[CONTRIBUTION FROM THE CHEMICAL RESEARCH INSTITUTE, SHANGHAI, CHINA]

THE ANALYTICAL CHEMISTRY OF ELEMENT 91, EKATANTALUM, AND ITS DIFFERENCE FROM TANTALUM

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In 1871 Mendelejeff,[1] on the basis of his periodic law, predicted the existence of a metal between thorium and uranium and named it ekatantalum (symbol Et). At present three isotopes of ekatantalum are known, all of them radioactive: brevium (Bv), discovered by Fajans[2] in 1913, protoactinium (Pa) and uranium Z (UZ, O. Hahn).[3]

Henceforth the author proposes to use as a synonym for element 91 the term "ekatantalum" (Et), meaning by it *all* of the isotopes of element 91. Under the term "protoactinium," according to its original meaning, will be understood only the parent substance of actinium, and by "brevium" only the disintegration product of UX_1.[4]

Brevium and uranium Z are very short-lived isotopes, their average life periods being 1.65 minutes and 9.7 hours. Naturally it is, and probably always will be, impossible to isolate them in pure form. Of the three isotopes, protoactinium is by far the most important, since it is the parent substance of actinium and all of the radio-elements of the actinium series. It was discovered in 1917 by Hahn and Meitner[5] in Germany, and simultaneously in England by the distinguished pioneer in radioactivity, Soddy in collaboration with Cranston.[6] Of the numerous radio-elements found since the splendid discovery of Mme. Curie, protoactinium is, in addition to radium, the only representative of a new radioactive chemical element which occurs in nature in considerable quantities. According to the author's latest determinations of the half-life period of protoactinium,[7] any uranium ore contains 0.6 g. of protoactinium for each gram of radium.

Until recently all attempts to concentrate and isolate the new element have been unsuccessful. These attempts have been based on the assumption that an analogy exists between the properties of ekatantalum and

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[1] D. I. Mendelejeff, *Ann. Suppl.*, **8**, 172, 191, 203 (1871).

[2] K. Fajans and O. Göhring, *Naturwissenschaften*, **1**, 339 (1913); *Physik. Z.*, **14**, 877 (1913).

[3] O. Hahn, *Ber.*, **54**, 1131 (1921); *Z. physik. Chem.*, **103**, 461 (1922).

[4] In this way the difference between the element "ekatantalum" and its isotope "protoactinium" will be emphasized, and such expressions as "protoactinium, free from brevium (or UZ)," or "brevium, free from protoactinium," will be definite.

[5] (a) O. Hahn and L. Meitner, *Naturwissenschaften*, **6**, 324 (1918); (b) *Physik. Z.*, **19**, 208 (1918).

[6] F. Soddy and J. A. Cranston, *Nature*, **100**, 498 (1918); *Proc. Roy. Soc.* (*London*), **94A**, 384 (1918).

[7] Their description is in preparation. The most reliable value for the half-life period of protoactinium is 32,000 years ±10%.

tantalum similar to that between radium and barium. This assumption has been supported by the authority of many prominent chemists and was one of the principal reasons for failure in attempts to isolate ekatantalum. The fallacy of this assumption has been demonstrated in the course of this investigation, and therefore it will be discussed here in greater detail.

Fajans,[8] in 1913, worked on this assumption during the discovery of the first isotope of ekatantalum—brevium—and shortly afterward Hahn and Meitner[9] concluded that any analytical reaction of tantalum can be used for the separation of element 91 from other metals. In the same year A. Fleck,[10] at the suggestion of Soddy, made a thorough study of the chemistry of the radio-elements, and wrote: "The chemistry of UX_2 (element 91) remains extremely vague. Tantalum is generally recognized by chemists to be a very difficult substance to work with, and an element of higher atomic weight occupying a position in the same group is not likely to have more distinctive reactions."

The attempts of Hahn and Meitner[11] to discover the parent of actinium in pitchblende by adding tantalum and recovering it by the acid and hydrogen peroxide method, and similar efforts of Göhring[12] to separate the then hypothetical protoactinium together with tantalum from solutions of alkali tantalates obtained from pitchblende gave negative results.

In 1917 success was attained in the long search for protoactinium and it was found in tantalum preparations. The supposedly close analogy between element 91 and tantalum appeared to be confirmed, so that Paneth and Hevesy remarked in their well-known manual on radioactivity; "The chemical properties of protoactinium are exactly those which should be anticipated from a higher homolog of tantalum; accordingly, its separation from tantalum is difficult."[13]

Soon after their discovery, Hahn and Meitner succeeded in obtaining highly radioactive preparations, but these contained at most only 0.01 to 0.1% by weight of the new element.[14] These preparations consisted generally of varying amounts of oxides and phosphates of zirconium, hafnium, tantalum, columbium, titanium and some other metals. All efforts to raise the protoactinium concentration proved futile, and in 1926 Hahn,[15] emphasizing the importance of isolating element 91, stated: ". . . . but

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[8] Fajans and Göhring, *Physik. Z.*, **14**, 880, 882 (1913); Fajans, "Die Radioaktivität," **1919**, p. 42.

[9] Hahn and Meitner, *Physik. Z.*, **14**, 759 (1913).

[10] Fleck, *Phil. Mag.*, **26**, 534 (1913).

[11] Ref. 5 b, p. 211.

[12] Göhring, *Physik. Z.*, **15**, 642 (1914).

[13] F. Paneth and G. Hevesy, "Lehrbuch der Radioaktivität," **1923**, p. 159.

[14] Ref. 5 b, p. 214.

[15] Hahn, "Handbuch der Physik," **1926**, Vol. 22, p. 282.

protoactinium, as a homolog of tantalum, evidently has in an exceptionally high degree its annoying chemical properties. Instead of normal chemical reactions of precipitation and substitution, colloidal precipitations, peptizations and as yet insufficiently explained adsorptions take place. In addition, the quantities are always very small, as compared with the accompanying elements, tantalum, niobium, titanium, zirconium and others, so that until now it has not been possible to obtain protoactinium in a highly concentrated state."

Such was the situation when the author took up the problem at the end of 1926. Inasmuch as the law of Mendelejeff had been employed advantageously in previous work on the chemistry of metal-organic compounds,[16] it was also applied in this case, and in November, 1926 the writer presented to Professor O. Hahn a report entitled "The Properties of Protoactinium and its Compounds, Calculated According to the Periodic Law."[17] The principal deductions were as follows. (1) Element 91, ekatantalum, will have its own characteristic properties and analytical reactions, differing from those of tantalum and columbium, just as its neighbors, thorium and uranium, differ greatly in their properties from their lower homologs, hafnium and zirconium, and tungsten and molybdenum. (2) Ekatantalum pentoxide (Et_2O_5) will have basic properties (similar to UO_3 and ThO_2) and form salts with acids, as contrasted with tantalum pentoxide (Ta_2O_5), which is a weak acid anhydride.

These predictions were verified recently through the isolation by the writer of 2 mg. of element 91 in pure form as its oxide.[18] Ekatantalum pentoxide, like tantalum pentoxide, is a heavy white powder with a very high melting point. The ignited oxide is practically insoluble in concentrated sulfuric, nitric or hydrochloric acid.

The author has recently succeeded in extracting about 40 mg. of element 91.[19] Part of this material has been used in the experiments described herein, which aimed at a more detailed study of the analytical reactions of ekatantalum and especially a comparison with tantalum.

The Reactions of Element 91 and Tantalum

The analytical reactions of the two elements were carried out with comparable quantities (10–50 mg.) of the pure oxides. Thus the quan-

[16] Grosse, *Z. anorg. allgem. Chem.*, **152**, 133 (1926); *Ber.*, **59**, 2646 (1926).

[17] This report is now in the possession of Professor Hahn, Berlin–Dahlem, Germany. A detailed account of the report was published in *J. Russ. Phys.-Chem. Soc.*, **60**, 843 (1928).

[18] A. V. Grosse, *Nature*, **120**, 621 (1927); *Naturwissenschaften*, **15**, 766 (1927); *Ber.*, **61**, 233 (1928); *J. Russ. Phys.-Chem. Soc.*, **60**, 847 (1928).

[19] An account of the technical extraction of protoactinium from radium residues, carried out through the courtesy of the German I. G. Dyes Trust at one of its factories in Ludwigshafen on the Rhine, is now being prepared for publication.

tities of element 91 used were not very much smaller than the amounts used in ordinary quantitative analysis. In small beakers (10–25 cc.), the reactions of this rare metal may be observed and studied as easily as those of any of the commoner elements.

1. **Material and Apparatus.**—All chemicals were E. Merck's guaranteed pure reagents. All operations with hydrofluoric acid and molten sodium bisulfate were carried out in platinum dishes. Pyrex or Jena glassware was used.

The ekatantalum pentoxide (Et_2O_5) was part of the first 30 mg. of the pure material recently separated by the author. It had been freed from all other metals and especially purified for a new determination of the average life of the protoactinium atom. The β-activity of the oxide was taken as a criterion of its purity; it remained constant throughout the various purification processes.[20]

The tantalum pentoxide (Ta_2O_5) was a sample of pure oxide from Merck and contained only traces of columbium and titanium. For further purification it was dissolved in 40% hydrofluoric acid, potassium carbonate added, the potassium fluotantalate separated and washed with 1% hydrofluoric acid. This material was then fractionally crystallized three times from 1% hydrofluoric acid in platinum dishes, the first and last fractions being discarded each time. The product was treated with sulfuric acid to expel the hydrofluoric acid, fused with sodium bisulfate, the melt dissolved in cold water and the precipitated tantalum pentoxide washed with boiling water until free from alkali metals. The oxide was then dried and ignited to constant weight.

Procedure.—Dissolved or insoluble matter was determined by difference in weight (using a micro-balance) or, in the case of element 91, also by estimating the amount of protoactinium electroscopically.[21]

Results

(a) Dissimilar Reactions

1. **Reaction with Sodium Bisulfate and Sulfuric Acid.**—Each oxide (10–50 mg.) was well mixed with 6–8 times its weight of powdered anhydrous sodium bisulfate and carefully melted in a platinum crucible until all of the oxide had dissolved and the melt was absolutely clear. The cooled melt was then treated with 10–50 cc. of 3% sulfuric acid at room temperature. In the case of *ekatantalum* almost all of the oxide *goes into solution*, leaving only a small residue (I, 6%; II, 4%); while in the case of *tantalum* only a small part of the oxide dissolves, most of it *remaining* as a fine, white powder (residue: I, 84%; II, 79%).

2 and 3. Reaction with Potassium Carbonate and Water.—Each oxide (10–50 mg.) was mixed with six times its weight of dry powdered potassium carbonate, melted and held in fusion with continuous stirring for ten to fifteen minutes. The oxide of *ekatantalum* is *insoluble* in the molten carbonate and remains suspended as a powder, giving the melt a milky appearance; *tantalum* pentoxide *dissolves completely* and clearly to give potassium tantalate.

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[20] The details of the purification methods will be published later.

[21] The method for exact determination of protoactinium and other isotopes of element 91 will be described in detail shortly.

The cooled melt was dissolved in 10–25 cc. of warm water (60–80°). The *ekatantalum* pentoxide remains as a fine, white *insoluble* powder (I, 99.9%; II, 99.8%), while the potassium *tantalate dissolves* to a clear solution with no residue.

4. **Reaction with Hydrogen Peroxide.**—*Ekatantalum* pentoxide hydrate is *completely precipitated* (99.9%) by an excess of hydrogen peroxide from a warm (40–60°) 2% sulfuric acid solution. On the other hand, a mixture of sulfuric acid and hydrogen peroxide *completely dissolves tantalum* pentoxide hydrate freshly precipitated from a potassium tantalate solution by sulfuric acid.

5. **Reactions with Phosphoric Acid.**—*Ekatantalum* pentoxide in solution in 20–30% hydrochloric acid, 15–20% sulfuric acid or in nitric acid, with or without hydrogen peroxide, is *completely precipitated* (99.9%) by an excess of phosphoric acid. A stable solution of *tantalum* pentoxide in concd. hydrochloric or sulfuric acid, with or without hydrogen peroxide, remains *absolutely clear* on the addition of an excess of phosphoric acid.

(b) Similar Reactions

6. **Reaction with Ammonia.**—*Ekatantalum* and *tantalum* in solution in mineral acids (hydrochloric, nitric, sulfuric and others) are *completely precipitated* on boiling with a slight excess of ammonia: Et_2O_5, 99.95%; Ta_2O_5, 99%. In the presence of *hydrofluoric acid or fluorides* the precipitation is incomplete (varying according to the concentration of ammonia, fluoride ion, etc.), owing to the formation of water-soluble double ammonium fluorides.

7. **Reaction with Hydrofluoric Acid.**—*Both oxides* are *completely dissolved* by 40% hydrofluoric acid on slow gentle warming, the ekatantalum pentoxide dissolving the more rapidly.

Discussion

A consideration of the reactions given above shows that except for the precipitation by ammonia, a reaction characteristic of almost all metals, *ekatantalum* and *tantalum* have *only one reaction in common*—the solubility of their oxides in hydrofluoric acid. (It is to be expected, of course, on the basis of the periodic law, that other reactions common to both will be discovered.)

Reaction 2 shows why Göhring[12] failed to isolate the hypothetical protoactinium together with tantalum, since actually he was purifying his tantalum preparations from the last traces of protoactinium which they may have adsorbed. Similarly, Reaction 4 indicates why the first attempts of Hahn and Meitner[11] were unsuccessful.

The behavior of the pentoxides of the two metals toward various reagents shows that while tantalum pentoxide is a feeble acid anhydride and forms more stable compounds with alkalies, ekatantalum pentoxide is a weak but decidedly basic oxide with no acidic properties.

All in all it may be said that the predictions made by the writer in 1926 as to the analytical properties of element 91 have thus far been proved by experiment; the expected characteristic properties of ekatantalum have been demonstrated. Once more Mendelejeff's law has proved its usefulness, and its application has rendered comparatively simple the solution of an apparently difficult task.

Summary

1. The unsuccessful attempts to isolate and obtain element 91—ekatantalum—were based on the assumption that it resembles its lower homolog—tantalum—just as radium resembles barium. The origin and development of this assumption and its contradiction to conclusions derived from the periodic law are discussed.

2. A study of the analytical chemistry of ekatantalum has been made with adequate amounts of its pure oxide. Its difference from tantalum predicted by the author on the basis of Mendelejeff's law, has been proved experimentally.

3. The behavior of ekatantalum toward different reagents is, in most of the cases observed, opposite to that of tantalum.

4. Ekatantalum pentoxide (Et_2O_5) is a distinctly, though feebly, basic oxide without acidic properties, whereas tantalum pentoxide (Ta_2O_5) is an acid anhydride and readily forms stable salts with basic oxides.

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THE BOILING POINTS OF CONSTANT BOILING HYDROCHLORIC ACIDS

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In connection with the work on the composition of constant boiling hydrochloric acid, recently published from this Laboratory,[1] we have made a precise determination of the boiling points of these acids over the same pressure range. The samples used were those whose analyses are given in the previous paper.

Foulk and Hollingsworth have shown[2] that the variation in boiling point of the acid which distils unchanged in composition at 750 ± 0.2-mm. pressure is not more than 0.003°, though they were not able to fix the temperature of boiling. In the work reported here a precision of 0.1 mm. was

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[1] Bonner and Titus, This Journal, **52**, 633 (1930).

[2] Foulk and Hollingsworth, *ibid.*, **45**, 1224 (1923).