[CONTRIBUTION FROM THE CHEMICAL LABORATORY, RHODE ISLAND STATE COLLEGE]

# The Solubility of Thorium in Mercury[1]

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Very few alloys of thorium have been prepared. The only reference in the literature to a thorium amalgam is the work of Kettembeil,[2] who was unable to prepare an amalgam by the electrolysis of an aqueous solution of a thorium salt using a mercury cathode. Insoluble basic compounds were always formed during the electrolysis. This investigation was undertaken to see whether an amalgam could be prepared and, if so, what its possibilities are for use in galvanic cells to determine the thermodynamic properties of tetravalent thorium salts.

## Experimental

**Mercury.**—Redistilled mercury was stirred under a dilute nitric acid–mercurous nitrate solution for three days. It was then redistilled three times in a slow current of air (15 mm.) by the Hulett[3] method, and finally under high vacuum.

**Thorium.**—Crystalline thorium prepared by the electrolysis of fused thorium chloride was kindly supplied by the Kemet Laboratories, Cleveland, Ohio. This metal analyzed 99.75% Th, by the oxalate method.[4] It contained small amounts of thorium oxide, silicon, iron and chromium due to the method of preparation. However, the amounts present are negligible for our purpose. It should be pointed out that very pure metallic thorium entirely free from thorium oxide has never been prepared; commercial samples rarely analyze better than 98.50%.[5] The samples for analysis were first fused with potassium bisulfate because when the metal is treated with acids, either singly or in combination, considerable oxide is formed which does not dissolve even in concentrated acids.[6]

**Thorium Salts.**—The best grade of C. P. thorium chloride, nitrate and sulfate were secured from Kahlbaum and were not further purified.

The preparation of a thorium amalgam was attempted by two methods. (1) Weighed quantities of thorium and mercury were heated together at 400° in small transparent fused quartz tubes for approximately eight hours. A higher temperature, although desirable, could not be employed due to shattering of the tubes. Furthermore, at elevated temperatures the thorium attacked the quartz badly. (2) An extensive series of experiments was carried out to determine the conditions under which an amalgam could be prepared electrolytically. These experiments included: electrolysis of thorium nitrate, sulfate and chloride in aqueous solution; $Th(NO_3)_4$ and $ThCl_4$ in 95% ethyl alcohol, and $ThCl_4$ in 12 $N$ hydrochloric acid. Both the test-tube and H-type cell vessel were employed using a mercury cathode. The mercury was stirred slowly during all experiments. The concentration of salts, current density, length of time electrolyzed, temperature and acidity were varied over a wide range. The results may be summarized as follows: in all aqueous solutions insoluble basic salts were formed causing the current to decrease gradually with no detectable amalgam formation. In the alcoholic solutions, the purpose of which was an attempt to prevent the formation of the basic compounds, no amalgam could be formed. The basic compounds still precipitated. The only electrolysis which appeared to have some degree of success was carried out in a saturated solution of thorium tetrachloride in 12 $N$ hydrochloric acid. A current of 0.5–1.0 amp. sq. cm. was passed through the solution for twenty-four hours. The H-cell was cooled continuously by running water.

The amalgams prepared by either method were placed in an oil-bath at 25 ± 0.01° and shaken for several days. The liquid mercury saturated with thorium was then separated for analysis by means of the special filter pipet previously described.[7] The analysis of mercury saturated with thorium offers very serious difficulties on account of the large quantity of mercury and relatively small quantity of thorium present. None of the ordinary methods of separation were found applicable. For example, no reagent could be found that would precipitate one without precipitating the other. It was found that hydrochloric acid would not react completely with the amalgam in the ordinary manner. The potassium permanganate oxidation method of Irvin and Russel[8] did not give satisfactory results. The distillation method also proved useless for quantitative work. The method finally adopted, although not entirely satisfactory, at least gives the order of magnitude of the solubility. For a more exact value an electrometric instead of a chemical method will have to be employed.

The samples to be analyzed were weighed carefully and then exposed to the atmosphere for at least two weeks in order that the thorium might separate from the mercury. This procedure has been found to be satisfactory for the separation of lanthanum and aluminum amalgams.[9] After standing the two weeks an excess of standard 0.5 $N$ hydrochloric acid was added and after shaking well the excess acid was determined by titration with standard carbonate-free sodium hydroxide using phenol red as an indicator. The sodium hydroxide was standardized against Bureau of Standards potassium acid phthalate. The analytical weights and burets employed were calibrated and corrections applied where necessary.

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(1) Abstracted from a thesis submitted by George E. Prime to the faculty of Rhode Island State College in partial fulfilment of the requirements for the degree of Master of Science.

(2) Kettembeil, *Z. anorg. Chem.*, **38**, 217 (1903).

(3) Hulett, *Phys. Rev.*, **21**, 388 (1905); *ibid.*, **33**, 307 (1911).

(4) Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York City, Vol. I, 1925, p. 524.

(5) Marsden and Rentschler, *Ind. Eng. Chem.*, **19**, 97 (1927).

(6) Driggs and Lilliendahl, *ibid.*, **22**, 1302 (1930).

(7) W. G. Parks and Campanella, *J. Phys. Chem.*, **40**, 333 (1936).

(8) Irvin and Russel, *J. Chem. Soc.*, 30, 891 (1932).

(9) Müller, *Monatsh.*, **53**, 215 (1929); Audrieth, Jukkola, Meints and Hopkins, THIS JOURNAL, **53**, 1805 (1931).

## Results and Discussion

The solubility of thorium in mercury at 25° is summarized in Table I. The data given represent the average of three determinations on five different amalgams. The second and fourth amalgams were prepared by method (1) while the others were prepared by method (2). The atomic per cent. was calculated from the weight per cent. by the graphical method of Ölander.[10]

TABLE I

THE SOLUBILITY OF THORIUM IN MERCURY AT 25°

| Weight, % | Atomic, % |
|---|---|
| 0.0158 | 0.0140 |
| .0157 | .0139 |
| .0156 | .0138 |
| .0145 | .0128 |
| .0154 ± 0.0005 | .0136 |

There are many factors which must be considered in the determination of the solubility of a sparingly soluble metal in mercury. The solubility may or may not be a definite quantity. Some metals like copper and zinc or lead[11] are known to form aggregates not only with themselves but also with mercury. This means that until the particle size in the amalgam has been determined the term solubility must be a loose one. A method other than filtration must be found for determining a homogeneous phase. Furthermore, we are not absolutely certain that all the thorium separates from the mercury on standing two weeks in contact with the atmosphere. The reproducibility of our results, however, leads us to place confidence in them. The amount of mercury that dissolves when the hydrochloric acid is added was found to be negligible at the concentration employed.

These data may be interpreted in terms of internal pressures and the metallic solution theory of Hildebrand.[12] The mutual solubility of thorium and mercury should follow from their position in the table of internal pressures provided that there is no compound formation. The physical constants necessary for calculating the internal pressure of thorium are not accurately known. However, if we adopt the method of Gilfillan and Bent[13] thorium is placed next to tin in the table given by Hildebrand, Hogness and Taylor.[14] This position indicates a large difference in the internal pressure of thorium and mercury and is in fair accord with the solubility found in this investigation. Joyner[15] found the solubility of tin in mercury to be 1.24 atomic per cent. at 25.4°. The mutual solubility of thorium and tin has not been determined.

According to the relationship between the melting point of a metal and its solubility in mercury as developed by Tammann and Hinnüber[16] our results are too high. However, this relationship is only an approximation. Considering all factors which enter into a problem such as this, we feel that our results indicate a very low solubility with our value as a maximum. This low solubility together with the difficulty of preparation leads to the conclusion that this amalgam is unsatisfactory for precise e. m. f. measurements. Further work on the amalgamation of thorium is in progress.

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[10] Ölander, *Ind. Eng. Chem., Anal. Ed.*, **4**, 438 (1932).

[11] Chuiko, *Ukrain. Khem. Zhur.*, **6**, No. 5-6, Sci. Part, 229 (1931).

[12] Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1936, p. 174 *et seq.*

[13] Gilfillan and Bent, THIS JOURNAL, **56**, 1661 (1934).

[14] Hildebrand, Hogness and Taylor, *ibid.*, **45**, 2830 (1923).

[15] Joyner, *J. Chem. Soc.*, **99**, 195 (1911).

[16] Tammann and Hinnüber, *Z. anorg. allgem. Chem.*, **160**, 249 (1927).