listed by Kelley,[13] but this was estimated entirely from the phase studies referred to above.[14]

The point of inflection in the C_p–temperature curve of solid lithium fluoride at approximately 700°K. (Fig. 1) is outside the experimental error, and leads to an interesting marked rise below the melting point. On the other hand it is probable that the corresponding curve for the liquid has a small negative slope. (The measurements on lithium fluoride cover too small a temperature range to establish this, but such has been found to be true in the case of almost every other liquid salt measured in this Laboratory.) Thus there is some evidence from the present case for regarding the process of fusion as partly a second-order transition.

Nevertheless, any such quantitative treatment of the available data on lithium fluoride would be difficult. C_p is generally regarded as the resultant of several rather delicately balanced factors. In the absence of compressibility measurements above 75°, it seems impossible to calculate reliable values of C_v at the high temperatures from the available C_p data. Using thermal expansion measurements made up to 800°,[15] the linear extrapolation of compressibilities measured at 30° and 75°[16] would lead to incredibly low values of C_v at high temperatures.

[15] A. Eucken and W. Dannöhl, *Z. Elektrochem.*, **40**, 814 (1934); the results of S. S. Sharma, *Proc. Indian Acad. Sci.*, **32A**, 268 (1950), obtained up to 400°, are in agreement within 1.5%.

[16] J. C. Slater, *Phys. Rev.*, **23**, 488 (1924).

WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

Phase Equilibria in the Condensed Systems Uranium Hexafluoride–Bromine Trifluoride and Uranium Hexafluoride–Bromine Pentafluoride

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Investigation of the systems uranium hexafluoride–bromine trifluoride and uranium hexafluoride–bromine pentafluoride has shown that the systems are simple eutectic types. The solid phases in equilibrium with saturated solutions are the pure components. The uranium hexafluoride–bromine trifluoride system exhibits positive deviation from ideality and the activity coefficients for uranium hexafluoride have been calculated. The uranium hexafluoride–bromine pentafluoride system shows only a slight deviation from ideality.

The systems uranium hexafluoride–bromine trifluoride and uranium hexafluoride–bromine pentafluoride were investigated to obtain the solubility of uranium hexafluoride as a function of temperature, and to determine the solid phases which exist in equilibrium with saturated solutions. A study of the systems was made by obtaining time–temperature cooling curves of synthetic complexes. In the system involving bromine trifluoride the visual isoplethal method also was used.

Experimental

Materials.—Bromine trifluoride and bromine pentafluoride obtained from the Harshaw Chemical Company were purified by distillation in a forty inch nickel fractionation column, one-half inch in diameter and packed with one-eighth inch nickel helices. The melting points of the bromine trifluoride shown in Table I and bromine pentafluoride shown in Table IV, agreed with the literature values[1,2] within 0.1°. The uranium hexafluoride has a melting point which also agreed with the literature value[3] as indicated in Tables I and IV.

Apparatus.—The apparatus used for the determination of the time–temperature freezing and thaw curves was similar to one previously described.[4] In order to prevent water from condensing and freezing on the apparatus at temperatures below the dew point, and to facilitate the attainment of cooling curves at low temperatures, the apparatus was placed in a box constructed of aluminum covered plywood. Dry air was passed into the box and when necessary Dry Ice and/or liquid nitrogen were added directly to the inside of the box. The components were introduced, under an atmosphere of helium, through a one fourth inch flared nickel fitting, into nickel or Monel tubes three-fourths inch in diameter and six inches long. Uranium hexafluoride, at 75 to 80°, was dispensed from a nickel buret containing a fluoroethene (Kel-F) sight glass.

Isoplethal analysis was also tried in the uranium hexafluoride–bromine trifluoride system. The apparatus used in determining the temperature at which the solid phase disappeared consisted of a three-fourths inch Kel-F tube, six inches in length, which was flared at the top so that it could be closed with a nickel fitting. The fitting was provided with a one-fourth inch nickel thermocouple well which extended into the sample, and a one-fourth inch flared tube through which a sample could be introduced. The temperature of the tube was controlled by placing it in a twelve cubic foot air-bath in which it was shaken with a Burrell wrist action shaker, keeping the temperature of the sample constant within 0.1°.

Temperatures were measured with iron–constantan or copper–constantan thermocouples in conjunction with a multi-point Brown Recording Potentiometer. The thermocouples and recorder were calibrated against a standardized platinum resistance thermometer employing a Leeds–Northrup G-2 Mueller bridge.

Synthetic complexes were prepared by weighing the components, under an atmosphere of helium, in the metal or Kel-F tubes. Total weights of complexes were approximately 50 g. The maximum cooling rate employed was 0.5 deg./min. Thaw curves were obtained by heating the solidified mixtures at somewhat lower rates.

Results and Discussion

The data for the system uranium hexafluoride–bromine trifluoride in terms of mole per cent. uranium hexafluoride are listed in Table I and are plotted in the usual fashion in Fig. 1. The values in Table I are the average of several determinations for any one complex. Where the datum is representative of four or more cooling curves for a complex, the average deviation from the mean is given after the value. All points plotted in Fig. 1 are assumed to be accurate within ±0.5°. Good agreements were obtained among the data taken from

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[1] G. D. Oliver and J. Grisard, THIS JOURNAL, **74**, 2705 (1952).

[2] O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **202**, 49 (1939).

[3] G. D. Oliver and J. Grisard, THIS JOURNAL, **75**, 2827 (1953).

[4] J. Fischer and R. C. Vogel, *ibid.*, **76**, 1497 (1954).

TABLE I

SOLID-LIQUID EQUILIBRIA OF THE SYSTEM URANIUM HEXAFLUORIDE-BROMINE TRIFLUORIDE

Data with asterisk obtained by visual observation of phase disappearance. M.p. lit. values: uranium hexafluoride,[2] 64.02; bromine trifluoride, 8.77

Mole % UF_6	Univariant point Cooling curve	Univariant point Thaw curve	Invariant point Cooling curve	Invariant point Thaw curve	Solid phase
100	..	..	64.0 ± 0.1	..	UF_6
96.4	62.3	62.8	..	..	UF_6
93.4	61.7	61.6	...	..	UF_6
90.4	61.4	..	..	..	UF_6
88.8	61.0 ± 0.2	60.7	..	..	UF_6
85.7	60.0	..	..	..	UF_6
83.1	60.4 ± 0.2	60.6	..	..	UF_6
81.8	60.0	60.2	..	..	UF_6
81.0	60.0 ± 0.1	..	..	..	UF_6
80.2	60.0	..	..	5.6	UF_6
76.8	59.6 ± 0.3	59.6	..	..	UF_6
72.9	59.1	59.3	..	6.0	UF_6
69.5	58.6	..	..	..	UF_6
67.0	58.4	58.4	..	..	UF_6
63.1	57.9	58.0	..	6.2	UF_6
58.8	57.7	..	6.4	6.5	UF_6
56.3	57.3 ± 0.2	..	..	..	UF_6
53.9	56.9	..	6.3	..	UF_6
51.9	56.7 ± 0.1	..	..	..	UF_6
48.7	56.5 ± 0.1	..	..	..	UF_6
45.4	55.9	..	6.1	..	UF_6
41.1	55.1	..	6.3	..	UF_6
38.2	..	55.0*	..	..	UF_6
35.6	53.3	..	6.1	..	UF_6
30.2	51.8 ± 0.4	51.9	..	..	UF_6
29.1	..	52.2*	..	..	UF_6
24.8	48.9	48.8	..	..	UF_6
19.5	..	46.5*	..	..	UF_6
19.3	46.5	45.4	..	..	UF_6
14.7	..	..	6.3	..	UF_6
13.4	..	38.9*	..	..	UF_6
9.9	..	..	6.5	..	UF_6
8.5	..	27.1*	..	..	UF_6
8.4	..	..	6.5	..	UF_6
7.6	..	..	6.4	..	UF_6
6.0	..	16.3*	..	..	UF_6
5.1	..	..	6.4	..	UF_6
2.6	..	7.1	6.7	6.3	BrF_3
0	8.7 ± 0.1	..	..	..	BrF_3

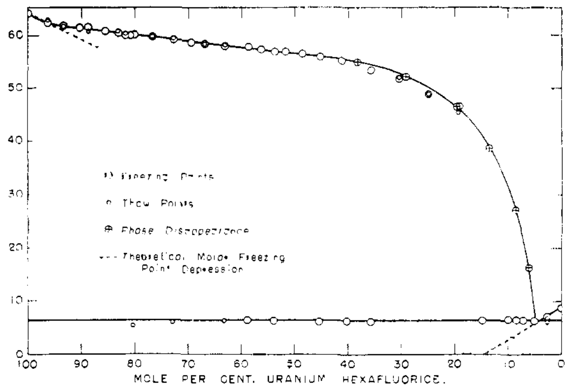

Fig. 1.—Solid–liquid equilibria of the binary system uranium hexafluoride–bromine trifluoride.

freezing and thaw curves, indicating that phase equilibria had been obtained. In the region of 20 to 40 mole per cent. uranium hexafluoride the results obtained from the visual observation of the disappearance of the solid phase are slightly higher, in terms of temperature, than the results obtained from freezing curves. These differences, however, are small enough to be within experimental error. Data on the liquidus curve could not be obtained from the thermal analysis of complexes containing less than 19 mole per cent. uranium hexafluoride because there was a marked decrease in the thermal effect upon solidification in this region. However, useful data for the eutectic halt were obtained in this region by this method.

It was difficult to obtain points on the liquidus curve for which the equilibrium solid phase was bromine trifluoride. The only point, obtained from thaw curves of a complex containing 2.6 mole per cent. uranium hexafluoride, was found to be coincident with the line representing the theoretical molar freezing point depression. The intersection of the theoretical freezing point line with the eutectic temperature 6.4° yields the eutectic composition 4.1 mole per cent. uranium hexafluoride. This value is in satisfactory agreement with the value of 4.8% obtained by extrapolating the liquidus curve to the eutectic temperature in Fig. 1. The molar freezing point depression lines, drawn on Fig. 1 for uranium hexafluoride and bromine trifluoride, were obtained from the familiar equation

$$\Delta T_f = (RT_0^2/\Delta H_f)X_2$$

The ΔH_f values for uranium hexafluoride and bromine trifluoride were 4.588[3] and 2.874[5] cal./mole, respectively.

In order to compare the system uranium hexafluoride–bromine trifluoride with the system uranium hexafluoride–chlorine trifluoride[6] and the system uranium hexafluoride–hydrogen fluoride,[7] the data were subjected to the following theoretical treatment used by Barber and Wendolkowski,[6] and Rutledge, Jarry and Davis.[7]

The solid–vapor and liquid–vapor pressure equations for uranium hexafluoride have been determined by Grisard and Oliver,[3] which makes an analysis of the data in terms of activity coefficients feasible.

One may calculate an ideal solubility based on Raoult's law. For a solid in equilibrium with a solution at a given temperature

$$P^0_{1,s} = \bar{P}_{1,g} = X^0_1 P^0_{1,l} \qquad (1)$$

$$X^0_1 = \frac{P^0_{1,s}}{P^0_{1,l}} \qquad (2)$$

where

$P^0_{1,s}$ is the vapor pressure of solid substance 1

$\bar{P}_{1,g}$ is the partial pressure of substance 1 in the gas phase

X^0_1 is the "ideal" mole fraction of substance 1 in the liquid phase

$P^0_{1,l}$ is the vapor pressure of pure substance 1 in the liquid phase

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(5) F. G. Brickwedde, H. J. Hoge and R. B. Scott, *J. Chem. Phys.*, **16**, 429 (1948).

(6) E. J. Barber and W. A. Wendolkowski, ORNL, Report No. K-846 (1951).

(7) G. P. Rutledge, R. J. Jarry and W. Davis, Jr., *J. Phys. Chem.*, **57**, 541 (1953).

The "ideal" mole fraction at a given temperature is equal to the ratio of the vapor pressure of the solid to the extrapolated vapor pressure of the liquid at that temperature. The "ideal" solubility curve for uranium hexafluoride is identical with the one calculated by Barber and Wendolkowski,[6] and is shown in Fig. 2, as a dotted line labeled "ideal."

The activity coefficient can be defined by

$$X^0_1 = \gamma^s_1 X^a_1 \qquad (3)$$

where γ^s_1 is the activity coefficient of component 1, where the standard state is the pure supercooled liquid of component 1 and X^a_1 is the experimentally observed mole fraction of component 1. The activity coefficient of component 1 can be formulated as

$$\gamma^s_1 = \frac{P^0_{1,s}}{X^a_1 P^0_{1,1}} \qquad (4)$$

and will be referred to as the experimental activity coefficient. For uranium hexafluoride the vapor pressure in mm. is given as a function of temperature in degrees centigrade by the following equations.

$$\log P^0_{1,s} = 6.38363 + 0.0075377t - \frac{942.76}{t + 182.416} \qquad (5)$$

$$\log P^0_{1,1} = 6.93718 - \frac{1091.537}{t + 217.22} \qquad (6)$$

It should be noted that the experimental activity coefficient is dependent on the validity of the extrapolation of the liquid–vapor pressure equation to temperatures below the triple point.

Employing the theory of real solutions, as developed by Scatchard, Hildebrand, Flory and Huggins,[8] the activity coefficient was formulated by Barber and Wendolkowski[6] as

$$RT \ln \gamma_1 = V_1\phi_2^2 \left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right] - RT \ln \frac{\phi_1}{X_1} - RT_{\phi_2}\left(\frac{V_1}{V_2} - 1\right) \qquad (7)$$

In the above equation ϕ_1 can be defined as

$$\phi_1 = \frac{X_1V_1}{X_1V_1 + X_2V_2} \qquad (8)$$

where the subscripts refer to the component, γ is activity coefficient with the same standard state as equation 3, ϕ is the volume fraction, V the molar volume in the solution, ΔE the molar energy of vaporization, X the mole fraction, R the gas constant and T the absolute temperature. In the following discussion component 1 is uranium hexafluoride and component 2 is bromine trifluoride. The energies of vaporization were calculated from the heats of vaporization ΔH, given in the following equations in which t is the temperature in degrees centigrade, by assuming perfect gas laws

$$\Delta H_1 = 4994.5 \left(\frac{t}{t + 217.22}\right)^2 \sqrt{\frac{1 - 1.9032P}{(t \times 10^{-2})^3 \text{ cal.mole}}} \qquad (9)^5$$

$$\Delta H_2 = 7714 \left(\frac{t + 2273.16}{t + 220.5}\right)^2 \text{cal./mole} \qquad (10)^6$$

The molar volumes of the components are given in the following equations as a function of temperature.

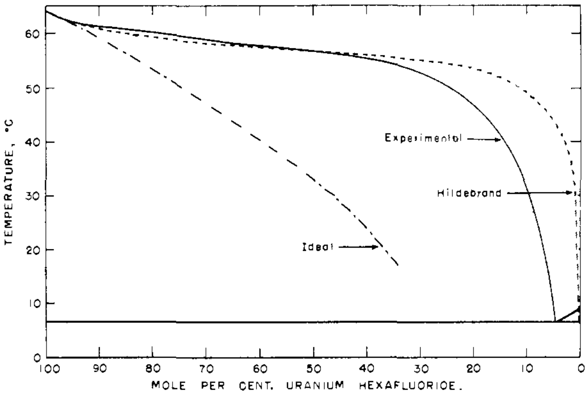

Fig. 2.—Solubility curves system uranium hexafluoride–bromine trifluoride.

$$V_1 = \frac{352.07}{3.674}\,[1 + 1.727(t - 64.05)10^{-3} + 3.59(t - 64.05)^2 10^{-6}] \qquad (11)^9$$

$$V_2 = \frac{136.92}{2.867 - 2.77 \times (10^{-3}\,t)} \qquad (12)^{10}$$

In equation 7 ideal partial molar volumes (see equation 8) are substituted for experimental partial molar volumes because there is a lack of data concerning the latter quantity. According to Barber and Wendolkowski,[6] for systems of this type, "this assumption normally introduces less than 5% error in the equation." Equation 7 expresses the deviation from ideality, in terms of the activity coefficient of one of the components of a solution as a function of the energy of mixing (dependent on the internal pressures of the constituents) and the entropy of mixing (dependent on the entropy change due to mixing molecules of unequal size). The activity coefficients calculated from equation 7 are listed in Table II as Hildebrand activity coefficients; Barber and Wendolkowski[6] refer to this as the "Theoretical activity coefficient."

TABLE II

ACTIVITY COEFFICIENTS OF URANIUM HEXAFLUORIDE

X_1 = mole fraction UF_6, γ^s_1 = activity coefficient UF_6.

°C.	Experimental X^a_1	Experimental γ^s_1	Hildebrand theoretical[a] X_1	Hildebrand theoretical[a] γ_1
64	1.00	1.0	1.0	1.00
63	0.980	1.0	0.978	1.00
62	.946	1.01	.955	1.00
61	.877	1.07	.912	1.02
60	.795	1.16	.855	1.08
58	.630	1.40	.665	1.33
56	.465	1.80	.411	2.05
52	.290	2.67	.153	5.05
50	.250	2.96	.108	6.83
40	.140	4.22	.028	21.2
30	.094	4.98	.011	41.8
20	.065	5.64	.005	74.0
10	.050	5.66	.003	106.0

[a] Called theoretical activity coefficients by Barber and Wendolkowski.

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(8) J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Third Edition, Reinhold Publ. Corp., New York, N. Y., 1950, Chapter XVII.

(9) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," Part I, First Edition, National Nuclear Energy Series, M.P.T.S., McGraw-Hill Book Co., Inc., New York, N. Y., 1951.

(10) O. Ruff, A. Braida, O. Bretachreidy, W. Menzel and H. Plant, *Z. anorg. Chem.*, **206**, 59 (1932).

The Hildebrand solubility was obtained by substituting the Hildebrand activity coefficients in equation 4 and solving for X_1 to obtain the Hildebrand solubility curve shown in Fig. 2.

It is obvious from Fig. 2 that the system exhibits positive deviation from ideality. Experimental and Hildebrand activity coefficients for uranium hexafluoride in bromine trifluoride, in chlorine trifluoride,[6] and in hydrogen fluoride[7] are listed in Table III for purposes of comparison. All three systems show positive deviations from ideality, the system uranium hexafluoride–chlorine trifluoride exhibiting the smallest deviations, and the system uranium hexafluoride–hydrogen fluoride, in which there is a liquid immiscibility gap, exhibiting the largest deviations of the three from ideality.

TABLE III

ACTIVITY COEFFICIENTS OF UF_6 IN VARIOUS SUBSTANCES

t, °C.	Experimental BrF_3	 ClF_3[6]	 HF[7]	Hildebrand theoretical[a] BrF_3	 ClF_3[6]	 HF[7]
64	1.0	1.0	1.0	1.0	1.00	..
60	1.16	1.10	10.4	1.08	1.00	..
50	2.96	..	18.5	6.83	1.01	130
40	4.22	1.23	23.5	21.2	1.03	250
30	4.98	1.42	31.1	41.8	1.06	410
20	5.64	1.63	33.3	74.0	1.13	600
10	5.66	1.78	42.0	106	1.16	740

[a] Called theoretical activity coefficients by Barber and Wendolkowski.

The system chlorine trifluoride–uranium hexafluoride deviates from ideality more than is predicted by the theory of real solutions, as expressed in equation 7. Since the final measure of the deviation depends on the theoretical solubility calculated by substituting the theoretical activity coefficients in equation 4, there may be some error because the results depend on extrapolated values of the vapor pressure equation for the liquid.

The deviations from ideality for the system uranium hexafluoride–bromine trifluoride, as calculated using equations 7 and 4, are in agreement with the experimental values in the region of 100 to about 40 mole per cent. uranium hexafluoride. At concentrations less than 40 mole per cent. the deviation from ideality is less than is calculated, and it is the reverse of the behavior in the uranium hexafluoride–chlorine trifluoride system. The differences from the theoretically calculated deviations from ideality in the uranium hexafluoride–hydrogen fluoride system are in the same direction as those in the uranium hexafluoride–bromine trifluoride system.

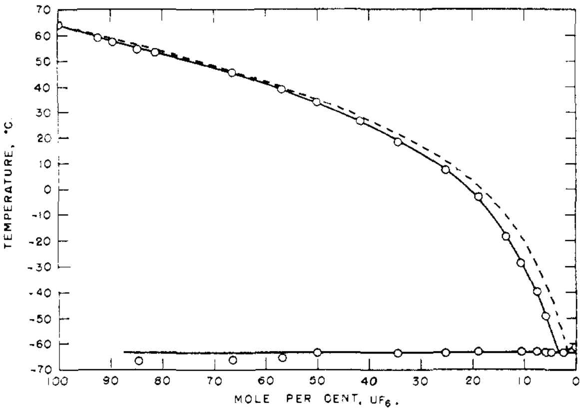

Fig. 3.—Solid–liquid equilibria of the system uranium hexafluoride–bromine pentafluoride.

The data for the system uranium hexafluoride bromine pentafluoride in terms of mole per cent. uranium hexafluoride, are listed in Table IV, and are plotted in the usual fashion in Fig. 3 where the points represent the average of the values obtained.

TABLE IV

SOLID–LIQUID EQUILIBRIA OF THE SYSTEM URANIUM HEXAFLUORIDE–BROMINE PENTAFLUORIDE

Melting points, lit. values: uranium hexafluoride, 64.02[1]; bromine pentafluoride, −61.3[2].

Mole % UF_6	Univariant point Freezing curve	 Thaw curve	Invariant point Freezing curve	 Thaw curve	Solid phase
100.0	..	..	63.9	....	UF_6
92.32	58.8	59.4	..	....	UF_6
89.52	57.3	..	..	....	UF_6
84.67	54.6	54.2	..	−66.7	UF_6
81.23	53.2	53.5	..	....	UF_6
66.40	45.6	..	..	−66.1	UF_6
56.81	39.0	..	..	−65.8	UF_6
50.07	34.0	34.1	..	−63.5	UF_6
41.68	26.7	..	..	....	UF_6
34.35	18.5	..	..	−63.5	UF_6
25.18	7.7	..	..	−63.8	UF_6
18.81	− 3.1	−2.9	..	−63.2	UF_6
13.32	−18.3	..	..	....	UF_6
10.53	−28.7	..	..	−63.2	UF_6
7.51	−40.1	..	..	−63.2	UF_6
5.78	−49.5	..	..	−63.5	UF_6
4.81	..	..	..	−63.5	UF_6
2.43	..	..	..	−63.5	BrF_5
0.00	..	..	−61.3	−61.3	BrF_5

In this work the recording potentiometer could be read with a precision of ±0.2°, and it is assumed that the data are accurate to within ±0.5°. Good agreements were found when both freezing and thaw curves were obtained for a given complex. Supercooling effects caused distortion of the freezing curves near the eutectic temperature. Therefore, thaw curves were employed in obtaining the temperature of the invariant point using the point of initial break in the thaw curve, which proved to be reproducible.

The "ideal" solubility curve for uranium hexafluoride, as calculated by Barber and Wendolkowski[7] from vapor pressure data, is shown as a broken line in Fig. 3. There is little deviation from ideality in this system.

Because of supercooling effects, it was impossible to obtain cooling curves in the region in which the solid phase is bromine pentafluoride. The eutectic composition of 3.2 ± 0.5 mole per cent. uranium hexafluoride was obtained by extrapolating the liquid curve to the eutectic temperature.

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