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FLUORIDE COMPLEXES OF TETRAVALENT PROTACTINIUM[1]

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MASTER

English Summary:

The compound $(NH_4)_4PaF_8$ has been made from NH_4F and PaF_4. It is isostructural with $(NH_4)_4UF_8$, $(NH_4)_4NpF_8$, $(NH_4)_4PuF_8$, and $(NH_4)_4AmF_8$. Details of the syntheses of this and other alkali fluoride complexes will be given along with structural data.

This paper was submitted for publication in the open literature at least 14 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

French Summary:

On a préparé le composé $(NH_4)_4PaF_8$ à partir de NH_4F et de PaF_4. Il a la même structure que $(NH_4)_4UF_8$, $(NH_4)_4NpF_8$, $(NH_4)_4PuF_8$, et de $(NH_4)_4AmF_8$. On décrit la synthèse de ce complexe et d'autres complexes alcali-fluorure et on présente des détails des données structurales.

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INTRODUCTION

Fluoride ion is known to form stable complexes with the tetravalent
states of the actinide elements. Indeed, for the heavy elements americium
and curium, fluoride complex stability is sufficiently great so that even their
tetravalent states (which are unstable with respect to reduction to the aqueous
2 trivalent state by more than 2.5 volts) can be studied in aqueous fluoride.[2]
Complexes of tetravalent protactinium have not been reported previously in
the literature. In aqueous fluoride, there would certainly be competition between
the stabilizing effect of fluoride on <u>both</u> tetravalent and pentavalent protactinium.
3,4 The sparingly-soluble M_2PaF_7 type is well-known.[3,4] As mentioned above,
Asprey and Penneman showed that tetravalent americium is stabilized with
respect to trivalent americium in saturated ammonium fluoride solution. However,
Haissinsky, Muxart, and Arapaki subsequently showed that when PaF_4 is
dissolved in saturated ammonium fluoride solution it must be protected from air
5 or it undergoes oxidation to the pentavalent state.[5]

In the work to be reported at this meeting, we chose to work with freshly
prepared anhydrous PaF_4 and attempted to make several complex fluorides by
intimately mixing PaF_4 with alkali (or ammonium) halides and subsequently
heating the mixture in an atmosphere of hydrogen and/or hydrogen fluoride.
6,7 Similar work by us on ammonium fluoride and UF_4,[6,7] and by Thoma and
8 co-workers on the alkali fluoride-UF_4 compounds[8] had provided X-ray data
for a series of fluoride complexes containing U(IV) and we anticipated that the
Pa(IV) compounds would be similar. We had previously observed similarities
9 with the pentavalent salts for $MPaF_6$ and MUF_6 compounds ($M = K$, NH_4, Rb).[9]

Experimental

Formation of PaF_4. — Amounts of Pa_2O_5 up to 100 mg. were placed in platinum dishes in a nickel reactor and heated at 350° - 500°C in a stream of hydrogen and hydrogen fluoride. Details of the reactor are shown in Fig. 1. At 500°, the red-brown PaF_4 was well-sintered and appeared to have crept up the sides of the platinum dish during the reaction; some weight loss was observed. When formed at 350°C, however, the PaF_4 product showed the expected gain in weight from $PaO_{2.5}$. Both preparations gave the X-ray powder pattern typical of anhydrous PaF_4 (and of UF_4). The preparation and purity of the protactinium is described in our first paper.

Preparation of $(NH_4)_4PaF_8$. — A sample of PaF_4 was ground with an excess of NH_4F in a Mullite mortar in an inert atmosphere (Argon). X-ray analysis of the product using 0.2 mm. Lindemann glass capillaries, with Cuα radiation gave the pattern of $(NH_4)_4PaF_8$. It was identified by comparison with $(NH_4)_4UF_8$ whose formula and X-ray properties are well-known.[6,7] The comparison is given in the following section.

X-ray Properties of $(NH_4)_4UF_8$ and $(NH_4)_4PaF_8$. — Figure 2 shows a diffractometer tracing obtained from $(NH_4)_4UF_8$. The corresponding $(NH_4)_4PaF_8$ was too radioactive to permit taking of diffractometer data. Therefore, visually estimated intensities obtained from a powder diffraction film of $(NH_4)_4PaF_8$ are given in the upper part of the figure. Other results will be given at the meeting.

Fig. 1 — Details of Protactinium Reactor.

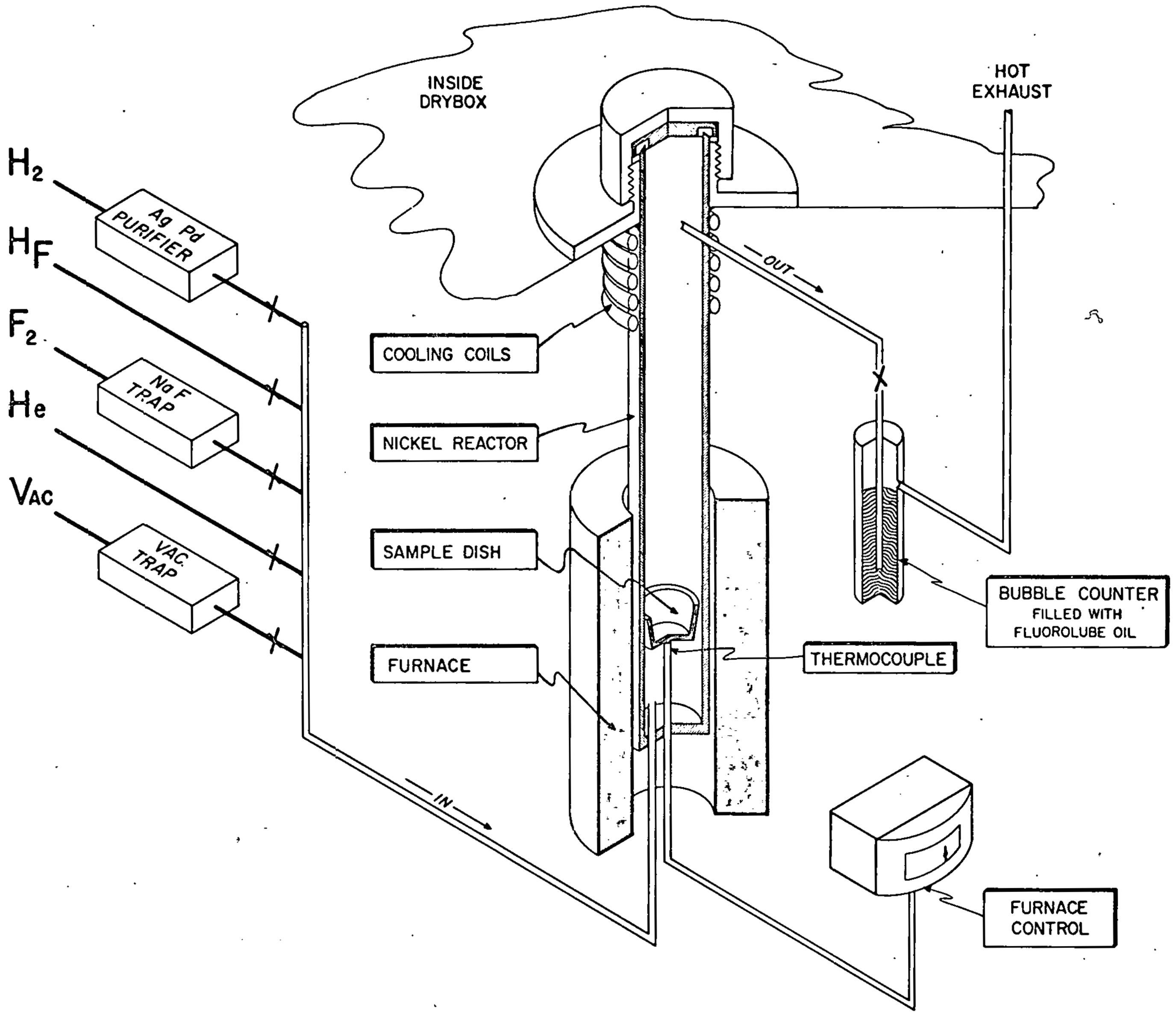


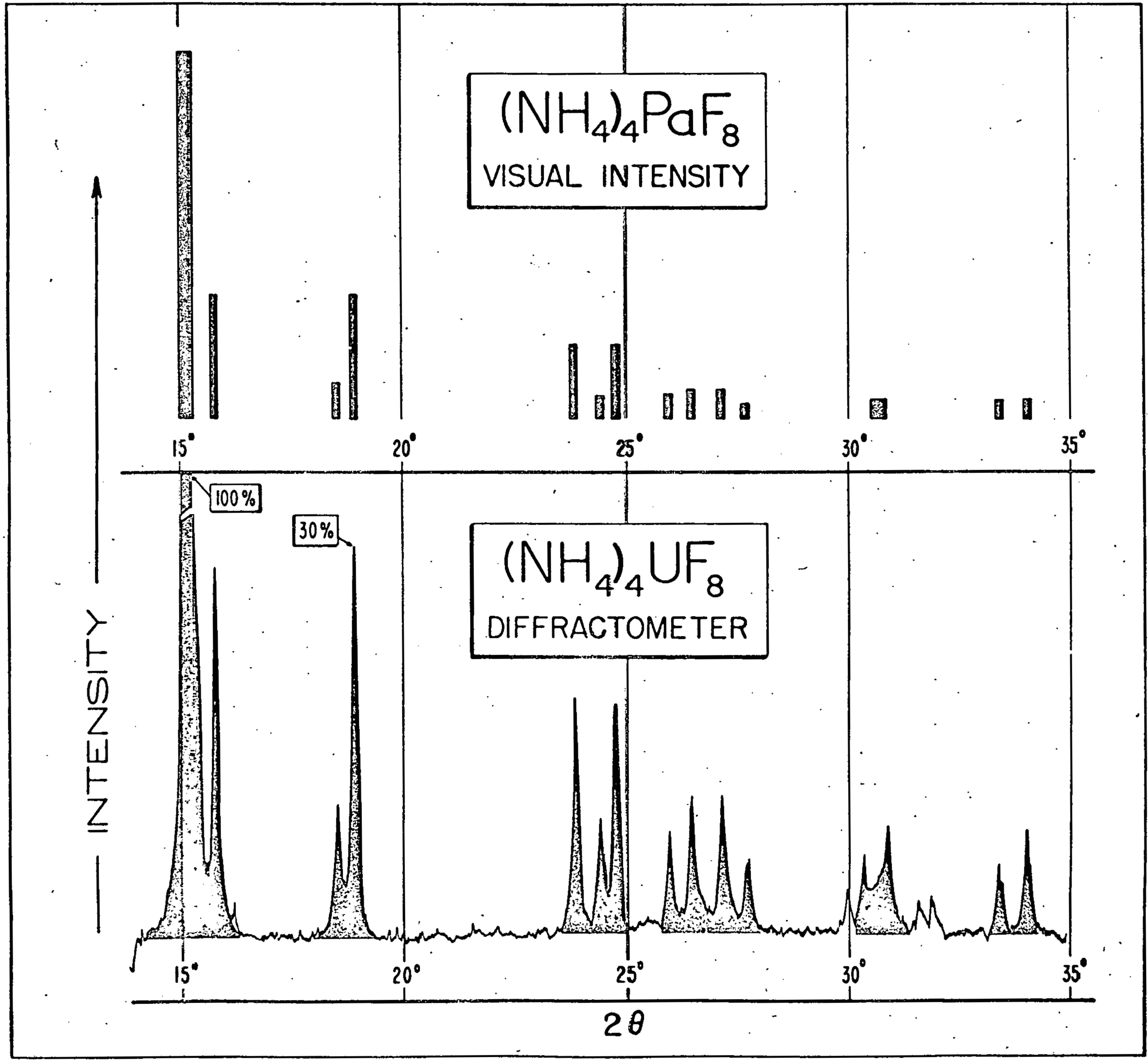
Figure 1. — PROTACTINIUM REACTOR

FLOW DIAGRAM

Fig. 2. — Comparison X-ray Data for $(NH_4)_4PaF_8$ and $(NH_4)_4UF_8$.

(a) Visually estimated intensities from X-ray powder diffraction data, Ilford film.

(b) Diffractometer scan of $(NH_4)_4UF_8$.



$(NH_4)_4PaF_8$
VISUAL INTENSITY
$(NH_4)_4UF_8$
DIFFRACTOMETER
INTENSITY
100%
30%
15°
20°
25°
30°
35°
15°
20°
25°
30°
35°
2θ

Discussion

From the present work, protactinium in the tetravalent state has been shown to form complex fluorides similar to those previously established with other tetravalent actinides. The $(NH_4)_4MF_8$ type of compound is now known for the series of elements where M = Pa, U, Np, Pu, and Am. The next lowest complex in the uranium series, $(NH_4)_2UF_6$, is known to have four polymorphs which have similar but different absorption spectra and X-ray diffraction patterns.[7] A similar situation is very likely with the $(NH_4)_2PaF_6$ complexes, but we have not yet investigated them.

An active investigation of other alkali fluoride complexes of Pa(IV) is under way at this time. In particular, the cesium, rubidium, and potassium systems will be studied especially in regard to their synthesis and their crystal structures. Results of this work will be reported at the Conference.

References

1. This work was performed under the auspices of the U. S. Atomic Energy Commission.
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