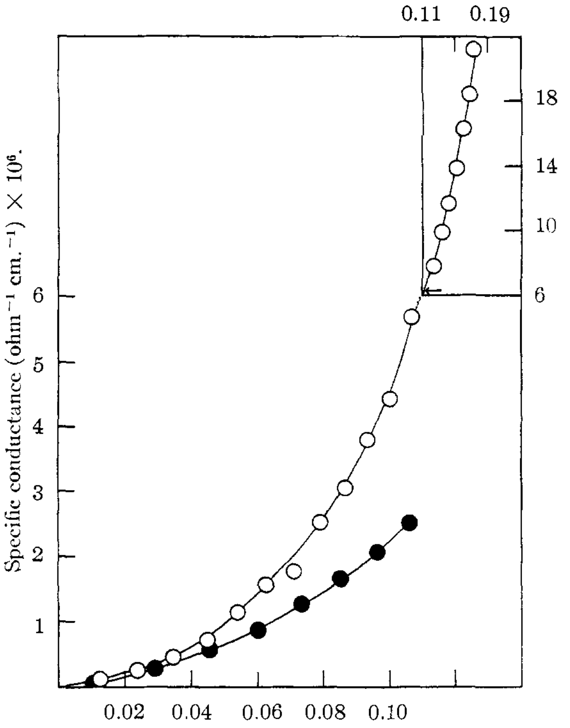

Fig. 1.—Conductivity of solutions of aluminum chloride in diethyl ether: ●, LiCl absent; ○, LiCl present.

Fig. 1 marks the point where equimolar amounts of the two chlorides were present.) We did not look for a change of conductivity with time in this experiment; but since none forced itself on our attention (which happened in the course of some related work), we consider that equilibrium is reached rapidly, during the period of not over one minute which is devoted to stirring before the taking of each reading.

(3) Solutions of aluminum chloride in tetrahydrofuran show much higher conductivities than do solutions in ethyl ether. The curve of specific conductance *vs.* concentration in tetrahydrofuran is almost a straight line when the solvent has been properly purified, but the slope of the line is different for different stock solutions even though the latter are freshly prepared. This variation does not show a systematic dependence on the concentration of the stock solution, and is probably to be traced to the combined effects of concentration, age, and temperatures attained in its preparation. It certainly indicates reaction between solute and solvent, which the following observation confirms.

(4) The addition of the first few ml. of the stock solution of aluminum chloride in tetrahydrofuran to a large volume of pure solvent causes the formation of an abundant white flocculent precipitate, which is gradually but completely dissolved by the addition of more stock solution. We propose for this substance the structure $Cl_2AlO(CH_2)_4Cl \cdot C_4H_8O$.

Anal. Calcd. for $C_8H_{16}O_2AlCl_3$: Al, 9.7; Cl (ionic), 25.6. Found: Al (by 8-quinolinol), 9.3; Cl (by Volhard), 26.2.

Such a structure could result from the attack of aluminum chloride, a Lewis acid, on the basic

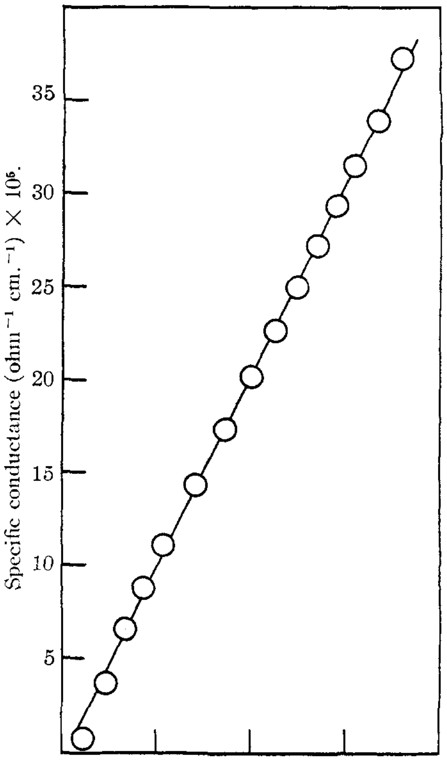

Fig. 2.—Conductivity of solutions of aluminum chloride in tetrahydrofuran.

oxygen atom of tetrahydrofuran, followed by a simple rearrangement. To the best of our knowledge, no material of comparable structure has previously been isolated; but such a substance may well be the intermediate in the formation of δ-chlorobutyl esters by the action of acid chlorides on tetrahydrofuran in the presence of zinc chloride[1] and stannic chloride,[2] both of which are likewise Lewis acids.

(5) Lithium chloride is soluble in tetrahydrofuran to the extent of approximately 2 g. per 100 ml. of solvent. The solubility is increased by the presence of aluminum chloride.

Acknowledgment.—We wish to express our appreciation of the support provided by the Office of Naval Research through Contract ONR 494(04).

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(1) J. B. Cloke and F. J. Pilgrim, This Journal, **61**, 2667 (1939).

(2) Ya. L. Gol'dfarb and L. M. Smorgonskiĭ, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1516 (1938); (*C. A.*, **33**, 4593^6 (1939)).

DEPARTMENT OF CHEMISTRY
TUFTS COLLEGE
MEDFORD 55, MASS.

Solid-Liquid Phase Equilibria in the Condensed System Bromine-Uranium Hexafluoride

BY JACK FISCHER AND RICHARD C. VOGEL

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Investigation of the system bromine-uranium hexafluoride has shown that the system is a simple eutectic type. The solid phases are the pure components and the system exhibits positive deviation from ideality.

The apparatus and procedure were those already described in previous publications.[1,2]

The uranium hexafluoride and bromine had melting points in agreement with the literature values[3,4] within experimental error as indicated in Table I.

TABLE I

SOLID–LIQUID EQUILIBRIA OF THE SYSTEM BROMINE–URANIUM HEXAFLUORIDE

Melting points, lit. value, uranium hexafluoride[3] 64.02°; bromine[4] −7.3°.

Mole % Br_2	Univariant temp., °C. Freezing curve	Univariant temp., °C. Thaw curve	Invariant temp., °C. Freezing curve	Invariant temp., °C. Thaw curve	Solid phase
0.0	..	..	63.9 ± 0.1	...	UF_6
6.34	60.6	60.9	...	...	UF_6
10.06	58.3	..	...	...	UF_6
14.99	56.9	..	...	...	UF_6
15.84	56.1	..	−7.2	−7.0	UF_6
20.30	54.6	..	...	...	UF_6
25.20	53.2	52.4	−7.3	−7.3	UF_6
28.22	52.8	..	...	...	UF_6
38.30	50.9 ± 0.3	50.4	−7.5	−7.4	UF_6
45.29	50.0	..	...	...	UF_6
51.04	48.7	..	−7.2	−7.2	UF_6
65.47	48.5	48.8	−7.5	−7.2	UF_6
80.83	46.9	47.6	−7.4	...	UF_6
86.84	45.1 ± 0.2	46.2	−7.5	−7.5	UF_6
92.32	38.8 ± 0.3	39.9	−7.4	−7.4	UF_6
95.16	31.7 ± 0.5	31.3	−7.3	−7.3	UF_6
96.92	19.9 ± 0.8	..	−7.4	−7.4	UF_6
97.79	10.3 ± 0.5	..	−7.5	−7.5	UF_6
98.77	0.0 ± 0.3	..	−7.4	−7.4	UF_6
100.00	..	..	−7.3 ± 0.1	...	Br_2

Synthetic complexes weighing about fifty grams were prepared by weighing bromine and uranium hexafluoride under an atmosphere of helium, in metal melting point tubes. The maximum cooling rate employed was 0.5 deg./min. Thaw curves were obtained by heating the solidified mixtures at somewhat lower rates. For details of the procedure, see ref. 3 and 4.

The data, in terms of mole per cent. bromine, are listed in Table I and are plotted in the usual fashion in Fig. 1 where the points represent the average values obtained from freezing curves. Where the datum is representative of four or more cooling curves, the average deviation from the mean is given after the value. Good agreements were obtained when both freezing and thaw curves were obtained for a given complex. The "ideal" solubility curve for uranium hexafluoride, as calculated by Barber and Wendolkowski,[5] is shown in Fig. 1 as a dashed line.

At concentrations greater than 15 mole per cent. bromine (Br_2) the system exhibits positive deviations from ideality. The eutectic composition lies between 99 and 100 mole per cent. bromine at −7.4 ± 0.1.

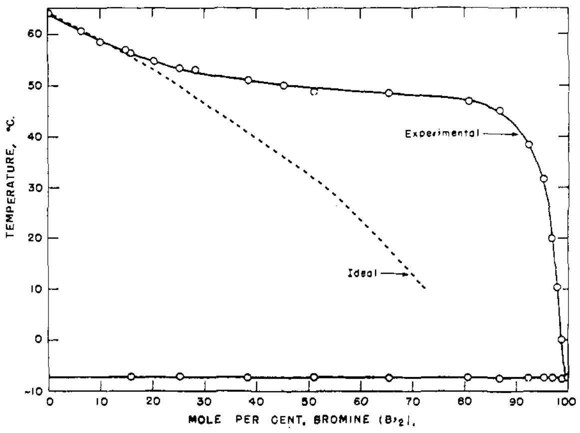

Fig. 1.—Solid-liquid equilibria of the system bromine–uranium hexafluoride.

Acknowledgment.—The authors wish to thank Mr. James Bingle for his assistance in performing the experimental determinations.

CHEMICAL ENGINEERING DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

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[1] J. Fischer and R. C. Vogel, THIS JOURNAL, **76**, 1497 (1954).

[2] J. Fischer and R. C. Vogel, *ibid.*, **76**, 4829 (1954).

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

[4] F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, 1952, p. 550.

[5] E. J. Barber and W. S. Wendolkowski, Oak Ridge National Laboratory, K-846, 1951.

The +4 Oxidation State of Protactinium in Aqueous Solution

BY S. FRIED AND J. C. HINDMAN

RECEIVED MARCH 25, 1954

Protactinium of oxidation state +4 has been prepared in the solid state as PaO_2, $PaCl_4$ and PaOS.[1,2] Bouissières and Haissinsky[3] have reported the reduction of Pa(V) to Pa(IV) in solution by use of amalgamated zinc, chromous chloride or titanous chloride as reducing agents. Titrations with ceric sulfate have been used by these authors to confirm the oxidation state.[4] In the present communication, the preparation of the +4 oxidation state in solution in the absence of other metal ions is described. The absorption spectrum in molar hydrochloric acid has been determined and the oxidation state tested by oxidation with neptunium(IV).

Experimental

Samples of 0.5 to 2 mg. of $PaCl_4$ were prepared in a thin quartz capillary by reduction of "$PaCl_5$" with hydrogen at 600–800°, the "$PaCl_5$" being prepared by action of CCl_4 on protactinium oxide. The Pa(IV) chloride, which was a golden yellow in color, was sublimed to one end of the capillary which was then sealed off to a length of about two inches. Dissolved oxygen was removed from a 1 *M* HCl solution by bubbling nitrogen through it for several hours. This solution was transferred to a dry-box whose nitrogen atmosphere acted as an inert environment. The sealed capillary containing the $PaCl_4$ was crushed inside an absorption cell and 1.5 ml. of the oxygen-free HCl added. The $PaCl_4$ appeared to go into solution readily. The stoppered cell was removed from the dry box and the

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[1] R. Elson, S. Fried, P. Sellers and W. H. Zachariasen, THIS JOURNAL, **72**, 5791 (1950).

[2] R. Elson, S. Fried and P. Sellers, reported in "The Actinide Elements" NNES, McGraw-Hill Book Co., Inc., New York, N. Y., 1954, Chapter 5.

[3] G. Bouissières and M. Haissinsky, *Compt. rend.*, **226**, 573 (1948); *J. Chem. Soc.*, S253, 554 (1949).

[4] M. Haissinsky and G. Bouissières, *Bull. soc. chim. France*, 146 (1951).