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PREPARATION OF MASSIVE SAMARIUM METAL

by

E. I. Onstott

CHEMISTRY

ABSTRACT[1]

Massive samarium metal of relatively high purity is made by heating a mixture of approximately 20-mesh barium metal and powdered anhydrous samarium (III) bromide. This mixture, contained in a tantalum crucible in an argon atmosphere, is heated to 1650-1700°C for about 20 minutes. The heating serves to agglomerate and separate the metal and distill out excess barium. A yield of about 10 g of metal, or 50%, is obtained with a batch of 50 g of bromide and 30 g of barium. Samarium metal distills at an appreciable rate when heated in an argon atmosphere at about 1700°C. Density data obtained on massive samarium metal samples are: metal as made, 7.499 g/cc; recast metal, 7.509 g/cc; distilled metal 7.495 g/cc.

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1. Introduction

In a recent Communication to the Editor, Daane, Dennison, and Spedding[2] described the preparation of samarium metal of at least 98% purity by reaction of samarium oxide with lanthanum metal. They also mentioned that barium metal had been tried with little success. In this laboratory, relatively pure samarium metal has been produced by reaction of barium metal with anhydrous samarium (III) bromide.[1] The technique used is similar to that described by Spedding and Daane.[3]

Samarium halides are difficult to reduce to the metallic state because of the high stability of the divalent halides. Calculations, based on data given in the tables of Brewer et al,[4] show that the alkali metals more electropositive than sodium react with the divalent halides of samarium (other than fluoride) with a free energy change which is negative, but small. The reaction of lithium with samarium (II) fluoride at 500°K also gives a small free energy change of ~-1 kcal. Of the alkaline earth metals only barium is sufficiently electropositive to effect reduction of samarium (II) bromide. A free energy change of ~-3 kcal at 1000°K was calculated for this reaction. However, the calculated free energy change for the reaction of barium metal with the other divalent samarium halides at this temperature was positive.

A review of the literature on the preparation of samarium metal has been made[2,3] and will not be repeated here.

2. Experimental

Samarium oxide of 99.9% purity, obtained from Research Chemicals, was used in preliminary experiments. However, this material proved to be too expensive to use in large batches. Subsequently, samarium oxide was purchased from Société de Produits Chimiques des Terres Rares. Spectrographic analysis showed this product to contain 2% europium, 1.5% calcium, and $<0.1\%$ sodium and magnesium. Other rare earths were not detected. The europium was separated by two electrolyses according to the method of McCoy.[5] Tracer europium, made by irradiation of normal europium oxide in the Los Alamos Water Boiler, was used to follow the course of the electrolysis. Two oxalate precipitations and ignition to the oxide served as the final purification steps. By a combination of gravimetric, colorimetric,[6] and tracer analyses, the europium oxide content of the purified samarium oxide was determined to be 0.08%.

Small batches of anhydrous samarium (III) bromide were prepared by heating a ground mixture of ammonium bromide and samarium oxide in an argon atmosphere. A ten to one atomic ratio of bromine to samarium was used. This method was not entirely satisfactory, however, since some ammonium bromide remained in the product. Subsequently, 25 and 50 g batches of samarium bromide were made by heating a mixture of the reactants in a vacuum at 400-425°C for about 15 hours. The product was shown to be relatively pure by gravimetric analysis for samarium as the oxide and potentiometric determination of bromine with silver nitrate. Anal. Calculated for $SmBr_3$: Sm, 38.55%; Br, 61.45%. Found: Sm, 38.8%; Br, 61.3%. A spot test for ammonia[7] was negative. The reaction of ammonium halides with rare earth oxides has been used previously for preparation of the anhydrous halides.[8]

Anhydrous samarium (III) iodide was prepared by essentially the same method as was used for preparing the bromide. However, the excess of ammonium iodide was removed by fusion of the samarium (III) iodide in an argon atmosphere.

Samarium (III) fluoride was prepared by precipitating it from 8N nitric acid with hydrofluoric acid, then washing with alcohol, and drying for one hour at 600°C.

Commercial barium from King Laboratories, Inc., and Kemet Labs Co., Inc., was used without purification. Spectrographic analysis showed that strontium, calcium, and magnesium were present in amounts totaling $< 5\%$. Silicon content was $<0.01\%$, and iron and aluminum were present in amounts $<0.1\%$. While the barium was being processed, it was protected with a covering of mineral oil or Gulf BT thinner. The barium was ground by first cutting it into small pieces and then passing it through a food chopper. It was screened through an 8-mesh screen onto a 30-mesh screen. The petroleum protector was then removed by washing with hexane, and the hexane was subsequently removed by vacuum distillation. A purified argon atmosphere was kept over the barium until it was mixed with the samarium bromide. A fresh batch of barium was made up on the same day that a reduction was made.

Commercial potassium from Baker Chemical Company was subdivided by melting under Gulf BT thinner in a glass-stoppered flask, and then shaking until the small particles of potassium had solidified. The petroleum thinner was then removed with benzene.

Crucibles of tantalum were first fabricated of thin foil by the method of Daane.[9] Later, seamless tubing was procured from Fansteel Metallurgical Co. and cupped bottoms were arc-welded in place in an argon atmosphere. Crucibles were made 3-1/2 inches long, 1 inch I. D., and had a wall thickness of 0.015 or 0.025 inch. The crucible served as the inductor for heating with a G. E. 5 KW Electronic Heater. It also served as the female member of the die for increasing the size of the charge by compacting with a punch. Fifty grams of samarium bromide mixed with 30 g of barium could be pressed into the crucible.

The anydrous samarium halides, except for the fluoride, were handled and stored in a dry box. In a typical experiment, 50 g of powdered samarium (III) bromide was mixed with 30 g (10% excess) of screened and dried barium by tumbling them in a flask. This mixture was then transferred to the tantalum crucible by alternate filling and pressing. A loose-fitting perforated tantalum lid was put in place, and the crucible was then inserted in a sintered magnesium oxide sleeve (for insulation). All of the previous operations were conducted in a dry box. The crucible assembly was transferred quickly to a quartz tube and held in place either by placing the assembly on a magnesium oxide pedestal or by suspending it by a tantalum wire. The quartz tube was then placed in a copper induction coil and flushed with purified argon (passed over phosphorous (V) oxide and hot copper turnings) after first evacuating to a pressure of $< 1\mu$. A slow stream of argon was allowed to flow through the quartz tube during the heating and cooling cycle. Heat was applied with the electronic heater at a low power setting until the reaction had started. This preheat period usually lasted 5-10 minutes. The power was then increased so that a temperature of 1650-1700°C was reached in about 5 minutes. This temperature was maintained for about 20 minutes, the power was then turned off, and the crucible was allowed to cool to room temperature before it was examined.

Temperature measurements were made with a Leeds and Northrup optical pyrometer. Direct measurement of temperature during a reaction was not possible, however, as vapors came out of the crucible continuously during the final heating cycle. Therefore, temperatures were determined by pre-calibration of the electronic heater.

The iodine boosted reaction[10] of samarium (III) bromide with barium was carried out in a steel bomb sealed with two copper ring gaskets. A magnesium oxide liner served as the insulator. Purified argon was used as the protecting atmosphere. The reaction was initiated by heating the bomb in a small muffle furnace. A rapid rise in the rate of heating, as determined from a thermocouple inserted in a well on one side of the bomb, indicated when the reaction had started.

Analysis of the metal product was done spectrographically. A typical analysis on a massive metal sample is as follows: Li, Na, Mg, Ca, Mn, Fe, Cu, each <0.001%; Ba, Si, Sn, each <0.01%; Bi, 0.001-0.1%. Europium was not determined in the metal, but is expected to be about 0.08%, the same amount as was present in the samarium oxide starting material. Slag inclusions in the metal are ruled out by the density determinations.

The density of the metal samples was determined by weighing the metal in air, then in acetylene tetrabromide (sample suspended from a platinum wire). Weight of the samples on which density was determined was between 0.6 and 2 g. Density measurements were made at 23.8°C, the temperature at which the density of acetylene tetrabromide was determined from a calibrated pycnometer to be 2.956_6 g/cc.

3. Discussion

3.1 Reaction of Samarium (III) Bromide with Barium. The reaction of samarium (III) bromide with barium proceeds instantaneously at about 500°C with sufficient evolution of energy to increase the temperature of the charge to about 1000°C. (ΔF was calculated to be $\sim$-59 kcal for this reaction at 1000°K.[4]) Further heating of the charge to 1650-1700°C permits agglomeration of the molten metal and separation of the slag by gravity. Excess barium is removed by vaporization at this temperature.

The yield of metal can be as high as 80% or as low as 1%, depending on the particle size and purity of the reactants. Samarium (III) bromide which has been fused, then broken up and mixed with large pieces of barium gives very low yields, while yields greater than 50% generally are obtained when the bromide is finely powdered and the barium has about a 20-mesh particle size. However, not all of the metal produced in the reaction is recovered in usable, massive form. Some is lost by vaporization, and some remains as a thin layer on the walls of the crucible, since tantalum is wet by molten samarium metal.

It was found that the thermal gradient from top to bottom of the tantalum crucible is fairly important. When the crucible is suspended from a tantalum wire and the bottom of the crucible is heated to a higher temperature than the top, some of the molten slag and metal can migrate to the top of the crucible. If the temperature is sufficiently high, a portion of the slag and metal will actually flow out of the crucible. However, if the crucible is set on a pedestal, conduction loss through the pedestal keeps the bottom of the crucible cooler, and thus both metal and slag remain at the bottom, effecting a good separation.

It has been pointed out by Daane, Dennison, and Spedding[2] that samarium metal has a relatively high vapor pressure. Their observation was confirmed in this work. When samarium metal was recast at about 1700°C, approximately 1 g of metal distilled to the lid of the crucible in a period of 5-10 minutes.

Samarium metal has a shiny appearance, resembling freshly cut iron. It was observed that it is relatively soft, thus confirming the report of Daane et al.[2] After weeks of exposure to air, it is scarcely tarnished. It dissolves slowly in cold, dilute strong acids, but rapidly in concentrated acids. Its reaction with distilled water is quite slow.

Ellinger and Zachariasen,[11] of this Laboratory, have found the crystal structure of samarium metal to be rhombohedral, with the unit cell dimensions of $a = 8.982 \pm 0.003$ Å and $\alpha = 23.31 \pm 0.02°$. The calculated density is 7.52 g/cc, and the mean metallic radius is 1.804 Å. Daane et al [2] had previously given an estimate of the unit cell dimensions.

The table below gives the density of samarium metal as determined by physical measurements on three different samples. Accuracy of the data is believed to be ± 0.005 g/cc.

Sample	Density (g/cc)
Metal as made	7.499
Recast metal	7.509
Distilled metal	7.495

These data compare favorably with the calculated density[11] and the value of 7.53 g/cc obtained by Daane et al.[2]

3.2 Other Reactions Tried. The reaction of samarium (III) bromide with barium in a sealed bomb with iodine as a booster[10] gives better than a 50% yield of metal in the form of semi-sintered black powder with a very small amount of fused metal. However, massive metal is not obtained in quantities large enough to work with. Post-heating of the charge with the induction heater after removal from the bomb does not materially increase the massive metal yield. The temperature developed by the boosted reaction is probably not sufficiently high to allow agglomeration of the metal and/or the presence of iodide interferes with agglomeration process.

Reaction of samarium (III) bromide with potassium in a sealed bomb gives a small yield of metal powder. Post-heating of the charge after removal from the bomb distills out most of the potassium and does not improve the metal yield.

Potassium vapor passed over samarium (III) bromide or iodide at ~ 800°C yields the divalent halide, but no appreciable amount of metal is formed. Lithium vapor is equally ineffective as a reductant for these halides.

A mixture of barium and potassium metals used in combination with samarium (III) bromide yields samarium metal, but it is believed that barium is the primary reductant, and that little of the potassium takes part in the reaction.

Lithium vapor passed over samarium (III) fluoride in a tantalum or molybdenum crucible at about 900°C gives the divalent fluoride. However, if a magnesium oxide crucible is used, some metal powder is formed. Possibly this method could be used for preparing milligram quantities of metal powder, but it would not be suitable for the preparation of large pieces of massive metal. L. B. Asprey[12] of this Laboratory has obtained similar results by using this method.

3.3 Samarium (II) Oxide. Samarium (II) oxide was identified from X-ray diffraction data by Ellinger and Zachariasen[11] as a contaminant in some of the products obtained by reduction of samarium (III) bromide with lithium or barium. Since these reactions were carried out on small scale, this compound could have resulted from oxygen contamination, or it could have been formed by reduction of oxyhalide present in the starting material. Ellinger and Zachariasen[11] also found that samarium (II) oxide is formed upon heat treatment of samarium metal. Samarium (II) oxide appears as a grey coating on the metal. Its crystal structure is of the sodium chloride type with a = 5.015-5.050 Å.

4. References

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