S 54. *A New Valency of Protoactinium.*

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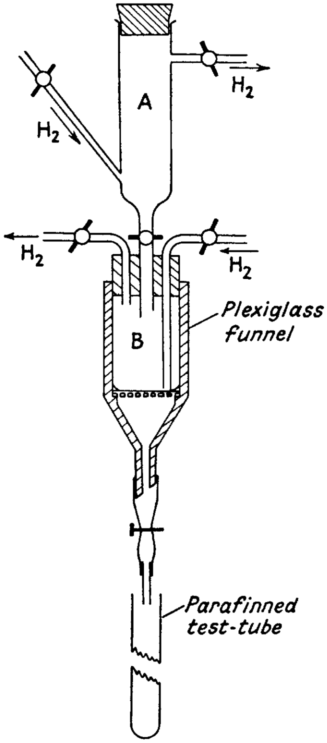
The reduction of protoactinium salts by means of zinc amalgam is described, and experiments on the product suggest that it is in the quadrivalent state.

WE have already shown (*Compt. rend.*, 1948, **226**, 573) that protoactinium, after reduction of its chloride with zinc amalgam, gives on treatment with hydrogen fluoride an insoluble fluoride. The experiments were carried out on tracer scale in the presence of a lanthanum salt used as carrier. We have now confirmed this result on weighable quantities of protoactinium and have established more exactly the conditions of the reduction. Furthermore, we have examined the behaviour of the reduced state towards certain reagents.

The reduction apparatus used consists of two superposed parts *A* and *B* (see figure). In most experiments the solution to be reduced is brought into contact with the amalgam in column *A*, and after reduction is allowed to flow into the " Plexiglass " funnel *B* containing the precipitating reagent. In other cases, the solution is with the amalgam in *B* and the reagent in *A* in order that the precipitation may be made in the presence of the reducing agent. When the reduction is carried out by a soluble agent, the latter is previously prepared on the amalgam in *A* and is later introduced into *B* which contains protoactinium in hydrofluoric acid solution. The operations are always carried out in an atmosphere of hydrogen.



We have thus found that reduction by the amalgam can be achieved either in hydrochloric or in sulphuric and even in hydrofluoric acid solution. In the last case the protoactinium is precipitated while it is being reduced. With amounts of protoactinium of the order of 0·1—2 mg. mixed with 10 or 20 mg. of zirconium or tantalum and with a comparable quantity of a lanthanum salt, we obtained yields of 80% or more, after 3 or 5 hours' reaction of the amalgam. We obtained about the same yield (75%) with 10 mg. of protoactinium mixed with 180 mg. of zirconium, tantalum, and titanium salts, but free from carrier for the insoluble fluoride formed. The fluorides of the three inactive elements, including that of Ti(III) formed during the reduction, remain in solution and are thus separated from the protoactinium.

We have observed a reduction with a yield of better than 50% using chromous chloride solution as reducing agent. It seems that even titanous chloride, freshly prepared, reduces the protoactinium, but only slowly. In any case, the presence of titanium salts is not an inconvenience for the reduction of protoactinium by zinc amalgam.

The precipitated fluoride may be washed, without re-oxidation, by oxygen-free water (the oxygen being previously eliminated by bubbling hydrogen for a sufficiently long time). It is quickly dissolved by a dilute solution of hydrofluoric acid if left in air, at least if the amount is only a fraction of a milligram.

For the reduced state one could presume ter- or quadri-valency, or even both. The insolubility of the fluoride does not give any information on this point, since the fluorides of all the elements of the seventh period corresponding to these two valencies are insoluble. On the other hand, there is a marked difference in the behaviour of the carbonates and the hypophosphates in the two oxidation states; the salts of thorium, zirconium, and U(IV) are soluble in an excess of ammonium carbonate and those of the rare earths and of actinium are not, if the solution is not too concentrated in carbonate. In an acid medium (N-hydrochloric or -sulphuric acid) salts of the former group are precipitated by hypophosphates while those of the rare earths and probably those of actinium remain in solution.

We have examined the action of the two reagents on solutions of protoactinium reduced to an extent of 80%, as has been verified by the precipitation of an aliquot part with hydrofluoric acid. The amount of protoactinium varied between 0·4 and 1·4 mg. in 10 c.c. containing zirconium and lanthanum as carriers of the two valencies. These experiments indicate that practically the whole of the reduced protoactinium follows zirconium, *i.e.*, it passes through in the carbonate filtrate and is retained by the hypophosphate precipitate. It seems then that the reduced state corresponds to the quadrivalency. This conclusion requires further confirmation, since, on the one hand, co-precipitation reactions alone are not always conclusive criteria and, on the other hand, it is not safe to draw conclusions about the chemical character of an element merely from analogy.

Whatever the new valency may be, the insolubility of the corresponding fluoride has already considerably furthered the enrichment and the purification of natural protoactinium. Indeed, the most troublesome elements in these operations are tantalum, zirconium, and titanium, whose fluorides are easily soluble.

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[*Read, March 28th,* 1949.]