more effective in bringing about dissociation of iodine in the solution than light corresponding to the discontinuous absorption, but that the difference is not large. Absolute values of the empirical specific rate constant have been measured.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Determination of the Zirconium–Hafnium Ratio[1]

BY GRANT WERNIMONT[2] AND THOMAS DE VRIES

The optical rotation of solutions containing potassium tartrate along with various amounts of zirconium or hafnium oxychloride has been studied by de Boer and Emmens.[3] They found that the effect of zirconium was somewhat less than that of hafnium and suggested that the polariscope might be used for determining zirconium–hafnium ratios. This paper describes such a procedure in which the fluorides were used.

Experimental

The rotation measurements were made with a Schmidt and Haensch No. 52b, Lippich type polarimeter using sodium D light from a monochromator.

Three samples of zirconium oxide were prepared (one by the method of Drophy and Davy[4] to remove completely small amounts of hafnium) from C. P. zirconium salts which were shown to contain no iron or titanium.

Measurement of Rotation Change.—To measure the rotation change, zirconium oxide samples were weighed into platinum crucibles, dissolved in 5 ml. of 50% hydrofluoric acid, evaporated to dryness on the steam-bath and the residues taken up with a little water. The solutions were transferred to volumetric flasks, 10 ml. of approximately 20% tartaric acid solution (about 14 millimoles) and 10 ml. of six normal potassium hydroxide were added along with sufficient water to make 50 ml. of solution. Blank solutions containing no zirconium were also prepared.

The rotations of the solutions and blank were determined in 2-dm. tubes, the differences being taken as the rotation change. When the weight of zirconium oxide was plotted against rotation change, a straight line resulted (Fig. 1). The equation for this is $\Delta\alpha_{Zr} = 5.37W_{Zr}$ where W_{Zr} is the grams of ZrO_2 and $\Delta\alpha_{Zr}$ is the corresponding rotation change in degrees. Twenty-six points ranging from 0.1017 to 1.002 g. of oxide were used to fit the equation. The maximum deviation of calculated rotation change from the observed value was 0.09° and the average of all deviations was 0.04°.

When less than 0.3 g. of ZrO_2 was present in solution, these results are in good agreement with those of de Boer and Emmens but when more than this amount of zirconium was present, the values found by de Boer and Emmens were less than those found in this investigation.

As the molecular ratio of tartrate to zirconium approached or became greater than two to one, the observed values were less than the calculated values. Therefore care must be taken that the ratio of tartrate to zirconium (and hafnium) is greater than two to one in the final solutions.

Hafnium salts, free from zirconium, were not available in this Laboratory; hence it was necessary to use the values of de Boer and Emmens for the rotation of hafnium tartrate solutions. Their results give a straight line (Fig. 1) and were fitted to the equation $\Delta\alpha_{Hf} = 1.16W_{Hf}$.

Calculation of Zirconium–Hafnium Ratios.—A convenient method of evaluating the ratio of hafnium to zirconium was devised by using the linear equations to derive a general expression for the relation between mole ratio, rotation change and weight of zirconium–hafnium oxide present in solution. The following equation was obtained

$$\frac{N_{Hf}}{N_{Zr}} = 0.5851 \times \frac{5.37W - \Delta\alpha}{\Delta\alpha - 1.16W}$$

where W is the grams of mixed oxides present in 50 ml. of test solution and $\Delta\alpha$ is the corresponding rotation change measured in a 2-dm. tube using sodium D light.

Preparation of Zirconium–Hafnium Oxide Samples for Analysis.—Two oxide samples were prepared from two fractions of a series of

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(3) De Boer and Emmens, *Rec. trav. chim.*, **49**, 955 (1930).

(4) Drophy and Davy, *Phys. Rev.*, **25**, 882 (1925).

fractional precipitations as follows. Five grams of the zirconium–hafnium phosphate mixture was dissolved in 50% hydrofluoric acid. The solution was filtered into cold 5% potassium hydroxide and the hydroxides were washed by decantation until free from phosphate.

The supernatant liquid was decanted and enough cold 10% sulfuric acid added to double the volume of the remaining mixture, which was then stirred and allowed to stand until the hydroxides had dissolved. Eight grams of tartaric acid was added, the solution was made alkaline with ammonia, saturated with hydrogen sulfide and the sulfide precipitate was filtered off. The filtrate was acidified, boiled and the zirconium and hafnium precipitated in the cold with a 6% cupferron solution. The precipitate was washed, dried and ignited to the oxide.

This procedure can be used quite generally to prepare samples of the mixed oxides for analysis with the polariscope. Titanium is not removed by the procedure but it was known to be absent from our samples. It should be noted that the incomplete removal of substances which have an effect on the rotation of the reference tartrate solution, makes the ratio of hafnium to zirconium appear to be less than it actually is.

Table I summarizes the results of the analysis of the two samples of mixed oxides. Three different weights of Sample No. 1 gave almost a straight line when plotted (Fig. 1). The ratios found by this method are in reasonable agreement with ratios found by the other methods indicated.

TABLE I

MOLE RATIO OF UNKNOWN MIXTURES OF ZIRCONIUM AND HAFNIUM

Sample	Expt.	Grams of oxide	Rotation change	Mole ratio Hf/Zr This method	Other methods
1	a	0.207	0.74°	0.43	0.45 (density of mixed
	b	.408	1.46	.43	oxides)
	c	.607	2.22	.40	
2	a	.635	2.79	.18	0.15 (spectroscopic method)

Millimoles of $H_6C_4O_6$ = 14.8; millimoles of KOH = 63.3; total volume of solutions = 50.0 ml.

The method is not thought to be more accurate than other methods which have been used for determining the zirconium–hafnium ratio. Of course it is not to be compared with a careful atomic weight determination. It is rapid and therefore convenient for following fractional separations of hafnium from zirconium.

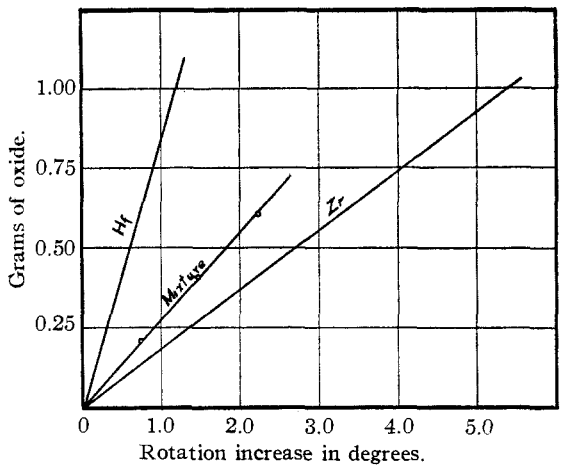

Fig. 1.

Summary

The optical rotation of basic tartrate solutions containing various amounts of zirconium have been measured and compared with the values obtained by de Boer and Emmens.

A procedure has been described for the rapid preparation of samples of zirconium–hafnium oxide suitable for analysis with the polariscope.

An equation has been given which may be used to calculate the mole ratio of hafnium to zirconium in mixtures of the two when the effect of a known weight of the mixed oxides on the rotation of certain reference tartrate solutions has been measured.

The mole ratios of two samples of zirconium–hafnium oxide have been determined and compared with the mole ratios found by other methods.

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