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MLM-175

Contract Number AT-33-1-GEN-53

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GAMMA SCALE CHEMISTRY PROGRESS REPORT

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Date: August 1-31, 1948

Prepared by: A. W. Martin

Distributed: OCT 12 1948

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GAMMA SCALE CHEMISTRY GROUP

B. Brody, M. Economides, E. Estabrook, E. F. Joy, and A. Martin

ABSTRACT

Oxide of Postum - A. Martin

A purified sample of metallic postum was dissolved in concentrated nitric acid. A white crystalline residue was obtained with removal of the liquid phase and after drying under reduced pressure. This crystalline nitrate residue was heated in a Pyrex tube at a maximum furnace temperature of 430°C. for five hours under a pressure of less than 1×10^{-5} mm. of mercury. The X-ray capillary end of the Pyrex tube containing the product, a yellow residue, was sealed off from the evacuated tube. This yellow residue was in appearance identical to that of the prepared dioxide of postum.[1] The X-ray capillary as sealed off was not suitable for use in obtaining an X-ray diffraction photograph. A repeat on this attempted preparation of an oxide of postum from a nitrate residue is planned.

In a memorandum by H. P. Knauss[2] it was suggested that a comparison of an X-ray diffraction pattern for thorium oxide be made with the X-ray diffraction pattern which had been obtained for postum dioxide.[3] A prepared sample of thorium oxide in an X-ray capillary of Pyrex was given to R. E. Brocklehurst for X-ray diffraction studies. It has been indicated by the X-ray Group that comparison of the X-ray diffraction patterns of thorium oxide with postum dioxide confirms the cubic crystalline pattern, unit cell size and formula, QO_2, which was obtained for postum dioxide.[1,3]

Microscopic Examination of Quartz Fibers from a Used Quartz Fiber Balance - A. Martin

In collaboration with R. G. Olt, sections from the quartz fiber balance which had been in use for some time in microassay determinations have been examined under a research microscope. Photomicrographs of these sections as examined are being made. When the necessary information has been obtained the detailed data together with the photomicrographs will be turned over to R. G. Olt for inclusion in a report on this quartz fiber balance.

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Density of Postum - B. Brody

Additional data confirming previous values[4] for the density of metallic postum have been obtained. The experimental data on the determinations for the density of postum are to be presented in a forthcoming report. No detailed report is included in this Progress Report.

Preparations - M. Economides

A comparison of water calibration of a 30 lambda pipet with a mercury calibration is being made in connection with determinations of possible errors involved in counting technique.

A preparation as requested by the Argonne Laboratory has been filled.

Seventy Simpson standards were prepared for the Counting Room.

Solubility of Tellurium in Dilute Nitric Acid - E. Estabrook

Standard solutions of titanium trichloride and potassium dichromate were prepared and quantitatively checked against each other by potentiometric titration. Tellurium oxide in four normal hydrochloric acid was prepared as a standard solution and titrated against a standard solution of titanium trichloride by potentiometric titration. The tellurium content of a prepared sample of tellurium nitrate was determined quantitatively by first converting the nitrate to the oxide of tellurium then dissolving the oxide in 5.7 normal hydrochloric acid. This hydrochloric acid solution was titrated potentiometrically against standard titanium trichloride for tellurium.

Samples of tellurium in ten per cent nitric acid containing an excess of tellurium have been prepared. When solution equilibrium at 25°C. has been reached the liquid phase will be analyzed quantitatively for tellurium content.

Postum Bromide - E. F. Joy

When metallic postum is reacted with an excess of bromine vapor at 250°C. dark red crystalline postum bromide is formed. Photomicrographs of a sample of this dark red crystalline postum bromide were obtained both in black and white and in color. Attempted analysis of this compound for bromide content was made using the potentiometric method.[5] The reason why

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no distinct end point was obtained is unknown. The amount of postum present in this sample of bromide was approximately two units. Better results may be obtainable if the postum bromide sample were to contain less activity. As an aid to the study of the crystalline structure of compounds of postum by optical and X-ray methods, a program of preparation of pure thorium compounds was initiated. The following compounds of thorium were prepared, oxalate, oxide, bromide and oxybromide. Comparison of the crystalline forms of thorium bromide and postum tetrachloride indicates that they are isomorphous.

DETAILED REPORT

Oxide of Postum - A. Martin

Microassay foils containing a total of approximately 1.5 units of postum were placed in a quartz volatilization tube.[6] Fractional volatilization was used to purify the metallic postum.[3] The purified sample of metallic postum was deposited as a metallic mirror on the walls of a 2 mm. I.D. quartz tube under reduced pressure by volatilization at a furnace temperature of 350°C. to 400°C. That section of the quartz tube containing this purified metal was broken out and then immediately inserted in a Pyrex tube containing ten lambda of concentrated nitric acid. The one end of this 10 mm. O.D. Pyrex tube was drawn out into a capillary of about 20 micron wall thickness and about 0.28 mm. diameter. The other end of this 10 mm. O.D. Pyrex tube was capped by means of a standard taper male and female glass joint. A side tube attached to the 10 mm. O.D. Pyrex tube was connected to a liquid air trap. The liquid air trap was a part of the vacuum system.

Twenty-four hours at atmospheric pressure was allowed for solution of the postum in the ten lambda portion of concentrated nitric acid. The liquid phase present was removed by gradually reducing the pressure in the system. A period of five days was required for removal of all visible liquid phase with the reduced atmospheric pressures used.

After removal of the liquid phase the pressure in the system was reduced to approximately 1×10^{-3} mm. of mercury. A white crystalline residue remained on the walls of the Pyrex tube and in a region above the capillary end and at a point where removal of the liquid phase had taken place. This white active nitrate residue contained in the Pyrex tube was brought to atmospheric pressure and the tube removed from the vacuum system. After removing the standard taper cap a small rod (1 mm. diameter) was inserted through the opened end. This glass rod was used to loosen the white nitrate residue from the walls of the Pyrex tube. A portion of this white residue was shaken down into the closed end of the X-ray capillary.

The standard taper cap was replaced on the Pyrex tube. This tube with its capillary end containing the white nitrate residue was connected to the liquid air trap of the vacuum system. After evacuation for several hours at a pressure of about 1×10^{-5} mm. of mercury a tubular electrically heated furnace was placed around that portion of the Pyrex tube which contained the active deposit, the X-ray capillary end. A furnace temperature of 394 to 430°C. was maintained for five hours. The white crystalline nitrate residue appeared as a yellow residue after heating and on cooling to room temperature. In appearance this yellow residue was observed to be identical with postum dioxide prepared by reacting metallic postum with dry oxygen.[1]

A seal off about 12 mm. from the closed end of the X-ray capillary was made. Although a major portion of the active yellow residue was contained in a region approximately 5 mm. from the closed end ot the capillary there was some active yellow residue scattered along the 4 cm. section of the capillary tube. It was found that in making the seal off of this X-ray capillary end activity was fused into the Pyrex glass. An attempt was made to remove the activity from the outside of the sealed X-ray capillary by rinsing with nitric acid, however, repeated rinsing over a period of two days removed most but not all the outside contamination. Because it was not desirable to expose X-ray diffraction equipment to possible contamination, this X-ray capillary containing the active yellow deposit was not turned over to the X-ray Group. In previous studies on the X-ray diffraction of postum dioxide it was observed that a freshly prepared dioxide of postum changes in crystalline pattern with time, therefore, X-ray studies on postum dioxide should be made with a freshly prepared sample.

Plans have been made to repeat this experiment since it has been indicated that there is a possible formation of the dioxide on heating the nitrate residue from a solution of metallic postum in nitric acid. Greater care will need to be exercised in locating a seal off point in the X-ray capillary which is free from scattered active residue as well as an improved procedure for sealing off such X-ray capillaries.

A suggested confirmation for the structure of the postum oxide as has been obtained from X-ray diffraction patterns was a comparison with thorium oxide.[2] Thorium nitrate was carefully recrystallized several times from water as the double ammonium nitrate. The final crop of crystals was dissolved in redistilled water and then filtered to remove any suspended impurities. The thorium in the filtrate was precipitated as oxalate from the strong nitric acid solution with pure oxalic acid. The crystals were filtered by suction, washed with alcohol and dried in a drying oven. This oxalate was converted to the oxide by heating to a red heat (800°) in an electric muffle.

A small portion (about 2 milligrams) of the white thorium oxide powder was placed in a Pyrex 10 mm. O.D. tube. One end of this tube was a closed end X-ray capillary (23 micron wall, 0.28 mm. diameter). The opposite end of this Pyrex tube was attached to the vacuum system by means of a standard taper joint. After thorough evacuation, a tubular electrically heated furnace was placed around the Pyrex tube. Heating at about 400°C. was continued for several hours. Upon cooling the 10 mm. O.D. Pyrex tube was sealed off from the vacuum system. A portion of the finely divided thorium oxide in the tube was shaken into the X-ray capillary end. The X-ray capillary was sealed off about 15 mm. from the closed end and contained a representative sample of white thorium oxide. This X-ray capillary of thorium oxide was given to the X-ray Group for X-ray diffraction studies. Results as indicated by the X-ray Group show that the X-ray diffraction patterns as obtained for thorium oxide compare with those of postum dioxide and give confirmation in the spacing in the unit cell, the cubic pattern, and the formula, QO_2, for postum dioxide.

It is suggested that this phase in the studies of postum dioxide, namely, X-ray diffraction data on postum dioxide, be summarized and presented in an Ad Interim Report.

A detailed report on the examination of the quartz fibers from the quartz fiber balance which had been in use for some time in microassay determinations is not included in this Progress Report. The information which is obtained in this examination will be given to R. G. Olt for a report to be presented by him.

<u>Preparations</u> - M. Economides

The 30 lambda pipet which was used in preparation of slides in study of counting technique was weighed empty and dry at 25°C. It was then weighed when filled with distilled water. The water content indicated a volume 2.9 per cent lower than the volume previously determined by mercury calibration.

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This pipet is to be checked further for volume. A proposed calibration by a titration method using a microburet will be tried.

A request in two parts was received from the Argonne Laboratory. Part one for postum plated on platinum was referred to Mr. Lowry. Part two for postum in dilute hydrochloric acid was prepared, packed, and dispatched.

Solutions F, K, E, L, and C prepared by Fainberg in 1944 were checked and found from counting to be 8.9 to 15.2 per cent low. Using the values as determined from counting, 70 standards were prepared and delivered to the Counting Room on August 24, 1948. Preparation of 40 postum Logac standards for the Counting Room is under way.

Solubility of Tellurium in Dilute Nitric Acid - E. Estabrook

A standard solution of potassium dichromate made by weight was 0.1041 normal as an oxidizing agent. A titanium trichloride solution when titrated potentiometrically against this standard dichromate solution was determined to be 0.0757 normal as a reducing agent. Tellurium dioxide was weighed quantitatively (0.7981 grams) and dissolved in four normal hydrochloric acid to a total volume of 200 milliliters. This solution of tellurium dioxide when titrated against standard titanium trichloride was 0.1037 normal.

A prepared 0.9116 grams sample of tellurium nitrate, basic nitrate, was weighed quantitatively. This weighed sample was placed in a porcelain crucible and after gradually drying in a muffle furnace was ignited in the furnace. This sample was heated in the muffle, cooled, and weighed until repeated treatment gave constant weight. The content of the crucible, tellurium oxide, was dissolved in 5.7 normal hydrochloric acid to a total volume of 200 milliliters. Ten milliliter portions of this tellurium oxide solution were titrated potentiometrically against standard titanium trichloride. Calculations based on the formula, basic nitrate, of tellurium, indicate 10 ml. of the tellurium oxide in hydrochloric acid would require 13.22 milliliters of 0.0717 normal titanium trichloride. Actually 13.2 to 13.3 milliliters of the 0.0717 normal titanium trichloride solution was required for 10 milliliters of the tellurium oxide solution.

An excess of tellurium, 5 grams, has been placed in 100 milliliters of 10 per cent (by volume) nitric acid. When solution equilibrium at room temperature or 25°C. has been reached, aliquots of the liquid phase will be evaporated. The residue from this evaporation will be ignited in the muffle.

The resulting residue will be taken up by hydrochloric acid and this solution titrated for tellurium content using standard titanium trichloride.

Postum Bromide - E. F. Joy

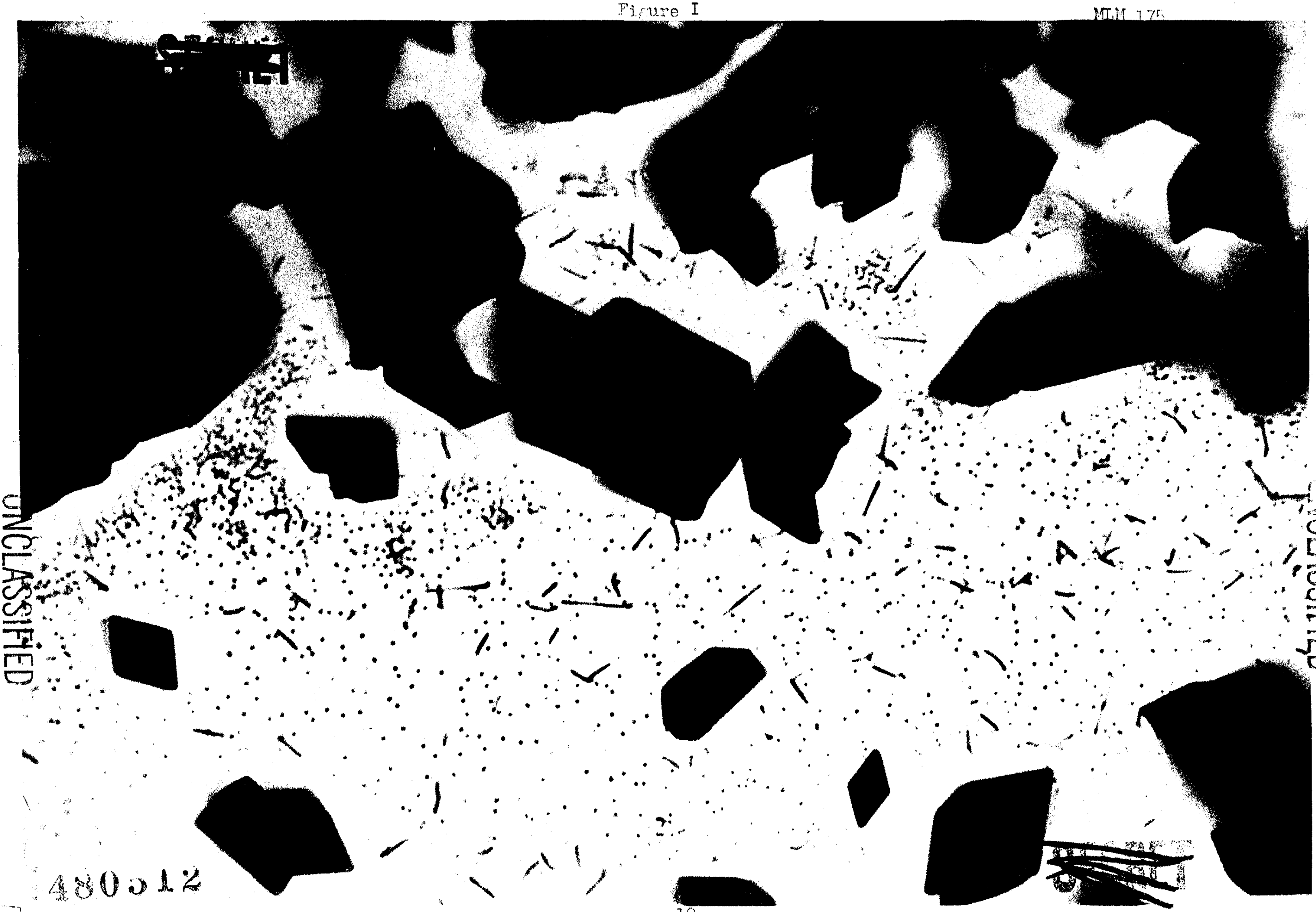
Two units of purified metallic postum were treated with dry bromine vapor at 200 mm. of mercury pressure in a Pyrex reaction tube. With standing overnight at room temperature a reaction occurred forming a yellow-brown mixture. The reaction tube was heated at 250°C. for one hour. A red crystalline product was volatilized in the presence of bromine vapor at 360°C. and condensed in the cooler portion of the tube as dark red crystals. Only the one crystalline phase was observed in the condensed crystals. Photomicrographs were obtained in black and white, Figure 1. A color photomicrograph was obtained, but was not reproduced for this report. These crystals resemble those of postum tetrachloride; however, the identity of crystalline form has not been established.

An attempt was made to quantitatively determine the bromine to postum ratio in the prepared sample of postum bromide. Calorimetric measurement of the sample gave 1.84 units of postum. This sample was dissolved in 500 lambda of 0.2 normal nitric acid and then titrated with 0.1 normal silver nitrate by the procedure already described.[5] The potential dropped rapidly from the initial value of 520 millivolts to 340 millivolts without addition of silver nitrate, but with the tip of the microburet containing silver nitrate dipping into the titration cell. Continuation of this titration with addition of silver nitrate gave no observable end point.

A second preparation of the red crystalline postum bromide has been completed. This preparation was started with 0.2 unit of postum. Quantitative analysis of this preparation by calorimetry and titration with silver nitrate will be attempted. It is hoped the reduction in postum content will give a sample which may be titrated for bromide ion.

Following the suggestion of W. H. Zachariasen[2] that thorium has approximately the same ionic radius as postum, and therefore, might serve as a "stand in", it was decided to prepare thorium compounds corresponding to those postum compounds on which X-ray data have been obtained. The comparison of thorium chloride and bromide to postum chlorides and bromides would serve in distinguishing between the divalent and tetravalent forms of the postum halides. If data on the crystal structure of the thorium halides are available comparison and interpretation of crystal structure of the postum tetrachlorides may be possible.

Figure I



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Purification and preparation of thorium compounds was started following the general method of Honigschmid and Horovitz.[7] Baker's cp. thorium nitrate was recrystallized as the double ammonium salt. Thorium oxalate was precipitated by addition of oxalic acid to a solution of the double ammonium nitrate. The oxalate was converted to the oxide by heating to 850°C. in a platinum dish.

Thorium bromide was prepared from thorium oxide by heating a mixture of two parts sugar charcoal with one part thorium oxide at 800°C. in a quartz tube while evacuating to remove moisture and oxygen. Bromine vapor was introduced at 200 mm. mercury pressure. The reaction tube was heated and the thorium bromide distilled to the cooler portion of the tube where it condensed as colorless crystals. Under the microscope the thorium bromide crystals resemble those of postum tetrachloride in structure. Measurement of the angles of 128° and 105° compare with 125.5° and 104° for the corresponding angles in the postum tetrachloride crystal.[8] The thorium bromide crystal is anisotropic and shows extinction at 7.5° from the long axis of the crystal, Figure 2.

An attempt was made to transfer crystals of the thorium bromide to an X-ray capillary in a dry atmosphere, however, sufficient moisture was present and was absorbed during the transfer to dissolve the crystals. Evaporation of the thorium bromide solution and heating to 160°C. formed thorium oxybromide, $ThOBr_2$, in the capillary.[9] The capillary was sealed and submitted to the X-ray Group for X-ray diffraction photographs.

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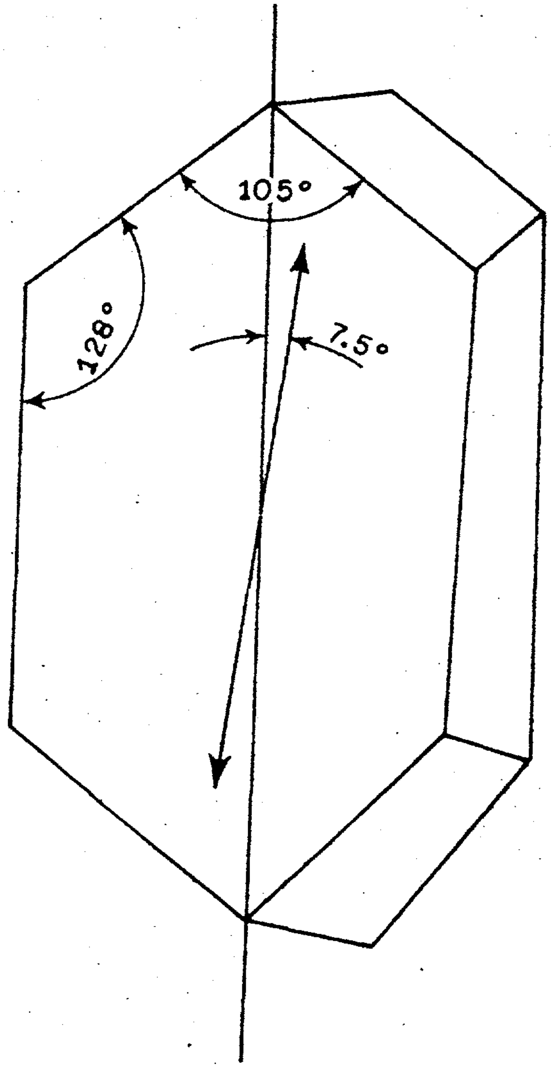
FIGURE 2

THORIUM BROMIDE



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