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.

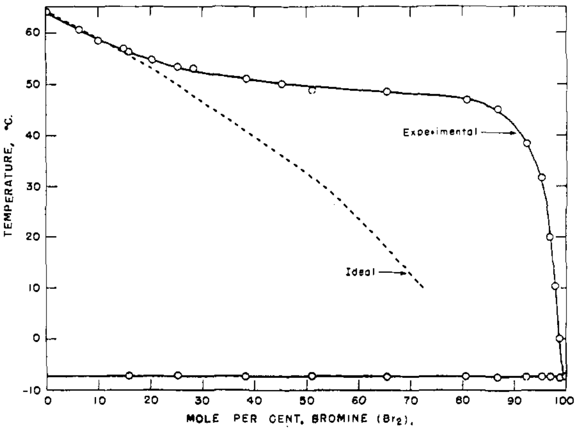

Fig. 1.—Solid–liquid equilibria of the system bromine–uranium hexafluoride.

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

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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).

absorption spectrum taken on a Cary recording spectrophotometer. The concentration of Pa^{231} was determined by radiometric assay using 3.4×10^4 years as the α half-life.[5] Spectrographic analyses showed Pa^{231} samples prepared in this manner were free of contamination by other metals. These analyses were performed by Mr. Faris of this Laboratory. In the oxidation experiments, the neptunium(IV) and Sn(II) were added as solutions in 1 *M* HCl. The Sn(II) solutions were prereduced with hydrogen gas to remove any Sn(IV) present. All operations were performed under nitrogen.

Discussion

The absorption spectrum of Pa(IV) is reproduced in Fig. 1. It is characterized by three maxima in the ultraviolet region, at 2760, 2550 and 2237.5 Å. There is no structure in the visible region up to 8000 Å. The spectrum is remarkably similar to the spectrum of Ce(III) (configuration $4f^1$). This is of some interest, since on the basis of the actinide hypothesis[6] protactinium(IV) might be expected to have the configuration $5f^1$. Also shown in Fig. 1 is the spectrum of the Pa(V) solution obtained after air oxidation of Pa(IV) and removal of the hydrolyzed protactinium by centrifugation.

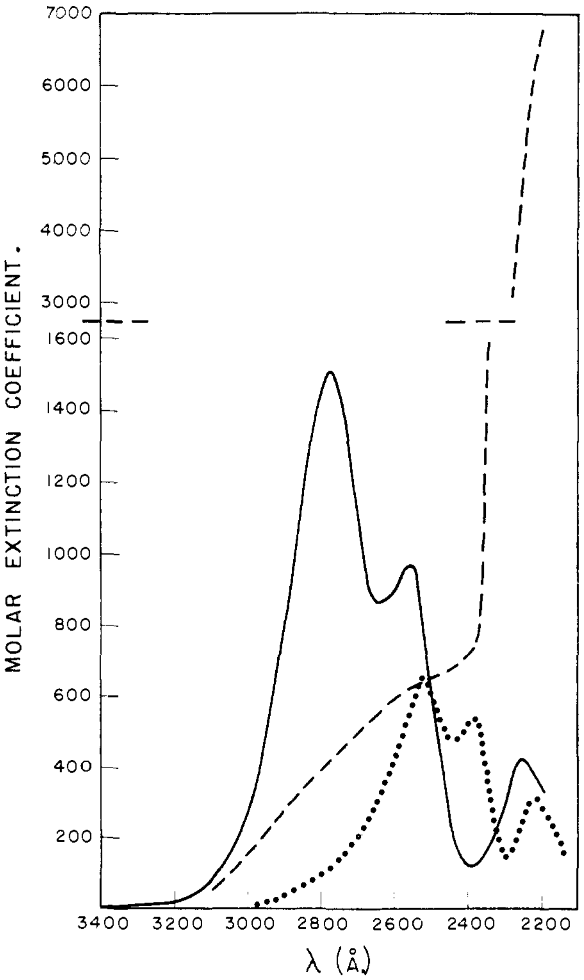

Fig. 1.—Absorption spectrum of Pa(IV) in 1 *M* HCl: ——, Pa(IV)-[Pa] = 1.1×10^{-3} *M*; - - -, Pa(V)-[Pa] = 4.2×10^{-5} *M*; · · ·, Ce(III).

The titrations of the Pa(IV) with Np(IV) were performed to (1) check the oxidation state of the protactinium and (2) to place further limits on the oxidation potential of the Pa(IV)-Pa(V) system. An excess of Np(IV) was used and the decrease in intensity of the Np(IV) band at 7230 Å. followed spectrophotometrically. There is no interference from protactinium absorption in this region. In two experiments, the calculated percentages of oxidation based on a one electron change were 95 ± 5% and 103 ± 6%, respectively. Within the experimental uncertainties, the oxidation of Pa(IV) to Pa(V) is quantitative. Since the potential of the Np(III)-Np(IV) couple is −0.14 volt,[7] the potential of the Pa(IV)-Pa(V) couple is fixed between −0.14 and +0.4 volt. This positive limit is set by the results of Haissinsky and Bouissières.[4]

Sn(II) in 1 *M* hydrochloric acid was added to give a solution containing about an eightfold excess. Apparently little or no oxidation of the Pa(IV) had occurred after a period of 24 hours since there was no evidence of precipitation of Sn^0 or Pa(V). Test of the solution indicated at least 85% of the Pa was still present as Pa(IV). Since the Pa(IV) solutions were found to oxidize slowly to Pa(V) on standing in the stoppered cells (estimated 5–10% in three days) it must be inferred that either Pa(IV) is not a strong enough reducing agent to reduce Sn(II) to Sn^0 or the rate is extremely slow. Although the slow rate of oxidation of Pa(IV) solution standing in sealed cells suggests that Pa(IV) is unstable to oxidation by H^+, further experiments are necessary before this can be considered unequivocally proved. We will tentatively estimate the potential of the $Pa(IV) = Pa(V) + e^-$ couple to be +0.1 volt on the basis of the above observations.

One hour and 15 minutes after blowing oxygen into the absorption cell, appreciable oxidation to Pa(V) had occurred. A marked Tyndall beam was observed. On standing overnight, the oxidation was complete. These qualitative observations on the air instability of Pu(IV) are in accord with those reported by Haissinsky and Bouissières.[4]

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[6] G. T. Seaborg, "The Actinide Elements," NNES, McGraw-Hill Book Co., Inc., New York, N. Y., 1954, Chapter 17.

[7] J. C. Hindman and E. S. Kritchevsky, THIS JOURNAL, **72**, 953 (1950).

Formation Constants of Metal Complexes of Tropolone and its Derivatives. IV. α-Bromotropolone, Tribromotropolone and 2-Aminotropone[1]

BY BURL E. BRYANT[2] AND W. CONARD FERNELIUS

RECEIVED APRIL 29, 1954

As part of an investigation of the coördinating tendencies of various ligands containing the cyclo-

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[1] Taken in part from a thesis submitted by B. E. Bryant in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, 1952.

[2] Public Health Service Research Fellow of the National Institutes of Health, 1953–1954.