THE PREPARATION AND PROPERTIES OF BORON TRISELENIDE

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ABSTRACT

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by William Earl Hutchinson

Boron triselenide was formed by passing selenium vapor over amorphous boron at 850° to 950°. A hydrogen sweep was employed and B_2Se_3, a yellow powder, was collected on a fritted disk.

The boron triselenide was amorphous as formed, but after being heated to a temperature between 195° and 235°, it became crystalline. Both forms were studied by infrared techniques and the characteristic bands were noted. X-ray powder photographs were taken of the crystalline form and "d-values" were calculated. These values were compared with those of the hexagonal and cubic forms of boric oxide and were similar to the values of the cubic form.

Melting point determinations were run and the solid product was found to decompose at $556 \pm 5°$ in an evacuated ampoule. The solubility of boron triselenide in various liquids was investigated, but because of its extreme moisture sensitivity, the accuracy of these findings is doubtful.

The reaction between boron and tellurium was attempted, but no reaction occurred.

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OF BORON TRISELENIDE

By

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INTRODUCTION

Historical

The reaction between boron and the chalcogenides was investigated by many persons prior to 1900. Berzelius[1] reported in 1824 that boron trisulfide could be formed by melting sulfur in the presence of boron. In 1858, Wohler and St. C. Deville[2] reported the preparation of the sulfide by the reaction of hydrogen sulfide with heated boron.

In the early 1890's, Sabatier[3] and Moissan[4], following the work of Wohler and St. C. Deville[2], also prepared boron trisulfide and attempted to prepare its analog, boron triselenide. Sabatier[5] found that the selenide could be prepared by passing hydrogen selenide over boron maintained at a bright red heat. Moissan[6,7] reported that selenium and boron would react at 610° to form boron triselenide. No additional work pertaining to the preparation and properties of this substance has been reported. Even at that time the majority of the investigations were carried out with boron and sulfur and their reaction product, boron trisulfide.

Both Moissan and Sabatier reported that the selenide reacted violently with water with the evolution of hydrogen selenide. This action was comparable to the reaction of boron trisulfide with water; a reaction which was accompanied by the evolution of hydrogen sulfide. These investigators, therefore, assumed that other reactions of boron triselenide would be the same as those of the corresponding sulfide, but they reported no further experiments to prove this hypothesis.

In 1926, Tiede and Thimann[8] again examined a modification of the sulfide reaction. They reported the formation of boron trisulfide by the reaction of boric oxide with aluminum sulfide at 1200° to 1300°. The product formed in this reaction was contaminated with silicon sulfide which was formed through the reaction of the aluminum sulfide with the quartz reaction tube. The reaction of boric oxide with aluminum selenide was not reported.

In the last few years the renewed interest in boron chemistry has led a few persons to re-examine boron trisulfide, but no one has reported data on boron triselenide. Zeeman[9], in 1950, published an article on the spectrum and structure of the boron monosulfide (BS) molecule. His apparatus consisted of a Pyrex glass vacuum system and a quartz discharge tube of the end-on type. Helium or argon was pumped through the system at low pressure with a mercury diffusion pump. Amorphous boron was placed in a silica boat which was contained in a quartz tube, while a reservoir which was filled with vacuum distilled sulfur protruded downward from the discharge tube and, when heated, provided sulfur vapor. This vapor was carried by the circulating gas over the boron which was heated by means of a cylindrical electrical heater. At about 700° the brilliant S_2-spectrum which was present at the early stages of the process disappeared and was superseded by a very intense spectrum resembling a "daylight" fluorescent lamp.

In a more recent study Greene and Margrave[10] reported additional spectral data on the boron monosulfide molecule. Their work was also conducted in the vapor phase. For their work, dried hydrogen sulfide was passed over amorphous boron at 700° and the vaporized product was collected on a cold finger. This product was introduced directly into a 2.54 centimeter diameter quartz or Vycor tube to which suitable windows had been attached. The spectrum of the gas over the boron trisulfide was examined by emission and absorption techniques; five bands were observed. The isotopic shifts which resulted from the enrichment of the boron sulfide with B^{10} gave support to a twisted zigzag model possessing C_2 symmetry.

These recent investigations did not include the examination of the boron-selenium reaction.

Purpose of Study

The purpose of the present study was to determine a suitable method for the preparation of boron triselenide, to investigate some of its physical properties, and to study some of its reactions. The lack of past knowledge of this compound and the availability of high purity raw materials led to the belief that this was a worthwhile endeavor.

EXPERIMENTAL

Raw Materials

The following raw materials were used throughout the present study. The purity and suppliers of these materials are listed when known.

1. Crystalline boron - 100 mesh
   U. S. Borax and Chemical Corporation
   50 Rockefeller Plaza
   New York 20, New York

2. Electrolytic boron - 99% purity
   Fairmount Chemical Company, Inc.
   117 Blanchard Street
   Newark, New Jersey

3. Sulfur - Triply distilled
   Purity and source unknown

4. Selenium metal - 99.99% pure powder
   Fairmount Chemical Company, Inc.
   117 Blanchard Street
   Newark, New Jersey

5. Prepurified nitrogen
   The Matheson Company, Inc.
   East Rutherford, New Jersey

6. Hydrogen gas
   Ohio Chemical and Surgical Equipment Company
   Cleveland, Ohio

7. Argon gas
   The Matheson Company, Inc.
   East Rutherford, New Jersey

8. Tantalum foil
   Fansteel Metallurgical Company
   North Chicago, Illinois

9. Molybdenum foil
   Fansteel Metallurgical Company
   North Chicago, Illinois

Reactions Between Boron and Sulfur

The preliminary work in the present study was carried out to determine the general type of equipment that would be needed to obtain good yields of product. In order to arrive at the best equipment design, the reaction between boron and sulfur was examined using the conditions reported by previous investigators. Eight series of reactions were run; each resulting in a modification of the equipment design.

Series I

To prove that a product could be formed when boron was reacted with sulfur, a simple, but crude, apparatus was set up. This apparatus consisted of a 2.5 centimeter diameter Vycor tube, 66 centimeters in length, which was inserted into a tube resistance furnace. Crystalline boron was placed in a Vycor boat which was then set in the tube. A quantity of sulfur was also added to the tube at the inlet end, outside of the heated zone. Rubber stoppers containing Pyrex tubing were placed in each end of the Vycor reaction tube. Prepurified nitrogen was passed through the inlet end of the system at an approximate rate of ten cubic centimeters per minute. The outlet end of the system was equipped with Tygon tubing which dipped into a water trap. A stream of air was directed at the outlet end of the reaction tube to cool it so that product crystallization could occur.

A Chromel p-Alumel thermocouple, attached to a Minneapolis Honeywell Model 2730 potentiometer, was placed inside the furnace to measure the temperature. A measurement of temperature, accurate to ±5°, could be made by first standardizing the potentiometer at room temperature and then measuring the millivolt potential difference when the thermocouple was heated. By comparing this millivolt reading with a standard chart the true temperature could be determined. This experiment was repeated varying the furnace temperature from 600° to 740°. Although a few small white crystals were formed at 680°, a higher yield was observed at 730°. The small amount of white crystals that was obtained was placed in water and found to be very soluble. Upon exposure to air these crystals emitted hydrogen sulfide.

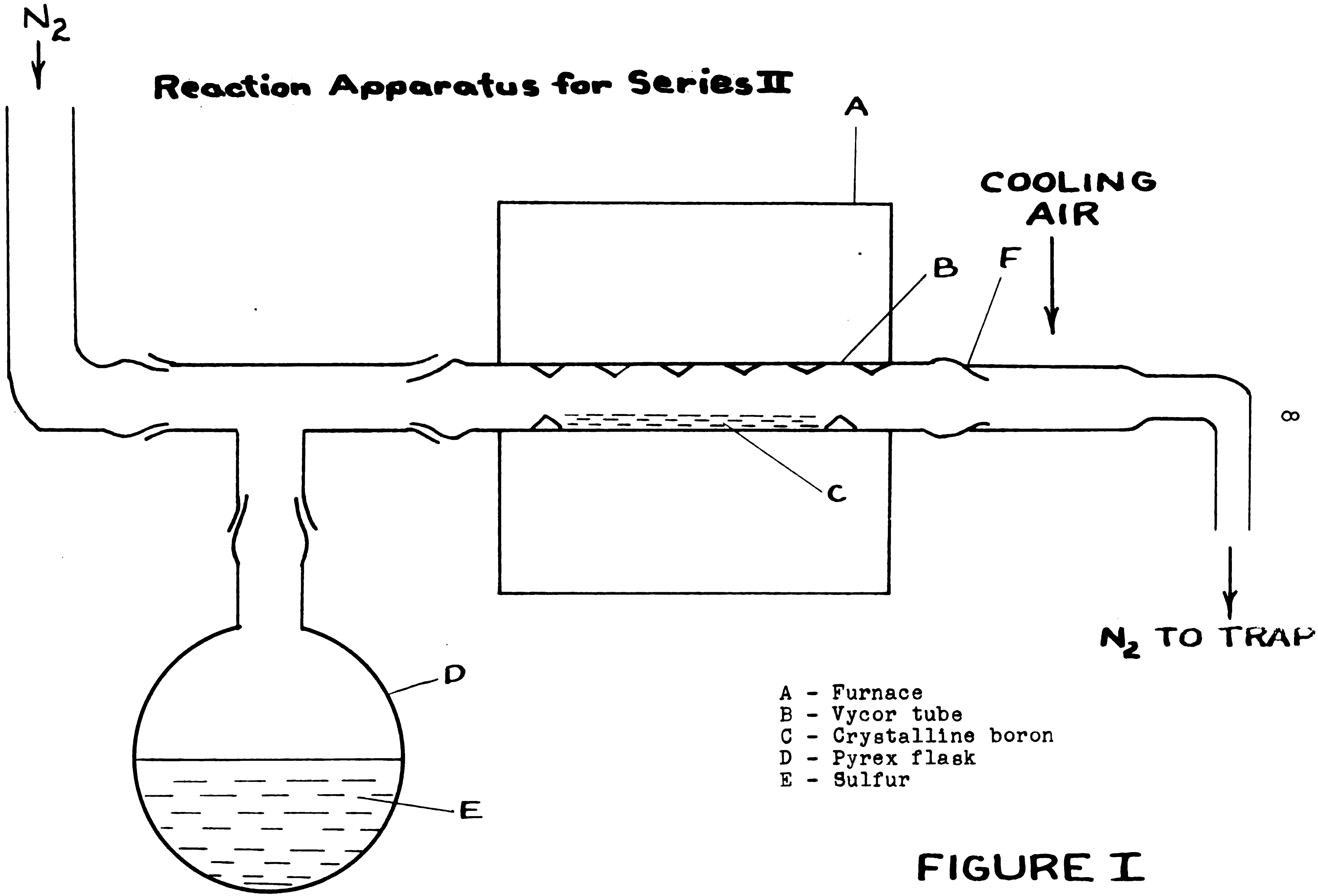
The above properties were identical with some of those previously reported for boron trisulfide. The poor yield of white material led to the belief that the rubber stoppers and Tygon tubing provided areas for product to escape. In an attempt to increase this yield a new apparatus was designed.

Series II

The failure of the apparatus described in Series I, page 5, led to the new apparatus as shown in Figure I. All of the glass-to-glass joints, except F, are 14/35 $\$$ joints. The 1.7 centimeter diameter Vycor reaction tube, B, was indented to promote turbulence and a longer contact time between the sulfur vapor and the crystalline boron, C. The boron was also spread thinly over the bottom of the tube to expose more surface for reaction. Triply-distilled sulfur, E, was placed in the 250 milliter flask, D, and prepurified nitrogen was used to sweep the system. After passing through the heated tube, A, the nitrogen was bubbled into a water trap at the approximate rate of ten cubic centimeters per minute. The furnace was maintained at 730° throughout the two hour reaction.

This arrangement also proved ineffective because it was difficult to carry enough sulfur vapor into the heated tube, even when the sulfur was boiled. No product formed in the cooled portion of the tube. The possibility of leakage at joint F resulted in replacing it with a standard tapered joint. The series of reactions using this setup was designated as Series III.

Reaction Apparatus for Series II

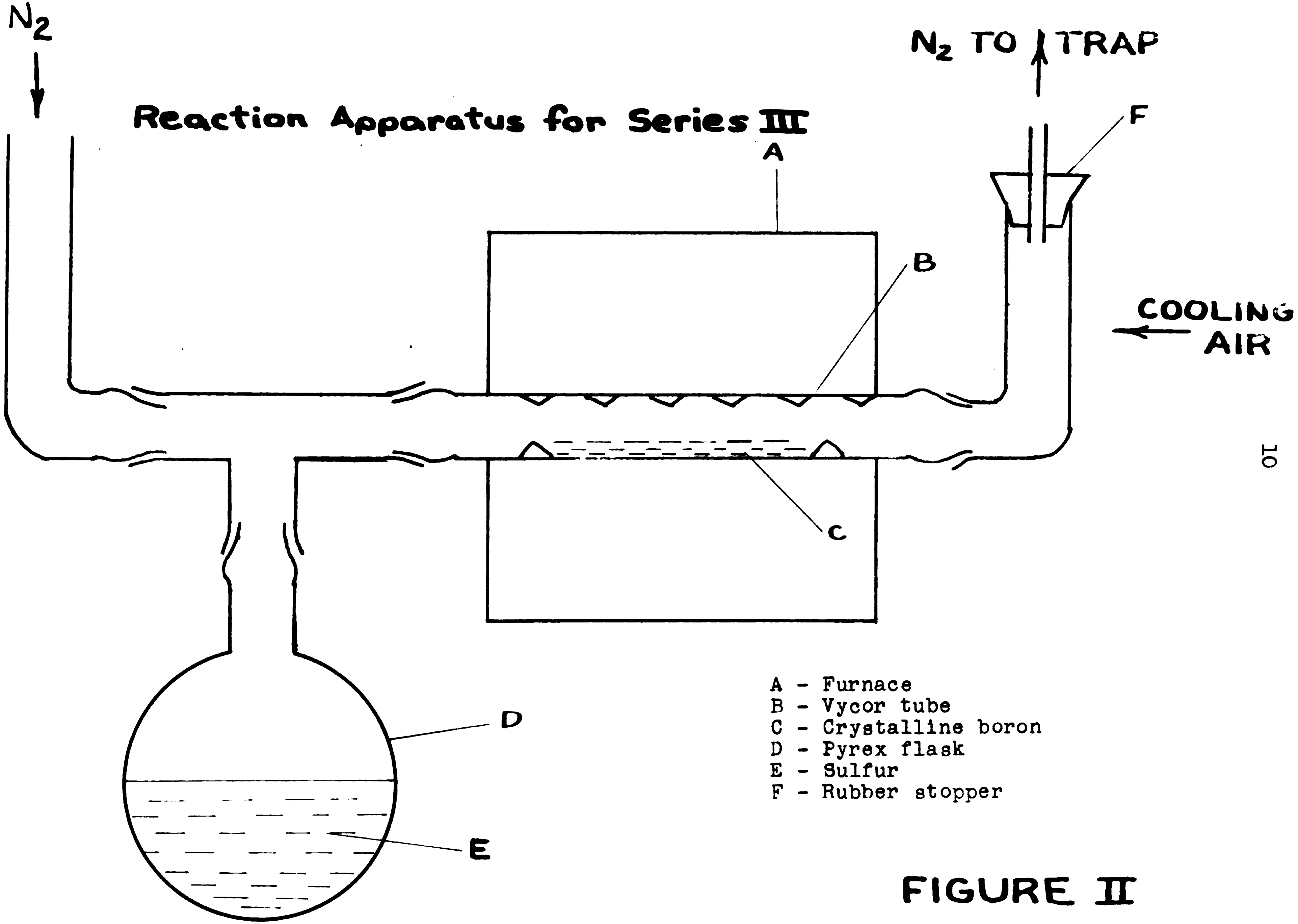


A - Furnace
B - Vycor tube
C - Crystalline boron
D - Pyrex flask
E - Sulfur

FIGURE I

Series III, IV, and V

An apparatus as shown in Figure II proved to be the basic apparatus which, after being modified as in Figures III and IV, was used for subsequent reactions between boron and sulfur. The transition of the flask, D, from the long necked flask of Figure II to the short necked flask of Figure IV was prompted by the need for getting sulfur vapor into the heated tube in sufficient quantity to promote reaction. A detailed explanation of these three series will be found in Appendix A.

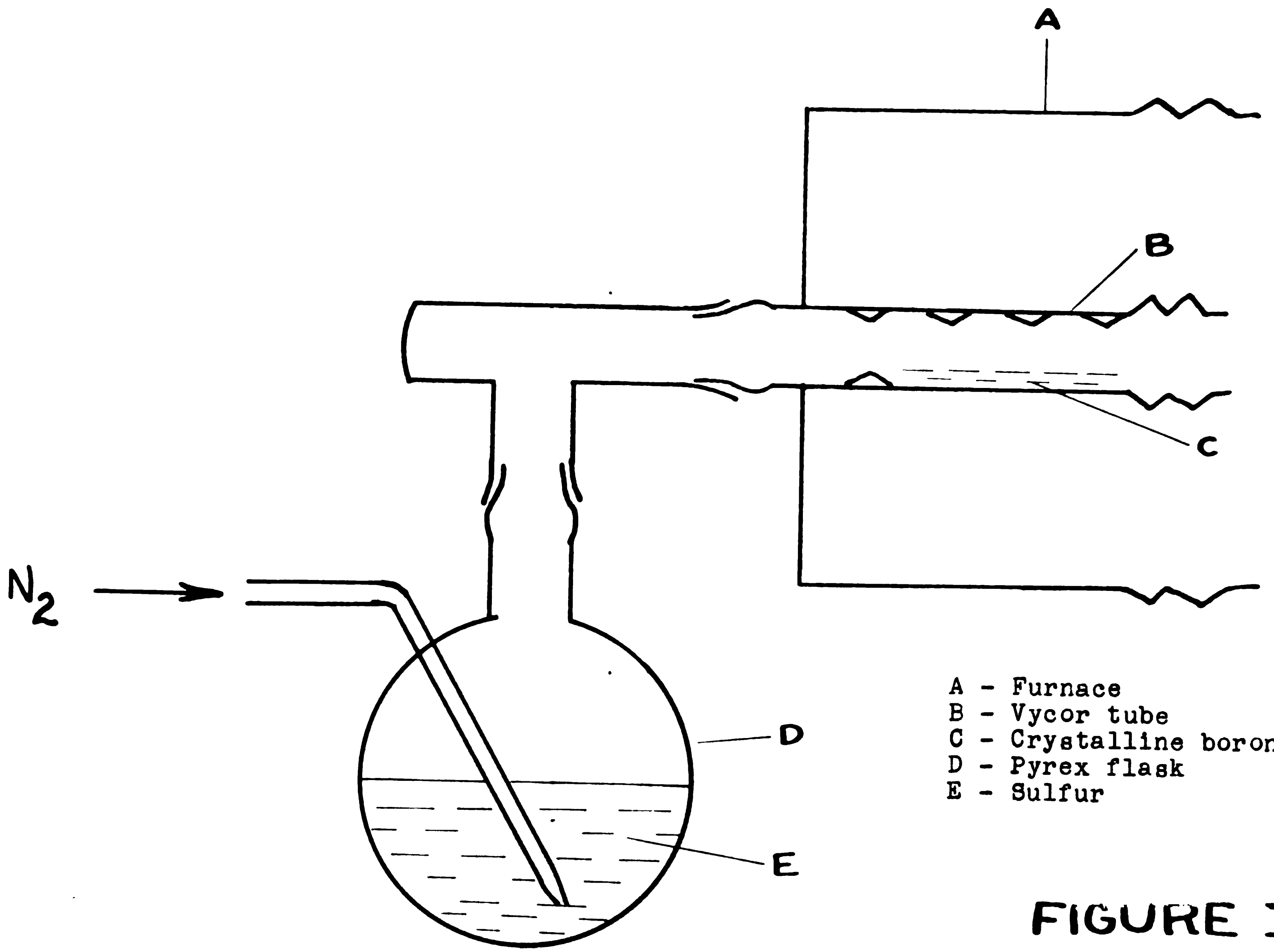


Reaction Apparatus for Series III

A - Furnace
B - Vycor tube
C - Crystalline boron
D - Pyrex flask
E - Sulfur
F - Rubber stopper

FIGURE II

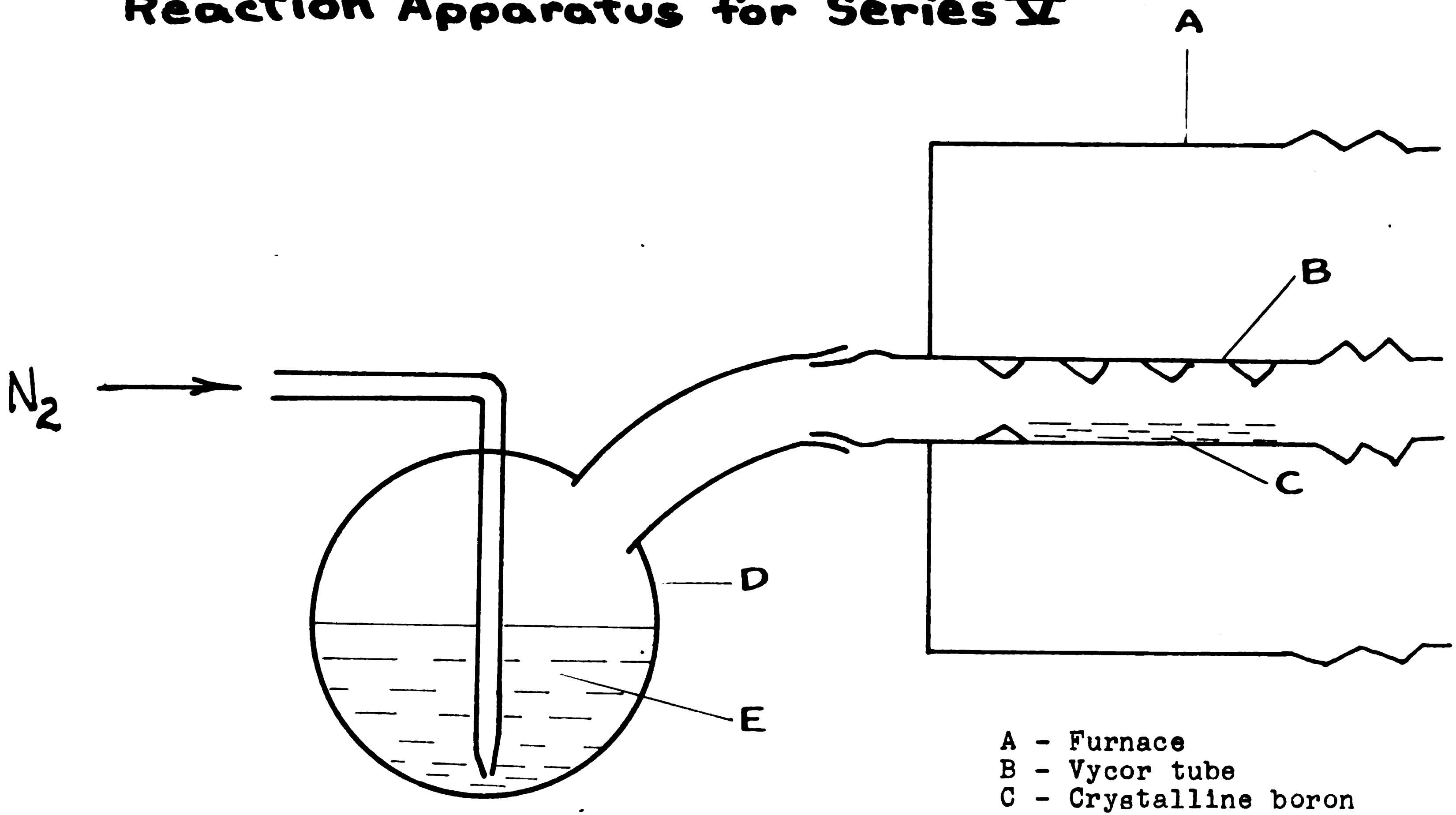
Reaction Apparatus for Series IV



A - Furnace
B - Vycor tube
C - Crystalline boron
D - Pyrex flask
E - Sulfur

FIGURE III

Reaction Apparatus for Series V



A - Furnace
B - Vycor tube
C - Crystalline boron
D - Pyrex flask
E - Sulfur

FIGURE IV

Series VI

After approximately ten reactions at temperatures of 700° to 740°, the indented Vycor reaction tube of Figures I through IV cracked. The boron apparently reacted with the Vycor, particularly at the indentations, developing a form, perhaps similar to Pyrex, which set up strains in the tube because of the difference in expansion. This inability to place the boron in direct contact with the Vycor reaction tube led to a search for a better carrier for the boron.

A piece of 0.018 centimeter molybdenum foil, approximately 1.3 centimeters by 7.5 centimeters, was bent to resemble a boat. To this assembly was added a quantity of crystalline boron. The boat was then placed in the 2.5 centimeter diameter Vycor tube of Series I, page 5, and a reaction was run. After a reaction time of two hours at 720°, the apparatus was cooled and the reaction tube was inspected.

Little or no product was formed even though sulfur vapor had been carried into the reaction zone as evidenced by a slight precipitate of sulfur at the outlet end of the reaction tube. However, the molybdenum boat was adhered to the Vycor tube with a syrupy red fluid. The sulfur vapor had apparently reacted with the molybdenum foil. When the reaction system cooled, the Vycor tube cracked at the molybdenum-Vycor interface. Molybdenum foil was, therefore, abandoned as a carrier for the boron.

Series VII

In the next series of reactions, a tantalum boat was substituted for the molybdenum boat. A piece of 0.013 centimeter tantalum foil, approximately 1.3 centimeters by 7.5 centimeters, was formed into a shallow boat by bending. To this boat was added crystalline boron. The boron was then placed in a 2.5 centimeter diameter Vycor tube, similar to the one described in Series I, page 5, with a quantity of sulfur at the inlet end. After several hours of reaction, using a nitrogen sweep, no reaction occurred between the sulfur and the tantalum foil, the boron and the tantalum foil, or the nitrogen and the tantalum foil. A small amount of white material formed during the reaction. The tantalum foil, therefore, appeared adequate as a carrier for the boron.

Series VIII

The previous series of reactions, using the prepurified nitrogen sweep, demonstrated that the crystalline boron was caked badly after the reactions were run. The compacted boron also smelled strongly of sulfur. These observations might be explained by postulating that the sulfur vapor was poisoning the surface of the boron, causing it to cake, and lessening the surface available for reaction. A dry hydrogen sweep was substituted for the nitrogen sweep on the assumption that the hydrogen would react with the surface sulfur to form hydrogen sulfide, or more logically the monohydrogen sulfide (HS) form[a]. This reaction would keep the surface fresh for further reaction because of the volatility of the hydrogen sulfide gas.

After a two hour reaction time at 740°, some white crystals formed.

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[a] Mellor[11] reports that hydrogen sulfide begins to dissociate at 400°, ultimately to hydrogen and sulfur at 1700°.

Reactions Between Boron and Selenium

Series IX

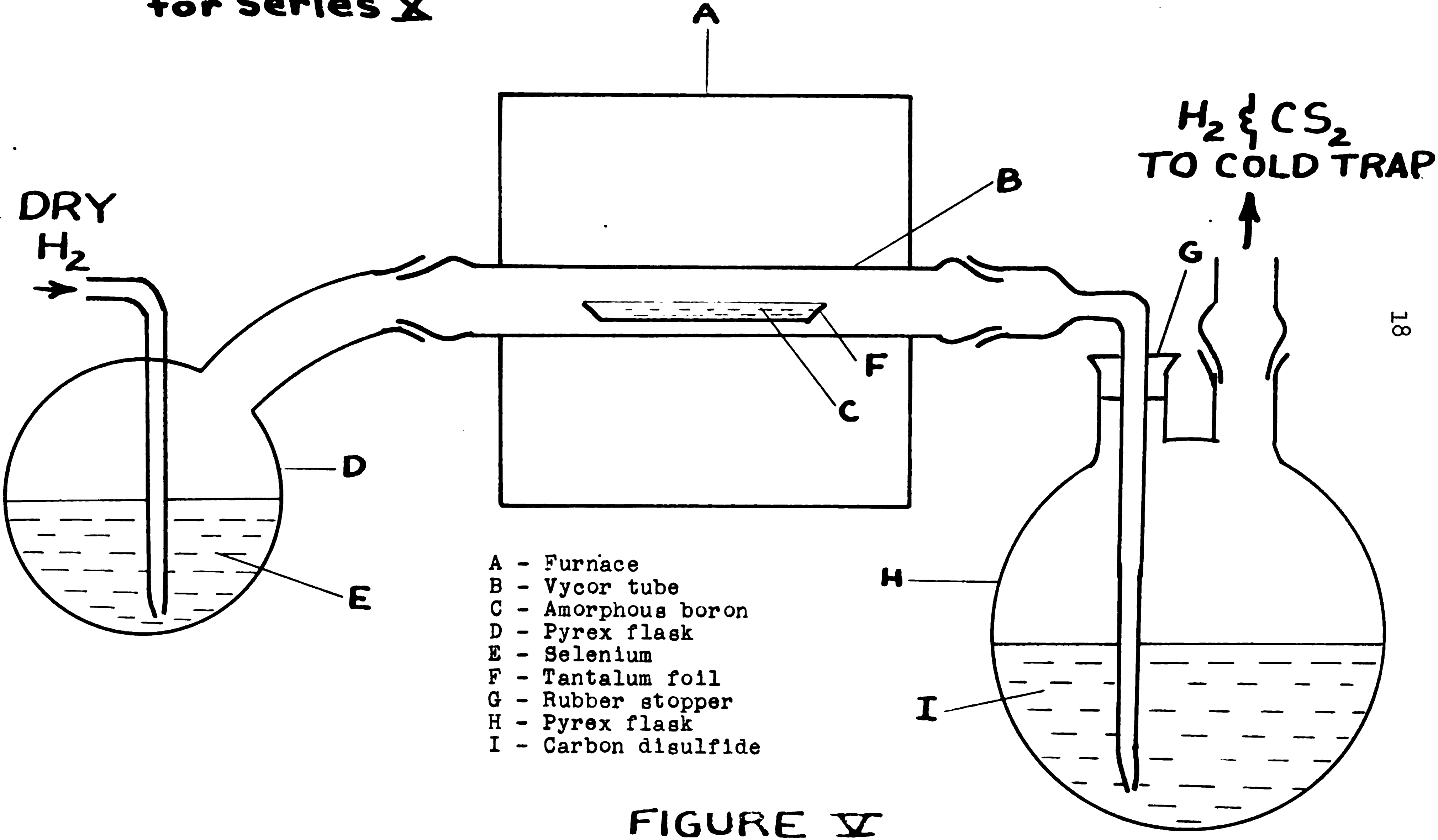
To determine whether selenium and boron would react, a series of reactions were run in an apparatus similar to that used previously in Series I, page 5. Selenium (99.99% pure) was placed at the inlet end of the 2.5 centimeter diameter Vycor tube and boron was placed inside the heated zone in a 0.013 centimeter tantalum foil boat. Hydrogen, dried by passage through a tower of calcium chloride, was used to carry the selenium vapors through the system. At temperatures from 800° to 820° a dark red-orange material deposited at the outlet end of the Vycor tube. This color did not agree with that reported by Sabatier[5] and Moissan[6,7]. The collection of the product was very difficult, and for this reason a new apparatus was developed.

Series X

An apparatus similar to the one depicted in Figure IV, page 12, was prepared. This newer system is shown in Figure V. In this figure the furnace is shown as A. The 1.9 centimeter diameter Vycor reaction tube, B, which is 66 centimeters in length, holds a tantalum boat, F, containing crystalline boron. Pure selenium powder (99.99%), E, is in the 250 milliliter Pyrex flask, D. A 600 milliliter two-necked Pyrex flask, H, has been added to the system. A rubber stopper, G, holds the dip tube in the carbon disulfide, I. After the hydrogen passes through the system into the carbon disulfide, it is sent into a dry ice-acetone cold trap to condense any carbon disulfide that may distill over from the flask, H. All joints except the one designated G are standard tapered ground glass joints.

It was hoped that any product which escaped into the carbon disulfide would be insoluble in the carbon disulfide and thus would settle out. After a reaction time of three hours at 840°, product was formed. The dense fumes which entered the carbon disulfide did not precipitate as a solid as anticipated. Instead the carbon disulfide turned yellow. It seemed probable that any product which formed would be soluble if any water was present in the solvent. The carbon disulfide was, therefore, distilled to determine if a solid residue would remain. The results will be discussed in the section entitled Results.

Reaction Apparatus for Series X



A - Furnace
B - Vycor tube
C - Amorphous boron
D - Pyrex flask
E - Selenium
F - Tantalum foil
G - Rubber stopper
H - Pyrex flask
I - Carbon disulfide

FIGURE V

Series XI

Since the boron-selenium reaction apparently took place at the surface of the red hot boron, it was felt that an increase in surface area of the boron would be beneficial to the formation of more product. Electrolytic amorphous boron powder of 99 per cent purity was substituted for the 100 mesh crystalline boron used in previous series. The apparatus shown in Figure V, page 18, was used with electrolytic boron, C, in the tantalum boat. At temperatures ranging from 850° to 900°, a bright yellow material was formed in a limited quantity. Upon exposure to air, this yellow solid turned orange and then red. This color change was a result of hydrolysis and indicated moisture sensitivity. The color of the solid material agreed with that reported for the possible boron triselenide product.

Series XII

The final apparatus used for the boron-selenium reaction is depicted in Figure VI. The fritted disk shown at G was inserted in the apparatus line to stop the product from being lost. The carbon disulfide trap, chilled with a dry ice-acetone bath, remained part of the system as shown in Figure V. Electrolytic boron was used in this series of reactions along with a 1.7 centimeter Vycor tube for the reaction chamber. The hydrogen gas sweep was increased from approximately ten to thirty cubic centimeters per minute for these reactions.

The reaction product, as formed, consisted of very minute, yellow particles which emanated from the furnace as dense yellow fumes. These fumes were readily collected on the fritted disk and isolated by transferring the entire disk unit to the dry box. In the dry box the product was placed in a dried container for further use in determination of properties.

The dry box was maintained at a fairly dry level by passing the air through two bubble towers containing concentrated sulfuric acid and Drierite, respectively. Quantities of phosphorous pentoxide were placed inside the dry box to remove any additional moisture which might enter the chamber. The samples were placed in an air lock at the rear of the chamber and brought into the dry box from that location.

Repeat reactions were run using the apparatus shown in

Reaction Apparatus for Series XII

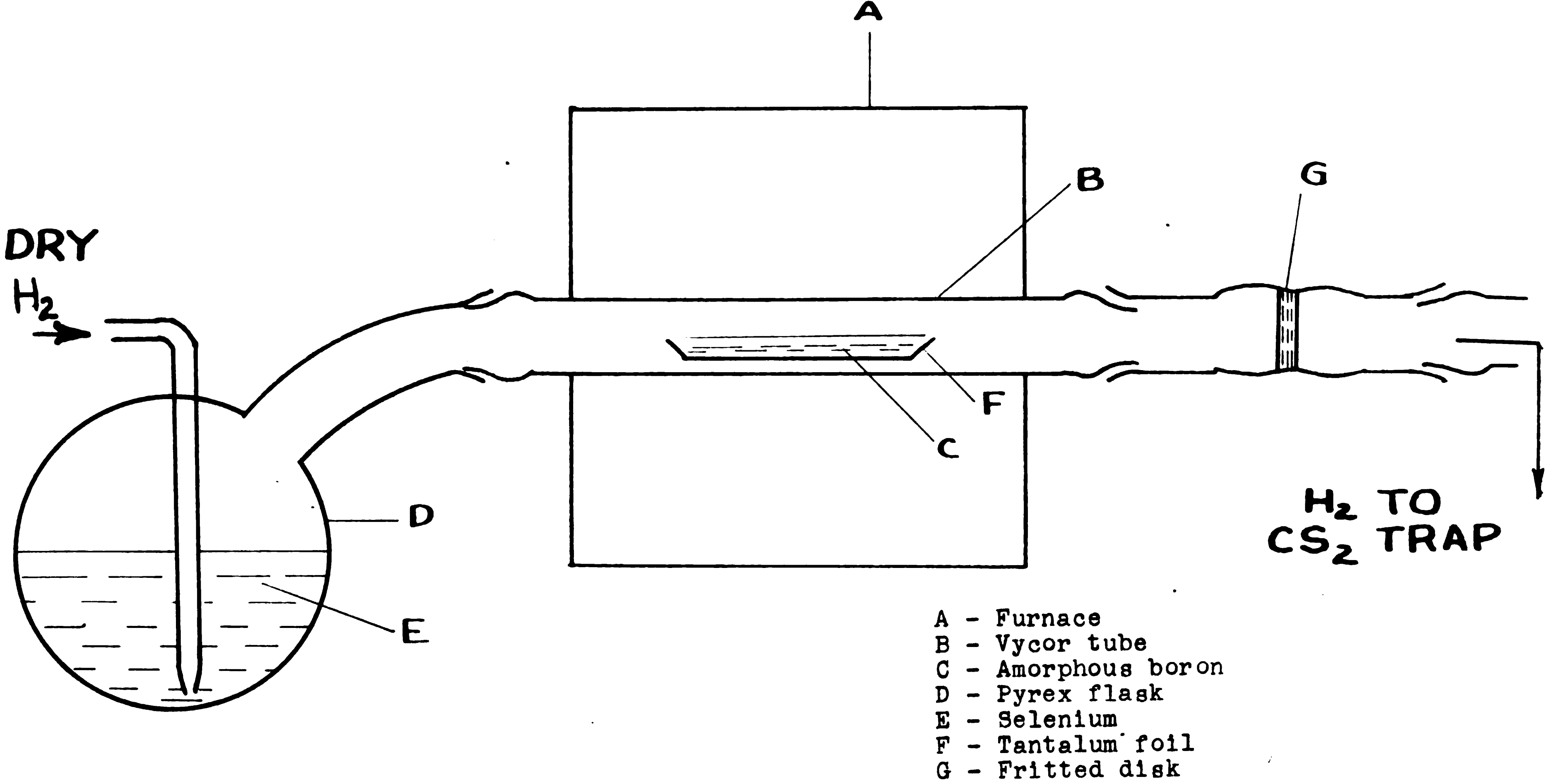


FIGURE VI

Figure VI because it was possible to re-run the reaction at least three times using the same boron and selenium. After three such runs, however, very little additional product formed, possibly because the more stable, metallic form of selenium was formed after repeated heating and cooling. The melting point of this form is reported[12] as 217° versus 170° for the monoclinic form. The metallic form was noted because of its lustre and its insolubility in carbon disulfide.

After a few reactions the tantalum boat became quite brittle and flattened, causing a quantity of boron to fall onto the Vycor reaction tube. As noted in previous runs, (Series II through V) boron in contact with Vycor tubing will react with that tubing causing it to crack. Using this premise, it was concluded that the boron which fell from the tantalum boat was probably not as reactive as that which remained on the boat due to the competition for reaction afforded by the Vycor tubing. After repeated heating and cooling under these conditions the boron also exhibited a tendency to cake, decreasing the surface area normally available for reaction. It was, therefore, concluded that the limitation found to exist on consecutive reactions was due to one or more of the above mentioned conditions causing inactivity of the reacting elements.

When in later experiments it was found that the dry box was not sufficiently dry to prevent hydrolysis, a Fisher No. 17-112 Isolator/Lab metallurgical stainless steel dry box was obtained. An argon atmosphere was employed with a quantity of magnesium perchlorate inside to remove additional moisture. The use of this dry box proved very effective by permitting 0.3 millimeter capillaries to be charged with the sample without the occurrence of slow hydrolysis. Final work was carried out using this arrangement.

The product was transferred to the dry box while still on the fritted disk. Rubber stoppers were inserted in each end of the unit and it was placed in the air lock. The air lock was then evacuated and the dry atmosphere from the dry box chamber was allowed to flow into the air lock before the sample was transferred to this chamber. At this point the sample was placed in a dried vial, a capillary, or an ampoule for future reference and study.

Analytical Procedures

Qualitative Tests

Tests for the Borate Ion

A. Tumeric paper[13]

A few drops of concentrated sulfuric acid are added to a solution containing the borate ion. If tumeric paper is dipped into this solution, it will turn red. Further treatment of this red paper with a solution of sodium hydroxide will cause the paper to change to green.

B. Methyl borate test[14]

If five to six milliliters of methyl alcohol and one to two milliliters of concentrated sulfuric acid are added to a substance containing boron and this solution is then heated on a steam bath, methyl borate will be volatilized. When this volatile borate is ignited, it will burn with a brilliant green flame whose intensity is proportional to the quantity of sample present.

C. Lead acetate test[15]

When lead acetate is added to a solution containing the sulfide or selenide ion, the black lead sulfide or lead selenide that is formed will precipitate. Likewise, if hydrogen sulfide or hydrogen selenide is emitted from an acidified solution it can be detected with moist lead acetate paper which darkens in the presence of both gases.

Test for the Sulfate Ion

A barium nitrate solution was used to test for the sulfate ion.

Quantitative Tests

Determination of Percent Selenium

A. Method I[16] - Gravimetric determination

Approximately 100 milliliters of hydrochloric acid are added to no more than 0.25 grams of the solid product and the solution is allowed to equilibrate. Following this addition, 50 milliliters of hydrochloric acid, saturated with sulfur dioxide, is added to the above solution to precipitate selenium in the red form. The selenium is then filtered, washed with alcohol and then with ether, dried at 30° to 120°, and cooled in a desiccator. The cooled selenium is then weighed and the percentage of selenium in the sample is determined.

B. Method II[17] - Volumetric determination

A mixture of nitric and sulfuric acids is added to the product. This mixture is allowed to cool and is diluted to 250 milliliters. A 25 milliliter aliquot is then acidified with 18<u>N</u> sulfuric acid and $Na_2HPO_4 \cdot 7H_2O$

is added. Twenty milliliters of 0.049N potassium permanganate is then added and the entire mixture is allowed to stand. The excess permanganate is then back-titrated with standard ferrous ammonium sulfate to an o-phenanthroline end point. The percent selenium is then calculated.

C. Method III - Gravimetric determination

Because air hydrolysis of the product results in the formation of selenium, it was thought that a method could be devised based on the hydrolysis of the product. A sample of the product is placed in a dried and weighed Gooch crucible and water is added rapidly. A thin sheet of rubber is placed over the crucible to keep all gases in the crucible. The red selenium thus formed is then filtered, dried, and weighed. When this method proved inadequate due to rapid escape of gaseous hydrogen selenide, the following alternative method was used.

The product is added to an Erlenmeyer flask equipped with a cork stopper and a drying tube containing glass wool saturated with nitric acid. Approximately 20 milliliters of water is added to 0.1 grams of product by injecting it through the stopper with a hypodermic needle. Upon this water addition the product is hydrolyzed to elemental selenium. Any escaping hydrogen selenide is oxidized to selenium in the nitric acid saturated glass wool. All glass parts are weighed and the resulting selenium is filtered, dried, and weighed. This modification of the original Method III also was not useful because of the violence of the water reaction, causing the escape of hydrogen selenide through the drying tube.

However, when sodium hydroxide is alternatively substituted for water in the method described above there is little or no evolution of hydrogen selenide. Hydrochloric acid is then added to this solution, followed by the addition of more hydrochloric acid saturated with sulfur dioxide. These additions, as given in Method I, page 25, precipitate the red form of selenium and prevent the escape of hydrogen selenide. The red selenium is filtered and weighed. The tared drying tube is also weighed and the percentage of selenium is determined. This modified gravimetric procedure will be referred to as Method III, alternative 2.

Determination of Percent Boron[19]

The sample is weighed and placed in an erlenmeyer flask. Water is added to the flask to hydrolyze the product without regard to the loss of selenium as hydrogen selenide. All red selenium which does form is filtered and mannitol is added to the filtrate. This solution is then titrated with standard sodium hydroxide to a phenolphthalein end point. The percent boron is then calculated.

Measurement of Physical Properties

Melting Point Determinations

Heated bath techniques

The yellow product samples were placed in dry Pyrex ampoules in the dry box. These ampoules were then evacuated by means of a vacuum pump and sealed immediately in the hot flame of an oxygen-gas torch.

After the ampoules were made they were placed in various hot baths to determine at what temperature the sample would melt, but no melting had occurred at a temperature of 480°, the maximum temperature at which it was convenient to use a lead bath.

Tube furnace technique

Since the melting point was higher than could be determined conveniently by conventional bath methods, a tube furnace was used. The solid product, sealed in a quartz ampoule under vacuum as described previously, was placed into a tube furnace. The temperature was raised slowly so that the sample could be examined at 5° increments to ascertain whether any melting or decomposition had taken place. This procedure was followed until melting or decomposition was noticed. This temperature was measured with an iron-constantan thermocouple.

Determination of X-ray Powder Data

X-ray powder photographs were obtained using a Norelco 114.6 millimeter diameter powder camera and nickel filtered copper Kα (λ_{unres}= 1.5418 A) radiation and used for qualitative guides. The 0.3 millimeter capillaries that were used were centered in the camera and exposed for times of one to four hours. Although X-ray powder photographs were taken of both forms of the product, only pictures of the crystalline form could be obtained since the amorphous form gave no lines.

In preliminary investigations an ampoule which was previously filled and heated was placed in the X-ray beam and the recording of a diffraction pattern was attempted. By this method it was proved that the heated form was crystalline and the powdered form was amorphous. Accurate photographs were not obtained because the large ampoule could not be centered in the camera.

In an attempt to correct this failure to center the ampoule an internal standard was added to the ampoule. Since the number of lines for potassium chloride were few, it was selected as the standard. If the product lines and the potassium chloride lines could be measured accurately, a comparison could be made. This comparison could be made accurate by plotting known "d values" for potassium chloride versus those obtained from the distorted X-ray obtained for the potassium chloride in the ampoule, and transposing the product lines to give their true values.

Determination of Infrared Spectral Data

Three methods were available and each was studied as to its applicability for use with the hygroscopic product.

Potassium bromide pellet method

The product was placed in a small amount of dry potassium bromide and mixed thoroughly. This mixture was placed inside a Perkin-Elmer potassium bromide pellet press and the unit was evacuated while pressure was applied. After three minutes, a pellet was removed from the unit and placed in a holder. The holder and pellet were placed in the sample beam of a Perkin-Elmer Model 21, Infrared Spectrophotometer, and a spectrum was obtained. The disadvantage of this method was that it did not prevent hydrolysis.

Solvent method

A small amount of the product was placed in dry carbon disulfide. This solvent was dried either by mixing it with phosphorous pentoxide and allowing the mixture to stand for twenty-four hours, then pouring off the solvent, or by distilling the carbon disulfide after the mixture had stood for sixteen hours.

The carbon disulfide containing the sample was placed in a special holder designed for liquid samples. This unit was placed in the sample beam of the Perkin-Elmer Model 21, Infrared Spectrophotometer and run against a control sample of carbon disulfide in the control beam. A spectrum was obtained.

Mineral oil mull method

This method entailed the mixing of mineral oil with the product. A few drops of this slurry were then placed onto a salt plate. Another salt plate was set on this first plate and the two were rubbed gently together to spread the drops into a thin continuous film. This set of plates was then placed in the infrared spectrophotometer in the sample beam and a spectrum was obtained using air as a standard. In initial trials sodium chloride plates and optics were used in the Perkin-Elmer Model 21, Infrared Spectrophotometer, but on final runs cesium bromide plates were used in conjunction with both cesium bromide and sodium chloride optics in a Perkin-Elmer Model 221, Infrared Spectrophotometer.

Since the samples were dispersed in mineral oil and the plates were prepared in a dry box, little hydrolysis occurred during plate preparation. The dispersion of the sample in mineral oil also inhibited hydrolysis during the run.

Determination of Solubility Data

Only limited trials were made to determine solubility data on the product. Samples were placed in hot and cold water and also in freshly distilled carbon disulfide, prepared as previously described on page 31. No exact solubilities were determined; only if the product was very soluble or sparingly soluble.

Reaction Between Boron and Tellurium

The apparatus shown in Figure VI (page 21) was used. Tellurium was substituted for selenium at E. Electrolytic boron was placed in a tantalum boat inside the Vycor reaction tube. A hydrogen sweep of approximately twenty cubic centimeters per minute was bubbled through the tellurium. The tellurium vapor was passed over boron maintained at 1050° for three hours.

RESULTS

Sulfur-Boron Reactions

In the reactions carried out between sulfur and boron, Series I-VIII, a white powder was obtained. Qualitative tests were run on this compound, but no quantitative data were obtained. A positive sulfide ion test was obtained using lead acetate paper.

When barium nitrate was added to an acidified solution of the product, no precipitate formed. It was, therefore, concluded that the sulfate ion was absent. An acidified sample was also tested with tumeric paper to test for the borate ion. A positive test was denoted when the paper turned red in the acidic solution and changed to green in a sodium hydroxide solution.

To verify the tumeric paper test, the ethyl borate test was tried to determine whether or not the borate ion was present. The appearance of a green flame, upon ignition, gave positive indication of the borate ion.

X-ray powder photographs were taken of the white solid product and compared with a boric acid control photograph. These proved identical and it was concluded that the sample was hydrolyzing in air according to the equation:

$$BS_x + 3H_2O \longrightarrow H_2S + H_3BO_3 + \frac{(3-2_x)}{2} H_2$$

When the material was placed in water, a violent reaction occurred with the evolution of hydrogen sulfide. The violence of this reaction was reported by Sabatier[3] and Moissan[4] when boron trisulfide reacted with water.

The positive borate and sulfide ion tests on the white solid product indicated that a reaction had occurred. The X-ray data proved that boric acid was formed upon air hydrolysis. These two facts plus reaction conditions reported by Sabatier[3] and Moissan[4] led to the belief that a boron sulfide had been formed.

Selenium-Boron Reactions

The reactions between selenium and boron, as described in Series IX through Series XII, eventually led to the formation of a bright yellow solid. The solid formed in Series IX, page 16, was undoubtedly contaminated with red selenium, which had been carried through the furnace. In the subsequent series, however, a dense yellow cloud emanated from the reaction chamber. The minute particles which formed this cloud were trapped in the apparatus of Series XII, page 21, and studied.

The attempt to trap the solid product in carbon disulfide (Series X, page 17) proved ineffective. No precipitate formed in the solvent, but it turned yellow, thus denoting the passage of a foreign substance into the carbon disulfide trap. When this discolored liquid was distilled to isolate the product, only a red material remained. This red substance turned metallic gray and formed a mirror-like finish on the distillation flask. It was assumed that this solid was selenium, and denoted either hydrolysis of the product or direct passage of selenium vapors into the carbon disulfide.

The substitution of electrolytic boron for crystalline boron (Series XI, page 19) led to the formation of a yellow solid in the outlet portion of the reaction tube, but the carbon disulfide in the trap discolored as in the previous experiment. The quantity of yellow material which formed, changed to orange and then to red upon exposure to air. This color change was accompanied by the evolution of hydrogen selenide and indicated possible air hydrolysis.

When the carbon disulfide was distilled, a small amount of selenium remained as before, but a second substance also was present. A positive borate ion test (methyl borate test) on the second substance, along with the formation of the previously mentioned yellow solid, indicated the passage of product into the carbon disulfide. A sample of carbon disulfide, which had been dried for twenty-four hours over phosphorus pentoxide, was substituted for the non-dried type. The product did not precipitate in this dried material, thus denoting its extreme moisture sensitivity. When the carbon disulfide was cooled to dry ice-acetone temperatures, a solid formed which, when dried, gave an X-ray powder photograph; which was identical with the X-ray photograph of the hydrolyzed product from the boron and sulfur reaction and the boric acid control.

The apparatus of Series XII, page 21, proved the most effective and the product formed by this technique was studied thoroughly. Following are the results of these studies.

Characterization of Product

The yellow solid formed in the reaction between selenium and boron using the apparatus of Series XII, page 21, was checked qualitatively and quantitatively.

When a qualitative borate ion test with tumeric paper (see page 24) was conducted on a solution of the product and a solution of freshly precipitated red selenium, each gave what appeared to be a positive test. A methyl borate flame test (page 24) gave a positive borate ion test on the product solution and on a boric acid solution, but gave a negative result on the red selenium solution. It was, therefore, concluded that the flame test was the most sensitive for borate ion in the presence of selenium and that the product contained boron.

A positive lead acetate test (page 24) on the product indicated the presence of selenide ion and coupled with the positive methyl borate test (page 24) denoted that a reaction had occurred. Quantitative tests to determine percent of selenium in the compound were then conducted using the various methods described in the experimental section (pages 25 to 28). Following are comparative results using each method:

Table I

Quantitative Results of Percent Selenium in Product

Method	Percent Selenium
I	67.8%
II	27.0%
III	67.2%
III-1	76.0%
III-2	91.02% 90.90% 91.87%

Methods I through III-1 proved ineffective and gave low results due to the escape of selenium as hydrogen selenide upon acid and water addition. Method III-2 proved effective when samples weighing approximately 200 milligrams were used. The substitution of sodium hydroxide in this latter method for the acids used in the other methods also prevented the escape of hydrogen selenide. Three separate determinations were, therefore, made using this method.

Two boron determinations were made following the method described on page 26 using 0.0858N sodium hydroxide for titration. The results showed 8.51 percent and 8.77 percent boron in the sample, compared with 8.36 percent theoretical for boron triselenide. The results obtained are somewhat high due to overtitration of the mannitol solution. The end point was masked by a slight discoloration which resulted from suspended red selenium which passed through the filter.

The average percent selenium obtained from Method III-2 was 91.26 percent. This value was compared with those of 91.64 percent for the compound formula B_2Se_3 and with 93.03 percent for the compound formula $HBSe_2$, another possible reaction product. The average percent boron, 8.64 percent, was compared with 8.36 percent (B_2Se_3) and with 6.37 percent ($HBSe_2$). Both the percent selenium and the percent boron compare more favorably with the compound formula B_2Se_3 than with the formula $HBSe_2$. Therefore, the yellow solid was assumed to be boron triselenide.

Melting Point (Decomposition Point)

When the boron triselenide was heated in a sealed quartz ampoule in a tube furnace, the sample was noted to decompose at 556±5° into a metallic gray portion and a red substance. At 800° the metallic portion glowed red, but did not melt. A new ampoule was therefore filled with more boron triselenide and placed in the hot furnace with one end of the ampoule at room temperature. Using this technique, it was possible to distill the red substance to the cooled end of the tube. When the ampoule was broken, a positive selenium test was obtained on this red substance using the lead acetate test. It was, therefore, concluded that the black solid was either boron or a lower boron selenide and the red material was selenium.

$$B_2Se_3 \longrightarrow 2B + 3Se$$

$$B_2Se_3 \longrightarrow 2BSe_x + (3-2x)Se$$

During the melting point determination studies, it was noted that at 195° to 235° the yellow powder form of boron triselenide changed to a more compact solid formation with a darker color. Infrared spectra and X-ray powder photographs were taken of these two forms to determine if they were similar. Because of the high decomposition point of the form obtained at 195° to 235°, and the known covalency of boron oxides, it was concluded that this form was at least partly covalent.

X-ray Powder Data

In the original qualitative tests, the product was placed in the capillaries without the aid of a dry box. When these X-ray powder photographs were compared with ones taken of boric acid and the boron-sulfur reaction product, they proved identical. This proved that the common hydrolysis product of boron triselenide and the boron sulfide was boric acid. Such X-rays were used as guides to determine the presence of product.

X-ray powder photographs of the yellow powder form in ampoules resulted in no lines on the film, while the heated product treated in the same manner, gave many lines. These lines were not accurate due to the inability to center the heavy ampoule in the camera. It was, therefore, concluded that the material as prepared was amorphous, but it became crystalline after heating to 195° to 235°. Since no decomposition was apparent, this product was assumed to be boron triselenide.

Attempts to use potassium chloride as a standard in the ampoule with the heated boron triselenide product proved futile. In a series of attempts, either all potassium chloride lines or no potassium chloride lines were evident, thus showing the need for proper mixing of a critical amount of potassium chloride in the ampoule. This series of attempts was abandoned upon the acquisition of the Fisher Isolator/Lab metallurgical stainless steel dry box.

By working in this dry box in an argon atmosphere and using standard 0.3 millimeter capillaries, good X-ray powder photographs were obtained. These photographs were read and the following "d values" calculated from the Bragg equation, $n\lambda = 2d\sin\theta$, where λ equals the wave length of CuKα radiation, 1.5418Å. Table II compares the observed "d values" with those of cubic and hexagonal boric oxide.

Table II

X-ray Spectral Data, "d values"

Hexagonal B_2O_3[b]	Cubic B_2O_3[b]	Observed B_2Se_3
3.75	6.08	6.77
3.42		4.11
2.78	3.80	3.90
2.230		3.78
2.165	3.21	3.26
2.096	2.92	3.10
1.920	2.60	2.82
1.872	2.49	2.64
1.822		2.36
1.710	2.26	2.30
1.659		2.16
1.522	2.09	2.11
1.418	1.98	
1.403		1.39

A comparison of values led to the belief that the heated boron triselenide is not like either hexagonal or cubic boric oxide, but that it was similar to the cubic form. The "d values" of boron triselenide, as noted, contain values for a triplet and two doublets, or alternatively, for four doublets. If these triplet and doublet values are considered as single lines the comparison to the cubic boric oxide is

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b. Values from ASTM X-ray diffraction card file.

more pronounced. It is reasonable to conclude that if selenium atoms were placed in a cubic lattice similar to that of boric oxide, the difference in size between large selenium atoms and small oxygen atoms would distort the lattice to a degree that would cause splitting of X-ray lines. These data are not conclusive, but tend to point toward a distorted cubic lattice for boron triselenide.

Infrared Spectra Data

Of the three methods described in the experimental section (pages 31 through 33) only the one which used mineral oil proved useful. The moisture sensitivity of the solid boron triselenide made the use of potassium bromide pellets and solvent techniques impractical. In both cases bands comparable to those reported by Miller and Wilkins[20] for boric acid were obtained. These techniques substantiated X-ray data which showed that boron triselenide hydrolyzes into boric acid upon exposure to moisture.

The first attempt at making a mineral oil mull was unsuccessful, producing a boric acid spectrum, because the mull was not made in a dry box. In all subsequent tests, a dry box was used and spectra were obtained for the amorphous and crystalline forms of boron triselenide using a Perkin-Elmer Model 221 spectrophotometer. Cesium bromide plates were used with a sodium chloride prism in the 15 to 37 micron range. After the spectrum for amorphous boron triselenide was run, the plates were allowed to remain open in air for 1.5 hours and another spectrum was obtained containing boric acid bands. This displayed proper dispersion of the sample. Table III gives the results obtained on the amorphous and crystalline forms of boron triselenide compared with the results on boron sulfide obtained by Greene and Margrave[10].

Table III

Infrared Bands - Amorphous and Crystalline Products

Amorphous B_2Se_3	Crystalline B_2Se_3	B_2S_3
1372 cm^{-1}	1300 cm^{-1}	1322 cm^{-1}
1250 cm^{-1}	1150 cm^{-1}	990 cm^{-1}
837 cm^{-1}		919 cm^{-1}
611 cm^{-1}		859 cm^{-1}
580 cm^{-1}		602 cm^{-1}

The values for amorphous boron triselenide were obtained by running the spectrum of the product over the entire 2 to 37 microns range and are shown in Figures VII and VIII. Figure IX shows the same sample from 2 to 15 microns after 1.5 hours in open air. The values for crystalline boron triselenide (Figure X) were obtained only in the sodium chloride region, 2 to 15 microns, to establish the similarity to the amorphous product. Shifts from 1372 cm^{-1} to 1300 cm^{-1} and from 1250 cm^{-1} 1150 cm^{-1} are noted when going from the amorphous to the crystalline form of boron triselenide. These are large shifts, but are apparently allowable when one is working with polymorphic substances.

Much investigation of various crystalline forms of minerals had been conducted. Hunt, Wisherd, and Bonham[21] made a thorough study of many such materials. Among the results given by them are various infrared data which show differences in spectra between the crystalline forms of inorganic materials. One such example was the comparison of spectra between quartz and alpha-quartz. Absorption peaks were obtained at 7.3, 12.2, and 14.2 microns for quartz and 9.2, 12.8 and 14.4 microns for alpha-quartz.

Infrared spectrum for amorphous product

FIGURE VII

SPECTRUM NO.
SAMPLE
ORIGIN Hutchinson
PURITY
PHASE
THICKNESS
1. Nujol Mull with CsBr
2. Plates
3.
DATE
OPERATOR
REMARKS

PRISM NaCl
RESOLUTION 927
RESPONSE 1100
GAIN 3
SPEED 16
SUPPRESSION 4
SCALE 5cm/μ

NO. C21-6308

No. D

Date 4/20/60 By NCA

Lab. No.

Ref.

Ident. B_2Se_3

From Hutchinson

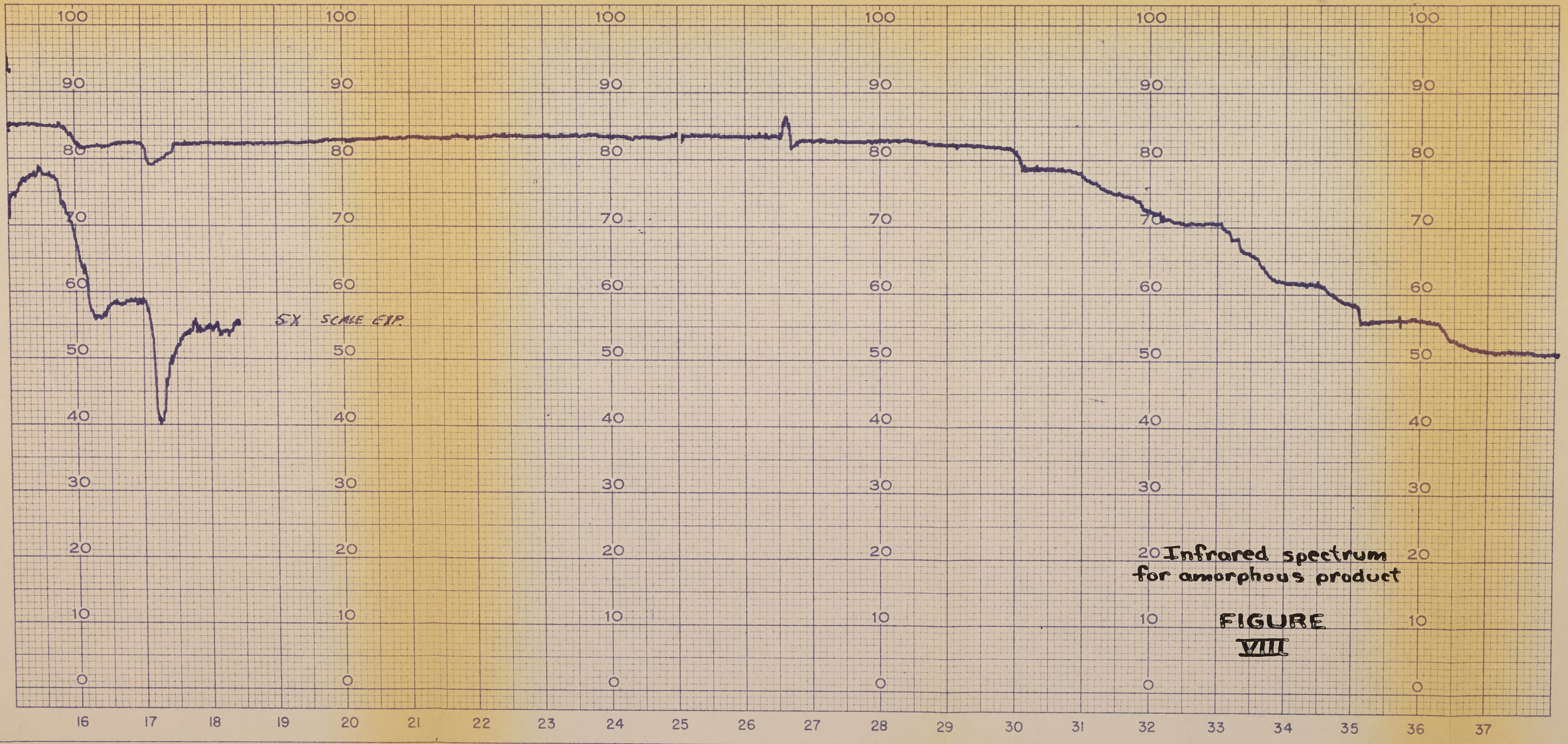
	CCl_4	CS_2	
Sample	mm	mm	
Comp.	mm	mm	
	%	%	%

FS	SW	PP	Mull	Film	Gas
			X		

Cs Br Prism

Attenuator 1100	Suppression 4
Slit 1000 2X	Source 0.3 AMP
Gain 3	AGC OFF
Speed 32	Expansion OFF + 5X

Dow Corning Corporation
Spectroscopy Laboratory
Midland, Mich.



Infrared spectrum for amorphous product

FIGURE VIII

Infrared spectrum
for crystalline product

FIGURE
IX

Infrared spectrum for amorphous product after exposure to air

FIGURE X

Ebert and Gottlieb[22] have also reported differences in infrared data between polymorphic forms of the same material.

These data show that a change of the order of magnitude observed in the transition of boron triselenide from the amorphous to the crystalline form is to be expected.

Solubilities

Boron triselenide decomposes in hot and cold water and is apparently insoluble in freshly dried carbon disulfide.

Boron-Tellurium Reaction

No product formed when solid boron and tellurium vapor were reacted at 1050°. That only tellurium metal collected on the fritted disk, was indicated by its lack of reaction with water. These results agree with those of Moissan[7] and Sabatier[5], each of whom reported that this reaction did not occur.

SUMMARY

Boron triselenide was synthesized by reacting solid boron with selenium vapor at temperatures from 850° to 950°. A hydrogen sweep was used to carry the selenium vapor over the boron in a tantalum boat.

The extreme moisture sensitivity of the yellow solid product made it necessary to carry out all essential work in a dry box. This moisture sensitivity which made it extremely difficult to obtain accurate physical data led to the hydrolysis equation;

$$B_2Se_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2 + 3Se$$

when all X-ray and infrared data on the hydrolyzed form proved identical with that for boric acid, and the resulting product was red.

By working in an argon atmosphere in a dry box, it was possible to load capillaries and obtain Bragg "d values" which tended to propose that the boron triselenide lattice was that of a distorted cube. Infrared bands were also obtained on the boron triselenide product by making mulls and preparing the plates in the dry box. Bands were obtained on the initial product, which was shown to be amorphous, and on the heated product, which was crystalline. A shift was noted when the bands for each form were compared.

The crystalline form of boron triselenide appeared to be partly covalent, having a decomposition point in vacuum of 556±5°. The decomposition products appeared to be selenium

and either boron or a lower boron selenide.

Suggestions for Future Research

Boron triselenide has proved to be a very interesting compound. It seems that other methods of synthesis should be tried and reactions of the resulting product studied. Perhaps reacting boric oxide with various metal selenides or reacting boron with selenium oxides would result in product formation. A measurement of vapor pressure over the solid could also be investigated. More precise information is needed on the crystal structure of this compound.

Since boron and tellurium vapor did not react at 1050°, it is possible that reactions between tellurium oxides and boron should be investigated. Infrared and X-ray data on a boron telluride, along with the present data on the other boron chalcogenides, would give much insight into both the chemistry of boron and of the oxygen family.

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APPENDIX A

Following, in detail, are the experimental apparatus changes involved in Series III, IV, and V.

Series III

An apparatus as shown in Figure II was used for this series of tests (see page 10). As in Figure I, page 8, A, B, C, D, and E are the furnace, the 1.7 centimeter diameter Vycor tube, the crystalline boron, Pyrex flask, and sulfur, respectively. A 14/35$ joint was placed at the outlet end of the reaction tube. A rubber stopper with a small Pyrex tube was placed at F to allow passage of prepurified nitrogen to the water trap.

As previously, this apparatus proved ineffective even when the sulfur was heated to boiling. After one hour of boiling, only a slight haze formed in the cooled portion of the system. The ease of boiling the sulfur led to the substitution of a new flask for the one used in this series of reactions. This modified apparatus was used in the next series of tests.

Series IV

Because of the ease of boiling the sulfur and passing nitrogen gas through it, the flask as shown in Figure III, page 11, was substituted in the apparatus of Figure II. Through the use of this flask it was felt that a large quantity of sulfur vapor could be forced into the reaction chamber. Crystalline boron, C, was spread thinly over the bottom of the Vycor reaction tube and a nitrogen flow rate of approximately ten cubic centimeters per minute was used as in previous trials. The reaction was carried out at 730°.

After the reaction had proceeded for thirty minutes a large quantity of a dust-like product was swept from the furnace, but it subsided quite rapidly. No other material was noted until the second hour of reaction when a slight amount formed. These observations may result from the variations in fluidity of sulfur as it is heated. The quantity of nitrogen gas entering the system apparently diminished as the sulfur passed from the first liquid stage to the syrupy stage and increased as the temperature increased sufficiently to transform the syrupy stage to the second liquid stage. The decrease in nitrogen flow resulted in a poor yield of product.

After five hours of reaction only a slight amount of product was formed. This apparatus was apparently inadequate because the sulfur vapor did not enter the reaction zone in a large enough volume to form the product. Some precipitated sulfur was found at the inlet end of the Vycor reaction tube, but none at the outlet end. An apparatus with a shorter path for vapor travel seemed necessary.

Series V

Figure IV, page 12, shows the re-designed apparatus used in the next series of reactions. The right hand portion of the apparatus is the same as in Figures II and III. A shorter path from the sulfur to the indented Vycor reaction tube has been made. The reaction was found to proceed at a very good rate at 710° using this apparatus. In fact, considerable product was lost in the form of white fumes which escaped into the water trap. The addition of a cold trap at the outlet end of the apparatus did not stop the escape of these fumes. The large volume of these fumes indicated that a product had formed and it was concluded that the shorter distance for vapor travel had improved this yield. As a result, this feature was incorporated into all subsequent apparatus designs.

APPENDIX B

Calculation of Percent Selenium

Weight of dry flask and product - 30.03395 grams
Weight of dry flask - 29.81621 grams
Weight of product - 0.21774 grams

Add NaOH, HCl, filter, dry, and weigh

Weight of selenium and filter paper - 2.54952 grams
Weight of filter paper - 2.43497 grams
Weight of selenium - 0.11455 grams

Weight of selenium and drying tube - 20.56765 grams
Weight of drying tube - 20.48400 grams
Weight of selenium - 0.08365 grams

Total selenium - 0.19820 grams

$$\text{PERCENT SELENIUM} = \frac{0.19820 \text{ grams}}{0.21774 \text{ grams}} \times 100$$

$$= 91.03\%$$

APPENDIX C

Calculation of Percent Boron

Weight of dry flask and product	- 10.84927	grams
Weight of dry flask	- 10.78264	grams
Weight of product	- 0.06663	grams

Titration of mannitol solution of product required
6.12 milliliters of
0.08585N NaOH

6.12 milliliters = 0.5254 milliequivalents

Therefore, the percent boron equals:

$$100 \times \frac{0.000525 \times 10.8}{0.06663} = 8.51\%$$

Where 10.8 is the molecular weight of Boron

APPENDIX D

Reading of X-ray film and calculation of "d values"

Right	Left	Sum	Delta	θ	$\mathrm{Sin}^2\ \theta$
18.645	5.220	23.865	134.25	33°33'	0.3054
16.215	7.650	23.865	85.65	21°24'	0.1331
16.100	7.760	23.860	83.40	20°51'	0.1267
15.845	8.020	23.865	78.25	19°33'	0.1120
15.730	8.125	23.855	76.05	19°01'	0.2061
15.335	8.540	23.875	67.95	16°59'	0.0853
15.100	8.755	23.855	63.45	15°52'	0.0748
14.810	9.040	23.850	57.70	14°26'	0.0621
14.660	9.205	23.865	54.55	13°38'	0.0556
14.290	9.570	23.860	47.20	11°48'	0.0418
14.215	9.645	23.860	45.70	11°26'	0.0393
14.100	9.765	23.875	43.45	10°52'	0.0355
13.290	10.575	23.865	26.15	6°32'	0.0129

$$\lambda = 2d\sin\theta$$

When $\lambda = 1.5418\text{Å}$ and $\theta = 6°32'$

$$1.5418\text{Å} = 2d\,(0.1138)$$
$$0.7709 = (0.1138)d$$
$$6.77 = d$$