

motive force of only about 10 mmv. and showed that the presence of copper in the amalgam of a Weston cell would not appreciably alter the electromotive force or temperature coefficient.

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[CONTRIBUTION FROM THE INSTITUTE OF THEORETICAL PHYSICS]

## THE SOLUBILITIES OF THE PHOSPHATES OF ZIRCONIUM AND HAFNIUM

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The unusually low solubility of zirconium phosphate in strong mineral acids insures an important role for the phosphate precipitate both in the qualitative and quantitative chemistry of zirconium. The appearance of such a precipitate in a strong acid solution containing hydrogen peroxide is the only simple qualitative reaction for zirconium. In the quantitative analysis<sup>1</sup> of zirconium the phosphate precipitate is no less important, especially when determining small amounts of zirconium occurring in rocks, as first proposed by Hillebrand.<sup>2</sup> All these conclusions have been somewhat modified by the discovery of hafnium. For example, the appearance of a precipitate in a solution of 20% sulfuric acid containing hydrogen peroxide upon the addition of sodium phosphate no longer proves with certainty the presence of zirconium, as hafnium is also precipitated under these conditions. Shortly after the discovery of hafnium, while investigating the fractional precipitation of a mixture of zirconium and hafnium by sodium phosphate from a strong acid solution, Coster and one of the present writers<sup>3</sup> found an accumulation of hafnium in the first precipitate, the method used being that of quantitative X-ray spectroscopy. In contrast to most of the other compounds of the two elements it was necessary to conclude from the above results that a not inappreciable difference exists between the solubilities of the phosphates of zirconium and hafnium. This result also showed that hafnium phosphate and not zirconium phosphate is the less soluble in strong mineral acids. The usefulness of the difference in the solubility of zirconium and hafnium phosphates as a method for the separation of these elements is here pointed out.<sup>4</sup> From the point of view of both the preparative and the analytical

<sup>1</sup> Bailey [*J. Chem. Soc. Trans.*, 49, 481 (1886)] first used the phosphate in the separation and quantitative determination of zirconium. Compare also Noyes, Bray and Spear, *THIS JOURNAL*, 30, 516 (1908). Biltz and Mecklenburg, *Z. angew. Chem.*, 25, 2110 (1912).

<sup>2</sup> Hillebrand, *U. S. Geol. Survey Bul.*, 176, 75 (1900).

<sup>3</sup> Hevesy, *Ber.*, 56, 1503 (1923). Coster, *Chem. News*, 127, 65 (1923).

<sup>4</sup> De Boer and van Arkel [*Z. anorg. Chem.*, 144, 196 (1925)] found that zirconium and hafnium phosphates are easily soluble in hydrofluoric acid. From this fact they evolved a method for the separation of zirconium from hafnium.

chemistry of hafnium and zirconium it therefore seemed desirable to determine the solubility of their phosphates in hydrochloric acid of different concentrations and to investigate the constitution of the phosphate precipitate.

### Preparation and Analysis of the Phosphates

We started with carefully purified oxychlorides of zirconium and hafnium, the former substance containing, however, about 0.4% of hafnium, and the latter about 0.1% of zirconium.

About 2 g. of zirconium oxychloride,  $ZrOCl_2 \cdot 8H_2O$ , dissolved in 1.5 liters of 6 *N* hydrochloric acid, was added drop by drop during constant stirring to 1.5 liters of 6 *N* hydrochloric acid containing about 2 g. of disodium phosphate. After the finely divided white precipitate formed had been washed several times with 6 *N* hydrochloric acid by decantation, it was filtered off and dried in an air-bath below 80°. The sample thus prepared was used for the solubility measurement and also for analysis.

About 0.1 g. of the sample was heated in an electric furnace to 120–130° without any appreciable loss of weight. Then the temperature of the furnace was gradually raised to 700° but even at this temperature a part of the water was not driven off. Only after continued ignition in the furnace at a still higher temperature could a constant weight be obtained. The total loss thus found was regarded as water and calculated as such.

The ignited sample was fused with about 3 g. of sodium carbonate. The melt was leached with hot water containing sodium carbonate, filtered and washed with sodium carbonate solution. The insoluble residue was fused again with sodium carbonate and treated as before. From the combined filtrates, the phosphoric acid was precipitated as magnesium ammonium phosphate; the precipitate was ignited and weighed as magnesium pyrophosphate. The insoluble residue obtained after the second treatment was fused with sodium acid sulfate. The melt was dissolved in water containing a little sulfuric acid. Zirconyl hydroxide was precipitated from this solution by ammonium hydroxide, ignited and weighed as zirconium oxide.

The result of the analysis was as follows.

Subs.	Found, %	Calcd. for $ZrO_2 \cdot P_2O_5 \cdot 2H_2O$ , %
$ZrO_2$	41.6	40.91
$P_2O_5$	46.6	47.14
$H_2O$	11.9	11.95
Total	100.1	100.00

About 0.5 g. of hafnium oxychloride,  $HfOCl_2 \cdot 8H_2O$ , dissolved in 400 cc. of 6 *N* hydrochloric acid was added to 400 cc. of 6 *N* hydrochloric acid containing 0.35 g. of disodium phosphate. The precipitate was washed, filtered, dried and analyzed by the same method that was used in the case of zirconium. The result of the analysis carried out with about 0.1 g. of the sample was as follows.

Subs.	Found, %	Calcd. for $HfO_2 \cdot P_2O_5 \cdot 2H_2O$ , %
$HfO_2$	54.2	54.18
$P_2O_5$	36.5	36.55
$H_2O$	9.4	9.27
Total	100.1	100.00

The values were calculated on the assumption that the compound has the formula  $ZrO(H_2PO_4)_2$  or  $HfO(H_2PO_4)_2$ . The agreement between the

values found and calculated being very satisfactory, we must conclude that the phosphate has the above formula and that it is presumably precipitated when the zirconyl cation  $(ZrO)^{++}$  unites with two primary phosphate ions  $(H_2PO_4)^-$ . However, we cannot decide on the basis of the results of the analysis whether the phosphate precipitated has the formula  $Zr(HPO_4)_2 \cdot H_2O$  or  $ZrO(H_2PO_4)_2$ . Considering the great stability of the zirconyl ions in contrast to the zirconium ions which practically do not exist in aqueous solution, we must regard the existence of the zirconyl compound  $ZrO(H_2PO_4)_2$  as being very much more probable.

When ignited, the resulting compound was found to correspond to either the formula  $ZrO(PO_3)_2$  or  $ZrP_2O_7$ . But since primary phosphates, for example, monosodium phosphate, form metaphosphates, such as  $NaPO_3$ , we must conclude that the first of the above formulas, that is,  $(ZrO)(PO_3)_2$ , is preferable.

### Solubility of Phosphates in Hydrochloric Acid

About 0.1 g. of the phosphate was shaken with about 150 cc. of hydrochloric acid in a thermostat at  $20^\circ$  for about three days. After several days in the thermostatic bath, the solution was filtered through a glass filter, and 100 cc. of the clear filtrate was evaporated; the residue was ignited and weighed. The results are shown in Table I.

TABLE I  
SOLUBILITY OF ZIRCONIUM PHOSPHATE

Concn. of acid <i>N</i>	Wt. of residue ignited per 100 cc. of solution, g.	$M^{IV}O(H_2PO_4)_2$ per liter of solution, Mole
10.00	0.0061	0.00023
6.01	.0033	.00012
SOLUBILITY OF HAFNIUM PHOSPHATE		
10.48	0.0046	0.00013
10.21	.0043	.00012
5.94	.0031	.00009

It is seen from the above values that the hafnium phosphate is less soluble than the phosphate of zirconium and that the ratio of the molecular solubilities amounts in 6 *N* acid to about 1:4 and in 10 *N* acid to 1:9. When separating hafnium from zirconium by the phosphate method it is thus desirable to precipitate the phosphate from a strongly acidic solution.

### The Analytical Determination of Zirconium and Hafnium

As the only phosphates "insoluble" in strong mineral acids<sup>5</sup> in the presence of hydrogen peroxide are those of zirconium and hafnium, we must conclude that either zirconium or hafnium is present when a precipitate is obtained in such solutions. Since hafnium is not found free from zir-

<sup>5</sup> With the exception of hydrofluoric acid in which they are readily soluble [De Boer, *Z. anorg. Chem.*, **144**, 190 (1925)].

conium in nature, the precipitate will in almost every case indicate the presence of zirconium. The quantitative determination of hafnium as phosphate can be carried out in exactly the same way as the determination of zirconium. If a mixture of the two elements is present, the composition of the phosphate precipitate can be calculated from the ratio  $\text{ZrO}(\text{PO}_3)_2 + \text{HfO}(\text{PO}_3)_2 : \text{P}_2\text{O}_5$ , or of that of the phosphates and oxides. The same result can also be secured through measurement of the density of the phosphate mixture or of that of the oxides.<sup>6</sup>

In addition to a great number of earlier researches<sup>7</sup> on the phosphate of zirconium the quantitative determination of zirconium as phosphate has recently been thoroughly investigated by Steiger,<sup>8</sup> Nicolardot and Reglade<sup>9</sup> and especially by Lundell and Knowles.<sup>10</sup> The last-mentioned investigators conclude that, by proper attention to the conditions under which the zirconium phosphate is precipitated and handled, the method will give reasonably accurate separations from aluminum, iron, chromium, titanium, tri- and tetravalent cesium, and thorium. They recommend the use of about 200 cc. of solution for 0.1 g. of zirconium dioxide containing 20% of sulfuric acid by weight. Assuming that the solubility of zirconium phosphate in sulfuric acid is about the same as in hydrochloric acid of equal concentration, 200 cc. of 20% acid should dissolve somewhat more than 6 mg. of zirconium phosphate, which introduces a very appreciable error. This error is eliminated by using an excess of the soluble phosphate. Lundell and Knowles found a loss of 0.0003 g. of zirconium oxide when the phosphate was precipitated from 2 *N* sulfuric acid containing ten times the calculated amount of phosphate; no loss in the presence of 100 times the calculated amount at room temperature; a loss of 0.0004 g. in 4 *N* acid, even in the presence of this large excess of phosphate; and a loss of 0.0026 g. when the latter solution was heated, an error of 14%. In spite of the slight solubility of the phosphates of zirconium and hafnium it is thus necessary to precipitate with a great excess of the phosphate and preferable to work in a cold solution.

### Summary

Zirconium phosphate precipitated from 6 *N* hydrochloric acid has the composition  $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ ; hafnium phosphate, that of  $\text{HfO}(\text{H}_2\text{PO}_4)_2$ . Upon ignition, the phosphate precipitates lose two molecules of water.

The solubility of the zirconium phosphate in 6 *N* hydrochloric acid amounts to 0.00012 molecular equivalent; that of the hafnium phosphate,

<sup>6</sup> Hevesy and Berglund, *J. Chem. Soc.*, **125**, 3273 (1924).

<sup>7</sup> Literature references up to 1922 may be found in Venable's monograph, "Zirconium and its Compounds," New York, 1922.

<sup>8</sup> Steiger, *J. Wash. Acad. Sci.*, **8**, 637 (1918).

<sup>9</sup> Nicolardot and Reglade, *Compt. rend.*, **16**, 348 (1919).

<sup>10</sup> Lundell and Knowles, *THIS JOURNAL*, **41**, 1801 (1919).

0.00009 molecular equivalent. In 10 *N* hydrochloric acid the values are 0.00023 and 0.00012.

The importance of the phosphate precipitation for the qualitative and quantitative determination of the two elements is discussed.

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## THE BINARY SYSTEM CONSISTING OF ORTHO-CRESOL AND PARA-CRESOL

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In a study of the methods of purifying organic compounds by fractional crystallization, the three cresols have been under investigation in this Laboratory. The freezing-point curves for the mixture of *o*-cresol and *p*-cresol are given below, with the evidence of the formation of a 1:1 molecular compound.

The *p*-cresol used was a Kahlbaum preparation; m. p., 33.5°. After fractional crystallization, rapid centrifuging and drying over phosphorus pentoxide for seven days it was not found possible to raise the melting point above 34.2°, which is 0.2° below that given by Kendall and Carpenter.<sup>2</sup> In the belief that the principal impurity in the cresols, after crystallization, is water absorbed because of their extreme hygroscopicity, an apparatus was devised in which the sample could be dried in the same tube in which the melting-point determinations were made. The inner tube of a Beckmann freezing-point apparatus was fitted with an inlet tube through which air, dried over phosphorus pentoxide, was aspirated; the glass stirrer was fitted with a mercury seal. This apparatus was used for the pure cresols and for the various mixtures investigated, the weights of the two components being determined directly in the apparatus. With its use the purified *p*-cresol rose to a maximum freezing point of 34.80° after 24 hours' drying, and that of the purified *o*-cresol rose to 30.08°.

TABLE I  
FREEZING POINTS OF *o*-CRESOL-*p*-CRESOL MIXTURES

<i>o</i> -Cresol, % by wt.	100	86.01	77.97	70.36	62.89	57.80	57.80	49.30
F. p., °C.	30.08	22.20	16.41	10.27	3.70	-0.58	+2.88	-6.62
<i>o</i> -Cresol, % by wt.	47.02	39.83	39.83	34.99	30.31	23.95	15.59	0
F. p., °C.	+7.65	6.40	-2.70	+3.70	9.28	15.67	22.94	34.80

In Table I and Fig. 1 are shown the data on the freezing points of mixtures of the two components. The usual technique of freezing-point

<sup>1</sup> The material of this paper is part of a thesis presented by Irving Mosbacher for the degree of Master of Science at New York University.

<sup>2</sup> Kendall and Carpenter, THIS JOURNAL, 36, 2498 (1914).