phoric acid diluted with $^1/_5$ of its weight of water) is saturated at the boiling point with zinc oxide. The water lost by evaporation is replaced and the solution rapidly cooled first to room temperature, then in cracked ice. About 10 volumes of ice-cold water are added and the solution violently stirred and poured through a filter into a large porcelain dish. The dish and its contents are heated with stirring on a water bath. A large quantity of shining plates of the neutral tetrahydrate will separate. The crystals are filtered out and washed clean with boiling water, sucked dry on a plate and spread out in a thin layer to air dry. This gives a pure product of constant composition, uncontaminated with alkalies and without excess zinc or phosphoric acid.

A microscopic study of the various phases was made with the following results.

$Zn_3(PO_4)_2 : 4H_2O$. Shining orthorhombic plates.

$ZnHPO_4 : 3H_2O$. Sticky, threadlike crystals agglomerating into cotton-wool-like masses. Optical properties could not be observed.

$ZnHPO_4 : H_2O$. Small, hard, transparent needles. Extinction oblique to long axis, probably triclinic.

$Zn(H_2PO_4) : 2H_2O$. Large, transparent triclinic rhombohedra.

Summary.

The isotherms at 25° and 37° of the ternary system $ZnO.P_2O_5 : H_2O$ have been traced to 55% phosphorus pentoxide.

The following solid phases separated at 25°: $Zn_3(PO_4)_2.4H_2O$, $ZnHPO_4.3H_2O$ $Zn(H_2PO_4)_2.2H_2O$.

At 37° an additional phase was noted, *viz.:* $ZnHPO_4.H_2O$.

A method of preparing pure neutral zinc orthophosphate tetrahydrate has been described.

PHILADELPHIA, PENN.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

THE DETERMINATION OF ZIRCONIUM AND TITANIUM IN ZIRCONIUM ORES.

BY G. E. F. LUNDELL AND H. B. KNOWLES.[1]

Received May 10, 1920.

CONTENTS.

I. Introduction. II. Decomposition of the Ore. III. The Bureau of Standards Method for the Determination of Zirconium and Titanium in Zirconium Ores—(*A*) Preliminary Remarks; (*B*) Procedure. IV. Confirmatory Analyses. V. Summary.

I. Introduction.

Zirconium ores may be expected to contain besides zirconium such elements as silicon, iron, aluminum, titanium, calcium, magnesium, sodium and potassium. In addition to these elements others such as thorium, cerium, tin, yttrium, uranium, manganese and phosphorus are often found,

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[1] Published by permission of the Director of the Bureau of Standards.

while tantalum, erbium, didymium, beryllium, scandium, lead, copper, bismuth, cobalt, zinc and lithium have been encountered. It is evident that an accurate determination of zirconium in mixtures so complex requires careful analytical procedures. When this Bureau was called upon to act as umpire in zirconium ore analyses during the war period, an extended study of the various published methods for this determination was made, and the cupferron method described in the following pages was finally adopted. Considerable difficulty was experienced at first in obtaining complete decomposition of zirconium ores, and this operation will, therefore, be discussed under a separate heading.

II. Decomposition of the Ore.

Various fluxes have been employed for this operation. Sodium carbonate has been recommended by Ferguson,[1] Brown,[2] and Wunder and Jeanneret.[3] Fusions with this reagent are usually tedious and often incomplete, even though the material has been ground to a very fine powder and well mixed with the flux.

Potassium hydrogen sulfate was employed by Dittrich and Pohl[4] and is specified in a method given by Johnstone.[5] This flux and the related one, potassium pyrosulfate, give good fusions of some ores like baddeleyite, and works very slowly and often incompletely on others, such as zircon.

Sodium hydrogen sulfate has been recommended by J. Lawrence Smith[6] as being far preferable to potassium pyrosulfate for the decomposition of emery. It may prove valuable in zirconium ore fusions.

Sodium peroxide has been recommended by Travers,[7] and also by Holladay.[8] Travers obtained excellent fusions by mixing one g. of the finely ground ore with 10 g. of sodium peroxide and fusing for a few minutes in a nickel crucible. Holladay recommends a sodium carbonate lining which is described as follows. "The sodium carbonate lining, which has for its object the prevention of attack of the crucible by sodium peroxide with consequent introduction of a large amount of nickel into the zirconium solution, is made by fusing sodium carbonate in the crucible at 1050–1100° and causing it to cool in an even layer on the bottom and sides. Several grams of peroxide are then melted in the crucible and allowed to solidify on the bottom, and the mixture of ore and peroxide is

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[1] J. D. Ferguson, *Eng. Mining J.*, 106, 793–794 (1918).

[2] Jas. Brown, This Journal, 39, 2358–66 (1917).

[3] M. Wunder and B. Jeanneret, *Z. anal. Chem.*, 50, 733–5 (1911).

[4] M. Dittrich and R. Pohl, *Z. anorg. Chem.*, 43, 236–241 (1905).

[5] S. J. Johnstone, "The Rare Earth Industry," C. Lockwood & Son, **1915**, p. 51.

[6] J. Lawrence Smith, *Compt. rend.*, 31, 48–50, 191–193 (1850); *Silliman's J.*, 10, 354–369 (1850).

[7] A. Travers, *Chimie et Industrie*, 2, 385–392 (1919).

[8] Private communication from J. A. Holladay, Electro Metallurgical Company, Niagara Falls, N. Y.

placed on top of this. The function of the layer of peroxide is to prevent particles of ore being caught in the carbonate lining and remaining unfused. Sodum carbonate does not melt at the comparatively low temperature required for the peroxide fusion and thus protects the crucible from attack."

Potassium hydrogen fluoride and also a recommended mixture of potassium pyrosulfate and potassium fluoride have been mentioned favorably. It seems quite possible that some zirconium may be volatilized as fluoride if the first named flux is used at high temperatures. Both fluxes require subsequent complete removal of all fluorine.

Borax has been used with success at the Bureau of Standards for the fusion of all zirconium ores as described under **III.** The flux does not cause any complications in the cupferron precipitation which is subsequently employed; if desirable, the boric acid can afterwards be easily removed by volatilization as methyl borate in the usual manner. Boric acid has not proven as satisfactory as borax.

III. The Bureau of Standards Method for the Determination of Zirconium and Titanium in Zirconium Ores.

A. Preliminary Remarks.

This method employs cupferron as a final precipitant and was adopted after a careful consideration of many possibilities. The following brief outline of the method indicates the manner in which the possible interfering elements are eliminated or provided for and will make clear the various steps in the method. After fusion of the ore with borax, solution of the melt in hydrochloric acid and evaporation to the appearance of fumes with sulfuric acid, the solution is cooled, diluted and digested in order to throw out, together with the impure silica, interfering quantities of phosphorus as zirconium phosphate. This insoluble matter is filtered off, ignited and treated with sulfuric and hydrofluoric acids to remove silicon. A sodium carbonate fusion of the non-volatile matter followed by a water extraction and filtration serves to remove the phosphorus. Zirconium and titanium in the water-insoluble are recovered by ignition, fusion with pyrosulfate, solution in acid and addition to the main solution.[1] Interfering quantities of such elements as calcium, magnesium, potassium, sodium, lithium, copper, cobalt, manganese, zinc and boron (introduced in the fusion) are next removed by an ammonium hydroxide precipitation followed by filtration. Solution of the ammonium hydroxide precipitate in acid, and treatment with hydrogen sulfide eliminates tin, lead, bismuth and any remaining copper. The filtrate from

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[1] Tantalum when present, should come down with silica in the sulfuric acid treatment and subsequently resist solution of the carbonate melt. Traces of tantalum left in solution would afterwards be caught in the hydrogen sulfide precipitation in sulfuric acid solution.

the hydrogen sulfide precipitation is next treated with tartaric acid, ammonium hydroxide and hydrogen sulfide to throw out iron and any cobalt, manganese and zinc which may have escaped the ammonium hydroxide separation. The above operations leave in solution at this point zirconium, titanium, thorium, cerium (and any other rare earths), aluminum, beryllium, uranium, and possibly some phosphorus. After acidification with sulfuric acid, and boiling to expel hydrogen sulfide, the solution is cooled and treated with an aqueous solution of cupferron, whereby zirconium and titanium are quantitatively precipitated together with varying amounts of thorium, cerium and other rare earths; while aluminum, beryllium,[1] uranium, phosphorus, and the remainder of the rare earths remain in solution. The ignited and weighed cupferron precipitate is then fused with potassium pyrosulfate, dissolved in sulfuric acid, and the solution divided into 2 equal parts for the determination of titanium and the rare earths. The procedure for the determination of titanium depends on its amount; for small amounts Weller's[2] colorimetric method is used, while for large amounts, the aliquot is reduced to Ti_2O_3[3] in a Jones reductor containing ferric alum in the receiver and then oxidized to TiO_2 by a standard permanganate solution. The rare earths oxides are determined in the second aliquot by a preliminary hydrofluoric acid precipitation followed by an oxalate separation as recommended by Hillebrand.[4] Zirconium oxide is then calculated by difference.

The following discussion of 3 other methods which were seriously considered may be of interest.

1. *The Substitution of Ammonium Hydroxide for Cupferron as the Final Precipitant.*—This proceedure would possess the advantage of a complete precipitation of the rare earths (and therefore provide for their determination in the same sample), and the disadvantages of requiring complete removal of tartaric acid before precipitation, as well as complicating the analysis by throwing down aluminum, beryllium, uranium and phosphorus. In case the ore was originally decomposed by a sodium peroxide fusion, followed by boiling with water and filtering, the greater

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[1] Beryllium and scandium were not considered by the authors in a paper on "The Use of Cupferron in Quantitative Analysis" (*J. Ind. Eng. Chem.*, 12, 344–350 (1920)). Subsequent quantitative tests made at this Bureau have demonstrated that beryllium when present alone or mixed with zirconium and titanium, is not thrown down by cupferron in sulfuric acid solution containing tartaric acid, and that scandium is partially precipitated.

[2] A. Weller, *Ber.*, 15, 2593 (1882); W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 700, pp. 155–162.

[3] F. Pisani, *Compt. rend.*, 59, 298 (1864); H. D. Newton, *Am. J. Sci.* (4th Ser.), 25, 130 (1908).

[4] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* 700, pp. 176–177.

part of these elements would go into the water extract and thus be eliminated. Perhaps a solution by acid of the water-insoluble portion, followed by neutralization with sodium hydrogen carbonate and peroxidation as described by Noyes, Bray and Spear,[1] would give a reasonably complete separation. Two difficulties arise in this last procedure, namely, complete precipitation of titanium in the peroxidized solution is accomplished only by vigorous boiling for at least 15 minutes, and this operation results in a partial precipitation of uranium.

2. Precipitation with Phenylhydrazine[2] in the Method as Given, after the Precipitation with Hydrogen Sulfide in Acid Solution.—This procedure would possess the advantage that no ammonium tartrate—ammonium sulfide treatment to remove iron would be required; and would possess the disadvantage of giving a complex precipitate similar in composition to that given by ammonium hydroxide, with the difference, however, that some elements, such as cerium, would be incompletely precipitated.

3. Direct Precipitation of Zirconium as Phosphate in a Sulfuric Acid Solution Containing Hydrogen Peroxide.[3]—This procedure would undoubtedly require preliminary separations such as are employed in the Bureau method. In case the amount of iron were not excessive, the precipitation would finally be carried out in the filtrate from the hydrogen sulfide precipitation. This procedure appears to be most attractive, since it affords a direct determination of zirconium. The authors do not, however, regard this method, at present, as entirely satisfactory for the determination of large amounts of zirconium, since uncertainties are introduced on account of various factors, such as: (1) Incomplete data as to the interference of elements such as uranium; (2) the tendency of zirconium phosphate to hydrolyze upon washing; and (3) difficulties during ignition owing to decrepitation.

B. Procedure.

Fuse 4 g. of borax in a platinum crucible, cool and place on top of the fused mass a 0.3000 g. sample of ore which has been ground to approximately 100 mesh. Cover the crucible and fuse thoroughly over a Meker burner, stirring the melt occasionally with a short, stiff platinum rod or wire kept in the crucible. When the decomposition of the ore is complete,[4] remove the platinum rod and put it in the beaker used for the solu-

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[1] A. A. Noyes, W. C. Bray and E. B. Spear, *Technology Quarterly*, 21, 36 (1908).

[2] E. T. Allen, THIS JOURNAL, 25, 421–444 (1903).

[3] W. F. Hillebrand. U. S. Geol. Surv., *Bull.* 700, pp. 173–175; G. E. F. Lundell and H. B. Knowles, THIS JOURNAL, 41, 1801–1808 (1919).

[4] This operation does not ordinarily require more than half an hour. If determinations of other elements such as aluminum, calcium and magnesium are desired, the substitution of sodium peroxide as a fusion medium (see II) is desirable, since otherwise all boric acid must be expelled by a methyl alcohol-hydrochloric acid treatment after solution of the melt.

tion of the melt. As the melt cools, gently twirl the crucible in order to run the fusion up on the sides.

Dissolve the cooled melt in 150 cc. of 1 : 5 hydrochloric acid in a 250-cc. beaker by filling the crucible with acid, inverting in such a manner that one edge of the crucible rests on the crucible cover, which has been placed on the bottom of the beaker, thus allowing free circulation of the solvent, and then gently warming on the steam bath.

Transfer the solution to a platinum dish, add 20 cc. of 1 : 1 sulfuric acid, and evaporate till heavy fumes escape. Cool, dilute to 100 cc. with water, filter off the impure silica, wash with hot water, and reserve for subsequent treatment. Digest the filtrate and washings, preferably warm and overnight, to throw down, as zirconium phosphate, interfering amounts of phosphorus. If a precipitate appears, filter, wash with 5% ammonium nitrate solution, reserve the paper and residue and treat the filtrate and washings as described below.

Add approximately 5 g. of ammonium chloride and then ammonium hydroxide in slight excess. Boil the solution for one or two minutes, filter, wash with 2% ammonium nitrate solution and discard the filtrate.[1]

Dissolve the precipitate in 100 cc. of hot 5% sulfuric acid, wash thoroughly with hot water and reserve the filtrate and washings.

Ignite the filter paper, together with the reserved papers containing impure silica and zirconium phosphate, in the original platinum crucible. Moisten the ash with water, add one cc. of 1 : 1 sulfuric acid, 5 cc. of hydrofluoric acid and evaporate to complete expulsion of sulfuric acid. Fuse the residue with a small amount of sodium carbonate, digest the melt in water and filter off the insoluble residue. Wash the residue with hot water, ignite it in a platinum crucible, fuse with potassium pyrosulfate, dissolve the cooled fusion in hot 5% sulfuric acid and add the solution to the reserved solution. (The above steps serve to remove phosphoric acid and to recover any zirconium that accompanies the silica, or that has been precipitated by ammonium hydroxide as phosphate and subsequently resists solution in 5% sulfuric acid.)

Dilute or neutralize with ammonium hydroxide till the solution contains approximately 1% (by volume) of sulfuric acid, treat with hydrogen sulfide, and filter if the hydrogen sulfide group is indicated. If indicated, wash well with a 1% sulfuric acid solution saturated with hydrogen sulfide.[2] Keep the volume of the filtrate at approximately 200 cc. To the solution add tartaric acid in amount equal to 5 times the aggregate weight

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[1] If a determination of such elements as copper, manganese, zinc, calcium and magnesium is desired, a double precipitation should be performed, and the combined filtrates treated as in ordinary analysis. Where extreme accuracy is desired, due attention should be paid to the slight recoveries of copper, cobalt, zinc and manganese subsequently made.

[2] The treatment of the acid solution with hydrogen sulfide instead of proceeding

of the bases to be held in solution; when the acid has dissolved, make the solution ammoniacal and saturate with hydrogen sulfide. Filter through the equivalent of an S. and S. blue-ribbon No. 589 paper, wash with ammonium sulfide-ammonium chloride solution and refilter, on a new filter, if traces of iron sulfide are suspected in the filtrate.[1]

Carefully acidify to a total acidity of 10% sulfuric acid (by volume) in 400 cc., boil to expel hydrogen sulfide, filter if sulfides are indicated, and cool the solution to from 5 to 14°.

Precipitate with an excess of a cold 6% water solution of cupferron. An excess of the precipitant is indicated by the formation of a fine, white precipitate, which redissolves, instead of a curdy one which persists.[2] Filter after a 5-minute digestion, using a filter paper and platinum cone with gentle suction. Thoroughly wash the precipitate with cold 10% (by volume) hydrochloric acid.[3]

Carefully dry and ignite the paper and precipitate in a tared platinum crucible and finally ignite over a blast lamp or its equivalent.[4] Cool in a desiccator and weigh as oxides of zirconium, titanium and rare earths.[5]

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directly with an ammonium sulfide treatment is carried out for the following 2 reasons: (1) it serves to show up immediately all members of the hydrogen sulfide group; and (2) unless the iron is reduced before precipitation as sulfide, titanium will be in part thrown down also (A. Cathrein, *Z. Kryst. Min.*, 6, 243 (1882); 7, 250 (1883); W. M. Thornton, Jr., *Am. J. Sci.*, [IV] 37, 407–414 (1914). The sulfide precipitate may contain tin, copper, lead and bismuth, together with some platinum resulting from attack of the crucible during the various previous operations. If desired, these may be determined after the recovery and inclusion of the copper present in the filtrate from the ammonium hydroxide precipitation.

[1] All of the iron in the sample taken, together with any manganese, zinc and cobalt, which came down with the ammonium hydroxide precipitate, are caught at this point as sulfides. In case a determination of iron alone is desired, the simplest procedure would consist in solution of the sulfide in sulfuric acid, elimination of hydrogen sulfide reduction in a Jones reductor, and titration with permanganate.

[2] The color of the precipitate furnishes an excellent indication of the amount of titanium present, since zirconium precipitates are pure white while titanium precipitates are yellow. A brownish tint indicates iron or vanadium.

[3] Clear filtrates and washings indicate complete precipitation of zirconium and titanium, while cloudy or opalescent ones indicate the reverse. The latter have occasionally developed and no satisfactory explanation has been found. In these circumstances, recoveries must be made as follows. Evaporate the solution to a small volume, destroy the organic matter by treatment with nitric acid, and finally heat till fumes of sulfuric acid appear. Cool, dilute, filter off any silica resulting from attack of the glassware, and precipitate with cupferron in a 10% sulfuric acid solution as directed above.

[4] A correction for silica in the mixed oxides is not ordinarily necessary. In umpire work and in cases where a recovery has been obtained from the first cupferron filtrate, this correction should be made, paying due attention to adding sufficient sulfuric acid to prevent volatilization of zirconium and titanium fluorides and avoiding mechanical loss during the expulsion of the sulfuric acid.

[5] Although vanadium has not been reported as a constituent of zirconium ores, it may be worth while to call attention to the fact that vanadium is partly precipitated

Fuse the mixed oxides with potassium pyrosulfate, take up in 10% (by volume) sulfuric acid, dilute to exactly 100 cc. and divide into two 50-cc. portions.

Determination of Titanium in Portion I.—If the percentage of titanium is low, determine it colorimetrically by Weller's method;[1] when the percentage is high, reduce to titanium sesquioxide[2] in a Jones reductor containing ferric alum-phosphoric acid in the receiver and then oxidize to titanium dioxide by titration with standard permanganate solution.

Determination of Rare Earths in Portion II.—Determine the rare earths in this portion by Hillebrand's method[3] as follows. Precipitate the hydroxides with an excess of potassium hydroxide, decant the liquid, wash by decantation with water once or twice and then slightly on the filter. Wash the precipitate from the paper into a small platinum dish, treat with hydrofluoric acid, and evaporate nearly to dryness. Take up in 5 cc. of 5% (by volume) hydrofluoric acid. If no precipitate is visible, rare earths are absent. If a precipitate is present, collect it on a small filter held by a perforated platinum or rubber cone and wash it with from 5 to 10 cc. of the same acid. Wash the crude rare-earth fluorides into a small platinum dish, burn the paper in platinum, add the ash to the fluorides and evaporate to dryness with a little sulfuric acid. Dissolve the sulfates in dil. hydrochloric acid, precipitate the rare-earth hydroxides by ammonia, filter, redissolve in hydrochloric acid, evaporate the solution to dryness, and treat the residue with 5 cc. of boiling hot 5% oxalic acid. Filter after 15 minutes, collect the oxalates on a small filter, wash with not more than 20 cc. of cold 5% oxalic acid, ignite and weigh as rare-earth oxides, which are to be deducted from the weight of the cupferron precipitate.

The above procedure does not give an absolutely quantitative recovery of the rare earths. Experiments indicate a recovery by the method

by cupferron in a 10% sulfuric acid solution. In case vanadium is present in the ore, either of 2 procedures may be followed. 1. Substitution of a peroxide fusion of the ore for the recommended borax fusion, followed by a water extraction of the cold melt and filtration to eliminate vanadium at the start of the analysis. 2. Fusion with sodium carbonate of the weighed oxides obtained as above in the method, followed by water extraction and filtration to separate vanadium from zirconium, titanium and the rare earths. The determination of titanium and the rare earths would then be performed as directed in this method, on the ignited water-insoluble; while the determination of V_2O_5 would be carried out by acidifying the sodium carbonate filtrate with sulfuric acid, reducing to V_2O_2 in a Jones reductor containing ferric alum in the receiver, and then oxidizing to V_2O_5 by means of a standard permanganate solution.

[1] A. Weller, *Ber.*, 15, 2593 (1882); W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol Surv., *Bull.* 700, pp. 155–162.

[2] F. Pisani, *Compt. rend.*, 59, 298 (1864); H. D. Newton, *Am. J. Sci.* [IV] 25, 130 (1908).

[3] W. F. Hillebrand, *loc. cit.*, pp. 176–177.

of approximately 85% of the rare earths present in residues containing 100 mg. of zirconia, 2 mg. of thoria and 2 mg. of ceria, the recovery of thoria being more complete than that of ceria.

Attempts which were made to omit the preliminary separation of the rare earths as fluorides were unsuccessful.

IV. Confirmatory Analyses.

The analyses listed in Table I were carried out by the Bureau Method on samples of diorite to which had been added various amounts of zirconium, titanium, thorium, cerium and phosphorus. All of the elements which might be present in zirconium ores were not added because researches by the authors and others[1] dealing with the use of cupferron in quantitative analysis had demonstrated that the ones added were most to be feared.

TABLE I.—ANALYSES.

	Weights taken in g. of:						Wt. of ignited cupferron precipitate.	Wts. found in g. of:		
Expt.	Rock.	ZrO_2.	TiO_2.[a]	ThO_2.	CeO_2.	P_2O_5.		ZrO_2.	TiO_2.	ThO_2–CeO_2.
1.....	0.0560	0.2096	0.0034	....	....	....	0.2129	0.2090	0.0039	....
2.....	0.0612	0.2151	0.0042	....	....	0.0100	0.2192	0.2149	0.0043	....
3.....	0.0607	0.2151	0.0042	0.0014	0.0013	....	0.2212	0.2152	0.0044	0.0016
4.....	0.0630	0.2151	0.0043	0.0054	0.0052	....	0.2235	0.2153	0.0043	0.0039
5.....	0.0621	0.2151	0.0042	0.0054	0.0052	0.0100	0.2234	0.2153	0.0043	0.0038

[a] Including a small amount of TiO_2 in the rock.

The results obtained show a gratifying accuracy for the method. It was expected that the values obtained for zirconium would be high in the analyses involving thoria and ceria on account of their probable incomplete recovery from the ignited cupferron precipitate. Thoria is more completely precipitated by cupferron than is ceria, and it is also more completely recovered by the fluoride-oxalate method. The rare-earth recoveries from the ignited cupferron precipitates in Expts. 3, 4 and 5 were therefore probably much better than the 85% obtained when equal parts of thoria and ceria were taken.

V. Summary.

1. Methods of decomposing zirconium ores are listed.

2. A cupferron method for the determination of zirconium and titanium in zirconium ores is given.

3. The method provides for the following elements which have been found in zirconium ores: zirconium, titanium, silicon, thorium, cerium, iron, aluminum, scandium, yttrium, erbium, didymium, beryllium, calcium, magnesium, sodium, potassium, lithium, uranium, phosphorus, tantalum, manganese, zinc, cobalt, tin, lead, copper and bismuth. It is also worthy of note that chromium and nickel do not interfere in a cupferron precipitation; that tungsten would not cause trouble since it is removed before

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[1] G. E. F. Lundell and H. B. Knowles, *J. Ind. Eng. Chem.*, **12**, 344–350 (1920).

the final precipitation; and that vanadium would require special treatment. Since this element has not been reported in zirconium ores, and since its presence in significant amounts would be indicated at various stages of the analysis, it would cause no trouble.

The authors desire to express to Dr. W. F. Hillebrand of this Bureau their sincere appreciation of his aid and counsel.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE ROYAL POLYTECHNICAL INSTITUTE OF COPENHAGEN.]

STUDIES ON SOLUBILITY. II. THE SOLUBILITY RATIOS OF SALTS IN STRONG HOMOIONIC SOLVENTS.

BY J. N. BRÖNSTED.

Received May 24, 1920.

I. Influence of Hydration of the Solute.

In a recent paper[1] a treatment of solubility equilibria in salt solutions was given on the basis of the provisional hypothesis that the stoichiometric activity coefficient in a mixed salt solution is the same for any ion of the same type. It was shown that the general features of the solubility curves in the case of homoionic as well as heteroionic solvents could be accounted for by means of this hypothesis.

The provisional character of the hypothesis was emphasized by pointing out several factors capable of causing deviations from the requirements of the simple assumption. As the principal of these factors we can name the secondary electric effect, which, besides the primary Milner effect, may influence the potential of the ions, and which manifests itself in a way similar to that of incomplete dissociation. Furthermore, there is the hydration of the dissolved ions and finally the electrostriction effect introduced by several authors[2] in order to explain the salting-out effect of salt solutions.

As a start on a general discussion of the influence of these factors we may conveniently put the simpler case of considering not the shape of the solubility curve itself, but the ratio of solubilities or solubility products for salts of varying concentration in the same solvent. If the secondary electric forces exert a similar effect upon the activity coefficients, which presumably is the case when the ions of the solute possess similar molecular structure, deviations from a constant solubility ratio would be due chiefly to changes in the hydration of the dissolved ions. If, on the other hand, constant solubility ratios are actually found, using a solvent of considerably changing vapor pressure, we may be entitled to conclude

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[1] *Kgl. Danske Vidensk. Selsk. Mathemat.-fysiske Medd.*, 2, 10 (1919); THIS JOURNAL, 42, 761 (1920).

[2] Euler, *Z. physik. Chem.*, 31, 360 (1899); Geffeken, *ibid.*, 49, 257 (1904).