8 without a noticeable change in D_L/u. On the other hand, the three Dacron fiber beds, with a fixed particle diameter, had widely different values of D_L/u. Although the porosity was different for each of these beds, it is believed that the observed difference in D_L/u was probably due to a difference in packing, or formation, of the beds rather than the difference in porosity. Thus, it appears that a single parameter, such as particle diameter, does not define a bed of fibrous media since geometric similarity is not necessarily maintained from bed to bed.

The theoretical equation for the washing of the viscose fiber beds was written with equilibrium assumed between the fibers and the surrounding solution. The assumption of equilibrium was found to be satisfactory over the range of flow rates investigated for the 1-denier fibers (16-μ diameter). For the 64-denier (120 μ) fibers, the assumption of equilibrium was satisfactory at low flow rates; however, at higher flow rates, this assumption was not satisfactory. In this case the experimental curve exhibited an appreciable tail due to the relatively slow intrafiber diffusion of the solute.

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NOTATION

c = concentration of fluid, g. solute/cc. solution
c_0 = concentration initially in bed at $t = 0$, g. solute/cc. solution
D_L = longitudinal dispersion coefficient due to flow pattern, sq. cm./sec.
D_L/u = mixing parameter, cm.
D_v = longitudinal molecular diffusion coefficient, sq. cm./sec.
d_p = particle diameter, cm.
K, K_0 = constants in Equation (3)
$k_0, k_1, k_2,$
k_3, k_4 = constants in Equation (7)
$k_1', k_2',$
k_3', k_4' = constants in Equation (8)
N_{Pe} = Peclet number = ud_p/D_L
R = ut/z
S = D_L/uz
t = time, sec.
u = average linear pore velocity, cm./sec.
z = longitudinal distance variable, cm.

Greek Letters

γ = constant in Equation (7)
γ' = constant in Equation (8)
ϵ = bed porosity
ϵ_f = porosity of fiber
η = quantity of solute sorbed by the solid per unit volume of solid, g. solute/cc. solid
λ = $1/(1 - K + K/\epsilon)$
ω = a variable of integration = $\sqrt{t/\tau}$
ω_1 = $[1 - (1/\omega^2)]R$

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Vapor-Liquid Equilibrium in the System Bromine Pentafluoride–Uranium Hexafluoride

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The system bromine pentafluoride-uranium hexafluoride is of interest in various fluoride volatility methods for the processing of nuclear fuel materials. These volatility methods are commonly based on distillation to purify and recover the uranium as the hexafluoride compound (*1*).

Two equilibrium studies have previously been published on the bromine pentafluoride-uranium hexafluoride system. One study was on the solid-liquid equilibrium; the results showed a simple eutectic at 63.5°C. at a composition of 3.2 mole % uranium hexafluoride (*2*). The solubility of solid-uranium hexafluoride in the liquid-bromine pentafluoride was stated to be essentially ideal (*2*). The other study gave some measurements on the vapor-liquid equilibria in the bromine pentafluoride-uranium hexafluoride system as obtained on a static type of apparatus; the results indicated that binary was nonideal and an azeotrope was reported at 90 mole % bromine pentafluoride (*3*).

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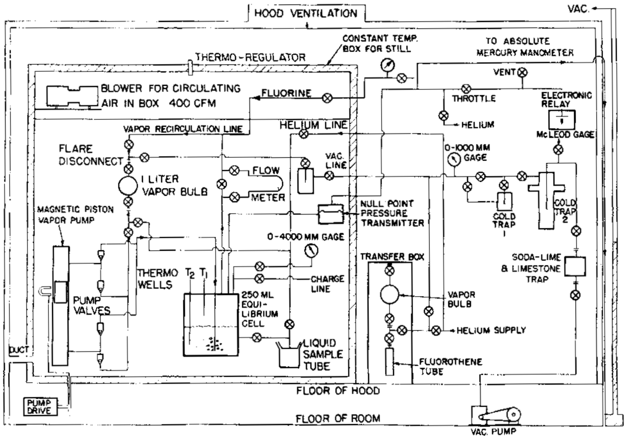

Fig. 1. Layout of recirculation type of vapor-liquid equilibrium still.

However, distillations performed in packed columns operating on the bromine pentafluoride-uranium hexafluoride system have indicated that for a wide range of still pot composition, substantially pure bromine pentafluoride could be obtained in the overhead fractions (*4*). Thus, these distillations suggested that no azeotrope exists.

In view of these differences between methods and investigators, the main objective of this study of the bromine pentafluoride-uranium hexafluoride system was to attempt to clear up the discrepancy on whether or not the binary had an azeotrope.

To obtain data for this binary system, an equilibrium still was designed and built which was capable of handling halogen materials. Nickel, Monel, and teflon were materials of construction for the still itself. Bellows seal valves were used with teflon to Monel seats. The still was of the mechanical circulation type. The vapor was bubbled repeatedly through the liquid during the operation of the still by means of a magnetic piston pump. The vapor flow rate was indicated by a thermal flow meter. The temperature was measured with a precision potentiometer as the millivolt output from copper-constantan thermocouples. The thermocouples were calibrated against a platinum resistance thermometer. The pressure was indicated on an absolute, well type of mercury manometer coupled to the still through a null point transmitter; the manometer had a range of 0 to 3,800 mm. Hg. The pressure inside the still was continuously balanced with helium on the other side of the flexible metal diaphragm on the transmitter. A diagram of the equilibrium still is shown in Figure 1. The still was contained in an isothermal box. The air inside of the box was recirculated at a rate of 400 cu.ft./min. by a blower. The temperature of the air was controlled by a precision mercury thermal regulator; the air was heated by electrical fin strip heaters. It was found that the temperature of the air within the box could be maintained constant to within plus or minus 0.2°C. of the set point.

Purification of commercial bromine pentafluoride was achieved by distillation in a 3-ft. packed nickel column, taking a middle cut consisting of about two thirds of the charge. The more volatile impurity was primarily hydrogen fluoride, and the less volatile was bromine trifluoride. The purified bromine pentafluoride was a colorless liquid at room temperature. The natural uranium hexafluoride was certified to have less than 0.01 wt. % hydrogen fluoride. 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 and wet chemical analysis and by vapor pressure measurements. It can be concluded that their purity was greater than 99.6%.

To operate the still after isothermal conditions were attained, the vapor pump was allowed to recycle for at least 4 hr. to insure equilibrium; then the two phases were sampled.

After equilibrium was established, a sample of the liquid phase was taken into an evacuated fluorothene tube, and a sample of the vapor phase was isolated by closing the two valves in the inlet and outlet lines on the vapor sample bulb. The bulb was then removed from the still, weighed on an analytical balance, and the contents transferred to evacuated fluorothene tubes. The tubes, containing the samples, were frozen in liquid nitrogen, sealed, and weighed. The material in the tubes was hydrolyzed, and the aqueous solutions were then analyzed for bromine or uranium by standard wet chemical methods. A Volhard analysis was used for the bromine and a volumetric analysis with ceric sulfate for the uranium.

To insure that corrosion (*5*) would not give spurious results, by producing extraneous components, very small amounts of elemental fluorine were added (~ 5 mm. partial pressure). This fluoride converted any bromine or bromine trifluoride corrosion species to bromine pentafluoride.

Since there were also conflicting data, with up to 17% difference (*3, 6, 7*) on the published values of the vapor pressures of bromine pentafluoride in the range above 1 atm., vapor pressure determinations were made on both of the pure components with the isothermal, vapor circulation equilibrium apparatus. The results obtained are summarized in Table 1. The pressures are given as millimeters of mercury referred to the density of mercury at zero degrees centigrade. It is evident that the experimental values for bromine pentafluoride are in agreement with the data of Long, et al. (*6*). Also, for uranium hexafluoride the data agree with the work of Oliver, et al. (*7*). Differences up to about ½% are present. It is concluded, therefore, that the equation for the vapor pressure of bromine pentafluoride given by Ruff and Menzel (*8*) cannot be extrapolated to pressures above 1 atm. Therefore, at positive pressures, the equation of Long, et al., must be used. Since Ellis and Johnson (*3*) indicated that their values for the vapor pressure of bromine pentafluoride were the same as those obtained by extrapolating the equation of Ruff, it is apparent that the values of Ellis and Johnson are too high.

Vapor density data were obtained from the weight of the vapor sample (in equilibrium with a given liquid composition) in a bulb of known volume at a known tempera-

TABLE 1. VAPOR PRESSURE OF PURE COMPONENTS OF THE SYSTEM BrF_5-UF_6

		Vapor pressure, mm. Hg		
Temp., °C.	Component	Observed	Previously* published	Difference, %
61.3	BrF_5	1,490	1,492	−0.13
69.5	BrF_5	1,924	1.916	+0.42
89.4	BrF_5	3,340	3,335	+0.15
89.3	BrF_5	3,332	3,326	+0.18
69.5	UF_6	1,350	1,350	0.00
69.5	UF_6	1,352	1,350	+0.15
69.6	UF_6	2,410	2,397	+0.53

* Values for BrF_5 were computed from equation given by Long et al. (*6*) and values for UF_6 from equation of Oliver et al. (*7*):

$$\text{for } BrF_5\text{: } \log_{10} P^o{}_1 = 6.4545 + 0.001101\,t - \frac{895}{t + 206}$$

$$\text{for } UF_6\text{: } \log_{10} P^o{}_2 = 6.9946 - \frac{1{,}126.288}{t + 221.963}$$

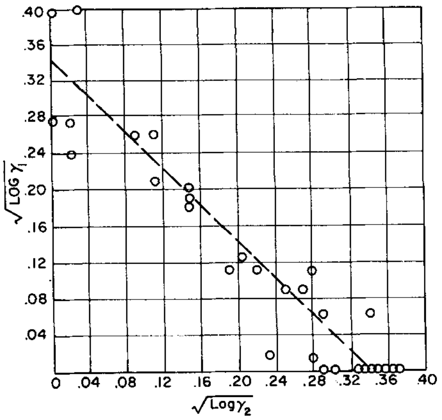

Fig. 2. Activity coefficients for 70° and 90°C. isotherms.

ture and pressure. From these data, the average compressibility factors for the vapor were computed to be Z equal to 0.936 at 70°C. and Z equal to 0.917 at 90°C. There is good agreement between the experimental values and values of Z predicted from various equations of state.

Tables 2 and 3 give the vapor-liquid equilibrium data obtained in this study. Activity coefficients were used as a measure of the degree of nonideality of the solution. The activity coefficients at the particular temperature, pressure, and composition were calculated by the equations

$$\gamma_1 = \frac{P y_1}{P^o{}_1 x_1} \tag{1}$$

and

$$\gamma_2 = \frac{P y_2}{P^o{}_2 x_2} \tag{2}$$

with lim $\gamma_1 \rightarrow 1$ as $x_1 \rightarrow 1$ and lim $\gamma_2 \rightarrow 1$ as $x_1 \rightarrow 0$. This method of determining γ is based on an ideal vapor phase with the standard state as the pure component at the temperature of the solution. The relative volatility α was computed from the defining equation:

$$\alpha = \frac{\dfrac{y_1}{x_1}}{\dfrac{y_2}{x_2}} \tag{3}$$

TABLE 2. VAPOR-LIQUID EQUILIBRIUM DATA FOR BrF_5-UF_6 SYSTEM: 69.5°C. ISOTHERM

Mole % BrF_5		Pressure,	Activity coefficients	
Liquid	Vapor	mm. Hg	BrF_5	UF_6
x_1	y_1	P	γ_1	γ_2
2.1	4.2	1,380	1.44	1.00
9.3	14.8	1,429	1.19	1.00
19.4	28.0	1,564	1.17	1.02
22.5	32.0	1,582	1.17	1.03
40.6	50.4	1,708	1.10	1.05
46.1	55.9	1,731	1.09	1.05
57.2	63.8	1,778	1.03	1.12
67.5	72.2	1,836	1.02	1.16
76.7	79.4	1,854	1.00	1.21
78.2	82.8	1,870	1.03	1.09
80.1	83.3	1,887	1.02	1.18
88.0	89.1	1,885	1.00	1.28
92.8	93.3	1,880	1.00	1.31
93.2	93.7	1,888	1.00	1.30
93.8	94.3	1,904	1.01	1.30
94.2	94.3	1,902	1.00	1.37
96.2	96.8	1,913	1.01	1.20
98.5	98.6	1,915	1.00	1.35

TABLE 3. VAPOR-LIQUID EQUILIBRIUM DATA FOR BrF_5-UF_6 SYSTEM: 89.3°C. ISOTHERM

Mole % BrF_5		Pressure,	Activity coefficients	
Liquid	Vapor	mm. Hg	BrF_5	UF_6
x_1	y_1	P	γ_1	γ_2
2.1	4.6	2,472	1.64	1.00
8.9	13.8	2,558	1.18	1.01
25.6	35.2	2,790	1.14	1.01
41.0	47.8	2,889	1.04	1.10
42.6	48.8	2,967	1.02	1.11
47.5	55.0	2,991	1.05	1.08
50.7	57.3	3,022	1.03	1.20
70.6	75.0	3,212	1.01	1.13
79.8	81.8	3,281	1.00	1.23
81.4	81.8	3,218	0.97	1.34
88.2	88.6	3,272	0.99	1.31
92.8	93.3	3,301	1.00	1.33
93.6	94.0	3,304	1.00	1.30

Calculations were made to correlate the activity coefficients with composition by the methods of Van Laar and Redlich-Kister. The approach of Snedeker in which the Van Laar equations are combined to give the linear form

$$(\log \gamma_1)^{1/2} = (A)^{1/2} - \left(\frac{A}{B}\right)^{1/2} (\log \gamma_2)^{1/2} \tag{4}$$

was used to evaluate the best values for constants A and B. Figure 2 gives a plot of the $\sqrt{\log \gamma_1}$ vs. $\sqrt{\log \gamma_2}$. Within the limits of the accuracy and precision of the data, the simple, symmetrical relationship with $A = B = 0.114$ gives a good correlation. This correlation gives the equations

$$\gamma_1 = 10^{0.114\,(1-x_1)^2} \tag{5}$$

and

$$\gamma_2 = 10^{0.114\,(x_1)^2} \tag{6}$$

From the equation

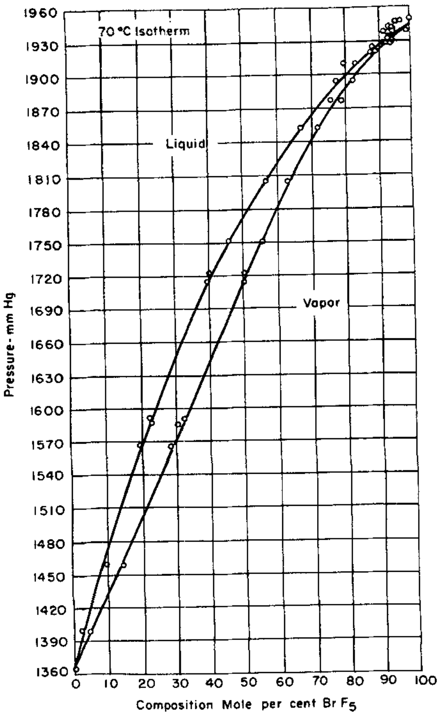

Fig. 3. Pressure-composition diagram, bromine pentafluoride—uranium hexafluoride.

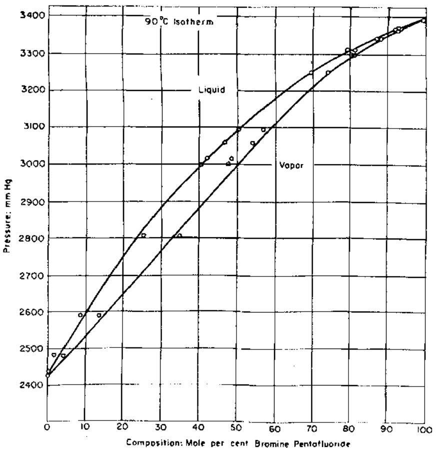

Fig. 4. Pressure-composition diagram, bromine pentafluoride—uranium hexafluoride.

$$P = (\gamma_1)(x_1)(P^o_1) + (\gamma_2)(1-x_1)(P^o_2) \qquad (7)$$

the smoothed total pressures were computed corresponding to given values of x_1 at 70° and 90.0°C. These computed pressure-composition curves are shown in Figure 3 and 4 together with the observed data points corrected to 70.0° and 90.0°C., respectively.

These results show that the bromine pentafluoride-uranium hexafluoride system has positive deviations from ideality with no azetrope. From these isothermal data, a 3 atm. isobar was calculated; this is shown in Figure 5 as an x-y diagram. At 3 atm., the relative volatility α varies as follows with composition:

x	α
$\lim x_1 \rightarrow 0$	1.80
50	1.41
$\lim x_1 \rightarrow 100$	1.09

Comparisons were also made with activity coefficients predicted by other methods (*9*). Data from the solid-liquid (*2*) equilibria gave estimated values of γ_2 ranging from 0.98 to 1.03 over the range of compositions $x_1 = 6$ to $x_1 = 79$ mole % bromine pentafluoride. Computations based on the theory of regular solutions (*10*) which assumes an ideal entropy of mixing gave the following:

x_1	γ_1	γ_2
0	1.06	1.00
0.3	1.02	1.01
0.7	1.01	1.03
1.0	1.00	1.07

Thus, the observed nonideality found in this study on vapor-liquid equilibria is in general agreement with the prediction for solid-liquid equilibria and from the regular solution concept. However, the observed activity coefficients are somewhat larger than the predicted values.

Subsequent to the completion of this study on phase equilibria, many distillations were made on bromine pentafluoride and uranium hexafluoride in a 0.5-in. diameter by 90 in. long column packed with 1/16-in. nickel helices (*11*). The organic system *n*-heptane–methylcyclohexane was first distilled as a reference.

The HTU_g was found to be 1.2 in. for flows of 50 to 450 lb./(hr.) (sq.ft.) for the *n*-heptane-methylcyclohexane system and 1.3 in. for flows of 285 to 1710 lb./(hr.) (sq. ft.) for the bromine pentafluoride–uranium hexafluoride system (*11*). The values for HTU_g for the fluoride system were computed from the equilibrium diagram obtained herein, Figure 5.

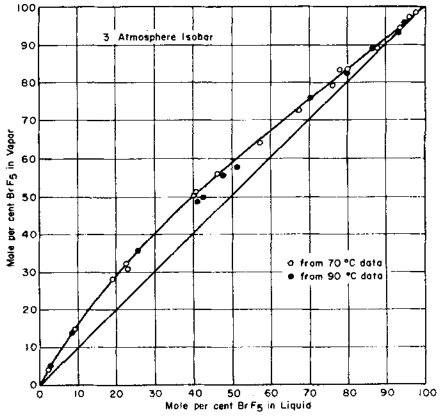

Fig. 5. Vapor-liquid equilibrium for the system bromine pentafluoride—uranium hexafluoride.

It was also found necessary in this distillation study to introduce fluorine into the column to inhibit the formation of bromine and bromine trifluoride. Several separations were performed which gave overhead concentrations from 1 to 0.01 mole % uranium hexafluoride with corresponding still-pot concentrations of from 10 to 30 mole % uranium hexafluoride (*11*). Therefore, no azeotrope was found at least above 0.01 mole % uranium hexafluoride in the bromine pentafluoride. At typical steady state conditions, with 76 mole % bromine pentafluoride in the still-pot, there was an overhead containing 99.8 mole % bromine pentafluoride (*11*). Thus the extensive distillation data (*11, 12*) give an independent confirmation of the equilibrium results. Both the phase equilibrium and distillation data indicate that no azeotrope exists in the bromine pentafluoride–uranium hexafluoride system.

NOTATION

x_1 = mole fraction bromine pentafluoride in liquid
x_2 = mole fraction uranium hexafluoride in liquid
y_1 = mole fraction bromine pentafluoride in vapor
y_2 = mole fraction uranium hexafluoride in vapor
γ_1 = activity coefficient of bromine pentafluoride in liquid
γ_2 = activity coefficient of uranium hexafluoride in liquid
$P_1{}^o$ = vapor pressure of bromine pentafluoride, mm. mercury
$P_2{}^o$ = vapor pressure of uranium hexafluoride, mm. mercury
P = total pressure, mm. mercury
t = temperature, °C.
A, B = constants in Van Laar equation

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