Hugo Müller Lecture.

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BY GEORGE VON HEVESY.

The Chemistry and Geochemistry of the Titanium Group.

MR. PRESIDENT, LADIES, and GENTLEMEN,—May I be permitted to express to you, Mr. President, and to the Council of the Chemical Society my hearty thanks for the great honour you have shown me in inviting me to deliver the Hugo Müller Lecture this year.

For the subject of the lecture I am to give to-day I have chosen the problem of the chemistry and geochemistry of the titanium group, a problem of equal interest to Chemistry and to Mineralogy.

1.

The head of the group, titanium, is one of the most abundant elements; the last member of the group, thorium, is the parent substance of one of the radioactive disintegration series. The intermediate members zirconium and hafnium are remarkable for a similarity unique in the periodic system. A comparison of the properties of the members of the titanium group is therefore extraordinarily interesting. Clarke and Washington consider titanium as number 9 in the series of abundance of elements in igneous rocks, with an abundance of 0·63%. This value is based on about 5000 analyses of igneous rocks. In stone meteorites titanium takes the 12th place, for the elements sulphur, nickel, and chromium, which are less common in igneous rocks, precede titanium in these substances. In iron meteorites, however, titanium advances to the 8th position. We desired to determine the abundance of all the members of the titanium group as well as of other rare elements in one and the same material, and for this purpose we prepared a standard mixture, using more than 300 samples of igneous rocks of all possible types.

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The composition of the standard mixture so far as the common elements are concerned was as follows :

SiO_2	56·35%	Na_2O	3·19%
Al_2O_3	13·08	TiO_2	1·02
MgO	8·06	P_2O_5	0·21
FeO	4·64	MnO	0·11
Fe_2O_3	2·87	H_2O (>110°)	1·56
CaO	5·70	H_2O (<110°)	0·06
K_2O	3·26		

Further, 1 gram contained :

Ti.	Zr.	Hf.	Th.
$0·61 \times 10^{-2}$	$1·9 \times 10^{-1}$	$3·2 \times 10^{-6}$	$1·3 \times 10^{-5}$ gram
V.	Nb.	Ta.	Pa.
$0·2 \times 10^{-3}$	$3·2 \times 10^{-7}$	$2·4 \times 10^{-7}$	$0·5 \times 10^{-12}$ gram

Although the determination of the elements of the titanium group in the available material of the earth's crust presents no difficulties, we encounter great difficulties when trying to determine the share of these elements in the building up of the whole earth's material. The solution of the latter question is of great importance, as the proportion of each element gives a measure of its nuclear stability upon the assumption that the earth is a fair sample of the solar system.

So far as titanium is concerned, it is comparatively easy to determine its share in the total mass of the earth. We can carry out the calculation in two different ways, using as its basis either the analysis chiefly of terrestrial rocks or solely the analysis of meteorites. According to the data of V. M. Goldschmidt, the masses of the four shells of the earth—the iron–nickel core, the intermediate shell, the eclogite shell, and the silicate shell—are in the ratio of about 31 : 37 : 30 : 3. Suppose we select the first way and start from the titanium content of eclogites, which is about 0·3%. We will assume this value for the total eclogite plus silicate shell, this assumption being justified partly by the fact that the eclogite shell is about ten times as heavy as the silicate shell, and also because the titanium content of the silicate shell is not very different from the above value, as the following table shows.

Average titanium content, %.

Granite, average. (Daly)	Basalt, average. (Daly)	Plateau basalt. (Niggli)	Peridotite. (Daly-Holmes)	Eclogite. (Eskola Wagner)	Igneous rock, average. (Clarke)	Our standard mixture.	Stony meteorites (average of 20 stones).
0·23	0·82	1·49	0·4	0·3	0·63	0·61	0·19

It follows from the above considerations that the titanium found in the eclogite plus silicate shell corresponds to 0·001 of the earth's total material. The titanium content of the intermediate shell

cannot be larger than that of the stone meteorites and will therefore only moderately increase the above-quoted figure, namely, from 0·001 to less than 0·0016. Moreover, the amount of titanium present in the iron core increases this figure only very slightly, for we found the average titanium content of iron meteorites to amount only to 4×10^{-4} g. per g., the titanium content of the 11 iron meteorites investigated varying between $3·4 \times 10^{-5}$ and $1·8 \times 10^{-3}$ g. per g.

The above considerations were based on the assumption that the second shell is chiefly composed of eclogite. An alternative view favoured by several geologists is that the material below the crust is more like peridotite in either crystalline or glassy state. For example, Holmes assumes that at a depth of about 60 km., crystalline peridotite is passing into a glassy substratum, which prevails down to the depth of 2900 km. where the metallic core begins. The average titanium content of peridotite works out to about 0·4%, and as according to the above assumption two-thirds of the total earth material is built upon similar lines to peridotites, the total titanium content of the earth may be put at somewhat less than 0·19%.

Our alternative method is to base the determination solely on the analysis of meteorites. As stone meteorites have a titanium content of 0·2%, if we regard two-thirds of the mass of the earth as having essentially the composition of the stone meteorites, we obtain a titanium content of the total earth not more than 0·14%. To this amount must be added the titanium content of the iron core, which leads to a slightly increased figure, *viz.*, 0·15%. The following table shows the titanium content of the total earth material calculated

(a) from the analysis of terrestrial rocks, assuming an
    eclogite shell .... 0·0016 g. per g.
(b) from the analysis of terrestrial rocks, assuming a
    peridotite shell .... 0·0019
(c) from the analysis of meteorites alone .... 0·0015

These figures are slightly too high, as the titanium content of the intermediate shell is probably less than that assumed.

The most important titanium minerals are ilmenite ($FeTiO_3$), rutile (TiO_2), titanite ($CaTiSiO_5$), and perowskite ($CaTiO_3$).

From a magma deficient in lime and iron, titanic oxide may separate as rutile; when lime is abundant, titanite or perowskite may form; in the presence of much iron ilmenite will be deposited.

In order to decide in which mineral the greatest part of the titanium exists, we have chosen the following method. Niobium and tantalum always occur together with titanium; the chemical similarity of these elements is well known and, as in chemical pro-

cesses, so also in geochemical separations, niobium and tantalum invariably follow titanium. If we determine the average niobium–titanium or tantalum–titanium ratio of igneous rocks, and simultaneously that of titanium minerals, we can conclude at once how far a titanium mineral can be the chief carrier of titanium in igneous rocks. We find, for example, that the ratio tantalum–titanium in titanite, perowskite, and rutile is so much larger than in igneous rocks that these minerals cannot be the chief carriers of titanium. The titanium–niobium ratio of ilmenite is not very different from that found in igneous rocks, and it is therefore apparent that ilmenite must be the mineral which contains the greatest part of the titanium present in igneous rocks.

The atomic ratio of niobium to titanium and of tantalum to titanium in certain minerals is seen in the following tables.

Atoms of niobium per 1000 atoms of titanium.

Rutile.	Titanite.	Ilmenite.	In our igneous rock standard mixture.
0·55	0·29	0·0024	0·0067

Atoms of tantalum per 1000 atoms of titanium.

Rutile.	Titanite.	Ilmenite.	In our igneous rock standard mixture.
0·052	0·23	0·0009	0·0027

These figures show that most of the earth's titanium, so far as it occurs in titanium minerals, must exist as ilmenite.

Titanium, however, is found not only as the chief constituent of the titanium minerals, but also as a vicarious constituent of silicates. Formerly it was thought that titanium could replace silicon, but recently Machatschki and others, in view of Goldschmidt's work, have concluded that this cannot occur, at least at lower temperatures, on account of the great difference in the ionic radii (0·64 A. and 0·39 Å.), but titanium may replace magnesium (ionic radii 0·64 A. and 0·78 Å.).* At high temperatures titanium might replace silicon, but when such a metasilicate cools, the titanium present would be expected to crystallise as ilmenite or another titanium mineral of similar constitution. To determine the amount of titanium which replaces magnesium in our " standard igneous rock mixture," we separated the latter into light and heavy constituents, and we could then distinguish between the vicarious titanium present in the lighter fraction and the titanium from titanium minerals present in the heavier fraction. It was found that the latter amounts to more than two-thirds of the total titanium present.

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* These are Goldschmidt's figures. Pauling gives the ionic radii as 0·68 and 0·80 Å. respectively.

2.

The increase of the nuclear charge by 18 units in the transition from titanium to zirconium causes a very appreciable decrease in the abundance of the element. It is probable that the lighter elements such as titanium and zirconium were built up by synthesis from lighter nuclei, and in this way very appreciably more titanium atoms than zirconium were formed.

The increase of the ionic size from 0·64 to 0·87 Å.* in going from titanium to zirconium had also important geochemical results. In his fundamental work on geochemistry, V. M. Goldschmidt has drawn attention to the fact that the products of magmatic crystallisation can be roughly classified into three groups. The first includes the minerals of the earliest separation from the magma, the second contains the dominating minerals of the main period of crystallisation, and in the third group are the minerals which separate from the magma at a very late stage of its evolution. The distribution of any given element between a liquid phase and a co-existing crystalline phase will depend on isomorphism between the element or its ions and the components of the crystalline phase. Isomorphism mainly depends on the size of the atoms or ions involved, and we have to expect a sorting of elements according to the size of their atoms and ions in relation to the sizes of the dominating constituents of the crystalline phases. Now, elements of very small ionic or of very large ionic size do not enter the crystal, but are forced to remain suspended in the liquid. In this manner, a number of rare elements are, or become, concentrated in mother-liquors or magmas, remaining there till the concentration reaches the saturation limit of their own crystalline phases. When that stage is reached they are precipitated as minerals of rare elements. This line of thought explains why, in the mother-liquors of silicate magmas, i.e., the pegmatite magmas, we encounter such a wealth of rare elements. Goldschmidt emphasises the idea that the process of fractional crystallisation has also important consequences for the vertical distribution of the elements throughout the silicate shell of the earth. The specific gravity of the liquid part of an ordinary silicate magma that is in process of fractional crystallisation decreases substantially as crystallisation proceeds, owing to the high density of early minerals and to the increase in such volatile compounds as water and carbonic acid in the mother-liquor. Therefore, residual magmas will have a strong tendency to migrate upwards to the uppermost levels of the earth's crust, so that in the highest levels of the silicate shell we encounter a relative enrichment of those

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* These are Goldschmidt's figures.

elements found concentrated in the light granitic rocks and pegmatites. For this reason many of the rare elements typical of pegmatite associations are found in comparatively high concentrations in the uppermost levels of the lithosphere. Three of the four members of the titanium group, namely, zirconium, hafnium, and thorium, are conspicuous members of the later group of the pegmatite magma although they are not found exclusively among the crystallisation products of residual magmas. On the other hand, a large proportion of the titanium enters into the products of early crystallisation.

The geochemical behaviour of titanium is, therefore, entirely different from that of the other members of its group. One of the most important consequences of this fact is that the titanium content of the igneous rocks is not very different from that of the eclogite and even of the intermediate shell, and therefore, as we saw, the titanium content of the igneous rocks supplies a fairly accurate measure of the titanium content of the total earth material. No such conclusion can be drawn from the zirconium, hafnium, and thorium content of the igneous rocks.

3.

It is of interest to recall that, even before the above geochemical considerations were known, the conclusion had been reached that thorium and uranium were practically limited to the lithosphere. The present Lord Rayleigh reached this conclusion through his considerations of the thermal equilibrium of the earth. At that time * it seemed quite arbitrary to say that the radioactive elements should chiefly exist only in the uppermost layer of the earth. To-day it seems to us to be quite obvious that the elements of residual crystallisation, such as uranium and thorium, have to concentrate in the uppermost shell of the earth. The decrease in the thorium content with increasing depth is beautifully shown by the following table, based chiefly on the work of Joly and Poole :

Granite	2×10^{-5}
Basalt, oceanic	$0 \cdot 6 \times 10^{-5}$
Basalt, plateau	$0 \cdot 5 \times 10^{-5}$
Ultra-basic dunite	$0 \cdot 3 \times 10^{-5}$
Eclogite	$0 \cdot 2 \times 10^{-5}$

Considerations, based on the heat equilibrium of the earth, allow us to calculate the thorium content of the total earth's material. I am much indebted to Professor A. Holmes for the more recent data. According to his calculations, the amount of thorium compatible with the requirements of the heat equilibrium is about 2×10^{-7} g. per g. in the layer corresponding to Goldschmidt's silicate, eclogite,

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* Holmes and Lawson have recently drawn attention to the fact that the heat production due to potassium disintegration must be also taken into account.

and intermediate shells combined; or, if distributed throughout the total mass of the earth, 1.3×10^{-7} g. per g.

The thorium content for the whole earth may also be computed by methods similar to those for computing the titanium content. The result is seen from the following table :

Thorium content of the total earth material.

From heat equilibrium considerations .... 1.3×10^{-7} g. per g.
From the analysis of terrestrial rocks .... 14×10^{-7}
From the analysis of meteorites alone .... 14×10^{-7}

The results in the second and third lines are somewhat too high, as the thorium content of the intermediate shell is presumably somewhat smaller than that assumed.

4.

According to Clarke and Washington, the average zirconium content of igneous rocks amounts to 0.026%. In our " standard mixture " we find a zirconium content of 0.019% and a hafnium content of 0.00032%. Thus the titanium/zirconium ratio is 32 : 1. The difference in abundance of these two elements is, however, more marked when one considers the whole earth's material. The arguments employed for the case of thorium can also be applied to zirconium in so far as the geochemical behaviour of this element follows that of thorium. The corresponding result is seen from the following table.

Zirconium content of the total earth material.

From the analysis of terrestrial rocks .... 2×10^{-5} g. per g.
From the analysis of meteorites alone .... 3×10^{-5}

The assumption of similar geochemical behaviour by zirconium and thorium could be questioned, but no objections can be raised against its application to the case of zirconium and hafnium. Owing to their great chemical similarity, zirconium and hafnium share the same fate during geochemical processes, and we may therefore consider the zirconium/hafnium ratio ascertained in the lithosphere to be a trustworthy measure of their general abundance in the material of the earth and, presumably, of the whole solar system. On account of the important conclusions which can be drawn from them, the ratios zirconium : hafnium, yttrium : holmium, niobium : tantalum, and so on, become of great interest. This applies to a still greater extent to the relative abundance of the isotopic atoms as determined by Aston's recent researches.

5.

In nature, zirconium is found chiefly as zircon ($ZrSiO_4$). This mineral is a product of the first crystallisations of the silicate melt

as well as of the chief crystallisation, but its chief occurrence is among the products of residual crystallisation. The last includes, according to Goldschmidt, about 80% of the total amount of zirconium. In nepheline–syenites, poor in silica but alkali-rich, zirconium occurs as eudialite, which weathers into baddeleyite. Zirconium is also found as a more or less important constituent of a large number of less common silicates.

The next member of the titanium group, hafnium, is never found as a dominating constituent of a mineral : no hafnium minerals are known. This is due chiefly to the unique similarity between zirconium and hafnium, but also to the fact that zirconium is much more abundant. In no case is the " camouflage " phenomenon, as Goldschmidt calls it, more conspicuous. In the fluid-gaseous stage of our solar system, a zirconium : hafnium ratio of about 60 : 1 prevailed throughout, and owing to their similarity, the same ratio is found also in the lithosphere.

The following example shows how weathering and other processes which can produce a very appreciable shift in the zirconium : titanium ratio are entirely ineffective in separating zirconium from hafnium. On the Chibina tundra of the Kola Peninsula there are found both unaltered and weathered eudialite. The original mineral shows a $TiO_2 : ZrO_2$ ratio of about 11, whereas in the weathered mineral a ratio of about 1 is found. The $ZrO_2 : HfO_2$ ratio was found to be exactly 100 : 1·3 in both cases.

In the course of the formation of minerals the original hafnium : zirconium ratio was, however, appreciably altered sometimes in favour of zirconium in the products of alkaline residual crystallisation, a zirconium poorer in hafnium than that of the gaseo-liquid earth thus being left behind. The lowest hafnium content is shown by those zircons which occur in nepheline–syenites with a low silica content, such as the zircons of Brazil. We find here zirconium : hafnium ratios up to 700 : 1. In the products of siliceous residual crystallisation, on the other hand, we sometimes find a very appreciable decrease in the above ratio. Some unaltered zircons of granitic origin, such as the zircons of Seiland investigated by Barth, exhibit an atomic ratio Zr : Hf of 40, and altered zircons, e.g., some alvites and cyrtolithes, show an atomic ratio up to 6 : 1 (the $ZrO_2 + HfO_2$ content of such minerals amounts to about 50%).

Minerals which contain a high hafnium–zirconium ratio contain mostly also large amounts of yttrium earths, such as thorium, uranium, niobium, tantalum, and beryllium. As Urbain has shown, the separation of closely related elements by fractional crystallisation can sometimes be promoted by the addition of a third element which crystallises between the elements to be separated. It is

possible that one or more of the elements mentioned above play this rôle.

Owing to the presence of thorium and uranium in such minerals as are products of residual crystallisation, we find a certain parallelism between hafnium content and radioactivity. Minerals which show a high hafnium content are often found in a " metamikt " state, which is also shown by the fact that such minerals give no sharp rings in their X-ray diagrams. Böhm and Ganter have taken X-ray diagrams of a large number of zirconium minerals but could not find a connexion between hafnium content and " metamikt " nature. Cyrtolithes from Parry Sound, Ontario (2·36% of HfO_2) or Karelia (2·3% of HfO_2) were found as distinctly " metamikt " as the cyrtolithes of Rockfort, Mass., which exhibited an uncommonly high hafnium content (up to 10% of HfO_2).

The elements of the titanium group are also found in the sun's spectrum. The titanium lines and also oxide bands appear with great intensity, but the zirconium lines are much weaker and the hafnium lines even fainter still.

The geochemical behaviour of the elements of the titanium group clearly indicates that the chemical resemblance between titanium and zirconium, on the one hand, and hafnium and thorium, on the other, is of the usual order, whilst the resemblance between zirconium and hafnium is exceptionally close. In the following we shall investigate how far the resemblance is borne out by the chemical behaviour.

6.

The most exact method for comparing the chemical similarity makes use of the ionisation potential of the elements, a magnitude which is best furnished by optical data. In spite of the great advances in optical spectroscopy, it has not yet been possible to disentangle the spectra of the elements of the titanium group to an extent that would enable us to calculate their ionisation potentials. There is, however, an approximate parallelism between ionisation potential and atomic magnitude, and this permits us to employ the atomic or the ionic size instead of the ionisation potentials in making chemical comparisons. Fig. 1 shows the ionic radii and atomic numbers of the elements of the titanium group, whereas Fig. 2 compares the values of their atomic radii and atomic numbers. The ionic radii were obtained by Dr. Böhm in my laboratory, and the atomic radii by van Arkel and de Boer at Eindhoven; the latter workers were able to prepare the metals of the titanium group and even single crystals by a very elegant method. Although the atomic radii of zirconium and hafnium show an appreciable difference, their ionic radii are identical within 0·05%.

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The molecular volumes of the oxides and the atomic volumes of the metals are given in the following tables.

Molecular volumes and densities of the oxides.

	Mol. vol.	Density.
TiO_2 (rutile)	18·75	3·97
ZrO_2 (tetragonal, nearly fluorite type)	20·10	6·13
CeO_2 (cubic, fluorite type)	23·99	7·58
HfO_2 (tetragonal, nearly fluorite type)	20·10	10·47
ThO_2 (cubic, fluorite type)	26·75	9·86

FIG. 1.
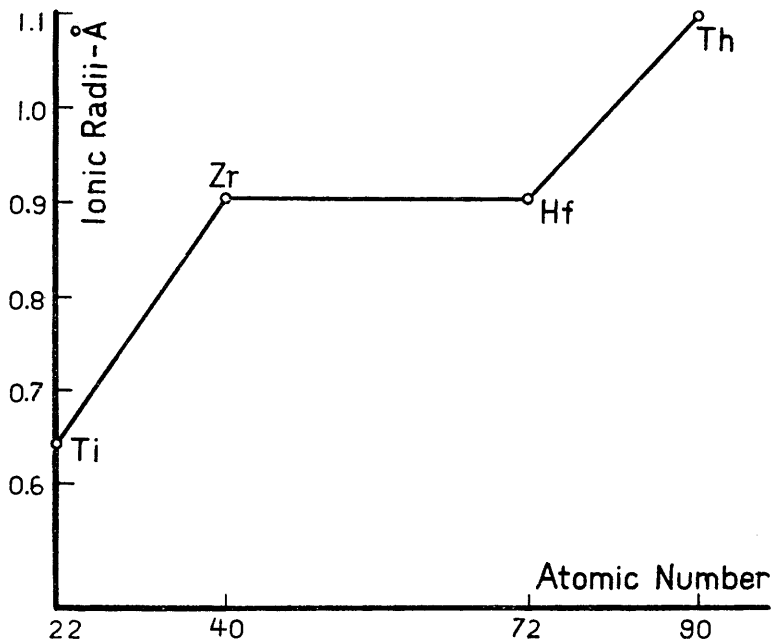
Second monoclinic modifications of ZrO_2 and HfO_2 have a somewhat higher molecular volume, *viz.*, 21·11, and accordingly a lower density, *viz.*, 5·84 and 9·98 respectively.   Under the usual conditions the latter modification is obtained.

Atomic volumes and densities of the metals.

|	Atomic vol.	Density.
Ti	10·93	4·5
Zr	13·97	6·52
Hf	13·42	13·31
Th	19·42	12·0

The melting points of the oxides and especially of the carbides of the elements of the titanium group are conspicuously high, as seen in the following table.

Melting points of the oxides and carbides.

TiO_2	....	1640°	TiC	—
ZrO_2	....	2687	ZrC	3532°
HfO_2	....	2812	HfC...........................	3887
ThO_2	....	2800	ThC	—

The solid solution containing 1 mol. of hafnium carbide and 4 mols. of tantalum carbide has the highest melting point yet found, for it melts at 3942°. The melting point of zirconium metal is 1580°, and that of hafnium 2230°.

Fig. 2.
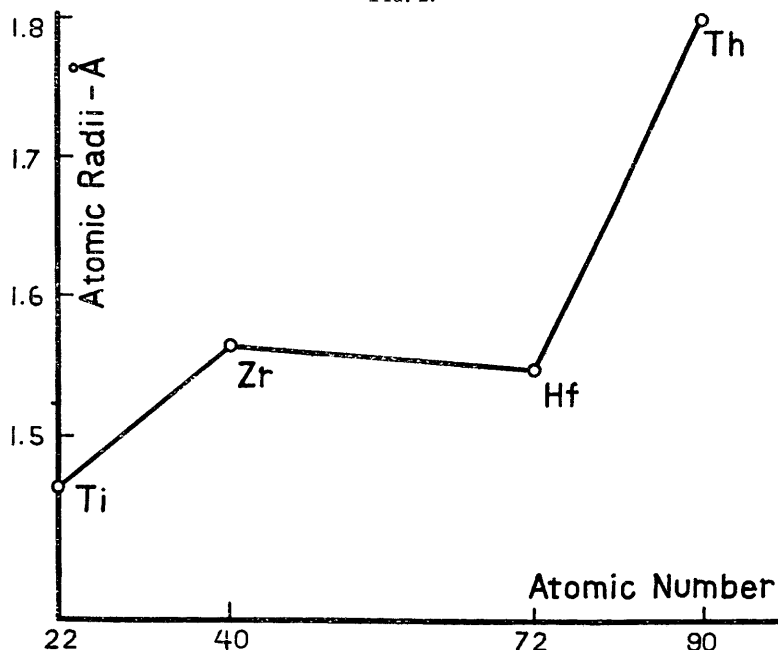
The great similarity of the ionic sizes of zirconium and hafnium is exhibited in the minute differences of solubility of most of the corresponding compounds, which account for the great difficulties of separation. In only a few cases are the differences not inappreciable; such an instance is afforded by the potassium and ammonium hexafluorides, as seen from the following table.

Solubility (mols. per litre) at 20° in N/8-hydrofluoric acid.

K_2TiF_6	....	0·0483	K_2HfF_6	0·1008
K_2ZrF_6	....	0·0655	K_2ThF_6,H_2O	Hardly soluble

The phosphates exhibit marked solubility differences in concentrated mineral acids :

Solubility (mols. per litre) of phosphates at 20° *in* 10N-*hydrochloric acid.*

Titanium phosphate	....	0·32
Zirconium ,,	....	0·00023
Hafnium ,,	....	0·00011

It is of interest to note that hafnium phosphate is the least soluble of all known phosphates.

The solubilities of the oxychlorides of zirconium and hafnium are practically identical in water and in dilute acids, but at greater acid concentrations very different behaviour is found. Instead of decrease of solubility with increasing acid concentration, we witness an increase in solubility after a concentration of about 8N-hydrochloric acid is reached. In this acid, these oxychlorides show a similar behaviour to that of lead chloride, where the increased solubility with increasing acid concentration is due to the formation of a complex compound. In the range of increasing solubility the oxychlorides of zirconium and hafnium show a distinct difference of solubility, presumably due to the greater tendency of the zirconium salt to form complex compounds. That complex hafnium compounds are less easily formed and more easily decomposed is also shown by heating zirconium and hafnium ammonium hexafluorides, the latter compound being more easily decomposed.

The oxybromides also show markedly different solubilities in concentrated hydrobromic acid : in 30N-acid the zirconium salt is 4·5 times more soluble than the hafnium salt. In the case of the oxyfluorides the greatest difference, 2 : 1, is found in 20N-acid.

The methods actually used to separate hafnium and zirconium are based on the fractional crystallisation of the ammonium or potassium hexafluorides and on the precipitation of the simple or the crystallisation of the complex phosphates.

7.

The anomalous behaviour of the titanium group has been described and illustrated. I shall now try to explain the anomaly by means of Bohr's quantum theory of atomic structure. According to Bohr's views, the chemical character of an element is conditioned by the charge on the nucleus of the atom and the attraction exerted by the charge on the electrons of the outermost shell. An increase in the nuclear charge without a change in the arrangement of the electrons has the effect of making the outer electrons more tightly bound, and the atom becomes less basic.

In the vertical groups of the Mendeléeff system, such an increase of charge takes place from the lower to the higher elements, but at the same time the valency electrons are displaced further and further
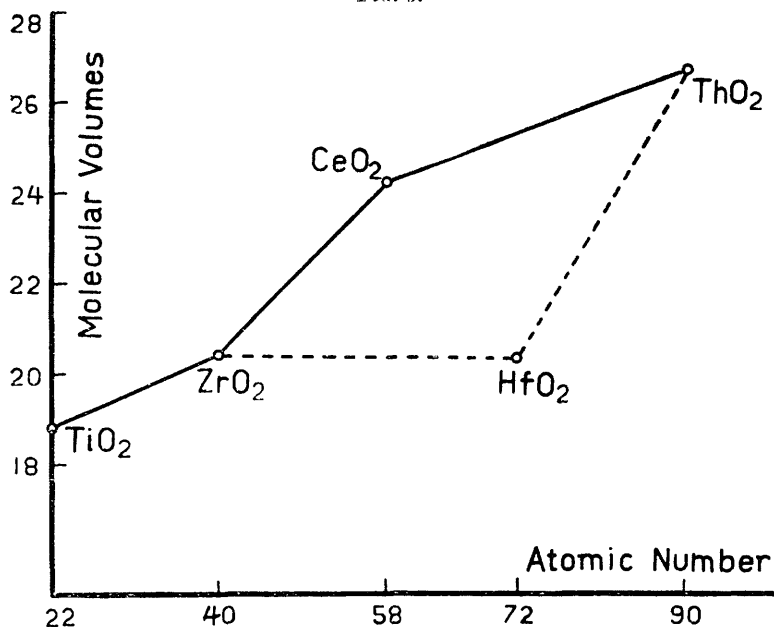
from the nucleus into quantum orbits of higher quantum number. Owing to this fact, this increased attraction—which is an effect of the increase of nuclear charge—is not only counterbalanced but even outweighed by the greater distance of the outer electrons from the nucleus, and the higher members become more basic than the lower. Barium has a nuclear charge 18 units higher than strontium, and yet it is the more basic element. In comparing hafnium with zirconium we find the difference in nuclear charge is 32 units, much more than in the case of barium and strontium, while the difference in the quantum number of the orbits is the same in each case. In comparing barium and strontium with zirconium and hafnium we have in both cases the same difference of quantum number of the valency orbits, but in the latter case the much bigger difference in nuclear charge of 32 units can no longer be compensated by the increase in the quantum number of the valency electrons, and hafnium is accordingly only inappreciably more basic than zirconium. We can always imagine two atoms of very different nuclear charge showing practically the same chemical behaviour if only the quantum numbers of the valency electrons are very different and exactly compensate the difference in the nuclear charge.

The next question which occurs is : Why has hafnium a so much larger nuclear charge than zirconium ? The difference is due to the introduction of the 14 rare-earth elements before hafnium. That the appearance of the rare earths is responsible for the extreme similarity of zirconium and hafnium, becomes apparent when we try to draw up a fictitious periodic table containing no rare-earth elements and then deduce the properties of an element which would follow lanthanum in such a table. Lanthanum is not considered in atomic physics as a rare-earth element. After lanthanum there would be a " pseudo-hafnium," then a " pseudo-tantalum," a " pseudo-tungsten," and so on. These pseudo-atoms would all be more reactive than the real ones, since their valency electrons would be less tightly bound. " Pseudo-hafnium " would have a density of 9, instead of 13, " pseudo-tantalum " 14 instead of 17, " pseudo-tungsten " 15 instead of 19. Although these pseudo-metals are purely fictitious, their compounds are not. The quadrivalent compounds of " pseudo-hafnium " are known and are, in fact, identical with the ceric compounds. This is obvious from a simple observation of the electronic grouping as shown in the table on p. 14.

As is to be expected, the anomalous behaviour of the ionic sizes and the molecular volumes of the oxides disappears if we replace the hafnium ion by the ceric ion (Fig. 3). This observation is not without interest in connexion with the earlier, apparently insuperable,

Hafnium.

N				O			P
s	p	d	f	s	p	d	s
2	6	10	14	2	6	2	2

Hafnium++++.

N				O			P
s	p	d	f	s	p	d	s
2	6	10	14	2	6	–	–

Pseudo-hafnium.

N				O			P
s	p	d	f	s	p	d	s
2	6	10	–	2	6	2	2

Pseudo-hafnium ++++.

N				O			P
s	p	d	f	s	p	d	s
2	6	10	–	2	6	–	–

Cerium.

N				O			P
s	p	d	f	s	p	d	s
2	6	10	1	2	6	1	2

Cerium++++.

N				O			P
s	p	d	f	s	p	d	s
2	6	10	–	2	6	–	–

Fig. 3.

difficulty of placing cerium in the third or in the fourth group of the periodic table. The cerium atom and the cerous ion are not directly related to zirconium, but the ceric ion is the pseudo-homologue of the zirconium ion. Similarly the quinquevalent praseodymium ion would be the pseudo-homologue of the niobium ion.

8.

I would like to mention the chief points in the analytical chemistry of the titanium group. Titanium can be colorimetrically estimated even when present only in traces, e.g., as little as 0·001% in iron.

The estimation of thorium also offers no difficulty.

Apart from chemical methods, the detection of thorium can be carried out conveniently by measuring the radioactivity of the thorium emanation. If the thorium content is too small, it can be concentrated chemically. This concentration is much facilitated by using the method of radioactive indicators. A known quantity of a thorium isotope (for example, U-X) is added to the solution of the mineral, and the quantity is checked by electroscopic measurements before and after the concentration process. In this way any thorium loss can be allowed for.

Zirconium can be easily determined by Hillebrand's method by the precipitation of the phosphate in acid solution, but the existence of hafnium introduces very great difficulties. The characteristic insolubility of zirconium phosphate in mineral acids is also shown by hafnium phosphate, as also are the colour reactions of zirconium, for example, the red colour developed with sodium alizarinsulphonate. One is, therefore, forced to turn to physical methods. In a mixture of the two oxides with no other constituent, a determination of the density supplies a simple means of analysis. A replacement of 1% of zirconium by the same volume of hafnium represents an increase of density of 0.7%. This method is useless except when a pure mixture of the oxides is available. Otherwise, only spectroscopic methods are possible, and quantitative X-ray spectroscopy is especially suitable. In order to determine the amount of hafnium in a mineral a known amount of lutecium oxide is added to the powdered mineral, and the intensities of the Hf-$L\alpha_1$ and Lu-$L\alpha_2$ lines are compared. These two lines lie very close together and are therefore especially suitable for intensity comparisons.

Quantitative X-ray spectroscopy is applicable to the determination of almost every element, but is indispensable in the above-mentioned case as in all other cases of elements difficult to determine chemically or those present in minerals only in traces.

Often the combination of chemical concentration and the X-ray method proves to be very useful. The determination of the abundance of niobium and tantalum already mentioned was only rendered possible by removing the titanium together with niobium and tantalum from the mineral, concentrating the last two in this fraction chemically until a concentration of $1 : 1000$ or $1 : 10,000$ was reached, and then using the X-ray method. Starting with a one-pound sample, in the part actually used for the X-ray analysis there was not more than $1/100$ mg. of tantalum, but this sufficed for the X-ray analysis.

X-Ray spectroscopy furnishes an unsurpassed method for the analysis of minerals, and it is greatly to be deplored that the late

H. G. J. Moseley, to whom we owe the discovery of the fundamental law of X-ray spectra and who laid the foundation for X-ray analysis, could not live to witness this and numerous other applications of his discovery.