THE DISCOVERY AND PROPERTIES OF HAFNIUM

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CONTENTS

THE DISCOVERY OF HAFNIUM AND THE QUANTUM THEORY OF ATOMIC STRUCTURE

1. *The rare earths. The complexity of Marignac's ytterbium*

In the course of the first half of the nineteenth century the problem of the atomic weight determination of most of the elements was taken up for the first time. The next step which suggested itself was to search after possible regularities which might exist between the atomic weights and the chemical characteristics of the elements. As is well known, Mendelejeff and Lothar Meyer first attacked successfully this problem to which additions from many sources have since been made gradually. We find when proceeding further in the order of increasing atomic weights of the elements, that the chemical properties change completely, but find later that the series periodically repeats itself. This periodicity does not occur, of course, without irregularities. After iron appear two elements, nickel and cobalt, which are closely related to each other, and further on ruthenium as well as osmium are followed by two intimately related elements and finally the most striking irregularity lies in the appearance of a large group of closely related elements, those of the rare earths after barium. To have ignored with gifted intuition these irregularities, when stating that fundamental connection between the chemical properties of the elements which has proved to be so important and instructive to us to-day, was one of the greatest services of the founders of the periodic system of the elements. Later in the course of the development of the system, the question of the source of the irregularities mentioned before, the appearance of the triads and the group of the rare earths naturally thrust itself repeatedly before the attention of scientists. That such irregularities can appear was somewhat disturbing because after iron besides nickel and cobalt there could follow other rare and as yet unknown elements and also other triads, as yet unknown, and such could also appear at other places and thus the number of elements could be considerably greater than would follow from the periodic system. In the group of the rare earths Mendelejeff considered the possibility of a larger number of elements and estimated the number of members of this group—of which 4 were known then—to be 20. Moseley performed the greatest service to science by eliminating this uncertainty with a single stroke. The linear relationship discovered by him between the atomic number and the square root of the frequency of the characteristic Röntgen rays of an element enabled him to state exactly the number of elements between hydrogen and uranium. It is clearly borne out that there are no other "triads" in this region except those already known, that the "triads" in reality contain only three members and further that between barium and tantalum in the region where the rare earths lie, there are only 16 elements—having the atomic numbers 57 to 72, both inclusive. Of these elements 14 were known at the time of Moseley's discovery. To have discovered and isolated nearly all of the rare earths without further theoretical guidance, in spite of their great similarity and the great rarity of some of these, is one of the most brilliant accomplishments that experimental chemistry has ever produced. Of these 14 rare earths those with atomic numbers 70 and 71 were discovered last. In the year 1878 Marignac isolated from the old erbium earth a new colorless earth slightly more basic than the others which was named ytterbium. In 1905 in the course of a systematic investigation on the separation of the rare earths Auer von Welsbach (2, 3) found that ytterbium was a mixture of two elements and also specified the method suitable for their separation. Then in 1907 Auer von Welsbach (4) published the optical spectrum of both constituents which, as we know from researches performed in Siegbahn's laboratory (24), have the atomic numbers 70 and 71, and for which he proposed the names aldebaranium and cassiopeium. Shortly previous to this publication (50) Urbain announced similar results and proposed the names neoytterbium and lutecium for the two constituents of ytterbium. The International Committee on atomic weights adopted the names ytterbium and lutecium.[1] The possibility seemed not

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[1] See *J. Am. Chem. Soc.*, **36**, +588 (1914): Ber. **47**, 8 (1914). See also the report of the German committee (Ber. **57**, 5, 1924) in which the consideration of the nomenclature is taken up in view of new evidence.

improbable to both investigators that Marignac's ytterbium—which consisted of about 90 per cent of the element 70 and 10 per cent of the element 71, as we know from the later researches of Auer von Welsbach—might contain yet a third still more easily soluble element than the two constituents already known. Auer von Welsbach started with 200 kgm. of gadolinite and secured after a fractional crystallization during several years one-half gram of the final liquor which, however, consisted entirely of cassiopeium and which showed no trace of the other supposed constituent; the latter, had it been present in ytterbium, should have been enriched in this fraction. Urbain (53) on the other hand believed that he had discovered the third constituent of Marignac's ytterbium in the year 1911. In his final liquor there appeared 21 new spectral lines which he had not previously observed and at the same time the paramagnetism of his preparation decreased very considerably compared with that of the element 71. The paramagnetism of this sample was found to be only between one-third and one-fourth of the preparation supposed to contain the element 71 in pure state. On the basis of this observation Urbain (53) announced in 1911 the discovery of a new rare earth for which he proposed the name celtium. Partly from the appearance of strong spectral lines and still more from the considerable decrease of the magnetic susceptibility we must conclude that Urbain's preparation must have contained a considerable amount of celtium. Eleven years later we learn from a communication of Dauvillier (21) that in addition to the familiar X-ray lines of the elements 70 and 71 those of the elements 69 and 72 have also been recognized in Urbain's preparation. Dauvillier explained the appearance of the two extraordinarily weak lines as due to the presence of a trace of the element which Urbain believed to have discovered on the basis of the observed optical lines. (Cet élément a été découvert par M. G. Urbain dans la préparation que nous avons étudiée grace a l'apparition d'un groupe de lignes inconnues dans le spectra d'arc.") From a later publication of Dauvillier (22) we also learn, that by this trace about 1/10,000 is to be understood. It is surprising that the discrepancy between the observation of strong optical spectral lines and of a very significant decrease of the paramagnetism on the one hand and the observation of these extremely weak X-ray lines on the other was not noticed. Moreover we read in a communication of Urbain (54) added to that of Dauvillier that now (after the discovery of celtium) "the question of the composition of the former ytterbium of Marignac is settled," ("la question des constituents de l'ancien ytterbium de Marignac est réglee").

This was the state of this question in 1922, when the quantum theory of atomic structure (12) enabled me to make a definite assertion as regards the characteristics of the element 72. This assertion was in full contradiction to the view that the element 72 should be the third constituent of Marignac's ytterbium and thus lead to the discovery of the true element 72, an element which was indeed a constituent of an "old element," but of "zirconium" and not of "ytterbium."

2. The element 72 and the quantum theory of atomic structure

All the older attempts to explain the periodic system were unsuccessful. Only after the discovery of the electron did a more hopeful method of explanation appear possible, and Sir J. J. Thomson was the first to attempt to reduce the periodicity in the chemical characteristics to a periodic arrangement of the electrons in atoms. At this time a closer pursuit of this idea was frustrated by a lack of knowledge concerning the arrangement of electrons in the atom. The proposal of the nuclear atom by Rutherford which was followed quickly by the foundation by Bohr of the quantum theory of atomic structure gave the necessary impulse. This development which leads also to a rational explanation of the periodicity in the chemical characteristics of the elements as they show themselves in Mendelejeff's system, was successfully accomplished by Bohr in 1922. As regard the question of position, Bohr asked how the electrons group themselves about the atomic nucleus in the atoms of different elements and what changes the grouping of the electrons suffer as one goes from element to element. The rational use of the laws of the quantum theory led him to the answer to this question and the numbers in the table shows his results. According to this theory the most common case is that, as one goes from element to element, the newly added electron (more correctly one of the electrons present in the completed atom) is fitted into the outermost group. With this addition the outer structure of the atom and therefore the chemistry depending in the first place on this outer structure undergoes a very essential change. The rational use of the quantum theory leads, however, to the result that, although this type is most frequent, a place is bound to come in the successive building up of the atoms from nuclei and electrons where the outer structure remains unchanged and the new incoming electron is fitted into a deeper group. We meet with such cases in groups of elements including the triads of iron, palladium and platinum metals and also the family of the rare earths. Various considerations insistently demand that after lanthanum (12) there must follow a series of elements whose inner groups only are completed by the addition of new electrons. This change in arrangement necessarily causes only a small chemical difference between neighboring elements. It can be seen from the table how, beginning with cerium, the inner lying 4 quantum groups are gradually completed until the number 32 is reached with the element 71 (Lu).

If now we go one step further the next element 72, in contrast to all preceding "rare earths," must differ in its outer structure. This causes a proportionally greater difference between the chemical characteristics of the elements 72 and 71 than those existing between the elements 71 and 70 or any other two members of the group of the rare earths; on the other hand the atomic structure of the element 72 shows an extraordinary similarity to the structure of the 40th element zirconium. The addition of another electron and simultaneously with this the increase by 1 of the number of electrons arranged in the outer group causes the element 72 to be quadrivalent in contrast to the trivalent constituents of Marignac's ytterbium. That the quantum theory of atomic structure requires unconditionally the quadrivalence of the element 72 can be shown by the

Number of electrons contained in the different groups of the neutralized atom

n k / N k	1_1	$2_1 2_2$	$3_1 3_2 3_3$	$4_1 4_2 4_3 4_4$	$5_1 5_2 5_3 5_4 5_5$	$6_1 6_2 6_3 6_4 6_5 6_6$	$7_1 7_2$
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 1					
⋮ ⋮	⋮	⋮					
10 Ne	2	8					
11 Na	2	8	1				
12 Mg	2	8	2				
13 Al	2	8	2 1				
⋮ ⋮	⋮	⋮	⋮				
18 A	2	8	8				
19 K	2	8	8	1			
20 Ca	2	8	8	2			
21 Sc	2	8	8 1	(2)			
22 Ti	2	8	8 2	(2)			
⋮ ⋮	⋮	⋮	⋮	⋮			
29 Cu	2	8	18	1			
30 Zn	2	8	18	2			
31 Ga	2	8	18	2 1			
⋮ ⋮	2	8	18	⋮			
36 Kr	2	8	18	8			
37 Rb	2	8	18	8	1		
38 Sr	2	8	18	8	2		
39 Y	2	8	18	8 1	(2)		
40 Zr	2	8	18	8 2	(2)		
⋮ ⋮	⋮	⋮	⋮	⋮	⋮		
47 Ag	2	8	18	18	1		
48 Cd	2	8	18	18	2		
49 In	2	8	18	18	2 1		
⋮ ⋮	⋮	⋮	18	⋮	⋮		
54 X	2	8	18	18	8		
55 Cs	2	8	18	18	8	1	
56 Ba	2	8	18	18	8	2	
57 La	2	8	18	18	8 1	(2)	
58 Ce	2	8	18	18 1	8 1	(2)	
59 Pr	2	8	18	18 2	8 1	(2)	
⋮ ⋮	⋮	⋮	⋮	⋮	⋮ ⋮	⋮	
71 Lu	2	8	18	32	8 1	(2)	
72 Hf	2	8	18	32	8 2	(2)	
⋮ ⋮	⋮	⋮	⋮	⋮	⋮	⋮	

N_k \ n_k	1_1	$2_1 2_2$	$3_1 3_2 3_3$	$4_1 4_2 4_3 4_4$	$5_1 5_2 5_3 5_4 5_5$	$6_1 6_2 6_3 6_4 6_5 6_6$	$7_1 7_2$
79 Au	2	8	18	32	18	1	
80 Hg	2	8	18	32	18	2	
81 Tl	2	8	18	32	18	2 1	
⋮ ⋮	⋮	⋮	⋮	⋮	⋮	⋮	
86 Em	2	8	18	32	18	8	
87 -	2	8	18	32	18	8	1
88 Ra	2	8	18	32	18	8	2
89 Ac	2	8	18	32	18	8 1	(2)
90 Th	2	8	18	32		8 2	(2)
⋮ ⋮	⋮	⋮	⋮	⋮		⋮	⋮

help of various considerations of which the following may be easily understood. A trivalency of the element 72 would be equivalent to the condition that in the successive building up of the atom as indicated above the sixty-ninth electron in the element 72 should be bound more strongly than in the element 73. The latter (tantalum) is in fact a quinquivalent element and so the sixty-ninth electron here belongs to the valency electrons. The loosening of the binding of an electron bound in a certain type of orbit in going from one element to the next is not compatible with the demands of quantum theory. This is due to the fact that such a transition is connected with an increase of the nuclear charge and therefore with an increase of the coulomb attractive force which determines the firmness of the binding.

After this unequivocal statement of the theory the discovery of Urbain, according to which Marignac's ytterbium should consist of the three constituent elements 70, 71 and 72, seemed to be a serious obstacle to the quantum theory. It was principally with the object of clearing up this point that induced Dirk Coster and the author to search for the element 72 which, according to the theory should be similar to zirconium.

Elements closely related chemically often accompany each other in minerals. Niobium (columbium) is very often accompanied by tantalum, molybdenum by tungsten, yttrium by holmium and other rare earths and so the immediate thing to do was to look for the missing element 72 in zirconium minerals. After the foundation of the X-ray spectroscopy by Moseley and its development in the hands of Siegbahn and his coworkers we have secured an ideal method for the identification of already known or as yet unknown elements and it seemed best to use this method of investigation.

3. The probable abundance of the missing element

It could not be predicted a priori whether the missing element was present in sufficiently large quantities to be recognizable in the minerals which were to be investigated. Yet there were many indications that the missing element was not rare. Elements with even atomic numbers are in general more abundant than those with odd atomic numbers. In the last year this question has been discussed many times by Harkins and others both on the basis of statistical data and in connection with speculations concerning the building up of the atomic nuclei.

These considerations appeared to us to be favorable as did also a comparison of the abundance of the elements Si, Ti, Zr and Th in the crust of the earth. The latter amounts in the lithosphere according to Clark, Washington and Jolly to

	per cent
SiO_2	59.09
TiO_2	1.05
ZrO_2	0.04
ThO_2	0.002

4. Discovery of hafnium

The investigation of the L-spectrum of the first Norwegian zircon enabled us to recognize at once the presence of two very distinct lines α_1 and α_2. These were situated exactly on the positions interpolated by means of the Moseley law. Shortly afterward the β_1, β_2, β_3 and γ_1 lines were also identified. Furthermore the comparison of intensities of the lines (which is an important control) was fully satisfactory and therefore the presence of not inconsiderable amounts of the element 72 in our mineral seemed to be definitely settled. This did not settle the question of the chemical properties of the element 72 at that time. Its presence in the zirconium mineral could indeed be purely accessory. The investigation of a great number of various zirconium minerals showed the presence of this new element in variable but in no case inconsiderable amounts in every one of them. We turned then to the commercial zirconium preparations labeled as pure and these also likewise showed the presence of the expected element. The near relationship of the new element to zirconium seemed therefore to be settled. The next problem was to separate the new element from zirconium. With this object we have fused the mineral with acid potassium fluoride and extracted the melt with hot water containing some hydrofluoric acid. Potassium zirconium fluoride is a substance very easily soluble in the hot and only slightly soluble in the cold water and is therefore adapted very well to a systematic crystallization (49). After a few crystallizations we investigated the different fractions. The new element was found to be enriched in the mother liquor while much weaker X-ray lines were emitted by the crystalline residue than by the original material. This same method starting from commercial pure zirconium preparations permitted us to secure rather quickly zirconium oxide which no longer showed the lines characteristic of the new element.

After the identification of the new element by means of X-ray spectroscopy was completely successful and after its presence in all the zirconium minerals and preparations investigated was proven and the partial separation from zirconium was successful, D. Coster and the present writer reported on January 2, 1923, in a letter addressed to *Nature* (16, 17, 18) the discovery of the new element and proposed for the new element the name Hafnium. This name was suggested by Hafnia the Latin name for the city of Copenhagen, in which the investigation was carried out, the work being done at the Institute for Theoretical Physics which is under the direction of Professor Niels Bohr.

5. *Earlier search for new elements in zirconium minerals*

Since the discovery of zirconium by Klaproth (1789), the discovery of new elements in zirconium minerals has often been announced.[2] Thus in 1845 Svanberg expressed the view that zirconium minerals contained an element similar to zirconium, which he called norium. Sjögren, another Swedish chemist, a few years later, again thought he had found Svanberg's norium in the zirconium mineral catapleiite. Then came Nylander's announcement (1869) of the discovery of jargonium, an element similar to zirconium, but having a lower atomic weight, and in the same year Church thought he had discovered the new element nigrium. We may add to this list the announcement of Ogawa (nipponium 1908), and of Hoffmann and Prandtl (1901), who believed they had found a new earth ("euxen earth") in the mineral euxenite. The genuineness of all these announcements was later disproved by different investigators, including Marignac, Weibull and Hauser, who showed the identity of norium and so on with zirconium. Most of these announcements were made on the basis of peculiar chemical reactions believed not to be characteristic of zirconium, and from this fact alone we can straightway conclude that the above announcements have nothing to do with the presence of hafnium, as zirconium and hafnium show the same chemical reactions. Nevertheless, the latter element was without exception undoubtedly present in the investigated samples.

At the time when X-ray spectroscopy was not yet known, the discovery of hafnium could hardly have been made by any other methods than by atomic weight determinations carried out with zirconium preparations of different origin, or by density measurements of these specimens. Such determinations were repeatedly carried out, but the methods used were (compare section V) not sufficiently accurate to enable the detection of the presence of 1 to 3 per cent hafnium in the preparations of

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[2] Compare P. Venable, Zirconium and its compounds, New York, 1922, where the whole reference on this subject may be consulted. The author wishes to acknowledge his indebtedness to Professor Venable for his excellent monograph on "zirconium and its compounds" which rendered the author an invaluable help during his investigations on the properties of hafnium. The author is also indebted to Messrs. Marden and Rich for the timely publication of Bulletin No. 186, Bureau of Mines in which the preparation of zirconium and its compounds is discussed.

zirconium investigated. Since the atomic weights of zirconium and hafnium are very appreciably different, it is to be expected that the percentage solubility of a zirconium compound will vary with its hafnium content. This ingenious method of attacking the problem of the possible presence of new elements in zirconium was chosen by Marignac. His failure was due solely to the fact that the technique of solubility measurements was at this time not sufficiently developed, to enable him to find the minute differences in the percentage solubilities of his different fractions.

We shall mention finally the attempt of Hauser to find new elements in zirconium, by investigating the optical spectrum of zirconium samples of different origin. The failure of his efforts was due to the intricate nature of the zirconium spectrum, and furthermore, to the fact that the variation of the intensity of the hafnium lines, which were all rather weak, was insufficient to enable the detection of the presence of a new element in his samples.

II. METHODS FOR SEPARATING HAFNIUM FROM ZIRCONIUM

In view of the great similarity between hafnium and zirconium, it is hardly possible to separate these two elements in a single operation. Methods based on repeated operations have therefore to be applied, from amongst which preference is given to crystallization methods, these being the easiest to carry out. The first condition which a compound used for this purpose has to fulfil is that of stability, viz., the compound must withstand decomposition even after a large number of crystallizations from water. This condition itself greatly restricts the number of the eligible zirconium compounds. Not a single zirconium compound, in which the zirconium atom is found in the cation, can be crystallized from water without decomposition, so that we have to have recourse to those compounds in which the zirconium atom is present in the anion. Owing to the great affinity of fluorine atoms for the electron, the complex zirconium fluoride anions are very stable ones. It was by crystallizing a compound containing such an anion that we were successful in achieving a complete separation of hafnium from zirconium.

1. Crystallization of the double fluorides

By adding the fluoride of potassium or ammonium to a solution of zirconium fluoride, two types of compounds can be obtained, viz., hexafluorides, $K_2Z^rF_6$; $(NH_4)_2ZrF_6$; and heptafluorides, K_3ZrF_7; $(NH_4)_3ZrF_7$. The heptafluorides of zirconium and hafnium having practically the same solubility (compare section III, page 21), we must crystallize the hexafluorides to obtain a separation. In preparing the double fluorides, it is thus necessary to avoid the addition of more than two molecules of the alkaline fluoride, to avoid the formation of the hepta salt. The solubility of both the potassium and the ammonium salt increases rapidly with the temperature; both crystallize in beautiful crystals, and are very suitable for a systematic crystallization (10, 34, 43). The difference in the molecular solubilities of the potassium salts is slightly greater than that of the ammonium compounds. Nevertheless, we gave preference to the latter compound on account of its much greater solubility, so long as we had to deal with large amounts of material. Starting with 2 kgm. of ammonium zirconium fluoride, containing about 3 per cent of hafnium salt, we obtained, after a great number of crystallizations ten fractions containing 30 to 80 per cent of hafnium. These fractions, the total weight of which amounted to 300 grams, were then converted into the potassium salt. After a few hundred operations, the best fractions of the potassium salt were found to be practically free from zirconium, but they contained an appreciable amount of columbium, the double fluorides of this element being still more soluble than those of hafnium, and thus accumulating in the best fractions. They also contained iron. To purify the hafnium from these and other impurities, we treated the K_2HfF_6 with sulfuric acid, ignited the sulphate obtained, and extracted the K_2SO_4 with hot water. The hafnium oxide was then converted into the neutral sulfate and dissolved in water, this solution being kept for some days at 40°, when a basic salt was precipitated. This was converted into hafnium hydroxide, dissolved in hydrochloric acid, and the oxychloride thus obtained was crystallized eight times from concentrated hydrochloric acid. The very pure product so obtained was used for the atomic weight determination described on page 17.

2. Crystallization of compounds other than fluorides

Similarly to the stable complex zirconium fluoride anions, complex zirconium oxalate can be obtained. A partial separation of hafnium from zirconium was also achieved by crystallizing the ammonium or the potassium zirconium oxalate (35, 37). Experience gained when carrying out these experiments seems to indicate that here again, as in the case of the double fluorides, compounds with a different content of oxalate exist. Furthermore, basic salts are formed. Only by the crystallization of some of these compounds can a reasonable separation be achieved.

When crystallizing the complex oxalate solution of zirconium hydroxide or zirconium nitrate, a minute concentration of the hafnium in the mother liquor was noted. We also partially separated hafnium from zirconium by crystallizing the double sulfates of potassium and ammonium, though the yield was here, just as in the case of the double carbonates, a rather poor one (37).

A much more successful separation was obtained by crystallizing zirconium oxychloride from about 12 N hydrochloric acid, whilst when less than 9 N acid was used, practically no separation of hafnium from zirconium occurred. In these crystallizations, hafnium is concentrated in the crystals, in contrast with all the above cases. This is of great importance, as all the impurities present concentrate in the mother liquor. When crystallizing the oxychloride in this way from concentrated hydrochloric acid, the elimination of casual impurities takes place simultaneously with a concentration of the hafnium content of the hafnium-zirconium mixture (35, 37).

3. Fractional precipitations

Numerous other methods of separation were tried, the results being more or less satisfactory.

a. Precipitation with bases. On fractionally precipitating a solution of zirconium oxychloride with ammonium or other bases, e.g., aniline, the first fractions were found to contain less hafnium than the last ones. The same was the case on precipitating potassium zirconium fluoride with ammonium. We also investigated the separation effected by the hydrolysis of the nitrates, when they were boiled with sodium thiosulfate. These experiments showed that hafnium nitrate hydrolyzed to a somewhat lesser degree than zirconium nitrate (33, 37).

b. Precipitation with basic chlorides. An amorphous precipitate of $Zr_2O_3Cl_2 \cdot 3H_2O$ is formed when an alcoholic solution of $ZrOCl_2 \cdot 8H_2O$ is precipitated with ether, acetone and the like. If a solution containing $ZrOCl_2 \cdot 8H_2O + HfOCl_2 \cdot 8H_2O$ is partially precipitated with ether, the first precipitates are poorer in hafnium than the later ones. Moreover, we have obtained hafnium preparations of high concentration in this way (35, 37).

c. Precipitation with hydrogen peroxide. Ten grams zirconium sulphate containing 1.5 per cent hafnium sulphate were dissolved in 300 cc. water. The solution was cooled with ice, and then 20 cc. of hydrogen peroxide of 30 per cent concentration, and 60 grams sodium hydroxide dissolved in 250 cc. of water were added. On warming the solution to 50° the hydrogen peroxide gradually decomposed and a precipitate was obtained. The solution was then cooled with ice, and the precipitate filtered off. After standing at room temperature for twenty-four hours, a new precipitate was obtained. On comparing the hafnium content of these two precipitates it was found that the second one contained about 1.5 times more hafnium than the first one, showing that the zirconium peroxide hydrate is less stable than the corresponding hafnium compound (37).

d. Precipitation with organic acids. To a very dilute solution of zirconium oxychloride a dilute solution of benzoic acid was gradually added. In this way seven consecutive precipitates were obtained. The fourth precipitate was found to contain slightly more hafnium than the first one, and the seventh slightly more than the fourth. Basic zirconyl benzoates have been prepared by Venable and Blaylock (59) by adding an aqueous solution of benzoic acid to a solution of zirconyl chloride. No definite compound was formed, but a series of basic zirconyl benzoates representing various degrees of hydrolysis, such as $ZrO(OH)_2 \cdot 2ZrO(C_6H_5CO_2)_2 \cdot 6H_2O$ and so on, were secured. Also, by gradually precipitating a dilute solution of zirconium oxychloride with salicylic or tartaric acid, a very slight accumulation of the hafnium content in the last fractions could be ascertained. In the last mentioned cases, especially in that of tartaric acid, it is difficult to secure equal consecutive fractions by adding the acid solution to that of the zirconium compound. At first no precipitation occurs, but later a very copious precipitate is obtained. The precipitated basic tartrates did not settle readily, and had to be whirled in a centrifuge (37).

e. Precipitation with phosphates. A mixture of zirconium and hafnium nitrates dissolved in concentrated nitric acid was precipitated with sodium phosphate in 11 equal fractions. It was found that the *eighth fraction* already contained less than one tenth of the hafnium amount present in the first precipitate (15, 33). It is of interest to note that zirconium was hitherto considered to have the most insoluble phosphate in concentrated acids; this rôle is now taken by hafnium.

From amongst all the precipitation methods, preference is to be given to the precipitation with phosphates. The conversion of the precipitated fractions into soluble compounds always requires, in contrast to the products of crystallization, more or less elaborate work; for this reason we did not carry out a total separation of hafnium from zirconium by the phosphate or any other precipitation method. It was recently suggested (9) to dissolve the phosphate precipitate in hydrofluoric acid and to crystallize the complex compound thus obtained, containing zirconium, phosphorus and fluorine. It is claimed (9) that the latter crystallization, or that of the ammonium or potassium salt of the above mentioned "acid," can be advantageously used to separate hafnium from zirconium.

4. Further methods of separation

The separation of hafnium from zirconium by distillation of their tetrahalides is rendered very inconvenient by the fact that the sublimation temperature of these compounds is lower than their melting point. The tetrachlorides, for example, can only be distilled at a pressure above 10 atmospheres. By sublimation, only an unsatisfactory separation could be obtained (35). It was also proposed to add to the zirconium tetrachloride compounds like phosphorus pentachloride, to lower its melting point (1). This and similar methods would only be practicable if it were possible to obtain a separation by not more than a few operations with their aid. Attempts to separate hafnium from zirconium, based on the different decomposition temperatures of their sulphates, were only partly successful.

By dialyzing a solution containing the nitrates of zirconium and hafnium, the dialysate was found to contain a slightly higher hafnium-zirconium ratio than the original solution. This is presumably due to a somewhat greater tendency of zirconium to hydrolyze, and thus to accumulate in the dialyzer.

III. PROPERTIES OF HAFNIUM

So far it was chiefly endeavored to elucidate the properties of the compounds of hafnium. The only statements available on the properties of metallic hafnium are the following: It has the same crystalline structure as the metallic zirconium. It was found[3] to crystallize in the hexagonal system, the side of the unit triangular prism being 3.32 and its height 5.46. Therefore the atomic volume works out to be 15.7. The metal was prepared by reducing H_2HfF_6 with sodium.

1. Atomic weight

Professor Hönigschmid kindly undertook to determine the atomic weight of hafnium by preparing the tetrabromide and

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[3] The determination of the crystal structure was carried out by Dr. Mark in Dahlem.

determining the ratio $\frac{HfBr_4}{4Ag}$. The last preparations supplied by us contained between 0.57 and 0.16 per cent ZrO_2 as revealed by X-ray spectroscopy. The values 177.79, 177.80 and 178.32, 178.33 were found for the atomic weight. Taking into account that the presence of 1 per cent ZrO_2 lowers the atomic weight by 1.4 units, the atomic weight works out in best agreement to be *178.64* to *178.59* (45).

2. Molecular volume of the oxide and double fluoride

The densities ($d_{20°}$) of ZrO_2 and HfO_2 were determined by the pyknometer method to be 5.73 and 9.68. Taking for the atomic weights of the two elements 91.3 and 178.6 the values 21.50 and 21.76 are obtained for the molecular volumes of the two oxides.

Hassel and Mark (30) determined the crystalline structure of $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$ by using X-ray methods. The volumes of the elementary cubes of the heptafluorides were found by them to be:

$(NH_4)_3ZrF_7$	818.2 Å³
$(NH_4)_3HfF_7$	830.6 Å³

The elementary cube containing 4 molecules, the molecular volumes of the two compounds are found to be 123.9 and 125.7, showing thus a difference of 1.5 per cent.

3. Solubility of the double fluorides

We determined (37, 41) the solubility of the $(NH)_2HfF_6$; $(NH_4)_3HfF_7$ in K_2HfF_6 and of the corresponding zirconium compounds both in water and in NH_4F solutions. Some data on the solubility of K_2ZrF_6 were already available from earlier researches (49, 50).

a. Solubility of the ammonium double fluorides. The results are seen from figures 1, 2 and 3. The first figure shows the change of solubility with temperatures, the second the effect of increasing NH_4F concentration on the solubility of the heptafluorides at 20° and in the third one the concentration of the

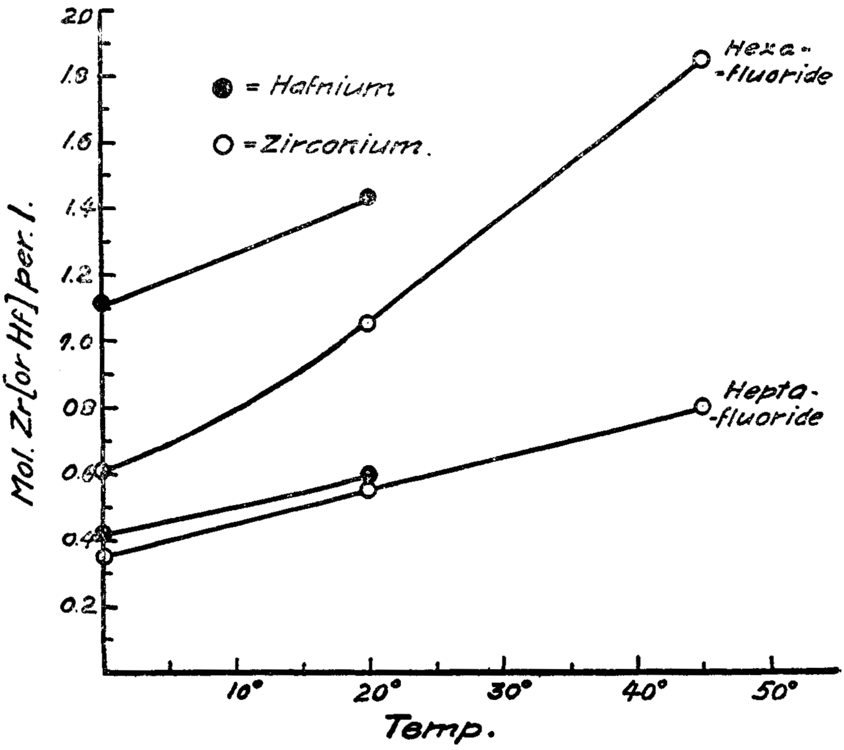
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Mol. Zr [or Hf] per l.
● = Hafnium
○ = Zirconium.
Hexa-fluoride
Hepta-fluoride
10°
20°
30°
40°
50°
Temp.

FIG. 1

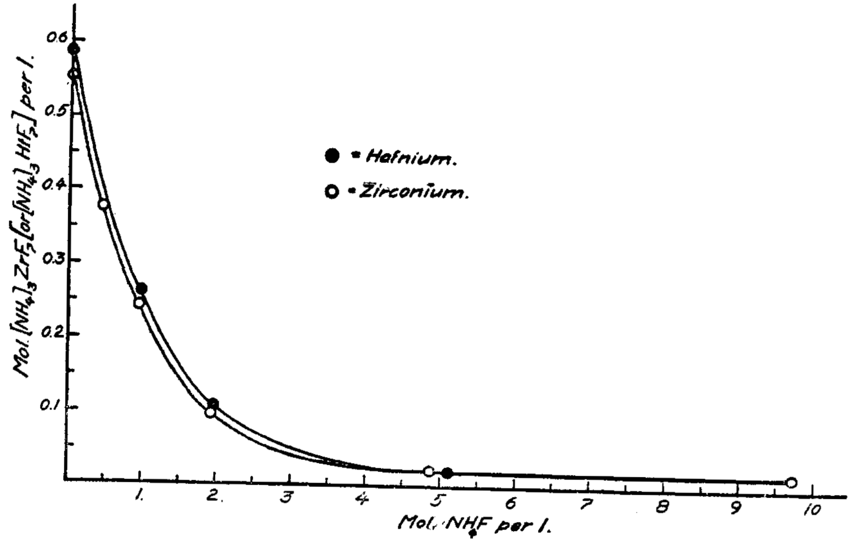
0.6
0.5
0.4
0.3
0.2
0.1
Mol. (NH4)3ZrF7 [or (NH4)3HfF7] per l.
● = Hafnium.
○ = Zirconium.
1.
2.
3
4
5
6
7
8
9
10
Mol. NH4F per l.

FIG. 2

heptafluorides is plotted on the abscissa and that of the hexafluorides on the ordinate.

When determining the solubility of the hexafluoride in a solution of ammonium fluoride the solubility first increases with increasing concentration of the latter due to the formation of heptafluoride. When the concentration of 0.165 mol. NH_4F per liter in the case of the zirconium salt, and of 0.160 mol. per liter in the case of the hafnium salt, is reached the solution is saturated, both as regards the hexa- and heptafluoride. If the ammonium fluoride concentration of the solution is further

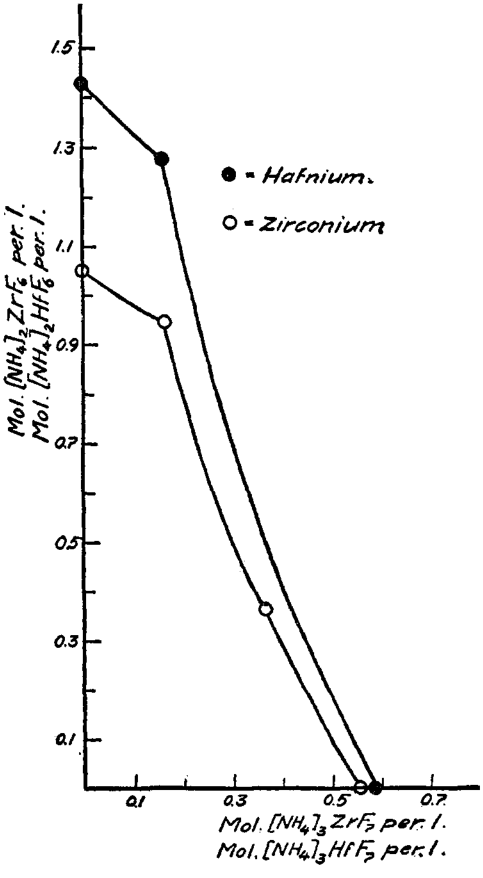

FIG. 3

increased, the crystal residue of the hexafluoride becomes transformed into heptafluoride. If we still go on, after the transfromation of the whole crystal residue into heptafluoride, to increase the ammonium fluoride concentration of our solution, the solubility of the zirconium or hafnium salt is bound to decrease. It is therefore we find at the point in which the solubility curves of the hexa- and heptafluorides cut each other a maximum solubility for the totality of the salt corresponding to 1.109 mol. zirconium, and 1.439 mol. hafnium per liter, whilst the solubility of the hexafluorides is only 1.050 and 1.425 mol. and that of the heptafluorides only 0.551 and 0.588 mol respectively.

b. Solubility of the potassium double fluorides. The molecular solubility of the potassium salts in 1/8 N and 5.89 N HF is seen from the following numbers.

SOLVENT	SOLUBILITY AT 20° OF	
	K_2ZrF_6	K_2HfF_6
1/8 N HF	0.0655	0.1008
5.89 N HF	0.1297	0.1942

The solubility of the potassium hexafluorides of the silicon group is seen from the figures below. The solubility increases when proceeding from silicon to hafnium and diminishes abruptly when proceeding further to thorium.

t°	SALT	SOLVENT	SOLUBILITY IN MOL. PER LITER
17.5°	K_2SiF_6	Water	0.00544
20°	K_2TiF_6	1/8 N HF	0.04825
20°	K_2ZrF_6	1/8 N HF	0.06545
20°	K_2HfF_6	1/8 N HF	0.10080
20°	K_2ThF_6	1/8 N HF	"insoluble"

4. Solubility of the oxychloride

The variation of the solubility of the oxychlorides at 20° with increasing hydrochloric acid concentration is shown in figure 4. It is to be observed that with increasing acid concentration the solubility first rapidly and later slowly decreases but after the concentration of about 9 mol. per liter is attained an increase of the solubility with increasing acid concentration begins. This increase of the solubility is possibly due to the formation of complex compounds such as H_2ZrOCl_4 and H_2HfOCl_4. It is of interest to note that while the solubility of the hafnium salt is practically the same as that of the zirconium salt in hydrochloric acid when the concentration of the latter does not exceed 9 mol. per liter, it is appreciably less soluble in more concentrated hydrochloric acid. When determining the solubility of hafnium oxychloride in still more concentrated acid (11.4 N) a smaller solubility, namely 0.0619, was observed. Further work on this point is in progress.

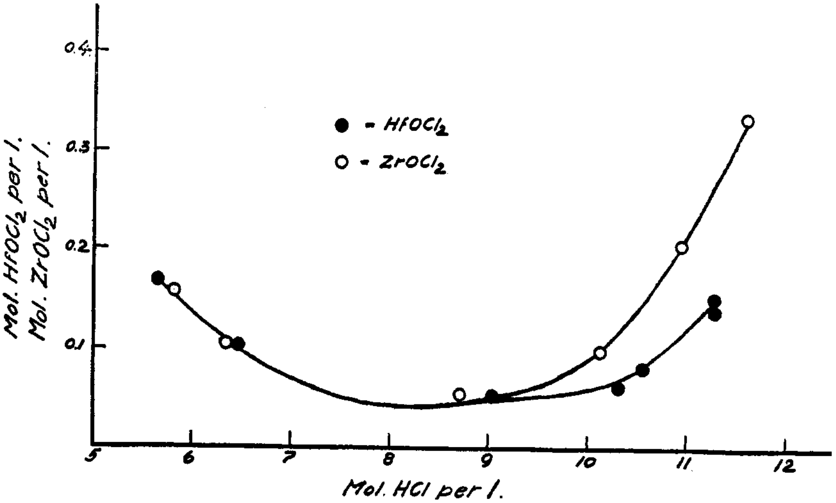

FIG. 4

5. *Magnetic susceptibility of the oxide*

The following values of the magnetic susceptibilities per gram (*X*) were found (37)

ZrO_2	-0.112×10^{-6}
HfO_2	-0.110×10^{-6}

Both oxides are thus diamagnetic.

6. Refractive index

These were determined for (*a*) the potassium hexafluorides, (*b*) the potassium and the ammonium heptafluorides and finally (*c*) for the oxychlorides (37). The following values were obtained.

a. K_2ZrF_6 monoclinic twins...... N (max.) = 1.466; N (min.) = 1.455
K_2HfF_6 monoclinic twins...... N (max.) = 1.461; N (min.) = 1.449

	N	Δ*N*
b. K_3ZrF_7 regular octahedron...	1.408	0.005
K_3HfF_7 regular octahedron...	1.403	
c. $(NH_4)_3\,ZrF_7$ regular octahedron......................	1.433	0.007
$(NH_4)_3\,HfF_7$ regular octahedron......................	1.426	

d. $ZrOCl_2+8H_2O$ Needle like crystals...................... $N(\omega) = 1.563$; $N(\epsilon) = 1.552$
$HfOCl_2+8H_2O$ Needle like crystals...................... $N(\omega) = 1.557$; $N(\epsilon) = 1.543$
$\Delta N(\omega) = 0.006$; $\Delta N(\epsilon) = 0.004$

7. Optical and X-ray spectra

The optical spectrum of hafnium has been investigated in the region between 7240.9 and 2253.95 A.U. where 760 lines have been measured in the arc and 683 in the spark spectrum (31).

It is of interest to note that several of the strongest hafnium lines are present as weak lines in the zirconium spectrum as measured by earlier investigators (6,23). This was to be expected, because all zirconium minerals and consequently all commercial zirconium preparations contain hafnium.

Detailed investigations on the X-ray spectra were carried out as well. The wave lengths of the principal 16 emission lines of the L-series (14, 51) and 2 lines of the M-series were determined. The K-absorption limit (13) and three L-absorption edges (14, 51) were also observed. From the above data the values for the different levels of the atom were calculated. The reader is referred to page 26 for a fuller discussion of this subject.

IV. METHODS FOR THE DETERMINATION OF THE HAFNIUM CONTENT OF ZIRCONIUM

Any chemical reaction which is characteristic of zirconium can also be used to identify hafnium, as for example, the precipitation of phosphates insoluble in concentrated mineral acids (33), the coloring of tumeric paper, and so on. Recently, different micro-reactions have been tried (52), using both zirconium which was purified from hafnium, and a concentrated hafnium preparation. The reactions tried were: precipitation with potassium dioxalate, with rubidium chloride and ammonium fluoride, with picric acid, with α-nitroso-β-naphthol, but not the slightest difference was found in the two cases.

As hafnium is always found associated with zirconium in nature, and considering the great difficulties which the separation of these elements involves, the practical analytical problem met with in dealing with hafnium is the determination of the hafnium content of zirconium preparations. When such preparations are purified from all impurities, their hafnium content can easily be determined by density measurements, or by the analysis of any well-defined compound, as for instance one of the double fluorides, the sulfate, or one of the tetrahalides. But if impurities are present, the method of quantitative X-ray spectroscopy has to be applied.

1. Density measurements

The oxide of hafnium has a density nearly twice as large as that of zirconium oxide (compare page 33). Density measurements of the oxide thus enable a fairly accurate determination of its hafnium content. The calculation of the latter is based on a standard value of the density of each of the two oxides. As the density varies with the mode of preparation of the oxides, care must be taken that these are always prepared by exactly the same method. In preparing the oxide of zirconium, for example, Venable and Bell[4] (59) ignited the oxychloride, and

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[4] This preparation probably contained about 1 per cent HfO_2 (compare p. 30), whilst Nilson and Pettersson's preparation had presumably a somewhat higher hafnium content.

found a value of 5.49, whilst Nilson and Pettersson (59) found the value of the density of a sample obtained by igniting the sulfate to be 5.85. This large difference in the densities found is presumably due to the presence of varying amounts of amorphous oxide, which has a lower density than the crystalline compound. By igniting the preparation at a sufficiently high temperature, or still better by melting it, the whole oxide can be converted into the crystalline state. Because of the extremely high melting point of zirconium oxide, such a procedure is fraught with very great difficulty, and it was for this reason that we compared the densities of the oxides prepared and treated in exactly the same way. The normal sulfates were first ignited at a moderate temperature, and then at 1000° for several hours, and their density determined by the pyknometric method. The hafnium oxide content of the preparation could then be calculated from the density (d) found, according to the formula

$$X = \frac{d - 5.73}{0.0394}$$

The presence of 1 per cent hafnium in a zirconium specimen can still be ascertained by this method.

As with the density of the oxide, so also that of the double fluorides indicates the hafnium content of zirconium. On account of the larger molecular weight of the double fluorides, this method is less sensitive. By crystallizing double fluorides, density measurements of such compounds may, however, be of great value. It is sufficient to remove tiny crystals of, for instance, $(NH_4)_2ZrF_6$ from the different fractions, and to determine their density by the flotation method. An increase in the hafnium content of the fractions will be at once revealed by the increasing density of the crystals. Mixtures of methylene iodide and bromoform can be used as the flotation liquid. The density of $(NH_4)_2HfF_6$ being greater than that of methylene iodide, this method cannot be used to determine the density of crystals with a very high hafnium content, though the density of methylene iodide can be increased somewhat by dissolving selenium or other substances of high density in it.

2. *Analysis of the double fluoride*

The determination of the ratio of the double fluoride to the oxide, or of the former to the ammonia content of the compound also provides us with quick and easy methods for determining the hafnium content of zirconium. For example:

a. Analysis of $(NH_4)_2ZrF_6$. The salt was dried at 60°, weighed, and its ammonia content determined.

The ratio $\frac{NH_3}{\text{salt}}$ was found to be 0.1149, from which it follows that the preparation contained 73.4 per cent HfO_2 and 26.6 per cent ZrO_2.

b. Analysis of $(NH_4)_3ZrF_7$. The same material analyzed as heptafluoride gave the following values:

$\frac{NH_3}{\text{salt}}$ = 0.1534, corresponding to 73.5 per cent HfO_2 and 26.5 per cent ZrO_2

$\frac{\text{Oxide}}{\text{salt}}$ = 0.5344, corresponding to 73.6 per cent HfO_2 and 26.4 per cent ZrO_2

The analysis of the K_2ZrF_6 previously used by Marignac to determine the atomic weight of zirconium, can also be used to ascertain the hafnium content of zirconium.

3. *Analysis of the sulfate*

By determining the ratio of the weights of the sulphate and oxide, the hafnium content of the zirconium sample can easily be calculated. Such determinations (33, 58) can be readily carried out, but no accuracy can be claimed (44).

Concerning the analysis of the tetrachlorides and bromides compare page 29.

4. *X-ray spectroscopy*

This method is based on the comparison of the intensity of one of the X-ray lines of hafnium with that of a standard substance, mixed in known amount, with the preparation to be investigated. For example, to determine the hafnium content of zirconium oxide we mix a sufficient amount of the oxide of the element 71 to our sample, to ensure that the L-β_2 line of the element 71 is as intense as the corresponding hafnium L-β_1 line. The next step is to mix with zirconium oxide free from hafnium suitable amounts of both the elements 71 and 72, so that the above mentioned lines appear with the same intensity. For example, if on the application of a field of 20,000 volts, the latter ratio were found to be 2.5, it follows that the amount of the element 71 which would have to be added to the zirconia to get the 71 L-β_2 line of the same intensity as the 72 L-β_1 would require to be divided by 2.5 to get the hafnium oxide content of the zirconia sample.

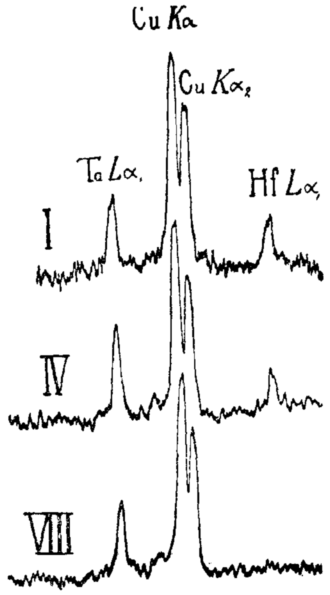

FIG. 5

It is advisable to compare the intensities of two lines lying very close to each other on the photographic plate, in order to diminish the possible error due to different exposure of the different parts of the plate. For this reason we give preference to the comparison of the 71L-β_2 with the 72 L-β_1 line to that of any other two lines, as with our apparatus the distance between these two lines on the photographic plate, using a calcite crystal, amounts only to 0.16 mm. (19, 37).

Instead of determining experimentally the intensity ratio of the two lines, this can be assumed to be unity when strictly corresponding lines of two neighboring elements, e.g. the L-α_1 lines of the elements 72 and 73, are compared (15). This procedure is simpler than that above described, but it is less trustworthy and can lead to erroneous results. It often happens that we do not want to know the absolute amount of hafnium present in zirconium preparations, but only wish to compare the hafnium contents of two samples; in such a case the latter method can be used advantageously. This case arises when we are investigating the effect of a partial crystallization or precipitation on the hafnium content of a zirconium compound. We convert the compound into zirconia, and mix the same amount of tantalum oxide with both samples; the comparison of the intensity ratio of the two lines indicates the effect of crystallization on the hafnium content of the preparation.

The effect of the partial precipitation of zirconium nitrate dissolved in concentrated nitric acid by sodium phosphate is shown in figure 5. This represents a photometric curve of the blackening of the photographic plate, taken with the Moll microphotometer. The copper lines are due to the copper anticathode. The original mixture contained about 4 per cent of hafnium oxide; 10 per cent of tantalum oxide was added to each of the different fractions. The figure gives the photometric curves of the first, fourth and eighth fractions. These curves show clearly that the hafnium phosphate is precipitated chiefly with the first fractions, and thus that the phosphate of hafnium is less soluble than that of zirconium.

V. THE ATOMIC WEIGHT OF ZIRCONIUM AND THE HAFNIUM CONTENT OF THE ZIRCONIUM PREPARATIONS USED IN ITS DETERMINATION

The values of the atomic weight of zirconium arrived at by different investigators show very appreciable variations. These variations were due to the unreliability of the methods used, and supply the reason why hafnium was not previously detected on the basis of atomic weight determinations. So far as we can ascertain, the hafnium content of the samples used in the different investigations, the results of which are shown in the following table, varied between 0.5 and 2 per cent (40, 36).

Values of the atomic weight of zirconium

YEAR	INVESTIGATOR	RATIO	ATOMIC WEIGHT	PER CENT OF HfO_2
1825	Berzelius	$Zr(SO_4)_2/ZrO_2$	89.46	2.0 (?)
1844	Hermann	$ZrCl_4/$?	88.64	1.0 (?)
1844	Hermann	$2ZrOCl_2$, 9 H_2O/?	89.98	1.0 (?)
1860	Marignac	K_2ZrF_6/K_2SO_4	90.03	0.5
1860	Marignac	K_2ZrF_6/ZrO_2	91.54	0.5
1881	Weibull	$Zr(SO_4)_2/ZrO_2$	89.54	2.0
1881	Weibull	$Zr(SeO_4)_2/ZrO_2$	90.79	2.0
1889	Bailey	$Zr(SO_4)_2/ZrO_2$	90.65	6.0 (??)
1898	Venable	$ZrO\ Cl_2$, $3H_2O/ZrO_2$	90.81	1.0
1917	Venable and Bell	$ZrCl_4/4Ag$	91.76	0.7–1.0
1924	Hönigschmid	$ZrBr_4/4\ Ag$	91.22	0*

* The sample used was purified by us from hafnium by the double fluoride method.

As the presence of 1 per cent HfO_2 increases the atomic weight of zirconium by 0.6 unit, the above hafnium contents correspond to errors of from 0.3 to 1.2 units, while the values found differ by as much as 3 units; and even values found by the same investigator, for example, those of Marignac, differ by 1.5 units. We can thus easily understand why the presence of variable amounts of an element of such a high atomic weight as hafnium in the zirconium preparations used could escape detection. It is of interest to note that all the earlier methods gave too low values for the atomic weight (except the second method used by Marignac), but the presence of hafnium fortunately partly compensated the error due to the method. This fact also explains why the atomic weight of zirconium as accepted by the international Committee of Atomic Weights (90.6), differs only by 0.7 unit from the true atomic weight, as quite recently ascertained by Venable and Bell, Hönigschmid, and Aston. Venable and Bell (61) and Hönigschmid (44) used modern and reliable methods, the first two distilling the tetrachloride and determining the ratio $ZrCl_4/4Ag$, while the last-named worker distilled the tetrabromide and determined the ratio $ZrBr_4/4Ag$. The material used by Hönigschmid was purified from hafnium, and found by us to be free from that element. Through the kindness of Professor Venable we were also able to investigate the hafnium content of the different specimens used by him and Dr. Bell, and we established the presence of 0.7 to 1 per cent of HfO_2 in them (62). Taking into account these results, the atomic weight found by Venable and Bell has to be reduced to an average value of 91.3, or in best accord with the value found by Hönigschmid. Moreover, considering that Aston obtained the value of 91.2 to 91.4 by the positive ray method, the intricate problem of the atomic weight of zirconium may now be regarded as settled.

VI. THE OCCURRENCE OF HAFNIUM IN NATURE

1. *The hafnium content of zirconium minerals*

In collaboration with Mr. V. Thal Jantzen, the hafnium content of practically every type of zirconium mineral has been determined (39, 37). The chief results of these determinations are seen in the following table, which shows the HfO_2/ZrO_2 ratio of minerals of both nepheline syenitic and of granitic origin.

MINERALS OF NEPHELINE SYENITIC ORIGIN (Products of alkaline residual crystallization)		MINERALS OF GRANITIC ORIGIN (Products of silicious residual crystallization)	
	$\frac{HfO_2}{ZrO_2}$		$\frac{HfO_2}{ZrO_2}$
Favas	0.007	Naegite	0.07
Catapleiite	0.01	Malacon	0.07
Eudialyte	0.01	Alvite	0.11
Elpidite	0.01	Cyrtolite	0.4
Baddeleyite	0.012	Thortveitite	0.5
Rosenbuschite	0.015		
Eucolite	0.02		
Polymignite	0.02		
Wöhlerite	0.03		
Zircon.*	0.015	Zircon	0.04

* Zircons are partly products of alkaline and partly of silicious residual crystallization.

It is clearly shown by the above table that while in zirconium minerals that are products of alkaline residual crystallization (25, 27) the HfO_2/ZrO_2 ratio is on the average about 0.015, an appreciably higher ratio—about 0.04—is found in minerals which are products of a less basic, silicious residual magma. Zirconium minerals of granitic origin being far more abundant, the average $\frac{HfO_2}{ZrO_2}$ ratio may work out to be about 0.03. In the primary gaseo-liquid earth material a constant Hf/Zr ratio prevailed. This is most conclusively borne out by the fact that a mixed element, for example chlorine, no matter from what source it may be derived, always contains the same admixture of Cl^{35} and Cl^{37}. This can hardly be accounted for otherwise than by assuming that in the material of the original gaseo-liquid earth, a homogeneous mixture of the two chlorines was present, (viz., that there was a constant ratio $Cl^{35}:Cl^{37}$), and that all the numerous geo-chemical changes which have taken place during and since the solidification of the earth's crust had no influence on this ratio. Zirconium and hafnium being chemically separable, some change was bound to occur in the original Hf/Zr ratio under the influence of the numerous geochemical processes to which this admixture would later be subject. Nevertheless, these changes, consequent on the great chemical similarity of hafnium and zirconium, would be less marked than those occurring in the ratio between tungsten and molybdenum, between tantalum and columbium, between yttrium and the elements of the rare earth group, and very probably in the ratio between any other pair of elements. In the course of the formation of minerals, the original Hf/Zr ratio was altered in favor of zirconium in the products of alkaline residual crystallization, thus leaving behind a zirconium richer in hafnium than in the gaseo-liquid earth. In the products of silicious residual crystallization, on the other hand, we find an appreciable increase of the above ratio. The greatest ratio is found in the case of the minerals alvite (26), cyrtolite and thortveitite, the highest ratio being that for the last mentioned mineral. It is well known, that all zircons exhibit radioactive properties, by virtue of the presence in them of minute amounts of uranium and thorium. Zircons with a large uranium or thorium content were also found in several cases to contain rather large amounts of hafnium, and the radioactivity of zircons accordingly shows a rough parallelism with their hafnium content. Radioactive measurements may thus prove useful when a search is being made for zircons with a high hafnium content (39, 37).

It is of interest to note that we have not been able to prove the presence of hafnium in any thorium mineral—even though thorium is the higher homologue of hafnium. Neither thorite, thorianite, nor orangite contain hafnium or zirconium. Furthermore, titanium minerals like rutile and ilmenite were found to be free from hafnium (37, 39).

2. The hafnium content of the earth's crust

Clark and Washington estimate the zirconium content of the earth's crust to be about 0.028 per cent. If we take the average hafnium content of zirconium to be 3 per cent, we find the hafnium content of the earth's crust to be 0.001 per cent. The actual hafnium content of the earth's crust is thus about 1/100,000. The above numbers represent the relative abundance of the two elements in the upper layer of the silicate phase, as rocks and minerals, the analysis of which lead to the above data, are only available for this layer. The average zirconium content of the *total* silicate phase must be less than 0.028 per cent and that of hafnium accordingly less than 0.001 per cent, as these elements, just like other lithophilic elements of residual crystallization, e.g., thorium, uranium, columbium and so on, are found comparatively strongly concentrated in the upper (the peripheral) layer of the silicate phase. For the average zirconium or hafnium content of the whole earth material very appreciably smaller numbers result, these elements being typically lithophilic ones, i.e., they are practically only found in the silicate mantle (25). In hardly any other case can the ratio of the abundance of two elements be determined so easily and conclusively as in that of zirconium and hafnium, owing to the great similarity of these two elements.

VII. GENERAL CONCLUSIONS

1. The relationship between hafnium and zirconium, as compared with the similarity between other pairs of elements

The close relationship between hafnium and zirconium is clearly borne out by the chemical and geochemical evidence adduced in the foregoing chapters. In this section we shall compare this relationship with the similarity between other closely related elements belonging to different periods of Mendelejeff's system. Numerical data are available about the following properties, and these we must therefore consider primarily:

a. Molecular volume of the oxides.

b. Solubility. (The ease with which they can be separated by crystallization and the like (degree of basicity).)

c. Refractivity. (Molecular refraction.)

The great similarity between zirconium and hafnium is so firmly established by what has already been said, that only the comparison of their similarity with that existing between the most closely related elements has any immediate interest; for example, the similarity existing between rubidium and caesium, strontium and barium, yttrium and the group of rare earths, columbium and tantalum, molybdenum and tungsten, requires consideration.

a. The density and molecular volume of the oxides of the titanium group is seen from the following table:

	DENSITY	MOLECULAR VOLUME
TiO_2	4.26	18.8
ZrO_2	5.73	21.5
HfO_2	9.68	21.7
ThO_2	10.22	25.8

The molecular volumes of the oxides of titanium and its higher homologues as functions of their atomic numbers are also plotted in figure 6. While we find appreciable differences between the molecular volumes of the oxides of titanium and zirconium, and likewise between those of hafnium and thorium, in the case of zirconium and hafnium, corresponding to the change from 42 to 72 in the atomic number, we only find a change of about 1 per cent in the molecular volumes. Appreciably greater values are found for the difference in the molecular volumes of the oxides of yttrium and most of the rare earth metals, or of columbium and tantalum. The close relationship between hafnium and zirconium, compared with that of zirconium and titanium on one side and hafnium and thorium on the other is far from being an unique phenomenon inthe periodic table. We find for instance similar regularities in the third, fifth and sixth vertical rows of Mendelejeff's system. Molybdenum and tungsten are much more similar than chromium and molybdenum, or tungsten and uranium. Of 49 analyses of vanadium minerals in Doelter's "Handbuch," we find none indicating columbium; of 211 analyses of titanium minerals zirconium is present in only ten cases, while the corresponding members of the fourth and fifth periods are found in most cases associated in nature (25, 37).

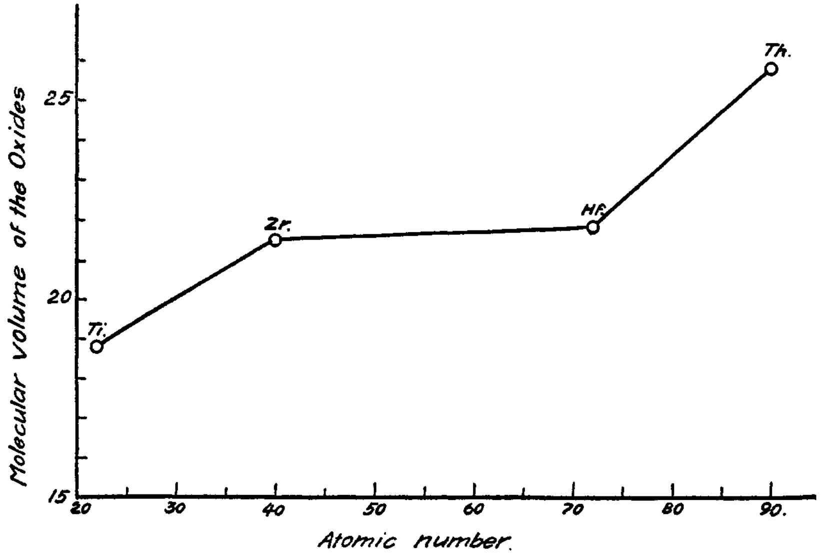

Fig. 6

b. The close relationship between hafnium and zirconium is best shown by the small differences in the solubilities of corresponding compounds. Even in the case of the potassium double fluorides the ratio of the solubilities of the corresponding compounds amounts only to 1.6. Much greater differences were found between the solubilities of K_2CbF_7 and K_2TaF_7 (in 5 N HF), for which a ratio of 5 was determined, and a ten times greater value was found between the solubilities of the fluorides (oxyfluorides) of these elements in an excess of potassium fluoride. The separation of tantalum from columbium, which, like that of hafnium from zirconium, can best be carried out by crystallization of the double fluorides, is in itself a difficult task, and we can only expect to get a separation of hafnium from zirconium after a very large number of crystallizations. In full accordance with this conclusion, we also found that geochemical processes, chiefly governed by the prevailing differences in basicity and solubility, influenced the original zirconium/hafnium ratio of the gaseo-liquid earth material much less than they influenced the molybdenum/tungsten, the columbium/tantalum, and even the yttrium/rare earth ratios. No zirconium is found in nature without hafnium, and no hafnium without very appreciable amounts of zirconium, whereas we know several tungsten and tantalum minerals, and several cases in which the original yttrium/rare earth ratio underwent very pronounced alterations (27).

c. The comparison of the refractive index (or of the molecular refraction) of corresponding compounds is also suitable for the comparison of the chemical similarity between two pairs of elements, in that it can be measured with great exactness, and because a very small amount is sufficient for the measurement.

In the four cases investigated (compare page 23), the refractive index of the hafnium salt was found to be very slightly less than that of the corresponding zirconium compound. The difference is in all cases much smaller than that between the refractive indices of such related compounds as the sulphates of rubidium and caesium, of strontium and barium, the potassium fluorides of columbium and tantalum (28), the molybdates, and tungstates of lead and the potassium cyanides of ruthenium and osmium. However, we find similar small differences between the refractive indices of yttrium and the corresponding compounds of the rare earth elements.

Owing to lack of data, it is difficult to compare the similarity between zirconium and hafnium with that between two neighboring elements of the rare earth group, e.g., between the closely related elements 70 and 71; but we may conclude with certainty from the chemical and geochemical data discussed in the foregoing chapters that hafnium and zirconium are more closely related than any other two elements belonging to different periods. The chemical similarity between two corresponding elements of the fourth and fifth series of the periodic system, namely, between rubidium and caesium, strontium and barium, yttrium and the rare earths, zirconium and hafnium, increases

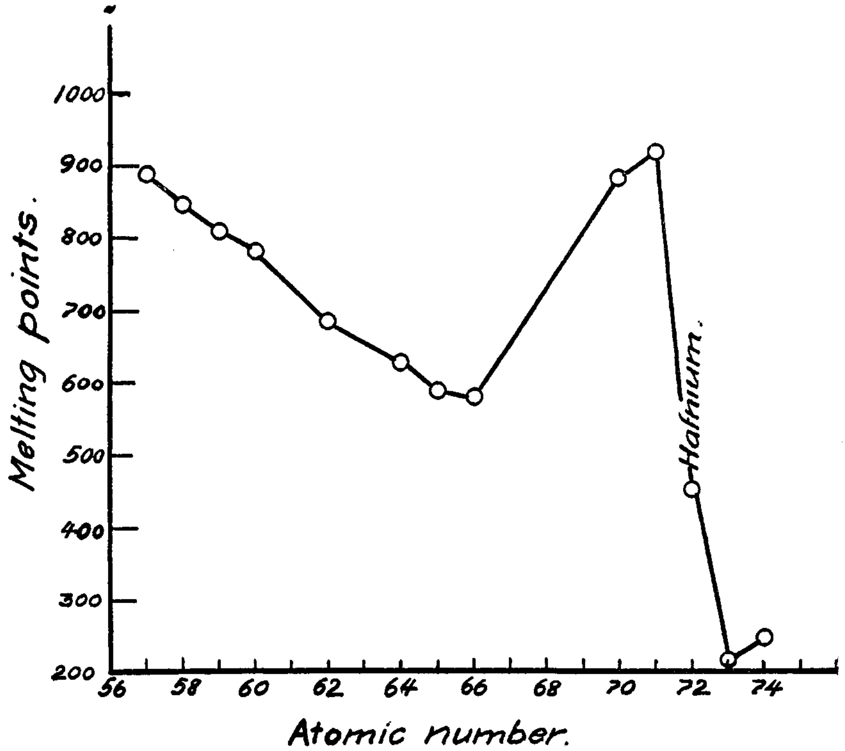

FIG. 7

in the order given, and reaches a maximum similarity in the last case. Columbium and tantalum are very closely related chemically, but not in as high a degree as the last-mentioned elements, and this applies still more to the case of the relationship between molybdenum and tungsten.

2. The properties of hafnium as compared with those of the other elements of the fifth period

In figure 7, the melting points of the chlorides of the elements between caesium and tungsten are plotted against the atomic number of their metallic constituent. The curve shows that while the melting point fluctuates between 920° and 588° in the long interval between the elements 55 and 71, a sudden drop amounting to 500° takes place when we pass from the element 71 to the element 72, and this clearly indicates the very great change which ensues in the course of the successive building up of atoms (compare page 6), when one more electron is added to a configuration containing 71 electrons, which represents the last member of the rare earth group. The reason why we consider only the melting points of the chlorides is that only for these compounds are numerical data available for practically every member of the fifth period. But also when we compare any of the chemical properties of the elements of this period, a very abrupt change will be found when we pass from the element 71 to the element 72. Similar very large differences are found between the boiling points of the elements 55–71 and that of 72. The solutions of the chlorides of the elements 55 to 71 show no signs of hydrolysis the solution of the chloride of the element 71 is neutral towards methyl orange (11), but the chloride of hafnium hydrolyzes at once to a very high degree when it comes into contact with water. The normal sulfates of the elements 55 to 71 can only be decomposed by prolonged heating at very high temperatures, whereas the sulphate of hafnium loses appreciable amounts of sulphuric acid even at 500°.

But the conspicuous change in the constitution of the atom after the completion of the inner groups of electrons which takes place with the last rare earth in most beautifully shown when we consider the energy levels calculated from X-ray data (51). These are shown in figure 8, in which the energy terms of different levels are plotted against the atomic number of the elements of the fifth period. The emphasized features are most distinctly shown in the curves relating to the levels N_{VI}, N_{VII}, O_{I} and $O_{II,\,III}$, where sharp bends occur at the element 71, showing the termination of the rare earth group in a remarkable manner.

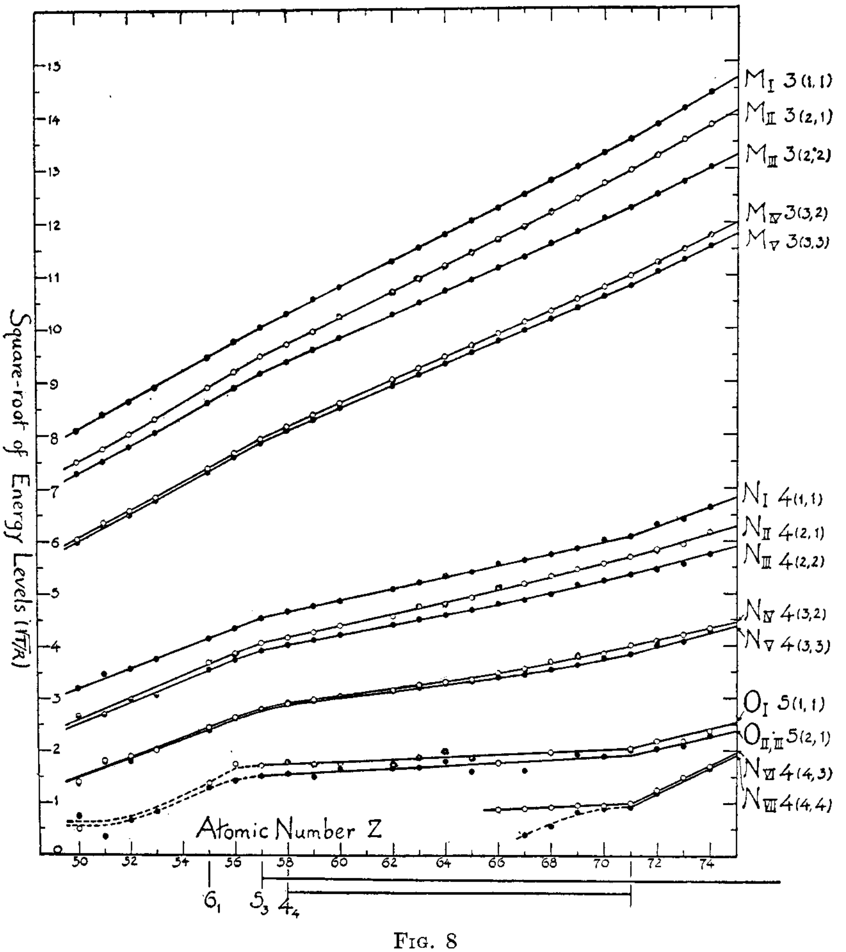

FIG. 8

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