

ents at their respective concentrations in the mixture. It is seen that with increasing concentration these two curves diverge more and more. For a more detailed discussion of this type of curve see the next paper. Briefly, this divergence seems explicable only on the assumption that with increasing concentration there is an increasing tendency to form higher order complexes between the various salt constituents due to their mass action. Thus, at low concentrations, where these complexes would be present only in small amounts, their specific effect should be negligible, and the two curves should tend to coincide. This is actually the case.

Summary.

1. The reversible molal heat of dilution has been determined for solutions of barium chloride of 3.2, 2.8, and 1.6 weight normal, and for solutions of the mixed salt $\text{NaCl} : 1/2 \text{BaCl}_2$ at 3.2, 1.6, 0.8, and 0.4 weight normal.

2. The heats of dilution of the mixed salt bear no simple additive relation to the heat effects of the simple components at equivalent concentrations.

3. The behavior of barium chloride in this respect is found to be analogous to that of strontium chloride.

4. These results can be explained on the same basis as the results obtained with the mixed strontium salts, namely on the basis of the formation of higher order compounds.

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THE SEPARATION OF ZIRCONIUM AND TITANIUM AS THE PHOSPHATES.

BY JAMES BROWN AND H. T. MADDEN.

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In a previous paper,¹ one of us made use of the Hillebrand method² of separating zirconium from titanium by precipitation of the former by use of hydrogen peroxide and alkaline phosphate in a faintly acid solution. The titanium, when large in amount, was determined as a difference or by the permanganate method, and by the colorimetric method when small amounts were present. The work recorded in the present paper was undertaken with the object of making a direct gravimetric determination of the titanium in the filtrate from the zirconium phosphate precipitation.

The standard solutions employed were prepared from pure potassium zirconium fluoride (K_2ZrF_6), and from pure potassium titanium fluoride

¹ THIS JOURNAL, 39, 2358 (1917).

² "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.*, 422, 141 (1910).

(K_2TiF_6), respectively. The pure salts of commerce were recrystallized from boiling water several times, and were then converted into the sulfates by evaporation with sulfuric acid in a platinum dish until all fluorine was expelled. The residues were diluted with water. Qualitative tests showed the absence of iron, aluminum, manganese, and rare earths from both solutions.

Standardization of Solutions.

The solutions of zirconium sulfate and of titanium sulfate thus prepared were standardized by precipitation with ammonia and ignition to the dioxide, in the usual way.

From other portions of the zirconium solutions, the base was precipitated as the phosphate, by disodium or diammonium phosphate, the solution containing 1-2% by volume of sulfuric acid. The zirconium phosphate was filtered off, washed, ignited and converted to the dioxide as follows: It was fused with sodium carbonate, the melt leached with water, and the insoluble residue dissolved either in hydrochloric acid or by fusion with sodium bisulfate and subsequent treatment with a dilute solution of sulfuric acid. The zirconium phosphate showed marked decrepitation during ignition. The zirconium was precipitated with ammonia, and weighed as ZrO_2 after ignition. The zirconium dioxide thus obtained from the phosphate corresponded in each case with the standard obtained by treating the original solution with ammonia. The amount of zirconium dioxide involved varied from 0.1608 to 0.3216 g. In view of the qualitative and quantitative checks thus obtained, the zirconium sulfate solution was considered free from interfering bases.

The solution of titanium sulfate, standardized by precipitation with ammonia, and ignition to titanium dioxide, was further standardized as follows:

Portions of the solution containing 1-2% of sulfuric acid by volume were precipitated by use of disodium or diammonium phosphate, filtered, ignited and weighed. The titanium phosphate thus obtained was of variable composition. It was, therefore, converted to the dioxide as with zirconium, and weighed as titanium dioxide. The dioxide thus obtained corresponded to the standard obtained by use of ammonia directly with the original solution. The titanium dioxide used varied from 0.1124 to 0.5726 g.

As a further check on the titanium solution, titanium was determined by reduction with zinc and sulfuric acid, addition of an excess of ferric sulfate, and titration of the reduced iron salt by use of permanganate.¹ The results thus obtained agreed very well with the standard obtained by use of ammonia alone, and the titanium solution was judged free from interfering bases.

¹ Newton, *Am. J. Sci.*, [4] 25, 130 (1908).

Separation of Zirconium and Titanium.

Measured amounts of the solutions of zirconium and titanium sulfates were mixed and made acid to the extent of 1-2% of free sulfuric acid by volume. An excess of hydrogen peroxide was added. A solution of disodium or diammonium phosphate was added in excess, and the solution allowed to stand overnight. The precipitated zirconium phosphate was filtered off and washed with water containing a few drops of sulfuric acid and hydrogen peroxide. The zirconium precipitate is colored yellow by titanium. To remove this titanium we proceeded as directed by Hillebrand¹ by fusing with sodium carbonate, leaching, and redissolving by fusion with sodium bisulfate and action of dil. sulfuric acid. The zirconium was reprecipitated by hydrogen peroxide and phosphate, allowed to stand, filtered and washed. In some cases this second zirconium precipitate contained small amounts of titanium, which were removed by repeating the above treatment.

The zirconium phosphate precipitated was converted to zirconium dioxide, as in the standardization, and weighed as such. The results for the zirconium are given in the table.

The combined filtrates from the zirconium phosphate precipitation were heated to get rid of the hydrogen peroxide. The volume of the solution was then adjusted so that the content of sulfuric acid was about 2% by volume, and disodium or diammonium phosphate solution was added to assure an excess. The liquid was allowed to stand about one hour, and the precipitate filtered and washed. The precipitate was converted to titanium dioxide as in the standardization and weighed as such. The results are given in the following table:

ZrO ₂ taken. G.	TiO ₂ taken. G.	ZrO ₂ found. G.	Error. G.	TiO ₂ found. G.	Error. G.
0.1287	0.0562	0.1282	-0.0005	0.0556	-0.0006
0.1287	0.0562	0.1281	-0.0006	0.0559	-0.0003
0.2594	0.0562	0.2588	-0.0006	0.0560	-0.0002
0.2594	0.1124	0.2592	-0.0002	0.1120	-0.0004
0.2594	0.1124	0.2585	-0.0009	0.1118	-0.0006
0.1287	0.1124	0.1284	-0.0003	0.1121	-0.0003
0.2594	0.0562	0.2591	-0.0003	0.0556	-0.0006
0.2594	0.0562	0.2592	-0.0002	0.0558	-0.0004
0.2594	0.1124	0.2589	-0.0005	0.1121	-0.0003

Summary.

The separation of titanium and zirconium by the Hillebrand method is quantitative, within the limits used in this work. The zirconium phosphate is converted to the dioxide and gives accurate results. The titanium in the filtrate from the zirconium phosphate may be completely precipitated by the use of sodium or ammonium phosphate, but as this precipi-

¹ *Loc. cit.*

tate is of variable composition, it should be converted to the dioxide to obtain quantitative results.

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THE ANALYSIS OF ACETONE BY MESSINGER'S METHOD.

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In the course of research work extending over the last 6 or 7 years, it was frequently necessary to make accurate determinations of acetone both in large and small amounts. Messinger's method¹ was found to give concordant results under all conditions, and since its accuracy has been disputed by one or two workers, and upheld by others, a résumé of the work on the subject and conclusions are herewith presented.

Since the publication of the original Messinger method, it has been subjected to an extended critical examination by Collischonn,² Edward R. Squibb³ and L. F. Kebler.⁴ Perhaps the only fault with all this work lay in the fact that no special precautions were taken to obtain pure acetone, and that the acetone was never weighed out accurately. Since, however, it was desired only to work out the conditions under which concordant results could be obtained, this hardly mattered.

Messinger's method has been seriously criticized only by Vaubel and Scheurer,⁵ and by Geelmuyden.⁶ The statements of the former authors were conclusively refuted by Keppeler,⁷ and those of the latter by Marriott.⁸

Messinger's original results were carried out to an accuracy of only one part in 200. Collischonn⁹ made very accurate experiments, but used only a sample of Kahlbaum acetone purified through the bisulfite compound, which distilled within 1°. He carried out other experiments with commercial acetone and showed that concordant results could be obtained.

Squibb and Kebler used sodium hypochlorite solutions, but appear to

¹ *Ber.*, 29, 3336 (1888). Other papers on the determination of acetone, not elsewhere referred to, are as follows: G. Kraemer, *Ber.*, 13, 1000 (1880); E. Hintz, *J. Soc. Chem. Ind.*, 7, 459 (1888); L. Vignon, *Ibid.*, 9, 639 (1890); E. Arachesquene, *Ibid.*, 9, 660 (1890); Otto Folin, *J. Biol. Chem.*, 4, 177 (1917); T. Stuart Hart, *Ibid.*, 4, 477 (1918); J. Rakshit, *Analyst*, 41, 246 (1916).

² *Z. anal. Chem.*, 29, 562-572; *J. Soc. Chem. Ind.*, 10, 166 (1891).

³ *THIS JOURNAL*, 18, 1068-1079 (1896).

⁴ *Ibid.*, 19, 316-320 (1897).

⁵ W. Vaubel and C. Sheuer, *Z. angew. Chem.*, 18, 215-216 (1905).

⁶ H. Chr. Geelmuyden, *J. Chem. Soc.*, 70, 679 (1896).

⁷ G. Keppeler, *Z. angew. Chem.*, 18, 464-465 (1905).

⁸ W. M. Marriott, *J. Biol. Chem.*, 16, 281 (1913).

⁹ *Loc. cit.*