THESIS.

The Preparation and Composition

of the

ZIRCONIUM CHLORIDES.

Presented for the Degree of B. S. in the School of Chemistry
of the University of Illinois.

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CLASS OF ’94.

M. J. 1894
The eleuther zirconium was discovered in 1789 by Klaproth in zircon, which is the natural silicate of the metal. He afterwards found the same element in hyacinth from Ceylon and proved the identity of this stone with zircon, hyacinth being a transparent variety.

The eleuther zirconium has at various times and for various reasons, been supposed to consist of several simpler bodies. For by in 1869 described a new eleuther in combination with zirconium in Ceylon hyacinth, which he called dijon (from Jargon, another name for the mineral). He based his conclusion upon the fact that the spectrum of the specimen was peculiar and differed from that
of any known constituent. Afterward, however, he found the spectrum was due to the presence of a little Uranium, the combination of Uranium with Zirconium affording a different spectrum from that produced by either constituent alone.

Sorby also induced Forbes to make a chemical examination of Zircon. The results of this examination led Forbes to the conclusion that Zirconium was not a simple body because the chloride formed from it was not entirely soluble in hydrochloric acid and because that part of the chloride which did dissolve differed materially from the soluble chloride in density and in physical properties.

In 1866 Cranberg thought he had decomposed Zirconium, calling the new earth
of its lower atomic weight, the easier solubility of its chloride in hydrochloric acid, the fact that its hydrochloric acid solution was not precipitated by potassium sulphate, and the easier solubility of its oxalate in oxalic acid.

The conclusions which both Forbes and Aarup drew, are, in the present state of our knowledge, explainable by the ready tendency of zirconium to form basic salts, so that the element has thus far resisted all efforts toward its decomposition.

We know that if the presence of oxygen in these basic salts were overlooked their analysis would lead also to errors in the atomic weight determination and we
find that the basic chlorides are less soluble in hydrochloric acid and the basic oxalates less soluble in oxalic acid than the normal ones.

Zirconium belongs to the fourth group in Mendeléeff's system. In its chemical behavior it resembles Carbon, Silicon &c. on the one hand and Aluminium, Iron &c. on the other. Its oxide is capable of forming salts with both acids and bases.

1. \( \text{Na}_2\text{OH}, \text{H}_2\text{O} + \text{Zr} \rightarrow \text{Zr(OH)}_2 \) precipitate zirconium hydroxide as a gelatinous, milk-white precipitate, easily soluble in acids when precipitated cold, but less easily when precipitated hot or when washed with hot water.

2. \( \text{Na}_2\text{CO}_3 \) precipitates the carbonate, soluble in excess.
$\text{Na}_2\text{C}_2\text{O}_4$ precipitates the oxalate, soluble in $\text{HCl}, \text{Na}_2\text{C}_2\text{O}_4$ and in $(\text{NH}_4)_2\text{C}_2\text{O}_4$

$\text{Na}_2\text{SO}_4$ precipitates the sulphate from a concentrated solution.

$\text{Na}_2\text{S}_2\text{O}_3$ precipitates a thiosulphate (?) mixed with sulphur.

$\text{H}_2\text{O}_2$ precipitates $\text{H}_2\text{O}_2$ from a dilute acid solution (Bailey). Complete precipitation took place readily according to Bailey.

If the $\text{H}_2\text{O}_2$ is 120 volumes strong, from slight traces of zirconium being thrown down, if the $\text{H}_2\text{O}_2$ was 20 volumes strong the precipitation was incomplete and only took place at all after some time.

In order to prepare pure salts of zirconium for investigation several methods have been
Firmanu gives the first (of which I have found record) in 1846. He fused the pulverized zircon at a good heat with four times its weight of NaOH. This fusion he dissolved in hydrochloric acid, separating silica in the usual manner from the filtrate he obtained a basic chloride from which he prepared the oxide by precipitating the solution with ammonia and igniting the precipitate.

In 1884 Stolba published a method for the disintegration of zircon by fusing with potassium fluoride (KBF₄) and potassium carbonate.

Lineman, in 1885, published a very valuable method for opening up zircon.
Linnemann treats the mineral several days with hydrofluoric acid, and then, after pulverizing, treats the powder several hours with boiling hydrochloric acid. He thus obtains snow-white material for fusion. The powder is fused with sodium fluoride and sodium hydrate in a silver crucible, using, for 25 gms. of 20 gms. of NaF and 10 gms. of NaCl. On digesting the fusion with water, sodium zirconate is left undissolved, and, after washing, is brought into solution by means of hydrochloric acid.

The hydrochloric acid solution is evaporated to dryness and the powdered mass washed on the filter with a mixture of hydrochloric acid, alcohol, and ether.

By extraction with this mixture, iron, and other impurities, are said to be gotten rid of to
a great extent.

In 1891, Venable proposed a method which is essentially a modification of Linnaeus's scheme. Venable uses in fusion, 400 grams of NaOH, 20 qm. of NaF and 100 grams of powdered zinc. Previous to fusion the powdered mineral is boiled several hours with hydrochloric acid, but Venable considers the treatment with HCl as unnecessary.

The powdered zinc is added to the flux while in fusion. From the product of fusion water dissolves sodium silicate leaving sodium zirconate (Na₂ZrO₄) undissolved. The sodium zirconate is dissolved in hydrochloric acid and the solution evaporated to separate silica. Zirconium hydrate is then precipitated with ammonia, and the precipitate washed.
repeatedly by decantations.

The crude hydrate is then dissolved in strong, hot hydrochloric acid. The solution is evaporated to dryness and the zirconium chlorides are washed in a funnel with a mixture of strong hydrochloric acid and alcohol. The chlorides, thus freed in large measure from impurities, are dissolved in boiling concentrated hydrochloric acid and repeatedly crystallized. Tambe says he finds it advisable to repeat this crystallization as many as twenty times.

In 1885 Bailey published a method for preparing zirconium salts involving the use of hydrogen peroxide. Hydrogen peroxide is added to a dilute sulphuric acid solution of zirconium sulphate where \( Zr_2O_5 \) (a hydrated oxide) is precipitated and the author says quite free
from iron, which is about the most difficult impurity to eliminate in preparing pure zirconium salts.

After the zircon has been opened up, the preparation of zirconium chlorides is a simple matter, but the preparation of a pure salt of definite composition, and especially a crystalline salt, presents far greater difficulty.

The chief chlorides of zirconium which have been described are zirconium tetra-chloride (or normal chloride) (\(\text{ZrCl}_4\)) and zirconium oxychloride, (\(\text{ZrOCl}_2\)).

The former it has been only thought possible to obtain in the dry way, i.e. by passing chlorine over zirconia in a combustion tube and condensing the volatile chloride in a suitable receiver, while the latter crystallizes out from
a hydrochloric acid solution under proper conditions.

Six zinconique oxychlorides have been described as having been separated from a hydrochloric acid solution. Their formulas are: 3\(\text{ZnCl}_2\cdot\text{HCl}\), \(\text{ZnCl}_2\cdot\text{Cl}_2\), \(\text{ZnCl}_2\cdot\text{HCl}\cdot\text{Cl}_2\), \(\text{ZnCl}_2\cdot \text{Cl}_2\cdot\text{HCl}\), \(\text{ZnCl}_2\cdot\text{HCl}\cdot\text{Cl}_2\cdot\text{HCl}\), and \(\text{ZnCl}_2\cdot\text{Cl}_2\cdot\text{HCl}\). Also, perhaps, \(\text{ZnCl}_2\). While Bailey says he thinks the highest chloride which can be isolated from solution is the oxychloride bearing the formula \(\text{ZnCl}_2\cdot\text{Cl}_2\cdot\text{HCl}\), Linnean calls the highest \(\text{ZnCl}_2\), but gives no authentic analyses of his product, simply remarking that the residue on ignition was 50% while that of \(\text{ZnCl}_2\) should be 52%.

I enable, in a private communication, also says some preliminary work done by him leads to this view.
The want of any unanimity of opinion on this point, and the doubtful need of the matter makes it desirable to undertake some analyses of zirconium chlorides, crystallized under various conditions from solution.

The most available resource of information upon zirconium chlorides in general are Graham-Otto, Lehrbuch der Chemie, and Emilin Krantz, Landbuch der Anorganischen Chemie.

A translation of some sections from these works may be of use as presenting in a concise form the most reliable work which has previously been done upon these points.

The "Lehrbuch der Chemie" of Graham-Otto says:

"If the solution of the tetra chloride (in water) is evaporated, half of the chlorine escapes..."
and one obtains, (as also by solution of zirconium hydrate in hydrochloric acid and evaporating the solution), crystals of a hydrate of zirconium dichloride, \( \text{ZrOCl}_2 \cdot 9\text{H}_2\text{O} \) (Kerimov).

According to Wellis these crystals contain only 4 ½ \( \text{H}_2\text{O} \). The crystals, which are needle-form, are soluble in water and alcohol.

By heating they part with water and hydrochloric acid, without change of form. They leave the compound \( 2\text{ZrOCl}_2 \cdot \text{ZrO}_2 \), which is insoluble in water.

The "Sodium Zirconium Peroxydichloride" of Gmelin—Kraut, says:

"The aqueous solution of chloride of zirconium loses by evaporation half its \( \text{HCl} \) and affords colorless, glistening needles of astringent taste. The same product
is obtained through solution of zirconia in HCl (Bergelsius). Formula: ZrOCl₂

"Nylander (Bidrag, 18) found in zirconium oxychloride of various methods of preparation not only from 27.9 to 37.8% Zr and from 21.5 to 28.7% Cl, which cannot be brought by variations in drying, but also, what is less easily accounted for, as high as 100% to 99.86% Cl while ZrOCl₂ affords the proportion 100:78.8

From the raw, alcoholic solution of ZrOCl₂ ether precipitates the crystalline body Zr₂O₃Cl₂, which contains about half the chlorine ZrOCl₂. Contains, this product dissolves in cold water.

Certainly nothing said here implies the formation of normal chloride in acid solution
Experimental Work.

We have, then, 1st, to find a convenient method, or a modification of an old method, for decomposing zinc oxide, and 2nd., to prepare a chloride which shall not only have a definite composition and be crystalline, if possible, but shall be prepared under those conditions most favorable to the formation of the normal salt.

As the higher basic chlorides are said to be less soluble (scarcely soluble at all) in hydrochloric acid this was looked to as a means of distinguishing and separating them.

As an initiative step zinc oxide was treated
with hydrofluoric and sulphuric acids and heated to ascertain to what extent it would decompose under these conditions. Decomposition, if it took place at all, was very slight.

Some acid potassium fluoride was then prepared and with it as a flux, some finely pulverized zircon ore was fused. The mineral was easily and completely decomposed.

Accordingly thirty-eight grams of the mineral, pulverized so as to pass a 100 mesh sieve, were fused with potassium acid fluoride at a high temperature over a blast lamp. The cold, porcelain-like mass was disintegrated with boiling water acidulated with hydrofluoric acid. In order to effect a complete disintegration and solution of the potassium flux, zirconate several digestions
were required.

The solutions of $K_4F_6$ thus obtained were
decanted from the residue of insoluble $K_4SiF_6$,
and on cooling, the salt crystallized in glistening
white crystals of small needles.

After two recrystallizations the salt
was dissolved in hot water and the zirconium
precipitated with ammonia; the hydrate
thus formed was then repeatedly washed
by decantation and finally out as filter.

The hydrate of zirconium was then dissolved
in hydrochloric acid. It dissolved readily
but upon heating an insoluble precipitate
immediately settled out which completely failed
to dissolve in more acid.

This was separated by filtering. Most of
the chloride obtained from this fusion was
in this insoluble form.

But Linneaner, Zincke, and others obtained a chloride soluble in concentrated HCl and crystallized from it. This insoluble material was reserved for investigation, and in order to ascertain the cause of having obtained the chloride in an insoluble state, a new amount of mineral was fused up.

This material (from North Carolina) was powdered so as to pass a 100 mesh sieve, and boiled with con. HCl for about fifteen minutes, then washed by decantation. HCl left a black carbamone residue from the iron of the plate used in pulverizing the mineral.

In order to destroy this the powder was ignited, and the powder again boiled with con. hydrochloric acid.
This treatment left a clean, white and apparently quite pure material; in notable contrast with the dark, brown mineral which was used. The dissolved out of two hundred grams of gizzard 10.5 grams of impurities, so that such previous treatment must be of great value in preparing the mineral for decomposition.

One hundred grams of this material were fused with 200 grams of HgO in a capacious platinum dish. The melt was pulverized and digested with boiling water so long as any salt n tough into solution. After two crystallizations the salt was dissolved in boiling water and precipitated with ammonia in a large jar, washed several times by decantation, and
finally on a filter.

As it was conceived that possibly the moisture in the hydrate was sufficient to cause a precipitation of basic guinea chloride from the acid solution on heating, the hydrate thus twice was dried at 100°C previous to its further treatment. The practically dry hydrate was then dissolved in concentrated, boiling hydrochloric acid. The great part of the hydrate went into solution and remained in solution.

The insoluble portion was filtered out and the acid solution of soluble chloride was evaporated over a free flame. The solution was dark colored and seemed to contain much iron.
Besides it seemed difficult to arrive at the point of crystallization. On the other hand the salt separated in an amorphous precipitate. However this amorphous material was taken, and washed on a grosh crucible with a mixture of alcohol and concentrated hydrochloric acid.

A very colored filtrate and a moderately white salt was the result. The purified salt was redisolved and placed in a vacuum desiccator to allow it to crystallize. Pure crystals, white, glistening octahedra were obtained which proved to be potassium chloride, from the potassium fluo-gironeate. These crystals were separated and the solution evaporated souff-
On cooling an amorphous mass was deposited. In order to eliminate any potassium chloride present the salt was redissolved, precipitated again with ammonia, and the dried hydrate again dissolved in concentrated hydrochloric acid.

The solution was placed in a vacuum desiccator and allowed to evaporate. Crystals were formed which were needle form and dehydrated in air. They had an astringent taste and were soluble in water, an amorphous salt precipitating on heating a moderately concentrated solution.

The crystals were submitted to analysis.
Sample #1 - was a salt which was allowed to deposit in vacuum without the aid of heat.

(Zirconia was precipitated with considerable excess of ammonia (boiling 1 minute), while chlorine was estimated as acid in the filtrate.)

The salt corresponds most nearly to the basic oxychloride $\text{ZrOCl}_2 + \frac{1}{2} \text{H}_2\text{O}$. (Hermann & Payer)

<table>
<thead>
<tr>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO</td>
<td>41.87</td>
</tr>
<tr>
<td>Cl₂</td>
<td>19.88 (%)</td>
</tr>
<tr>
<td>$\frac{1}{2}$H₂O</td>
<td>38.25</td>
</tr>
</tbody>
</table>

Sample #2 - the solution was evaporated nearly to dryness and crystallization completed in vacuo.

Corresponds to $\text{Zr}_2\text{O}_3\text{Cl}_2$ (Scheidemann).

<table>
<thead>
<tr>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr₂O₃</td>
<td>52.44</td>
</tr>
<tr>
<td>Cl₂</td>
<td>16.95</td>
</tr>
<tr>
<td>$\frac{1}{2}$H₂O</td>
<td>30.61</td>
</tr>
</tbody>
</table>
In order to further purify these salts and to get them in shape for another analysis, the samples were redissolved in hot, conc. hydrochloric acid and allowed to evaporate spontaneously in a vacuum until entirely free from hydrochloric acid.

The product crystallized well in blades.

Duplicate samples of one half gram each were submitted to analysis with the following results:

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>43.92 - 44.20</td>
<td>41.11</td>
</tr>
<tr>
<td>Cl₂</td>
<td>23.38 - 23.39</td>
<td>27.49</td>
</tr>
<tr>
<td>½ H₂O</td>
<td>32.70 - 32.41</td>
<td>31.40</td>
</tr>
</tbody>
</table>

These results show that the salt corresponds nearly again, as in sample #1, to the oxychloride ZnOCl₂ + 4½ H₂O.
In regard to the disagreement I regard it must be borne in mind that the analyses were not made upon chemically pure salts, though it will be observed that the last analyses, where the salt was further purified, agree better with theory.

Then, too, it must be borne in mind, that these salts all lose hydrochloric acid very easily and there is a consequent tendency for the chlorine to be lowered and the zirconia to be raised in proportion.

As a result of this work the conclusion must be drawn that the normal chloride of zirconium is not formed on crystallization of zirconium chlorides from concentrated hydrochloric acid under the conditions which have here been observed.
As even concentrated hydrochloric acid must contain water—which is prejudicial to the formation of \( \text{FeCl}_4^- \)—we must deem it an impossibility, so far as this thesis proves, to prepare such a salt by crystallizing from it.

On the other hand, while it was impossible to bring a solution to crystallization by evaporating by aid of heat, by evaporating at normal temperature in a vacuum, a salt was obtained which, on analysis, proved to be \( \text{FeCl}_2 + \frac{1}{2} \text{H}_2\text{O} \), an oxychloride having about one half the amount of chlorine required to make it a normal salt.
Appendix.

a. On some attempt to precipitate zirconia by oxidation.

Bailey (ref. 5) found that by adding hydrogen peroxide to a dil. acid solution of zirconium sulphate he could precipitate all the zirconium free from iron, titanium etc. and even separate traces of zirconium from all excess of other elements.

But to do this he had to employ N/10 or 120 volumes of oxygen strength. This fact presents the practical or now general scientific use of the reaction as hydrogen peroxide of only 15 vol. strength is all that is obtainable, and this is far too weak for the purpose.

The experiments made were with a view to finding some convenient substitute for hydrox
peroxide.
It is apparent that the value of hydrogen peroxide depends on its furnishing nascent oxygen. Sodium hypochlorite was prepared and a little being added to a dilute solution of zirconium sulphate, the mixture was heated. Oxygen was evolved and a fraction of the zirconia was precipitated. But to condense considerable work, the method proved unsuccessful as the zirconia was neither completely separated nor purified.
Potassium permanganate was then added to a solution of zirconium sulphate slightly acid with $\text{H}_2\text{SO}_4$, and enough $\text{H}_2\text{O}_2$ added to decompose the $\text{K}_2\text{Mn}_2\text{O}_8$. Oxygen was copiously evolved and continued to come off for some hours, but by no variation
In treatment could a precipitate of girocine be produced free from manganese or iron. Moreover the separation was not complete. Time was wanting for extensive research on this point, but if a good substitute for hydrogen peroxide can be found even unpractical method will be rendered practical and of great use to the lithologist as well as to the chemist.

b.- On the effect of boiling gr/100 of precipitated in excess of ammonia and its solubility in an excess of ammonia.

Previous to making the analyses recorded on pages 23 and 24 some experiments were made upon the method of precipitation.
zirconium as hydrate (and weighing as dioxide.)

To determine the effect of boiling, three samples, each containing the same amount of zirconia, were analyzed.

#1 was precipitated cold with a considerable excess of Ammonia: \( \text{H}_2\text{ZrO}_2 = 0.1888 \)

#2 was precipitated, excess \( \text{NH}_4\text{OH} \), filtered in min., \( \text{H}_2\text{ZrO}_2 = 0.1820 \)

#3 added slight excess \( \text{NH}_4\text{OH} \), filtered in 10 min., \( \text{H}_2\text{ZrO}_2 = 0.1634 \)

From these results we see that long boiling can not be thought of in making a determination of zirconium by this method, the last (#3) being carried out precisely as an aluminium determination.

In order to determine the effect of an excess of ammonia on the precipitate three more samples were taken.

#1- added slight excess \( \text{NH}_4\text{OH} \), \( \text{H}_2\text{ZrO}_2 = 0.1212 \)
#2 Added 10 cc. Am.    VI. $\text{Fe}_2\text{O}_3 = 1.277$

#3 20 "

Boiled all of these just one minute.

From these results it is shown that $\text{Fe}(\text{OH})_4$ is quite insoluble in an excess of ammonia.

Accordingly the following details were adopted in making a zirconium determination, and the method was successful. The solutions were treated with 5 cc. Ammonia in excess while cold. Then they were just brought to a good boil and filtered.

No trouble was experienced in washing $\text{Fe}^{3+}/_4$ thus precipitated and there was not one turbid filtrate.
Articles referred to in Margin.

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2. - Deutsch Chem. Ges. 1869-126-193
3. - 337-383
4. - Ann. Chem. u. Pharm. 56-223
5. - Jour. Chem. Soc. 49-149-481
8. - Chem. Yearb. 5-2 233-240
10. - Arr #5.

Besides these the following references were used and are all which were found on the subject of Zirconium in the libraries.
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   5-477-8-478-23-569
   6-345-17-227
5. Ann. Chimie 1875-326 (Vol. 2-3-3-4 fr. 8)
   1873-704-1876-275 1884-70-460 49-169-451
7. Z. für f. Phys. 1893-662-60-6
11. Bull. de la société Chimique 20-65
13. Comptes Rendus 1891-218