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## GAMMA SCALE CHEMISTRY PROGRESS REPORT

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Date: May 1-31, 1948

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GAMMA SCALE CHEMISTRY GROUP

M. Economides, E. Estabrook, L. Fauble, F. Joy, and  
A. Martin

Note: Mr. Fauble and Mr. Joy temporarily transferred to  
"Y" Group.

ABSTRACT

Reaction of HBr and KBr with Oxide of Postum - A. Martin

An attempt has been made to prepare a compound of postum analogous to  $K_2TeBr_6$ . A preliminary experiment indicates possible preparation of bromides of postum and that these bromides are analogous to the chloride of postum. Photomicrographs of two crystalline forms of a product resulting from the reaction of bromine and postum are included in this report together with procedure used to form these crystals. Intermediate compounds were formed in the attempted preparation of potassium postum bromide. These were (1) a white residue from nitric acid containing postum and (2) a yellow material formed on the ignition of this white residue. This yellow residue was identical in appearance to the yellow dioxide of postum. A red crystalline precipitate resulted when the yellow residue, which may well be  $QO_2$ , was treated with solution of hydrobromic acid and potassium bromide.

Preparations - M. Economides

The work investigating counting technique is continuing. That portion of the work completed is being written up and will be presented as Information Paper Counting Technique I.

Titration of Tellurium Dioxide with Titanium Trichloride - E. Estabrook

Investigation of the use of titanium trichloride as a reducing agent to titrate quantitatively tellurium dioxide has not yielded concordant results. An effort is being made to determine the best conditions for such a titration potentiometrically. Variations in concentrations, temperature of titration, electrode surface, acid concentration, and degree of agitation are in suspect. This investigation of variables in the titration method is to be continued. No detailed report is included.

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## DETAILED REPORT

Reaction of HBr and KBr with Oxide of Postum

Victor Lenher, J. Am. Chem. Soc. 31, 20 (1909) prepared potassium tellurium bromide for atomic weight determinations of tellurium. This salt according to Lenher is "a salt readily obtained in a high degree of purity and one of the most strongly crystalline derivatives of tellurium." For the preparation of this tellurium salt of definite composition, the nitrate of tellurium was converted to the dioxide by ignition, the tellurium dioxide was dissolved in pure hydrobromic acid and the molecular proportion of potassium bromide was added. The resulting bright red crystalline compound was definitely established by analysis to be anhydrous potassium bromide,  $K_2TeBr_6$ .

Preparation of  $K_2QBr_6$  analogous to the tellurium compound described by Lenher was attempted. A bright red crystalline precipitate resulted when the yellow dioxide of postum was treated with hydrobromic acid and potassium bromide, however, there is as yet no analytical data to give the needed information as to what atoms are present or in what ratio these atoms are present in the precipitate formed.

There was no available information for compound formation between postum and bromine; therefore, it was desirable to attempt preparation of a bromide. This was done as outlined below. Photomicrographs of crystals formed from the reaction of bromine and metallic postum are included with this report. Color photomicrographs of these bromide crystals were made; however, copies were not reproduced for this report. A description of the quartz tube containing the two crystalline forms referred to in the photomicrographs (Figures 1 and 2) is given in the sketch (Figure 3).

A. Procedure Used in Preparation of Bromide or Bromides of PostumPurification of Postum

Microfoils on which postum was deposited, containing approximately two units of postum were placed in a quartz tube similar to that previously described in "Ad Interim Report No. 8, Oxide of Postum, May 14, 1947", and in particular, Figure 1 of Ad Interim Report No. 8. Volatilization of postum from the microfoils under a reduced pressure of less than  $1 \times 10^{-6}$  mm. of mercury was accomplished by heating the outside of the quartz tube with an

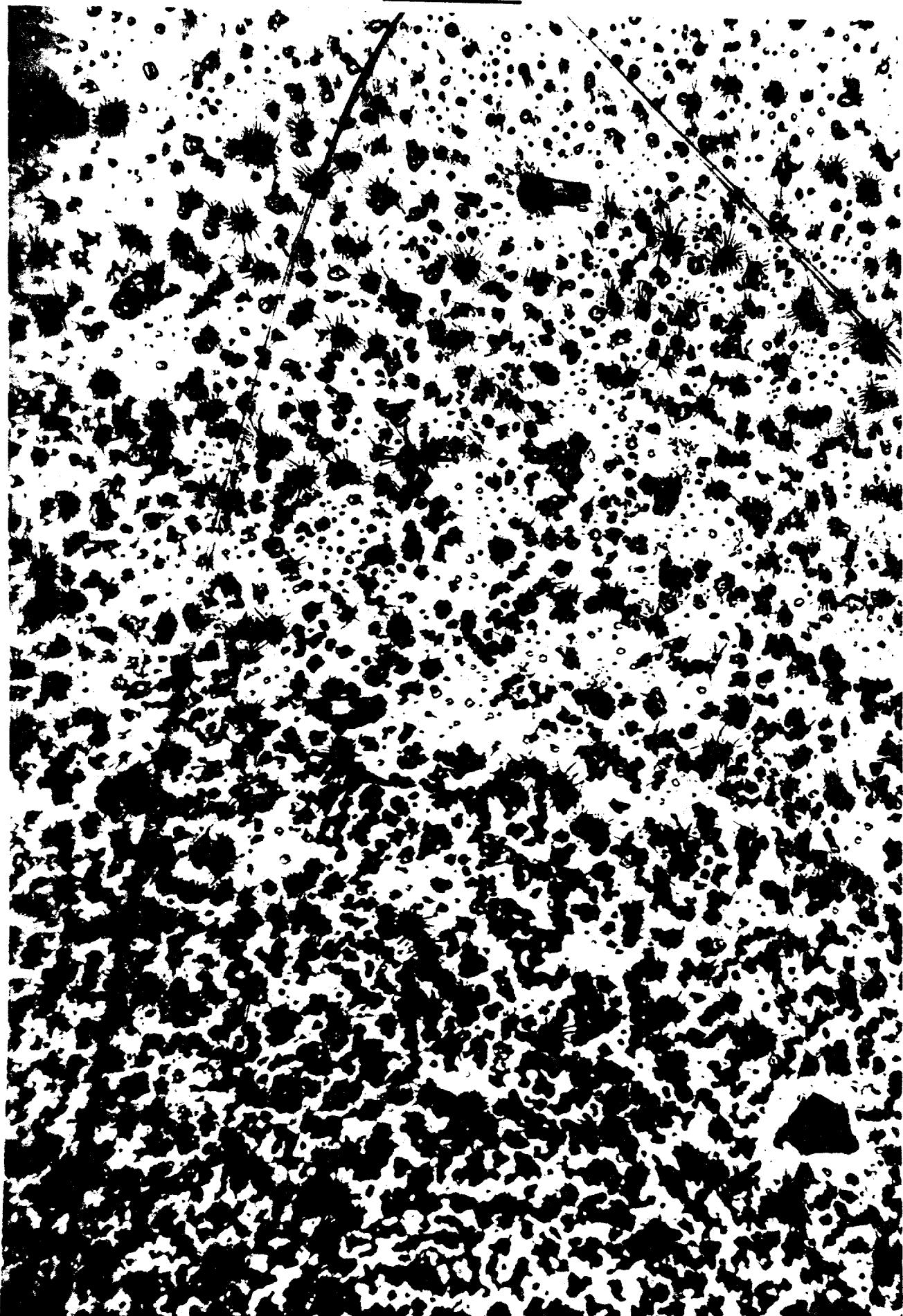
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—FIGURE 1—

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— FIGURE 2 —

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— FIGURE 3 —  
**QUARTZ TUBE OF BROMIDE CRYSTALS**  
— FULL SIZE SCALE —

## THIS PORTION IN FURNACE

THIS PORTION OUTSIDE FURNACE

A technical drawing of a glass tube. The tube has a flared top and a narrower bottom. A horizontal line extends from the top of the tube to the left, with a dimension of  $1\frac{3}{8}$ " indicated. Another horizontal line extends from the bottom of the tube to the left, with a dimension of 3" indicated. A vertical line extends downwards from the center of the tube. A bracket on the right side of the tube is labeled "X-RAY CAPILLARY" at the top, "0.45 MM. DIAMETER" in the middle, and "36 MICRON WALL" at the bottom. A line labeled "6 mm. O.D." and "4 mm. I.D." is located at the bottom right.

**PHOTOMICROGRAPH**

**PHOTOMICROGRAPH** **FIGURE 2.**  
**BLACK CRYSTALS**

**ASBESTOS SHIELD  
AT FURNACE EDGE**

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oxygen-gas flame with the vacuum pumps on during heating. The quartz tube containing the activity was sealed off from the vacuum system and placed in a electrically heated tubular furnace. Volatilization into the cooler portion (4 mm. diameter) of the quartz tube was made at a furnace temperature of 500 to 550°C. The 4 mm. diameter quartz tube containing the volatilized activity was sealed off from the larger diameter quartz tube. This 4 mm. diameter quartz tube containing the active deposit was placed in a small tubular furnace maintained at a temperature of 450°C. for three hours. Elimination of components volatilizing below 200°C. was accomplished by turning the 4 mm. tube end-for-end in the furnace and removing these more volatile components from the metallic mirror at furnace temperatures up to 200°C. That portion of the 4 mm. diameter quartz tube containing the metallic mirror of postum was placed in a quartz tube similar to the one previously described, Figure 1 of Ad Interim Report No. 8, loc. cit. After thorough evacuation of this quartz tube, oxygen free dry hydrogen gas was admitted. The end of this quartz tube containing the active deposit and hydrogen gas at one atmosphere of pressure was heated by means of a tubular furnace at 200°C. for three hours. After heating and upon cooling to room temperature, the hydrogen gas was removed by evacuation. That portion of this quartz tube containing the active deposit was sealed off from the vacuum system. Final volatilization of metallic postum into the capsule end of the quartz tube, Figure 6 of Ad Interim Report No. 8, loc. cit., was made at a furnace temperature of 400°C. for a period of three hours.

Preparation of Crystalline Compounds Formed in the Reaction of Bromine with Postum

Postum from the above purification steps and contained in the quartz capsule was inserted into the reaction end of a Bourdon gauge apparatus similar to Figure 7 of Ad Interim Report No. 8, loc. cit. The procedure for following a reaction using this Bourdon gauge apparatus has been previously described. Bromine vapor was admitted to the evacuated apparatus instead of dry oxygen gas as was used in the preparation of the oxide of postum, Ad Interim Report No. 8, loc. cit.

The reaction of bromine vapor over metallic postum was followed at room temperature for twenty-eight hours. A slight decrease of pressure from an initial pressure of 123.5 mm. of mercury was noted. Further pressure measurements were interrupted by a fracture of the sensitive Bourdon gauge caused by a drop of over 15 mm. of mercury in the atmospheric pressure which occurred on standing overnight. Although the broken gauge prevented further

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pressure measurements, the change of appearance of the deposit formed between postum and bromine could be followed since the apparatus was a closed system and bromine vapor was in contact with postum. It was observed that a dark red almost black deposit was forming with the postum.

That portion of the Bourdon gauge apparatus containing the postum and bromine vapors was immersed in liquid air and broken off from the remainder of the apparatus. This end containing the activity and condensed bromine vapors was immediately transferred to a quartz tube (Figure 4) and the open end of this quartz tube sealed. Heating of the active deposit contained in this quartz tube by means of a tubular furnace maintained at a temperature of 383°C. to 394°C. volatilized the active deposit which in turn condensed as a crystalline orange-red to black deposit in the cooler portion of the quartz tube, that portion of the quartz tube extending outside and beyond the furnace edge. This condensed crystalline orange-red to black deposit fluoresced in semi-darkness. An excess of bromine condensed as a liquid in the cooler portion of the quartz tube, considerably removed from the active deposit. After cooling to room temperature a portion of the excess bromine was removed by condensing in one end of the quartz tube by means of liquid air and then sealing off this end containing the condensed bromine vapors. That portion containing the active deposit as well as some remaining bromine vapor was placed in a tubular furnace and heated to 400°C. A crystalline deposit containing two crystalline edges one orange-red and the other black in appearance was observed (Figure 3). An examination of this crystalline deposit was made with the aid of a microscope. Photomicrographs were made (Figures 1 and 2). The sketch (Figure 3) of the quartz tube containing the crystalline deposit formed by bromine and postum indicates the position at which the photomicrographs referred to in (Figures 1 and 2) were taken. The center portion of this deposit was too dense for detailed observation. Figure 1 shows the deposit which condensed just inside the edge of the furnace at a furnace temperature of 400°C. This deposit was orange-red in appearance. Figure 2 shows the deposit condensing outside the furnace at the same furnace temperature of 400°C. These crystals were black, however, without metallic luster, and were unlike a deposit of metallic postum in appearance.

An effort was made to transfer this crystalline deposit, formed with bromine and postum (Figure 3) to a tube suitable for X-ray diffraction studies. After condensing the crystalline deposit into the X-ray capillary, it was observed that severe checking of the thin walled capillary was taking place due to the activity present.

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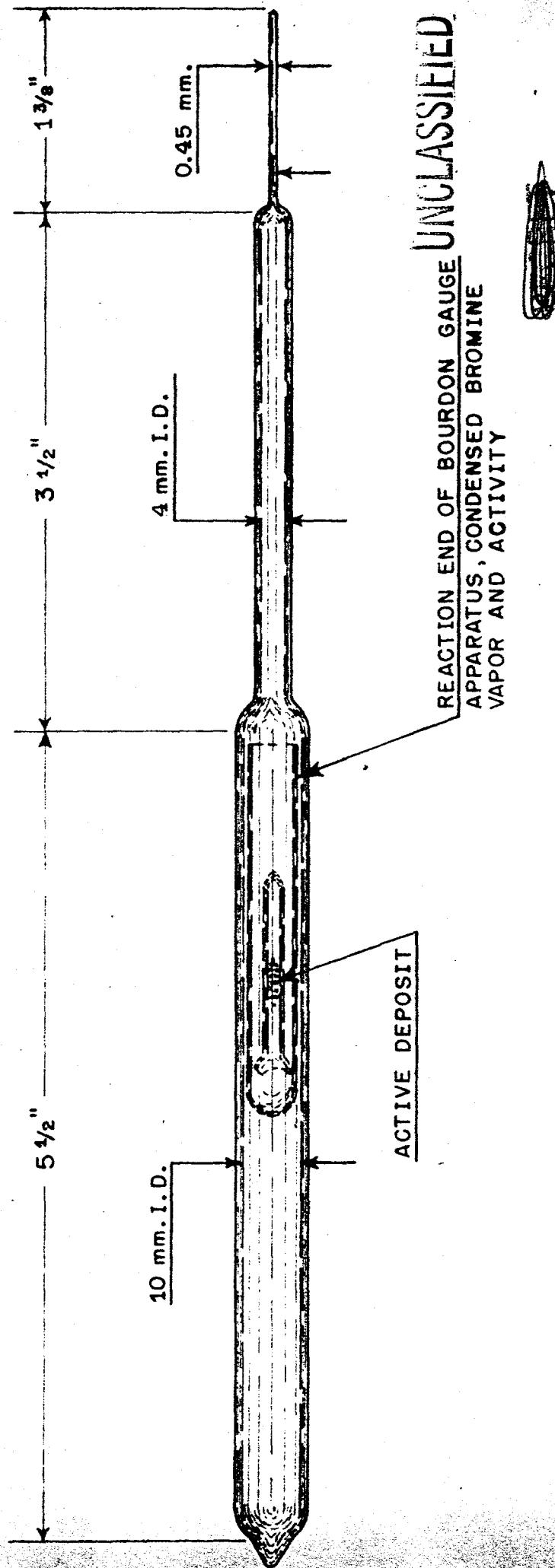
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FIGURE 4

ALL QUARTZ  
TUBE



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Therefore, no X-ray diffraction powder photograph was made because of danger of contamination of X-ray equipment with such a cracked tube. Checking of this thin walled quartz capillary by the activity present resulted in breaking of the tube on standing less than forty-eight hours at room temperature.

B. Preparation of Yellow Oxide of Postum by Ignition of Residue Obtained from Postum Dissolved in Nitric Acid

Metallic postum as received on microfoils was further purified in essentially the same manner as already described under part A of this report. The purified metallic postum was deposited by volatilization in a quartz capillary and the amount of postum determined by calorimetry. This quartz capillary was broken and then inserted in a quartz reaction tube (Figure 5). Two milliliters of concentrated nitric acid was added, the reaction tube placed on the vacuum line and allowed to remain overnight under atmospheric pressure. All activity was dissolved and there was no appearance of a precipitate. The pressure was then reduced from atmospheric 741 mm. of mercury to 380 mm. of mercury. Approximately one third of the liquid volume was removed with 380 mm. pressure and at room temperature after three days, when there appeared a white precipitate. Gradual reduction of the pressure to 28 mm. of mercury pressure removed all visible liquid and a white residue remained. This residue fluoresced in semi-darkness. The pressure was reduced and maintained at approximately  $1 \times 10^{-5}$  mm. of mercury for three hours. With the vacuum pumps on and a tubular furnace around the reaction end containing the white residue (active deposit) the temperature of the furnace was gradually (1°C. per five minutes) raised to 312°C. This temperature, 309°C. to 312°C., was maintained for three hours. Upon removal of the furnace a yellow residue with an edge of white was observed. The furnace was replaced around the active yellow-white edged residue and a furnace temperature of 399°C. to 418°C. maintained for three hours. A yellow residue of active deposit remained after this heating and on cooling to room temperature. The appearance of this residue was identical to that observed for the dioxide of postum,  $QO_2$  formed when dry oxygen was allowed to react with metallic postum at 300°C., Ad Interim Report No. 8, loc. cit.

C. Treatment of the Yellow Residue Obtained by Ignition of the Residue from Postum Dissolved in Nitric Acid with Hydrobromic Acid and Potassium Bromide

That portion of the quartz tube in part B of this report containing the active yellow residue which was in appearance identical to postum dioxide was broken off and inserted into a Pyrex tube (Figure 6). Five lambda of 40 per cent hydrobromic

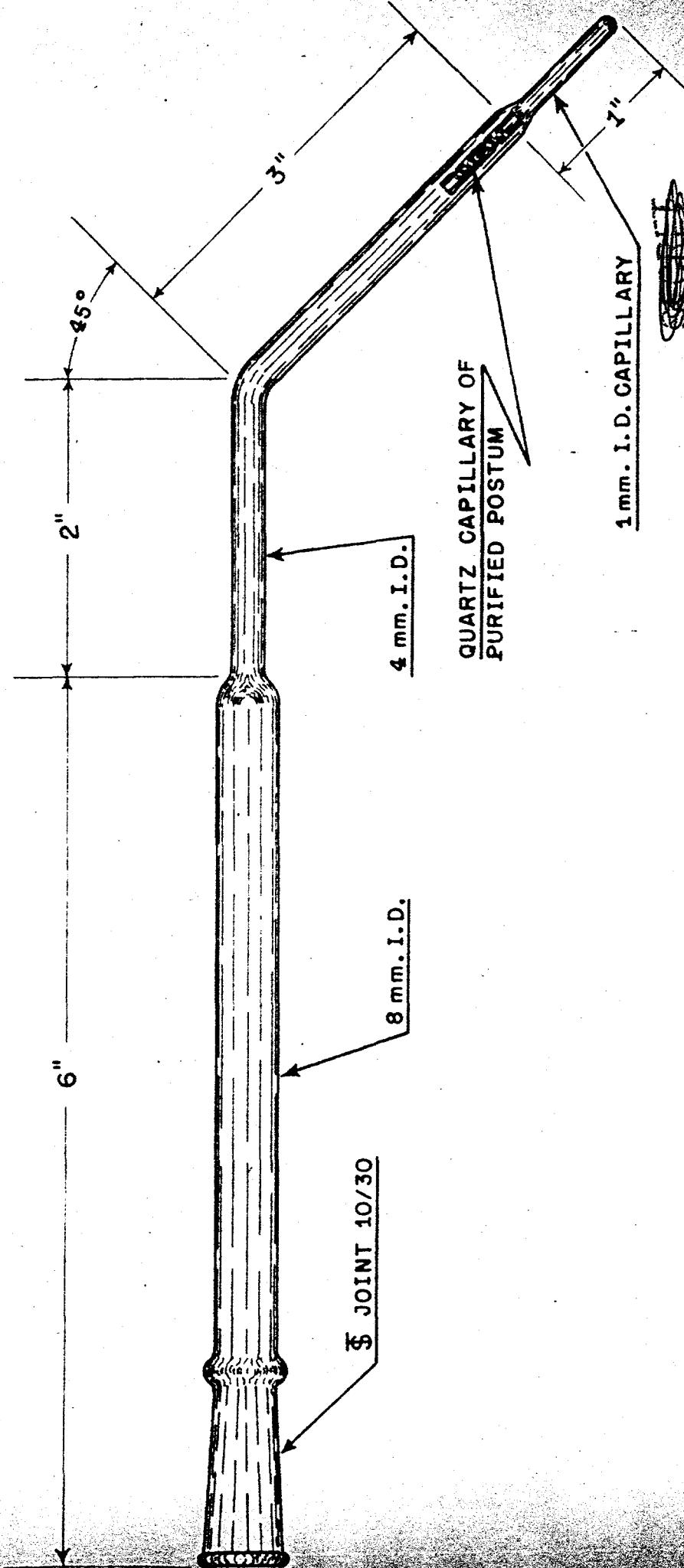
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-FIGURE 5-

ALL QUARTZ REACTION TUBE

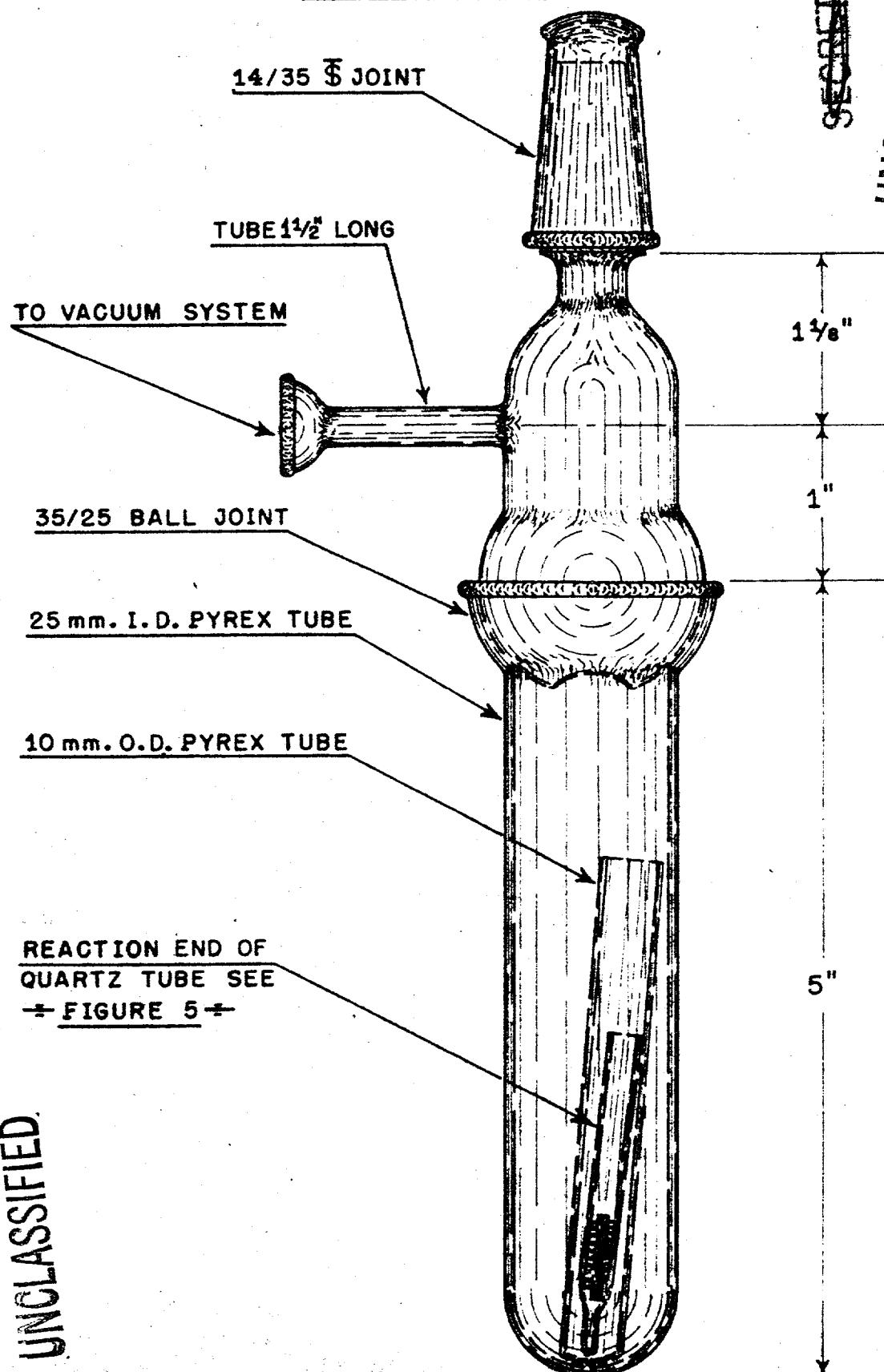


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— FIGURE 6 —

PYREX REACTION TUBE, DIOXIDE OF POSTUM  
PLUS HBr AND KBr SOLUTIONS

— FULL SIZE SCALE —



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acid and five lambda of a solution of potassium bromide (5 grams of KBr per 100 ml. of water) was added. Upon addition of these two solutions to the yellow residue, a bright red solution resulted. This solution was subjected to reduced pressure (ca. 600 mm. mercury) and approximately two thirds of the liquid present removed. A bright red precipitate formed. A recrystallization of the red crystalline precipitate with microscopic examination of the precipitate is planned.

FUTURE PLANS

The experiments on new compounds of postum reported above are qualitative and preliminary to a thorough investigation. Formation of a crystalline residue obtained from bromine in contact with postum appears analogous to formation of the chlorides of postum, two crystalline forms of the bromide being present. Separation and analysis of the crystalline product formed in the experiment with bromine and postum should be carried out.

The white residue obtained from nitric acid on postum upon removal of the liquid phase, may or may not be the nitrate, analogy to tellurium suggests the composition  $Q_2O_3(OH)NO_3$ . However, this white residue may be a hydrated oxide. Further investigation and analysis of this residue should be attempted. There is no confirmatory evidence that the active yellow residue obtained by ignition of the white residue from nitric acid and postum is the dioxide of postum other than identical appearance to the oxide obtained in reacting dry oxygen gas and postum. Analogy to tellurium compounds would postulate the ignition of the nitrate and would produce the dioxide. Further investigation of this active yellow residue is contemplated.

Analysis should be undertaken of the bright red crystalline precipitate formed when hydrobromic acid and potassium bromide solutions are reacted with the active yellow residue. An important factor in attempting the preparation of  $K_2QBr_6$  is to prepare such a compound in a pure form which could be produced in weighable quantities; further, that in such a compound the ratio of the weight of postum to the total molecular weight should be as small as possible. Quantitative determination of the bright red crystals are planned.

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