[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 516]

AN ATTEMPTED SEPARATION OF HAFNIUM AND ZIRCONIUM BY THE IONIC MIGRATION METHOD

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RECEIVED AUGUST 23, 1926 PUBLISHED OCTOBER 6, 1926

The success of the method of ionic migration in causing separation of certain rare earth mixtures[1] suggested the investigation of its application to another pair of difficultly separable elements, hafnium and zirconium, and accordingly experiments have been performed with a carefully purified zirconium preparation containing some 5% of hafnium kindly furnished us by Professor Hevesy.

In this method, an agar gel containing the mixture is placed in a long glass tube behind a gel containing a faster ion of the same sign as those to be separated, and in front of a gel containing a slower ion. On electrolysis, the two boundaries of the middle section remain sharp, and if the constituents of the mixture possess appreciably different mobilities, the faster ion gradually concentrates in the front of the section, and the slower in the rear. Recovery of the separated mixture can then be effected by slicing up the gel at the conclusion of the run.

Previous experience in the method has indicated that a considerable separation can be effected when the constituents of a mixture differ in ionic mobility by more than about 1.5%.[2] No quantitative data are available from which an estimate can be made of the relative mobilities of ions derived from zirconium and hafnium, but the very close similarity in almost all the physical and chemical properties of the two elements suggests that the speeds of their ions will be nearly alike. It was hoped, however, that any difference in mobility would be accentuated in ions in which the metals formed part of a negative complex, for there seemed to be a possibility that the slightly greater basicity associated with the more electropositive nature of hafnium in comparison with zirconium would cause complex hafnium anions to be somewhat less stable than the corresponding zirconium ions. There would thus be a greater tendency for hafnium than for zirconium to strive towards the cathode, and if the complex hafnium anion were slower than that from zirconium, the two factors would operate in the same way and increase the effective difference in mobility. Some justification for expecting the heavier hafnium ion to be slower than the zirconium is afforded by the comparison of the mobilities of chlorides, bromides and iodides with those of chlorates, bromates and iodates for, while the extreme difference in mobility of the simple ions is 3%, and the series exhibits the well-known anomaly in which the atom of

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[1] Kendall and Clark, *Proc. Nat. Acad. Sci.*, **11**, 393 (1925).

[2] Kendall and White, *ibid.*, **10**, 458 (1924).

lowest mass yields the slowest ion, the mobilities of the more complex chlorates, bromates and iodates show an extreme difference of about 50% and they decrease with increasing mass.

As it happens, the possibility of a successful migration with zirconium and hafnium in agar gel, not to speak of a separation, depends upon the use of complex anions, for when the zirconium is present as the positive zirconyl ion, a precipitate is formed between the metal and the agar which prevents migration. This behavior was noted with all of the salts tried in which zirconium was present largely in the ZrO^{++} condition, the chloride, bromide and nitrate; a gelatin gel, on the other hand, is not precipitated by the zirconyl radical. A solution of the sulfate, $Zr(SO_4)_2$, however, does not cause precipitation of agar and, on electrolysis, the migration of the zirconium is almost entirely towards the anode, a fact which confirms the transport experiments of Ruer and the widely held opinion that zirconium sulfate dissolves in water as complex zirconium sulfuric acids.[3] The preliminary experiments were made with the alkali salts of the complex sulfuric acid, the necessary quantity of alkali sulfate being added to a solution of zirconium sulfate on the assumption that the salts possess the formula $M_4[Zr(SO_4)_4]$.[4]

Choice of Front and Rear Ions.—The general principles regulating the choice of front and rear ions have been formulated in previous reports.[1,2] An attempt to secure a difference in color at the moving boundaries by the use of chromate in front and of picrate behind was unsuccessful owing to the formation of precipitates at the boundaries. Sulfate, however, was found to serve well as front ion, but the discovery of a suitable rear ion presented difficulties. Slow ions such as chloride, acetate and trichloroacetate were tried without success; the zirconium, instead of moving towards the anode as a compact section, partially lagged behind and the section increased four- or five-fold in length. The solution of the problem thus presented was found to lie in the use of a rear ion which, besides being slower than the zirconium ion, was also capable of forming a stable complex with zirconium. The lagging behind appears to be due to slight decomposition of the complex ion, which gives rise to small quantities of ZrO^{++} ions tending to reverse the migration; any such ions formed are captured on entering the rear section, a complex ion is again formed and moves in the desired direction. Of the ions capable of forming complexes with zirconium, oxalate, tartrate and gallate were tried. The oxalate ion proved faster than the zirconium complex, and of the others, tartrate was chosen as the more convenient.

The existence of a completely sharp rear boundary was, however, found to depend on the fulfilment of still another condition; a hydrogen-ion con-

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[3] Ruer, *Z. anorg. Chem.*, **42**, 87 (1904). Hauser and Herzfeld, *ibid.*, **106**, 1 (1919).

[4] Rosenheim and Pinsker, *ibid.*, **106**, 9 (1919).

centration of at least 0.1 N had to be maintained in the whole tube throughout a run. Otherwise, although the use of tartrate as rear ion greatly diminished the tendency of the rear boundary to become diffuse, small but appreciable quantities of zirconium remained behind the main section. This second condition is somewhat unfortunate for, since much of the current is carried by the fast hydrogen ions, the rate of migration of the zirconium section is reduced; moreover, the presence of hydrogen ion causes the gel to disintegrate to some extent in regions of high resistance, although no actual trouble was experienced due to the latter effect.

Choice of Zirconium Complex.—Trials were made with various complex zirconium anions; the complex sulfate $[Zr(SO_4)_4]^{----}$, the complex fluoride, ZrF_6^{--}, the complex oxalate $[Zr\overline{Ox}_4]^{----}$, and the complex tartrate. The fluoride offers the advantage of relatively high mobility but since, owing to the low solubility of the potassium salt, it must be used in conjunction with ammonium, an ion that increases the difficulties of obtaining good gels already introduced by the presence of hydrogen ion, it was finally rejected in favor of the complex oxalate.

Concentrations.—The following concentrations were found by trial to permit the accomplishment of a successful run, in which the length of the zirconium-hafnium section did not alter materially in a movement over 400 cm.

Front gel	Na_2SO_4	0.8 N + $NaHSO_4$	0.2 N
Zr-Hf gel	$Na_4Zr(Hf)(C_2O_4)_4$	0.7 N	
Rear gel	$Na_2C_4H_4O_6$	0.3 N + $NaHC_4H_4O_6$	0.2 N
Anode liquid	Na_2SO_4	0.8 N + $NaHSO_4$	0.2 N
Cathode liquid	$H_2C_4H_4O_6$	2 N	

The concentrations of the electrode liquids were maintained by renewal once or twice a day according to the current passing through the tube.

To prepare the complex oxalate, a quantity of ammonium fluozirconate containing about 5% of hafnium was dissolved in water, precipitated with ammonium hydroxide, the hydroxide filtered, washed and dissolved in the calculated quantity of sodium hydrogen oxalate solution. The hot solution was poured into half its volume of hot 9% agar sol, so that the resulting gel was 3% in agar. The length of the zirconium section varied in different experiments from about 4 to 7 cm.

Tubes 3 meters long and, in the final experiments, of 4 cm. internal diameter were used. The electrolysis was performed by a motor generator capable of yielding 0.3 amp. at 1000 volts. With the smaller tubes, of 2.7 cm. diameter, used in the early experiments, a potential difference of 500 volts between the electrodes caused migration through a distance of 5 meters in 30 days; the rate of movement with the large tube was much less, amounting to 4 meters in 35 days.

Method of Following the Boundaries.—Two circumstances conspired to make the location of the boundaries easier than the lack of a color difference between the various solutions led one to anticipate. The zirconium-hafnium mixture used contained a trace of iron. Within a few hours of the commencement of a run, practically all of the iron in the section had concentrated at the front boundary, where it showed as a remarkably sharp, pale green ring, the iron evidently being in the form of the complex ferri-oxalate. The separation of iron from zirconium is thus accomplished very readily by the ionic migration method.

At the rear boundary a very characteristic constriction appeared in the gel and followed the boundary in its course throughout a run. The cause of this may lie in a concentration of tartrate ion behind the rear boundary, such as was noted with chromium in the rare-earth separations.[1] It is known that the lyotropic effect in the case of anions in diminishing the swelling of agar becomes apparent at high concentrations,[5] and the contraction observed would be in accordance with the position of tartrate ion in the Hofmeister series.

Analysis of the Sections.—After the completion of a run, the zirconium-hafnium section was sliced as in previous applications of the method. Carbonaceous matter having been removed by ignition and fusion with potassium pyrosulfate, the zirconium-hafnium mixture was recovered from the dissolved melt by precipitation with ammonium hydroxide. The hydroxide from the first section was always tinged with brown (Fe); the others were white. For removal of the iron, the hydroxide was dissolved in 1 N sulfuric acid, about 1 g. of tartaric acid was added, the solution made alkaline by the addition of ammonium hydroxide (precipitation of hydroxides being prevented by the tartaric acid), the iron precipitated as sulfide by hydrogen sulfide, and the zirconium-hafnium recovered from the filtrate by precipitation with Cupferron.[6] Ignition of the Cupferron precipitate gave the mixed zirconium-hafnium oxides as a pure white powder, free from iron. All segments were purified in this way.

An attempt was made to analyze the segments by determining the densities of the oxides,[7] a pycnometer of 1 cc. capacity and a microbalance being used. The results, however, were subject to erratic variations, and since the small quantities of oxide available from each segment (0.1–0.2 g.) seemed to prevent the attainment of sufficient precision, the method was abandoned in favor of the determination of the atomic weight from an analysis of the sulfate.

For this purpose the weighed oxide was dissolved in hydrofluoric acid and the solution evaporated nearly to dryness; concd. sulfuric acid was

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[5] Michaelis, "The Effects of Ions in Colloidal Systems," Williams and Wilkins Co., **1925**, p. 91.

[6] *U. S. Bur. Mines Bull.*, **1923**, No. 212, p. 312.

[7] Hevesy and Berglund, *J. Chem. Soc.*, **125**, 2372 (1924).

added and most of the excess of acid removed by heating in an electric furnace to as low a temperature as possible; the last traces of acid were removed by heating at 380–390° for several hours while a current of dry air was passed through the furnace, zirconium sulfate being stable up to 400°.[8] Two separate determinations were made on the oxides from each segment.

The analysis of the sulfate in the determination of the atomic weight of zirconium has been criticized as giving too low a value owing to incomplete decomposition of acid sulfates.[9] While this may be true for determinations that purport to be standard, the absolute values of the atomic weights are not essential for our purpose of ascertaining whether separation has occurred, provided the values for the different segments derived from a run are mutually comparable. That results reproducible within narrow limits can be attained by the analysis of the sulfate is shown by Bailey's figures,[8] and was shown in the present investigation in determinations on the original sample; and as the conditions of heating were the same in the analyses of the different segments, one can conclude that they were comparable among themselves. The results are given in Table I.

Table I

Atomic Weights from Segments after Migration[a]

Expt.	Length of run, cm.	Segment 1	2	3	4	5
5	340	Front 92.6, 92.7 Av. 92.7	....	....	Rear 94.3, 94.2 94.3	....
6	500	92.4, 92.2 Av. 92.3	93.0, 92.0 92.5	Lost	93.0, 93.7 93.4	Rear 94.1, 93.9 94.0
7	406	92.3, 91.9 Av. 92.1	93.4, 92.5 93.0	94.8, 94.6 94.7	Rear 94.8, 94.3 94.6	....

[a] Atomic weight of metal in original sample, 94.0.

Table I immediately shows that no considerable separation had occurred; in none of the runs did even the first section consist of pure zirconium (at. wt., 91.2).

Nevertheless, there is a distinct trend towards values of the atomic weight lower than that of the original sample at the front, and towards higher values at the rear. The difference in the figures for the first and rear sections amounts to some 2%, while the mean deviation of the extremes for the individual values is 0.4%, and it must be concluded that a slight separation had indeed been achieved in all three cases. While, then, the experiments show that ionic migration is not a practicable method of obtaining pure hafnium or pure zirconium from a mixture of the two,

[8] Bailey, *Proc. Roy. Soc.*, **46A**, 74 (1889).

[9] Hönigschmid, Zintl and González, *Z. anorg. Chem.*, **139**, 296 (1924).

the results demonstrate sufficient difference in mobility between the complex anions formed from these elements, closely related as they are, to yield a detectable separation.

Discussion.—The success of the ionic migration method in separating certain rare earths naturally raises the question why for practical purposes it fails with zirconium and hafnium.

There are four properties of a small charged particle which might possibly determine its motion through a liquid, the mass, the size, the shape and the charge.[10] Now, all experience indicates that the mobility of an electrolytic ion is governed to a relatively slight degree by the mass of the particle, but to a great extent by the size, where by the size is understood the sum of the parts contributed by the ion itself and by the envelope of solvent molecules which accompanies it. In aqueous solution the contribution of the solvent atmosphere to the size of the total ion aggregate is of great importance. Concerning the true volumes of the ions derived from hafnium and zirconium, the existing data show that the differences are small. For instance, an estimate of the relative volumes of hafnium and zirconium cations can be made from the values for the molecular volumes of the oxides, whose values, 21.72 and 21.50, respectively, show a difference of 1%; the sizes of the cations must therefore be nearly alike. Again, on the basis of the crystal structure, the molecular volumes of the compounds $(NH_4)_3ZrF_7$ and $(NH_4)_3HfF_7$ are calculated to be 123.9 and 125.7[11] so that only a slight difference can exist between the volumes of the anions.

In the formation of the solvent envelope of the ion aggregate, it appears possible to distinguish between two kinds of actions. One is to be identified with that which causes ions to become associated with other molecules or ions to form coördination compounds, an effect that may be determined by the endeavor of the ion to attain to certain favored electronic structures in the outermost subgroups. In the second effect, highly polar molecules are held by relatively weaker forces which may be regarded as due to an electrostatic field emanating from the interior of the ion. While, for mathematical simplicity, it has been customary in the development of the modern theory of ionic solutions to consider the ion as a charged sphere, the effect in reality will be subject to influences that depend on the composition of the individual electron shells, so that ions of the same valence and similar size may exhibit differences in their external fields if the composition of a shell within the outermost is different. Such influences will be most prominent in the transition elements and in the rare-earth group. All the rare-earth ions possess the inert gas structure in the outermost shell of electrons, and the coördination forces, as is shown in fact by the similarity in hydration of the crystalline salts, are therefore nearly the same; but

[10] Jette, forthcoming publication.

[11] Hassel and Mark, *Z. Physik*, **27**, 89 (1924).

throughout the group there is a continuous change in the constitution of the inner N shell, and it seems necessary to attribute the considerable differences in mobility, which are shown to exist by the success of the migration method in causing separation, to differences in hydration induced by the changing N shell. The members of the rare-earth group, although so closely similar in chemical properties, exhibit great variation in the magnetic susceptibility, a property originating in the electrons in the outermost subgroups of the N shell. Corresponding differences in the external fields of the ions would cause hydration to different degrees, and thus confer different mobilities; in fact, separation in the rare earths was most successful where the difference in susceptibility was greatest. Probably the most remarkable separation by the migration method was that between samarium (at. wt., 150.4) and gadolinium (157.4) in which, despite the proximity in weight and in the molecular volume of their salts,[12] an almost complete separation was achieved in a comparatively short time. The magnetization numbers of the ions of samarium and gadolinium are 0.87 and 28.2×10^6, respectively,[13] and the difference appears to be connected with the entrance of electrons into the seventh sublevel of the N group in Main-Smith and Stoner's scheme, a level that is unoccupied in samarium. Differences in the external electrical field of the ions, with consequent differences in hydration and mobility, might well originate in the same way.

In hafnium and zirconium, however, there is an almost complete similarity in the electronic arrangements both of outer and of inner groups. Hevesy has pointed out that of all the closely related pairs of homologs, rubidium and cesium, strontium and barium, yttrium and lanthanum, zirconium and hafnium, neobium and tantalum, molybdenum and tungsten, the pair in the fourth group exhibits the greatest similarity,[12] and if, as is stated, the difference in basicity between hafnium and zirconium is less than that between cesium and rubidium, the effect by which we had hoped to convert a slight difference in mobility into one yielding a practicable separation will be very slight. Nevertheless, the existence of slight differences in chemical properties is shown by the possibility of causing a partial separation of zirconium and hafnium by fractional precipitation with aniline or ammonium hydroxide, and by the difference in stability of complexes of the metals with hydroxy-anthraquinones,[14] and we have here the ground for concluding that the difference in ionic mobility is increased very slightly by the different basicities.

The similarity in ionic volume and in electronic structure of all the groups precludes the possibility of any considerable difference in hydration due to electrostatic attraction, and the small separation that was achieved is

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[12] v. Hevesy, *Z. anorg. Chem.*, **147**, 217 (1925).

[13] St. Meyer, *Sitzb. Akad. Wiss. Wien*, **133**, 491 (1925).

[14] De Boer, *Rec. trav. chim.*, **44**, 1071 (1925).

therefore in accordance with the predictions that would be made from a consideration of the properties of the two elements.

Summary

The method of ionic migration has been applied to the separation of zirconium and hafnium. After prolonged electrolysis of an agar gel containing these elements as complex anions, a slight but nevertheless distinct concentration of hafnium in the rear of the section occurred, a difference of some 2% in the average atomic weights of front and rear segments being consistently established. The degree of separation, however, was much smaller than that previously attained in the application of the method to the rare-earth metals. An attempt is made to correlate the similarity of the velocities of zirconium and hafnium ions, contrasted with the considerable differences which apparently exist in the rare-earth group, with prevalent notions of the atomic structures of the elements in question.

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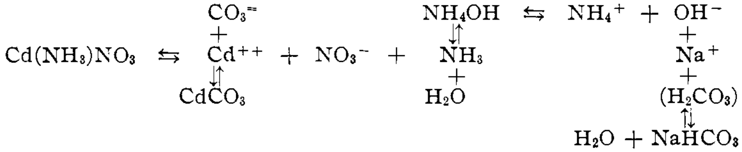
NOTE

A Test for Cadmium in the Presence of Copper.—In the course of development of schemes of qualitative analysis numerous methods have been devised for the separation of cadmium from copper; perhaps the most satisfactory of these is the cyanide method. Most of the other methods present difficulties of one sort or another. The following is a test for cadmium in the presence of copper.

The test is based on the fact that there is a marked difference in the solubility of copper and cadmium carbonates and also a difference in the stability of the copper- and cadmium-ammonia complexes which results in a still greater difference in the solubility of the carbonate salts in the presence of ammonia. When ammonium chloride is added to a solution of a copper salt and an excess of sodium bicarbonate is then added, there is a deepening of the blue color, indicating that one of the copper-ammonia complexes has been formed. When a solution of a cadmium salt is similarly treated a precipitate of cadmium carbonate is formed which is insoluble in an excess of either reagent. This is probably due to the fact that the equilibrium



$$\begin{array}{ccccccccc}
 & & CO_3^{=} & & & & NH_4OH & \leftrightarrows & NH_4^+ + OH^- \\
 & & + & & & & \downarrow\uparrow & & + \\
Cd(NH_3)NO_3 & \leftrightarrows & Cd^{++} & + & NO_3^- & + & NH_3 & & Na^+ \\
 & & \downarrow\uparrow & & & & + & & + \\
 & & CdCO_3 & & & & H_2O & & (H_2CO_3) \\
 & & & & & & & & \uparrow\downarrow \\
 & & & & & & & & H_2O + NaHCO_3
\end{array}$$

is not shifted far enough to the left to form the complex with cadmium as it does with copper. If the normal carbonate is used in place of the bicarbonate, the equilibrium is shifted sufficiently to allow no precipitate with either cadmium or copper.