

THE PURIFICATION OF BORON IN  
AN ATOMIC HYDROGEN FURNACE

by

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A THESIS

submitted to

OREGON STATE COLLEGE

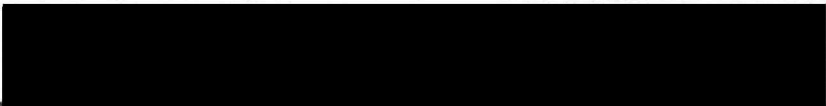
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degree of

MASTER OF SCIENCE

June 1957

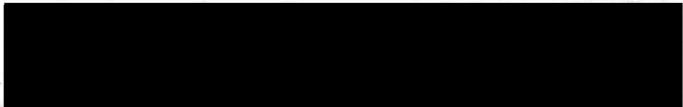
NEENAH BOND  
23% RAC CONTENT  
MADE IN U.S.A.

APPROVED:

  
\_\_\_\_\_  
Professor of Chemical Engineering

In Charge of Major

  
\_\_\_\_\_  
Head of Department of Chemical Engineering

  
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Chairman of School Graduate Committee

  
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Dean of Graduate School

Date thesis is presented October 23, 1956

Typed by Margaret Gunn

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# THE PURIFICATION OF BORON IN AN ATOMIC HYDROGEN FURNACE

## INTRODUCTION

Many of the compounds of boron such as boric acid and borax have long been familiar, and their properties have been thoroughly explored. About the pure element, however, comparatively little is known. A high melting point, high susceptibility to transmutation, unusual electrical properties, and an undetermined crystal structure make it a material of considerable interest.

Boron, with its atomic number of five, lies in the periodic table on the division between metals and non-metals. Its small atomic size and the large charge of its simple ion give it a tendency toward covalent, non-metallic behavior. The three valence electrons indicate metallic action. This combination results in oxides that are very difficult to reduce, a great reactivity of the element at high temperatures with either metals or non-metals, a very high melting point, and, undoubtedly, unusual co-ordination and bonding systems (11, pp.734-735). In the solid state it exists in a non-metallic amorphous form and a more metallic crystalline form.

The properties and earlier methods of attempting purification are summarized by Laubengayer, Newkirk, and Brandaur (9, pp.382-385) and only a brief discussion will be included here. There are many claims of preparation over 99% boron, but most are unsubstantiated and the many properties attributed to pure boron indicate that the same material is not being described. Much of the confusion is due to the lack of a satisfactory analytical method for the determination of boron.

Spectrographic methods do not indicate the presence of all impurities such as oxygen; a x-ray diffraction pattern uniquely characteristic of boron is not described; and x-ray methods are complicated by impurities and the long exposures that are necessary (9, p. 382). Sufficiently large crystals of pure boron have not yet been produced to allow determination of the single crystal properties. However, Shaw, Hudson, and Danielson (15, p. 7) have had some success in measuring the electrical properties of boron crystals weighing less than ten micrograms by micromanipulative techniques.

The most successful methods of the preparation of high purity boron have been by decomposition of the boron halides by an electric arc, ie. Weintraub (19, pp. 165-184) and Hackspill (5, pp. 776-8); decomposition of the boron halides on a heated filament, ie. Laubengayer (8, p. 1924) and Shaw (14, p. 31); and by thermal decomposition of diborane, ie. Schlesinger (13, p. 27). The amount of product obtained in each case is very small, usually less than a gram.

As previously mentioned, the melting point of boron is quite high, about  $2300^{\circ}\text{C}$ . (18, p. 114 and 11, p. 735). The boiling point has not been reliably determined and sublimation near the melting point was observed by Weintraub (19, p. 178). A boiling point of  $2800^{\circ}\text{C}$ . at atmospheric pressure is recorded by Quill (12, p. 59). Investigators agree that there is a liquid range. It should be possible to heat impure boron to its liquid range and to distill off or to decompose the impurities. Since boron is very reactive at this temperature, a vacuum or inert atmosphere would be necessary.



This high temperature method was first explored by Weintraub (18, pp. 112-3). He prepared "Moissan Boron" (boron prepared by reduction of  $B_2O_3$  with magnesium) of up to 92% purity. The material was placed in a water-cooled copper crucible and used as an electrode in an electric furnace. He obtained a product that was 97% to 98% boron. A very high voltage (15,000 volts) was needed to start the reaction because of the high electrical resistance of the boron at low temperatures. Warth (16, pp. 55-6) states that he observed crystals up to 6.4 millimeters in size in Weintraub's laboratory. A study of these crystals has not been reported nor were they ever mentioned by Weintraub. Kahlenberg, H. H. (6, p. 30) repeated Weintraub's experiments and was able to prepare a small quantity of fused material. Visible crystals were not found (6, p. 57). Kremers (7, p. 221) also purified boron in the arc.

All these investigators used a single metallic electrode with the boron as the other electrode. While this has the advantage of obtaining a large melt, it leads to contamination by the electrode metal which is carried by the arc. This difficulty was reported by Weintraub (19, p. 133).

The atomic hydrogen flame should provide considerably less contamination. The purpose of this investigation is to study the formation and purification of crystalline boron by heating it in an atomic hydrogen flame.



## THEORY

## MOISSAN BORON

The reaction between boric anhydride and magnesium is:



The products are separated by treating with alkali, hydrochloric acid and hydrofluoric acid (11, p. 738). Moissan claimed to have obtained 98% to 99% boron by this method. This purity could not be obtained by other workers when duplicating his experiments (19, pp. 167-173 and 6, p. 30). However, this is the best commercial method of producing boron discovered thus far. Recently, the Pacific Coast Borax Company of Los Angeles has prepared 91% and 96% boron by a modification of the Moissan reaction.

The nature of the impurities in Moissan boron is not fully understood. Magnesium, nitrogen, and oxygen are the main elemental impurities, but the combined forms in which they exist have not been determined.

Oxygen is particularly in doubt.  $\text{B}_2\text{O}_3$  is water soluble and should have been removed by the leaching process.  $\text{B}_2\text{O}$ ,  $\text{B}_4\text{O}_5$ ,  $\text{B}_4\text{O}_3$ ,  $\text{B}_2\text{O}_2$ ,  $\text{B}_3\text{O}$ ,  $\text{B}_6\text{O}$ ,  $\text{BO}$  have all been reported, but little is known about their properties. Apparently, most of these compounds have melting points over  $3000^\circ\text{C}$ .

Magnesium would be expected to be present in the form of  $\text{Mg}_3\text{B}_2$ , its only known boride. However, this compound reacts with water to give  $\text{MgO}$  and  $\text{B}_2\text{H}_6$  and, consequently, should have been removed by the leaching process. Either the magnesium boride is trapped by the

amorphous boron or a boron-oxygen-magnesium complex if formed. At about 1500°C. magnesium returns to the elemental form.

Nitrogen probably exists as  $B_3N_3$  which is a highly stable compound that sublimates near 3000°C. and melts under pressure at that temperature. It will react with  $H_2O$  at high temperatures to form  $NH_3$  and  $B_2O_3$ . Fortunately, the amount of  $B_3N_3$  in Moissan boron is quite small.

The use of atomic hydrogen would cause the formation of boron hydrides. Decomposition of the hydrides occurs below 600°C., so that contamination by hydrogen is not likely. On the other hand, tungsten vapor from the arc would form  $WB_2$  or  $WB$ , which have melting points of over 3000°C.

With the liquid range of boron approximately 2300°C. - 2550°C., the melting of Moissan boron would be expected to effect the following:

1. Complete removal of the magnesium by vaporization.
2. Possible removal of the oxides by vaporization or reduction by the atomic hydrogen.
3. Little change in the nitride composition unless dissociation of the oxides produces  $H_2O$  to cause the  $NH_3$  reaction.
4. Some contamination by the electrode vapor.

The exhaust gases would contain toxic and inflammable hydrides, hydrogen, a wide variety of vaporized metallic compounds, and possibly some  $NH_3$  or  $H_2O$ .



## ATOMIC HYDROGEN

The very high temperature that can be obtained by blowing hydrogen through a tungsten arc is due to the following reaction:



As hydrogen molecules enter the arc, they are dissociated at the high temperature of the arc. Upon leaving the arc, the reverse process takes place: molecular hydrogen is again formed and a tremendous amount of heat is liberated. Tungsten rods can be melted (melting point  $3660^\circ\text{K}$ .) by this process (8, p. 158). The temperature obtained is determined by the material upon which the flames impinge. Materials that catalyze the molecular hydrogen formation give the highest temperature. Caeilleron (2, p. 468) used a small atomic hydrogen torch to convert amorphous boron to crystalline boron. He reported obtaining a temperature of  $2075^\circ\text{C}$ . He did not investigate the purity of his product.

Commercially these principles have been applied to the atomic hydrogen welding torch (17, pp. 160-8). It consists of two tungsten rods, mounted to form a "V". The arc is formed at the bottom of the "V" and hydrogen is blown along the electrodes and through the arc. The striking voltage and the arc voltage are much higher for an arc in hydrogen than in air. Consequently, a higher voltage source must be used than for the normal arc welder. The atomic hydrogen welding torch is a logical source of design data for construction of an atomic hydrogen furnace. Though hydrogen atmospheres are frequently used in arc furnaces, and the atomic hydrogen torch is often used in the



laboratory, a furnace employing this high temperature method has not been described in the literature.

The advantages of the atomic hydrogen furnace are the high temperatures obtainable, little contamination from the electrodes as compared to the usual arc furnace, and the availability of hydrogen in the highly active, atomic state. The main disadvantage commercially is that it gives a concentrated heat which is not easily applied to the heating of large areas.

#### PRINCIPLES OF TUNGSTEN ARCS

Fundamentally, the arc consists of a stream of electrons emitted from a hot cathode. The electrons are drawn through the arc stream by the electric field and condense on the anode where they release a considerable amount of energy. The energy supplied to the cathode is that required to emit electrons and to maintain the temperature of the cathode. The current at the cathode is concentrated in a small area called the cathode spot, just outside of which is a positive space charge produced by ionization of the surrounding gas. The space charge sets up an electric field, thereby causing a cathode voltage drop aiding the extraction of electrons from the electrode.

The current enters the anode at a small area the size of which is determined by the conditions of temperature, electrode shape, and impurities at the anode surface. There is little voltage drop at the anode (1, pp. 290-300).

At low currents the total voltage drop in an atmosphere of helium

is less than 25 volts per centimeter. In hydrogen it is 150 volts per centimeter because of the energy needed to form atomic hydrogen (4, p. 156).

## SEMICONDUCTORS

The theory of semiconductors and the derivation of the equations used is given by Shaw (15, pp. 13-29) and will not be included here.

Three properties of semiconductors of interest in this investigation are:

1. Room temperature resistivity approximately in the range of  $10^{-2}$  to  $10^8$  ohms - centimeters.
2. Resistance which decreases with heating and which varies exponentially with the reciprocal of the absolute temperature through at least parts of the temperature range.
3. Decrease in resistivity with the introduction of small amounts of certain impurities.

A study of these properties might provide some information as to the nature of impurities found in crystalline boron and offer a basis for comparison with other workers.

Electrical conduction is dependent upon the number of electron carriers available and upon the mobility of the carriers. A certain quantity of energy called the activation energy is necessary to produce the carrier by moving an electron from the filled electron band to the conducting band. This forms two carriers: the hole left in the filled band and the addition of an electron band. Any impurities



present will also contribute carriers, but requiring a different activation energy. When all sources of carriers are considered, the electrical conductivity can be expressed as: (15, p. 21)

$$\begin{aligned} \sigma &= (u_h + u_e) S_g \exp (-E_g/2kT) \\ &+ u_h \sum_h S_h \exp (-E_h/kT) \\ &+ u_e \sum_e S_e \exp (-E_e/kT). \end{aligned} \quad (3)$$

where:  $\sigma$  = the electrical conductivity

$u_h$  and  $u_e$  = the mobility of the holes and of the electrons respectively

$S_g$ ,  $S_h$  and  $S_e$  = coefficients

$E_g$  = activation energy of pure material

$E_h$  = activation energy of impurities that contribute holes

$E_e$  = activation energy of impurities that contribute electrons.

When the number of different types of impurities is small, then each term in equation 3 usually has some range of temperatures where its contribution to conduction is the only significant term. In such a range where the  $r$ th term has control:

$$\sigma = u_r S_r \exp (-E_r/kT). \quad (4)$$

$$\log \sigma = \log u_r S_r - 0.434 (E_r/k) (1/T). \quad (5)$$

Letting:  $R$  = the resistance

$\rho$  = the resistivity

$l$  = length of conduction

$A$  = cross sectional area of conduction



By definition:

$$p = \frac{RA}{l}, \quad (6)$$

$$\text{and } \log p = \log R + \log A - \log l. \quad (7)$$

Again by definition:

$$p = \frac{1}{\delta}, \quad (8)$$

$$\text{and } \log p = -\log \delta. \quad (9)$$

Substituting:

$$\log R = \log l - \log A - \log u_r S_r + 0.434 \left( \frac{E}{k} \right) (1/T). \quad (10)$$

If  $u_r$ ,  $S_r$ , and  $E_r$  are constant over the temperature ranges studied, equation 10 takes the form of:

$$\log R = b (1/T) + C, \quad (11)$$

where  $b$  and  $C$  are constants. A plot of  $\log R$  against  $1/T$  should yield a straight line segment with a slope of  $b$  or  $(0.434) (E_r/k)$ .

Over a large plot a series of almost straight line segments should be obtained. Values obtained from the literature are plotted in figure 1. Data used for this plot is in the appendix.

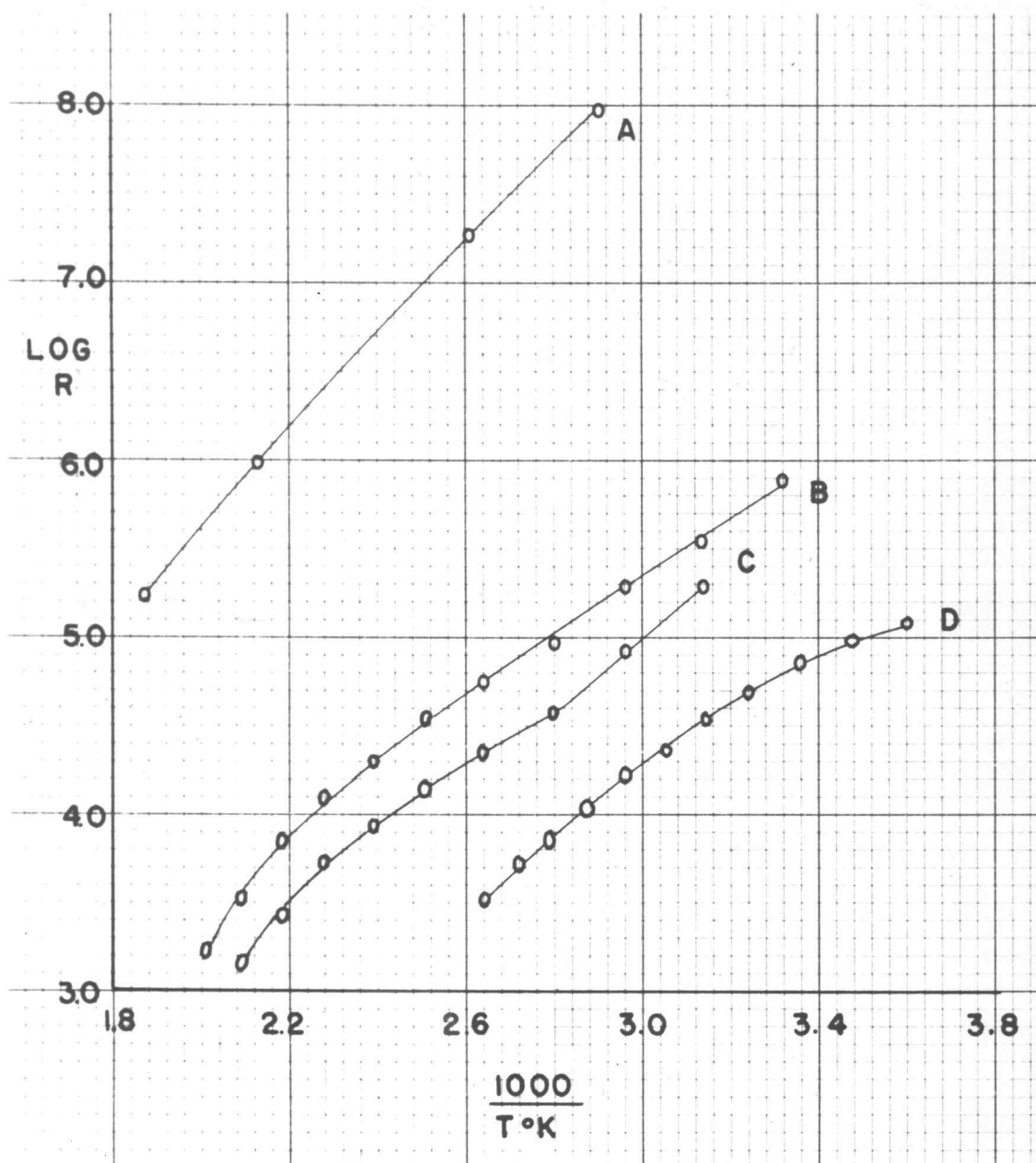


Figure 1. Plot of the log of resistance versus the reciprocal of temperature of crystalline boron as recorded in the literature.

A - Shaw (15,p.115); B - Weintraub's crystal 1 (18,p.106); C - Weintraub's crystal 2 (18,p.106); D - Freyman (3,p.1109). Values used for this plot are listed in the appendix.

## EXPERIMENTAL

## INTRODUCTION

The starting material used in these experiments was Moissan boron, furnished by the Pacific Coast Borax Company of Los Angeles. Two grades were furnished. One grade was 91.4% boron, 6.2% magnesium, and 2.6% other impurities. The other was 96.3% boron, 1.6% magnesium, and 2.1% other impurities. The lower grade was used in most experiments because of the high cost of the purer material.

The study of the purification of boron in an atomic furnace was conducted in the following steps:

1. A suitable furnace was designed and constructed.
2. The proper operating conditions and the best methods of control of the atomic hydrogen arc were determined.
3. The identity of areas of maximum purity and the conditions that best produced these areas were established.
4. The methods for continuous purification of a large quantity of material were investigated.
5. The products of the furnace were analyzed and a few of its properties were investigated.

There was, of course, some overlapping of these steps since modification of the furnace continued throughout the study as new ideas were tried and furnace malfunctions occurred.



## THE FURNACE

Since a description of an atomic hydrogen furnace is not available in the literature, the design of the furnace was based on the atomic hydrogen torch and the principles of the ordinary arc furnace. The basic design considerations were:

1. The materials of construction must be unreactive to boron, hydrogen, and the gases of the furnace at high temperatures.
2. The use of a refractory material also must be unaffected by the above, or the need for a refractory be eliminated.
3. A means must be devised which will allow convenient starting and control of the arc between two electrodes and directing the flame onto the material to be heated.
4. An atmosphere void of  $N_2$  and  $O_2$  must be maintained.
5. Maximum flexibility and adaptability must be obtained.

Copper successfully met the requirements for the material of construction and was used where possible. It also had a high heat conductivity which dissipated the heat so fast that a lining of refractory material was not needed. To meet condition three, both electrodes were made adjustable, and three gas ports were provided to direct the flame. Condition four required the removal of air by a vacuum system and maintenance of a positive pressure by an inert gas system to prevent re-entry of air. Changes in design and operating conditions were made easier by the flat wall construction (instead of cylindrical) and by making inside dimensions larger than in normal

arc furnace designs.

The furnace shell with electrodes in place is shown in figure 2. It consisted of 3/16 inch copper sheet, butt welded to form a tetragon with inside dimensions of five inches by five inches by twelve inches. The end flanges were  $1\frac{1}{2}$  inches wide. The bottom flange contained eight - 3/8 inch bolt holes, while the top contained twelve - 3/8 inch bolt holes. The additional holes in the top flange were deemed necessary because of the additional wear caused by continually opening and closing the furnace. An opening in the center of one furnace wall, two inches square, was cut to provide observation of the arc. A  $\frac{1}{2}$  inch thick heat resistant glass was mounted three inches in front of the hole by means of a flanged cylinder. Two - 1 3/8 inch diameter tubes were mounted at a  $45^\circ$  angle to the furnace axis on opposite sides to house the moveable electrodes.

A blow hole, three inches in diameter, was cut on the back side of the furnace and fitted with a rubber diaphragm cut from an inner tube. A perforated plate prevented collapse of the diaphragm when a vacuum was pulled in the furnace. Protection from heat was afforded by sheet asbestos. Cooling of the diaphragm was found necessary; a continuous blast of air or occasional spraying with water was found effective. The rubber diaphragm was later replaced with a piece of "durable" gasket material which required much less attention.

The use of copper in the furnace construction caused some difficulty in welding because the heat from the welding torch was conducted away from the weld so fast that the proper welding temperature could



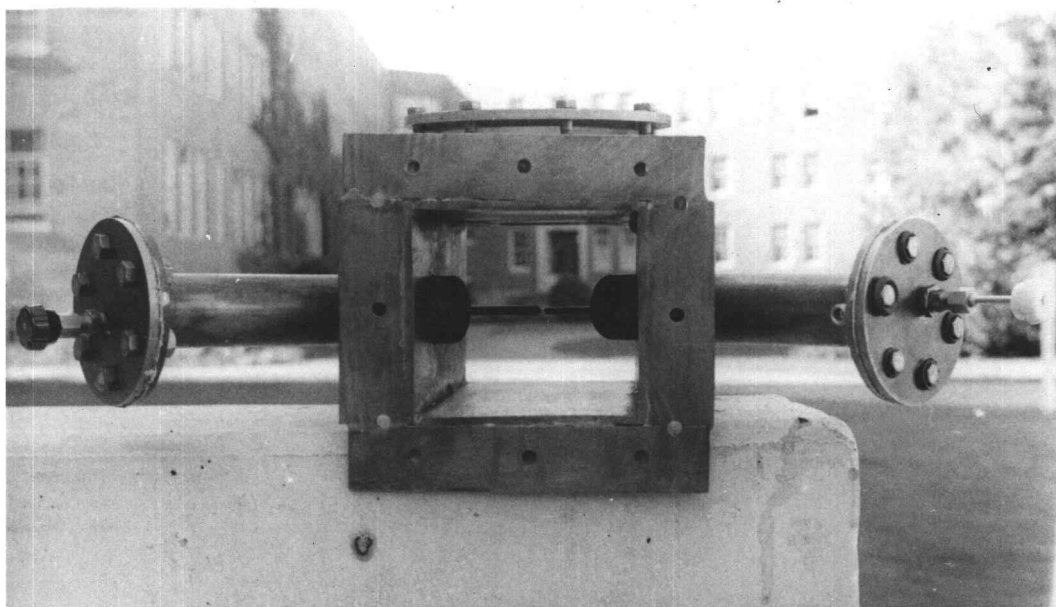


Figure 2 - Top view of the furnace shell. Gas-cooled electrodes in place. Flange for observation hole is on top. The electrode on the right is electrically insulated from the furnace.

not be obtained. Prolonged pre-heating by a gas burner was necessary before good welds could be made.

The observation glass cracked once when the arc flame impinged upon it. The use of a watch glass between the furnace and the window was tried. The watch glass broke each time it was used so that this method of protection was abandoned. Better furnace operating techniques prevented impingement and no further difficulty was experienced.

"Durable" sheet protected by asbestos sheet was found to be an adequate gasket material. A rubber gasket, protected by asbestos sheet was used on the window to prevent setting up unnecessary stresses in the glass.

The electrode assembly is shown in figure 3 partially dismantled. The electrode assembly shown is at the same electric potential as the furnace. The other electrode (not shown) is identical except that a quartz cylinder instead of a copper cylinder was used. Different coefficients of expansion for the holder and the quartz cylinder caused some cracking of the quartz cylinder. Tungsten rods were used as electrodes. A 3/16 inch rod was tried, but it began to melt even at the minimum current settings. Two 1/4 inch rods were subsequently used and found satisfactory. The electrodes were centered in a copper holder and held in place by means of a set screw. Several small holes were drilled in the holder to allow passage of hydrogen over the electrodes. The holder was fitted inside of the cylinder and the entire assembly moved up and down the tube by means of a threaded rod, which



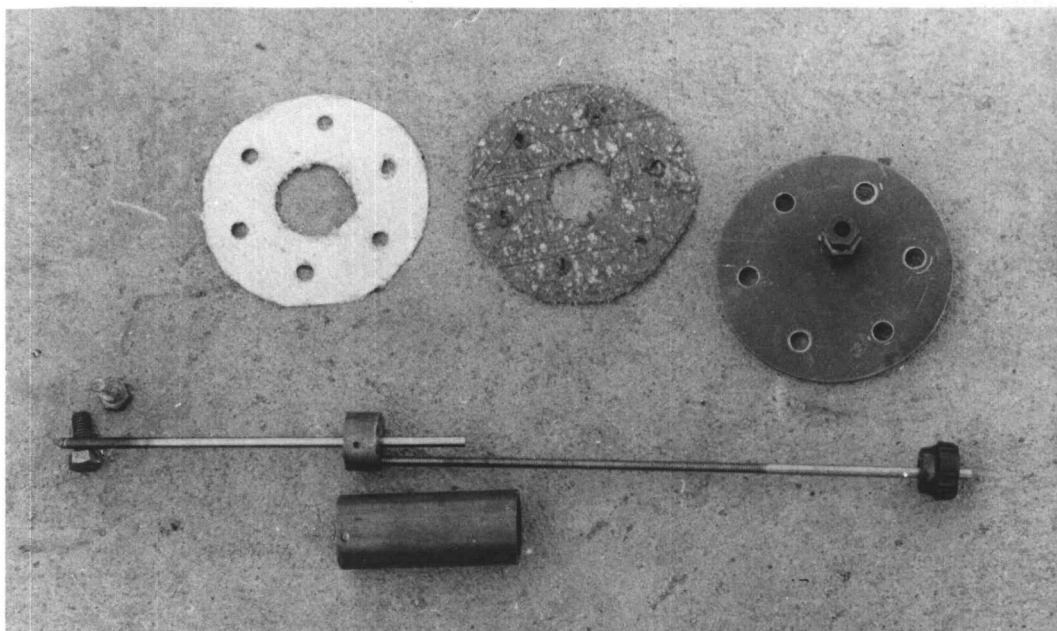


Figure 3 - Electrode assembly. Shown are the asbestos and "durable" gaskets, and flange plate. The tungsten electrode was held in the copper holder by means of a set screw. The holder was moved up or down by means of the threaded copper rod. The copper cylinder at the bottom was used to give steadier slide operation and fit over the electrode holder.

was manipulated from outside of the furnace.

Originally one arc welder was used supplying an open circuit voltage of 90 volts. An arc in hydrogen could be maintained only with difficulty. A second welding generator was added in series. The arc could be maintained but overheating of the anode occurred. A water-cooled electrode, figure 4, was thereafter employed at the anode. The water-cooled electrode was electrically insulated from the furnace by a piece of pyrex tubing.

The arc welding generators used to supply direct current for the furnace were a General Electric, 400 ampere unit and a Lincoln, 250 ampere unit, figure 5. Maximum open circuit voltage was 150 volts. The electrical circuit is diagramed in figure 6 and the electrically insulated flange in figure 7.

The gas system used is shown in figure 8. It consists essentially of a hydrogen feed system, a helium feed system, and an exhaust system. A plastic beach balloon was used as a reservoir and surge tank during air removal, starting, and cooling operations. The basic solution in the wash bottle for the exhaust system was to trap toxic  $B_2H_5$  and to prevent air from entering the furnace during runs. Should the air go out, a sudden drop in furnace pressure occurs. The vacuum pump was used only for initial air removal and was disconnected during the actual run.

The equipment is assembled in figure 9.



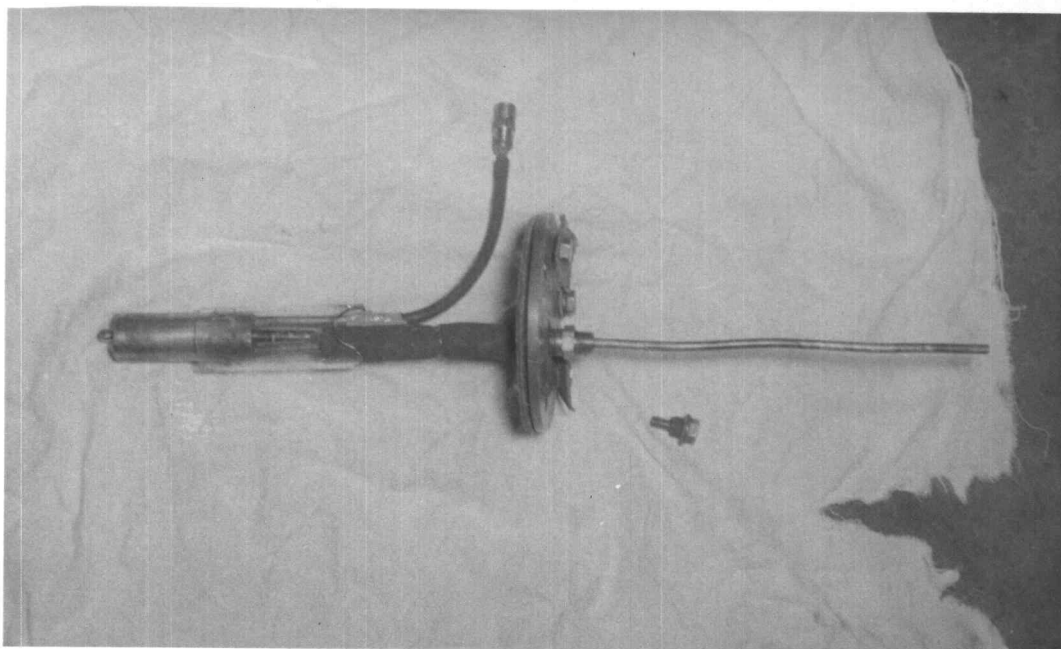


Figure 4 - Water-cooled electrode. This was used as the anode for most of the furnace runs. The electrode could be adjusted by means of the long copper tube in the center of the picture. Water flowed into the copper jacket and exited through the small rubber tube. The long tube also served as the electrical conductor. The electrode was electrically insulated from the furnace by the glass tube and large rubber tube.

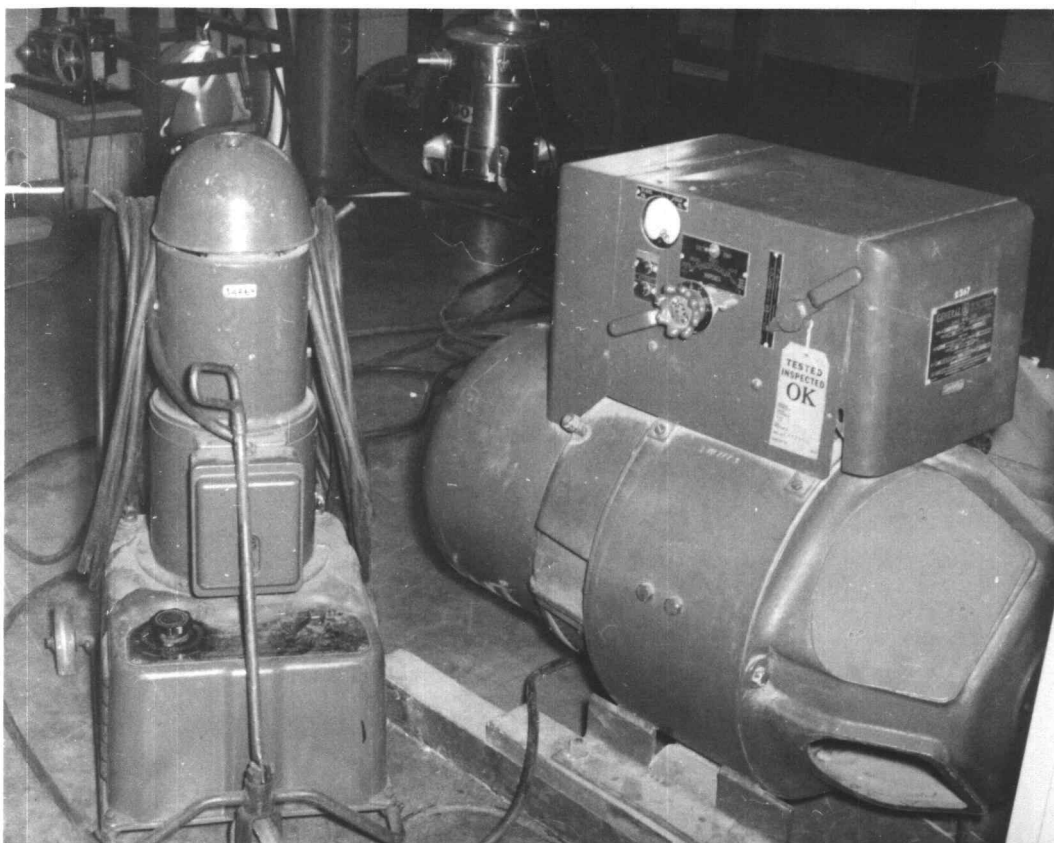


Figure 5 - Electric welding generators used during runs. They are hooked in series to give maximum voltage output.



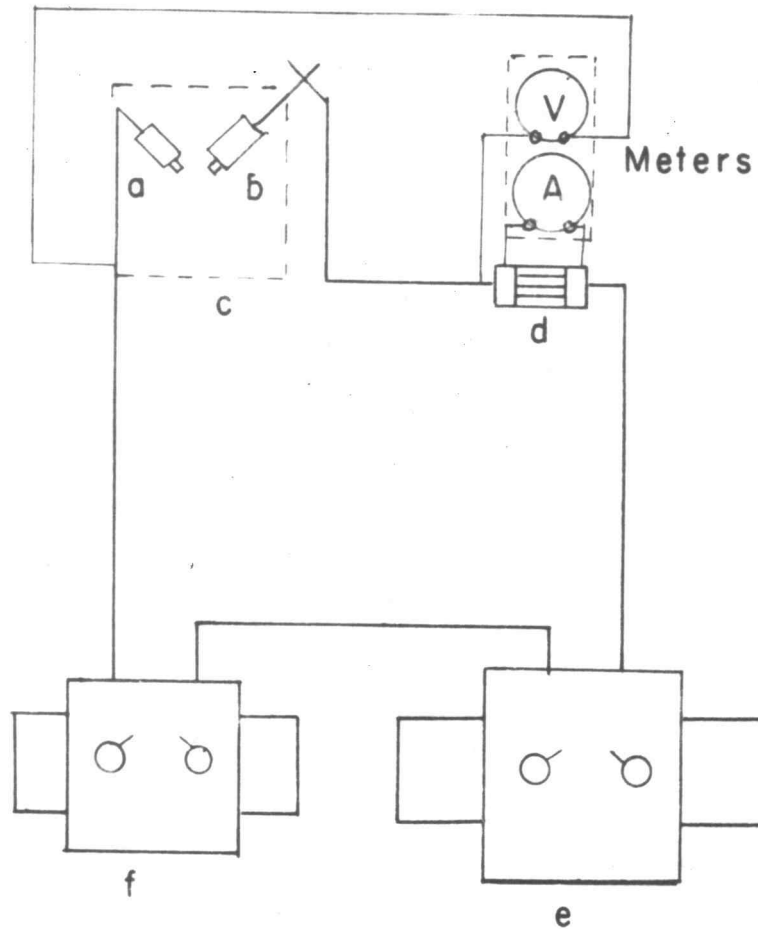


Figure 6. Diagram of the electrical system. a- electrode; b- insulated electrode; c- furnace; d- shunt; e- General Electric welding generator; f- Lincoln welding machine.





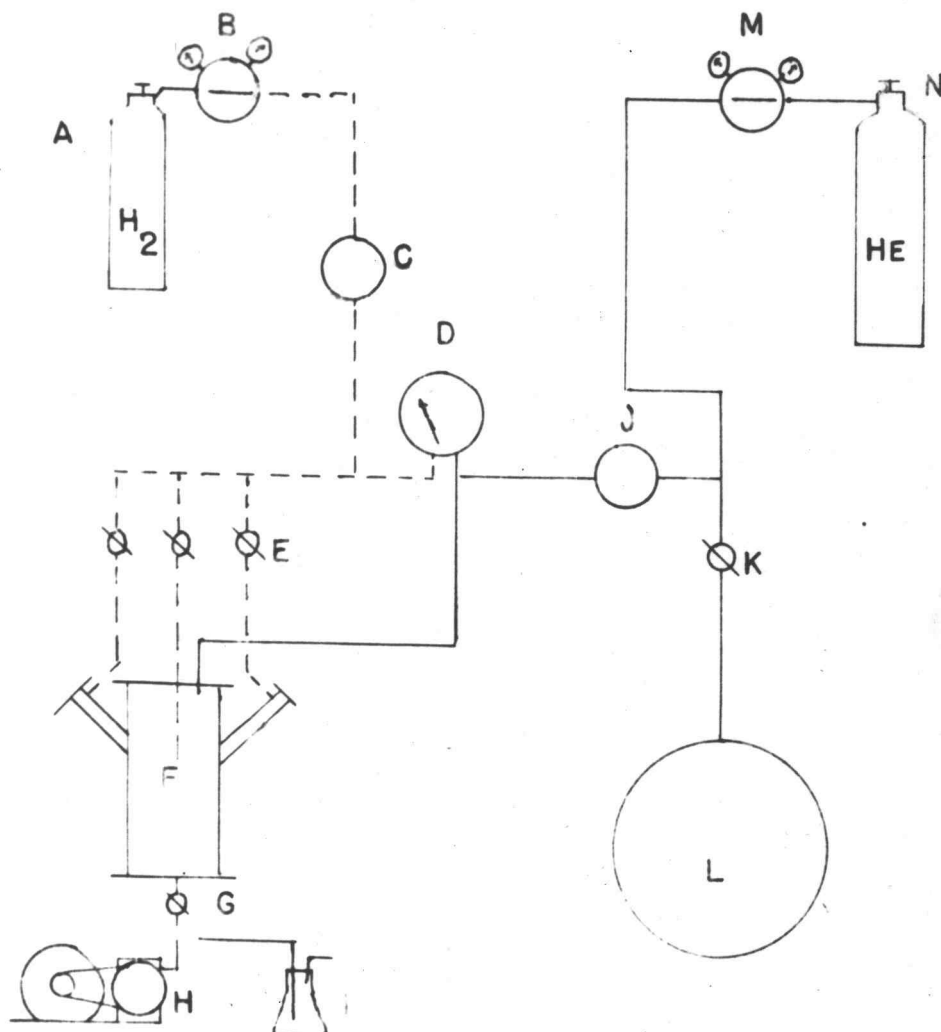


Figure 8. Diagram of the gas system. A- hydrogen cylinder; B- hydrogen regulator; C- drying bulb; D- duplex pressure gauge; E- needle valves for hydrogen control; F- furnace; G- needle valve for exit stream; H- vacuum pump; I- scrubbing bottle; J- drying tube; K- pinchclamp; L- beach balloon; M- helium regulator; N- helium cylinder.

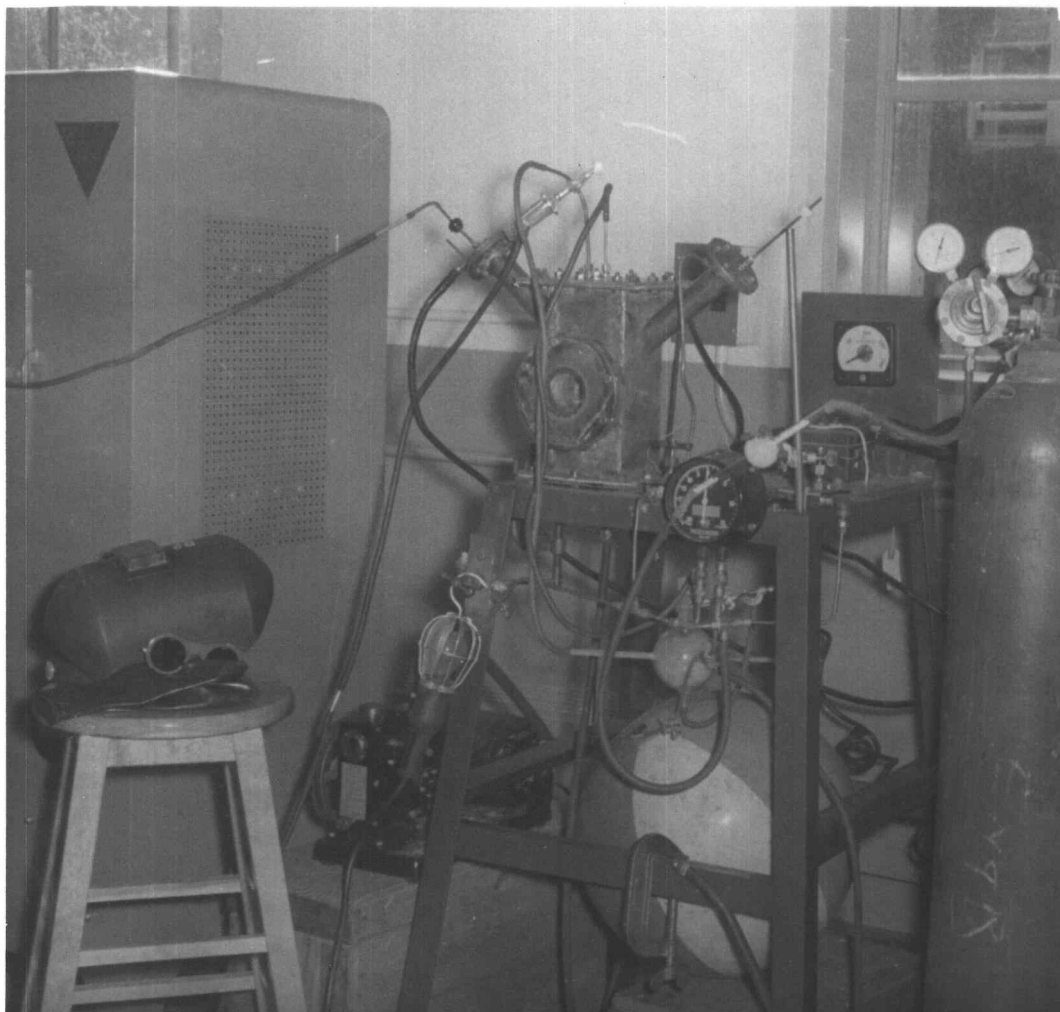


Figure 9 - Furnace mounted on stand. The water-cooled electrode was installed.



## OPERATION OF THE FURNACE

A considerable amount of experimentation was necessary before satisfactory control of the arc was accomplished. The arc had a natural tendency to climb up the "V" of the electrodes and the hot rising exhaust gases tended to push the flame upward instead of downward on the object to be heated. A mixture of helium and small quantities of hydrogen yielded a very unstable arc atmosphere and its flame shot wildly around in the furnace. Furthermore, with the "V" type construction and rounded electrode ends the shortest distance between the electrodes was on the top side of the electrode ends. The cathode and anode spots were continually moving on the electrode to find areas of least resistance. Unless the electrodes were correctly positioned these spots would get too far apart and the arc would go out.

The furnace was designed to send hydrogen through the arc from three places - along each electrode and directly above the arc. Best results were obtained when hydrogen was emitted only from directly above the arc. A small flow from this position was found sufficient to keep the flame pointed in a downward direction. Positioning the cathode slightly above the center of the "V" was found to give the least spot wandering and maximum arc stability. An electrode separation of one to three millimeters gave best results. The arc must be started by bringing the two electrodes together.

Disregarding the high current, low-voltage arc occurring when the

furnace atmosphere was chiefly helium, three distinct types of arc positions were noted, each with their own typical current-voltage relationships. Figure 10 is a plot of power versus voltage and shows the range in which each were operated. When the arc stream took the shortest route between the electrodes, a low-voltage, low power arc was formed. By separating the electrodes slightly more, a long pointed arc was formed. This was a medium voltage, high power arc that delivered maximum heat. Unfortunately, this flame was not particularly stable and pointed in different directions and to the side. The most stable arc was a round reddish flame of high voltage and medium power with electrode spots on the lower edges of the electrodes. Figure 11 shows the three types of arcs.

Chemical cleaning of the electrodes was accomplished by the use of concentrated  $\text{HNO}_3$  and then hot  $\text{KOH}$ . This was found to be necessary only after continued use. A complete list of operating procedures is included in the appendix.

The boron was prepared for heating by pressing into bricks two inches by two inches by one inch at a pressure of 5,000 pounds per square inch by a hydraulic press. It was then heated to  $200^\circ\text{F}$ . in a vacuum for several hours. The bricks were placed in the atomic hydrogen furnace on an adjustable stand that could be raised or lowered by means of a copper rod protruding from the bottom of the furnace. Other shapes were pressed and treated in the same manner.



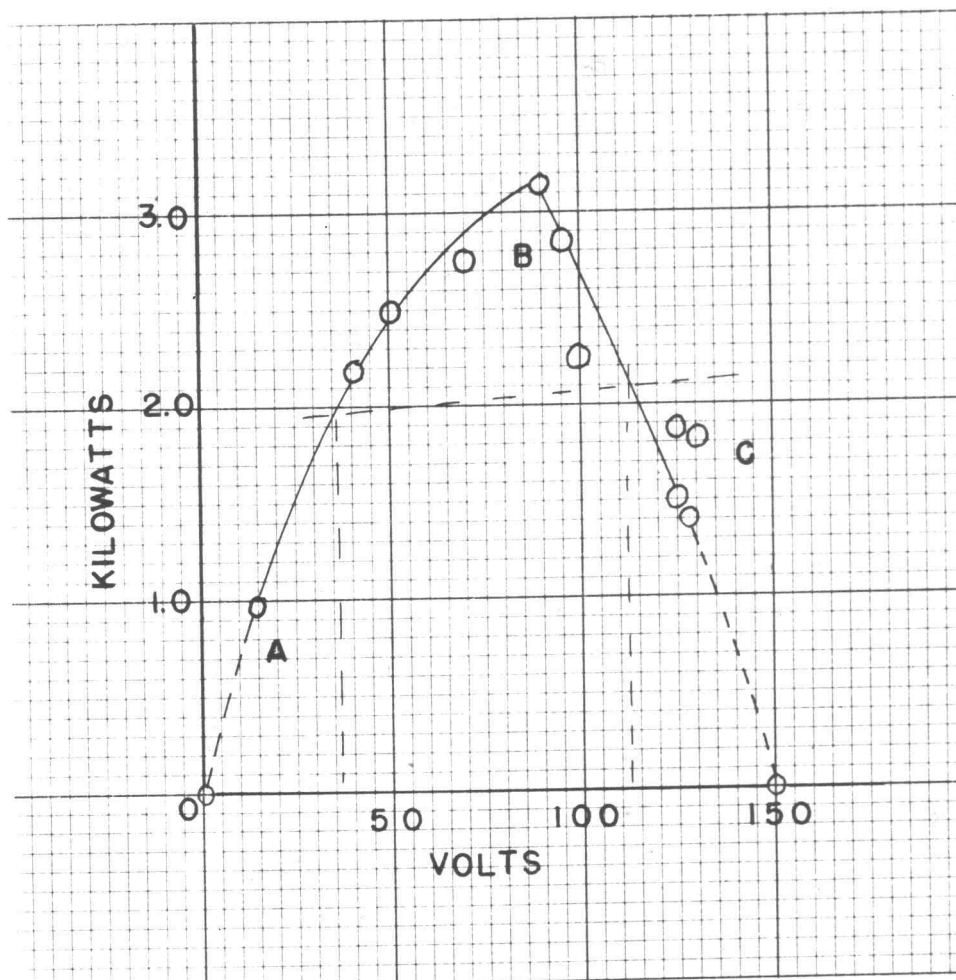


Figure 10. Power input versus arc voltage for maximum voltage, minimum current welder settings. Areas A, B, and C indicate the power-voltage characteristics of the three types of arc flames.

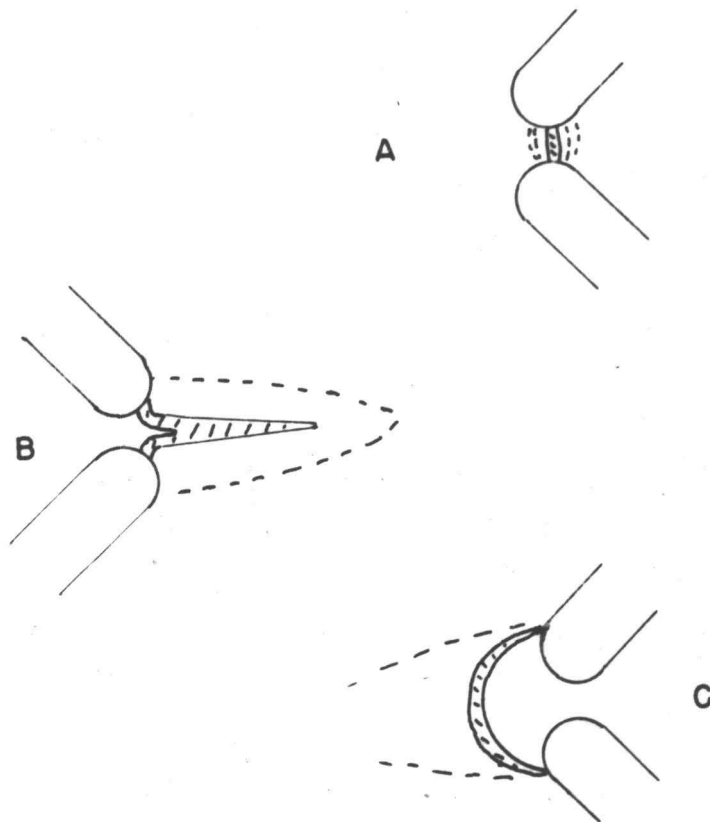


Figure 11. Flame shapes of the arc. Each has its own power-voltage characteristics. A- a low power, low voltage flame; B- high power, medium voltage flame; C- medium power, high voltage flame.

## OPERATING CONDITIONS

The proper operating conditions for maximum boron purification were studied by adjusting the following variables:

1. Distance of the brick from the arc.
2. Length of exposure to the flame of the arc.
3. The composition of the furnace atmosphere.
4. The type of arc used.
5. The purity of the initial boron.

The brick was then broken and the fused layer sent for analysis. A detailed report of the findings is included in the RESULTS.

## CONTINUOUS OPERATION

When the brick was exposed to the flame, a cup was formed, averaging  $1\frac{1}{4}$  inches in diameter and  $\frac{3}{8}$  inches deep. Further exposure caused little increase in the amount of boron melted. It was therefore necessary to investigate means to obtain a larger melt. The main difficulty encountered was that boron had little tendency to flow even in the molten state, presumably due to high surface tension. Several cylindrical shapes were tried in an effort to get the boron to drip off the hot end. A tapped hole was also tried.

The most promising method was to feed boron into the melted cup, melt the feed, and add more boron. Since the powdered amorphous boron possesses poor free flow qualities, and in order to prevent the material from being blown away by the flame, it was necessary to pelletize the boron. The Stokes tableting machine shown in figure 12 was



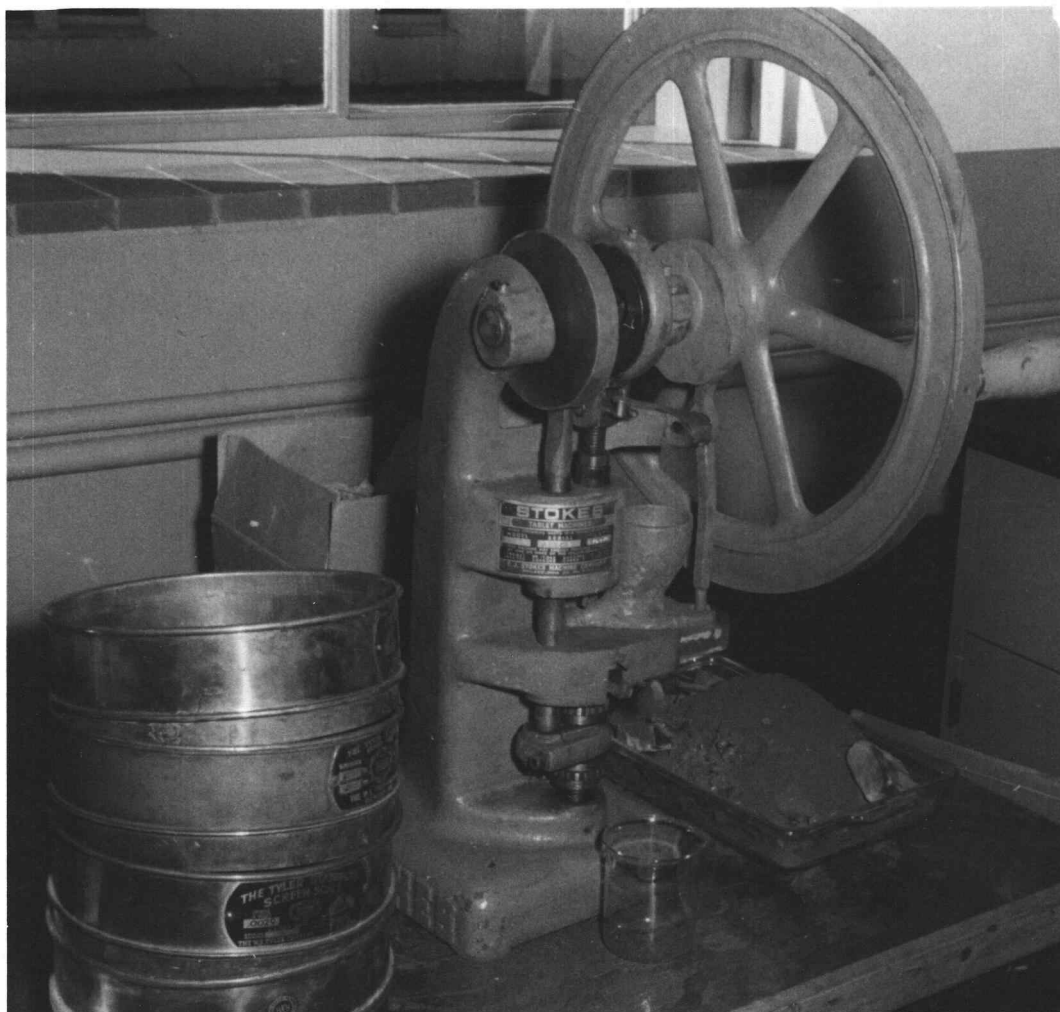


Figure 12 - Stokes tableting machine used to prepare boron for feeding.

used for this purpose. It was found that boron from thirty-two to forty-eight mesh could be used to obtain satisfactory pellets  $5/32$  inches in diameter and  $1/8$  inch high.

Several feeder designs were tried. The first design, shown in figure 13, consisted of a curved copper tube of such a length that it could be positioned directly over the edge of the cup. The tube was placed in back of the water-cooled electrode when not in use. The tube entered the furnace through the rubber diaphragm. Boron was directed into the copper tube from a glass tube by means of a copper push rod. Results were far from desirable. The pellets on entering the hot cup, caused severe spattering; the copper feeding tube got so hot that it melted the rubber diaphragm; and the pellets stuck in the hot copper tube.

The furnace was placed in the horizontal position, figure 14, and the flame was directed on the side of the brick instead of on top of it. The feeder and the boron brick arrangement used is shown in figure 15. The feeder was water-cooled and pellets could be fed by merely increasing the angle of the glass tube.

Another feeder is shown in figure 16 and the furnace arrangement is diagramed in figure 17. The furnace was in a vertical position. The feeding was accomplished by means of the push rod. Pellets dropped into position for feeding from the vertical tube, pushed out of the feeder onto the boron slide, and dropped into the cup. The bricks were lowered to feeding position; and when feeding was accomplished, slowly returned to the flame. The boron slide shielded the

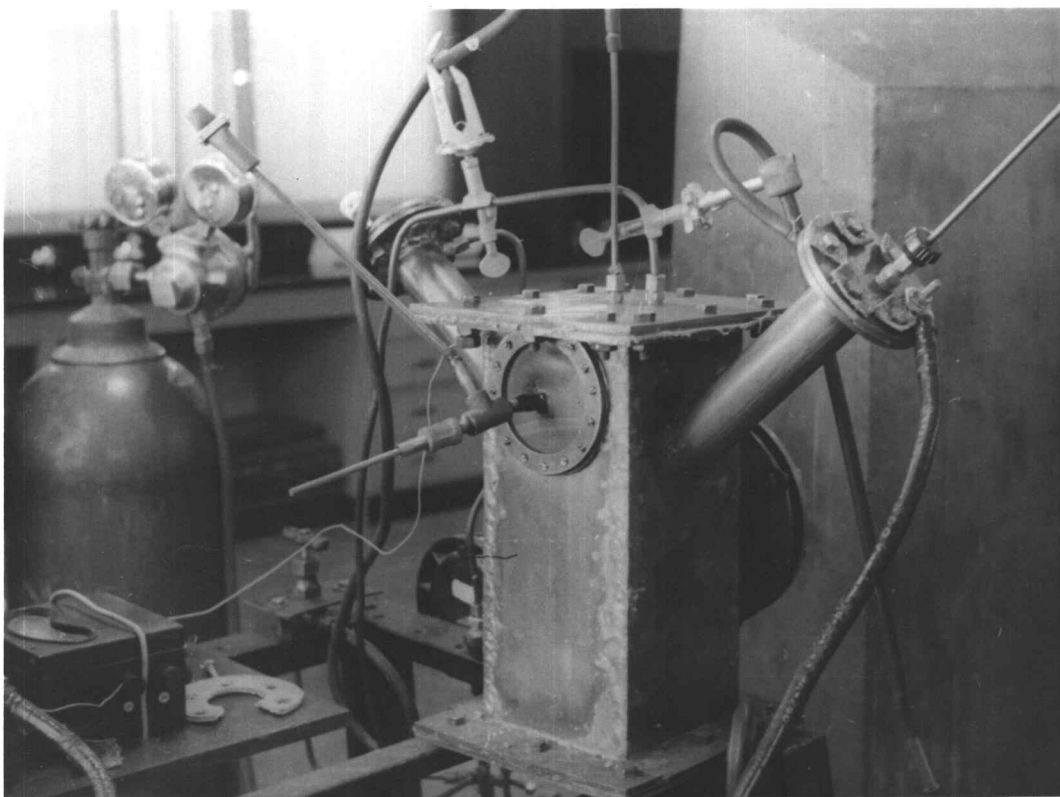


Figure 13 - Back of furnace showing first feeder tried.



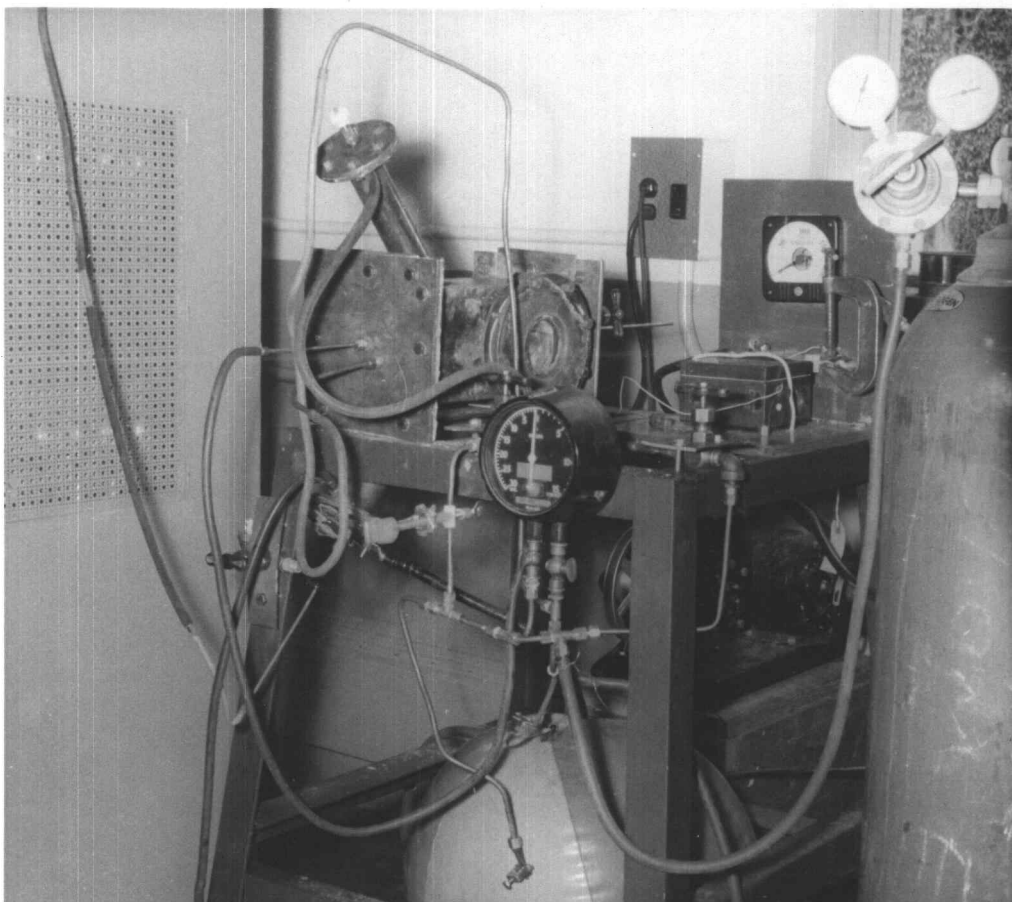


Figure 14 - Furnace in horizontal position.

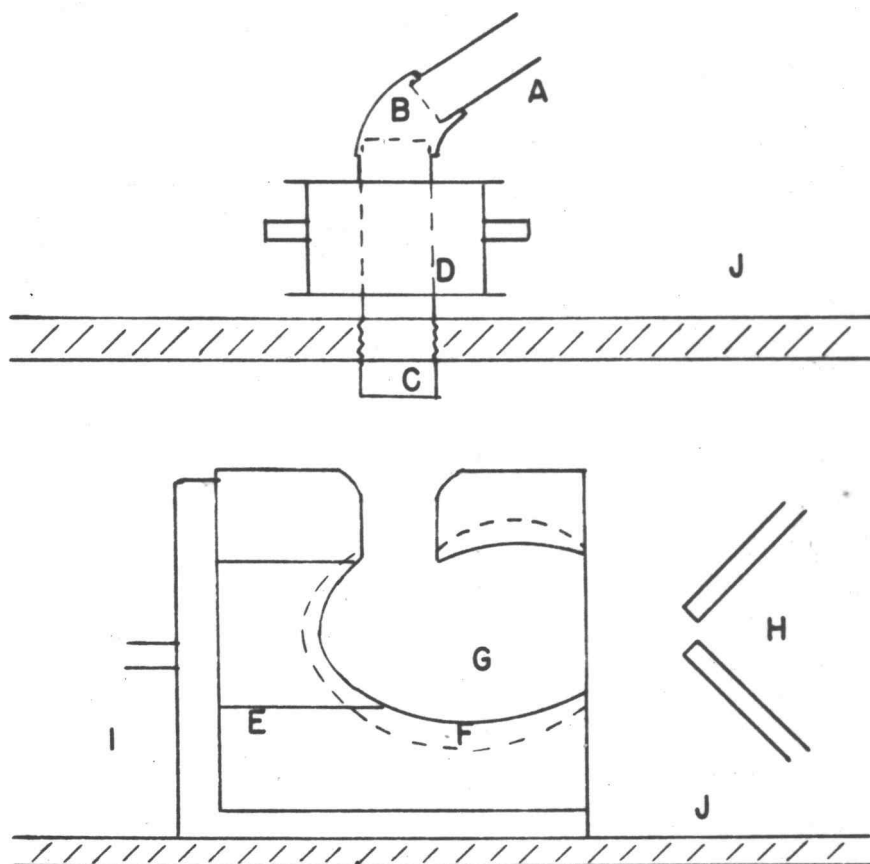


Figure 15. Horizontal feeder, brick, and cup arrangement. Pellets in tube A are dropped through tube C into cup G. A- glass tube; B- rubber tubing; C- copper tubing; D- water jacket; E- boron bricks; F- crystalline boron layer; G- cup; H- electrodes; I- adjustable, copper holder; J- furnace walls.

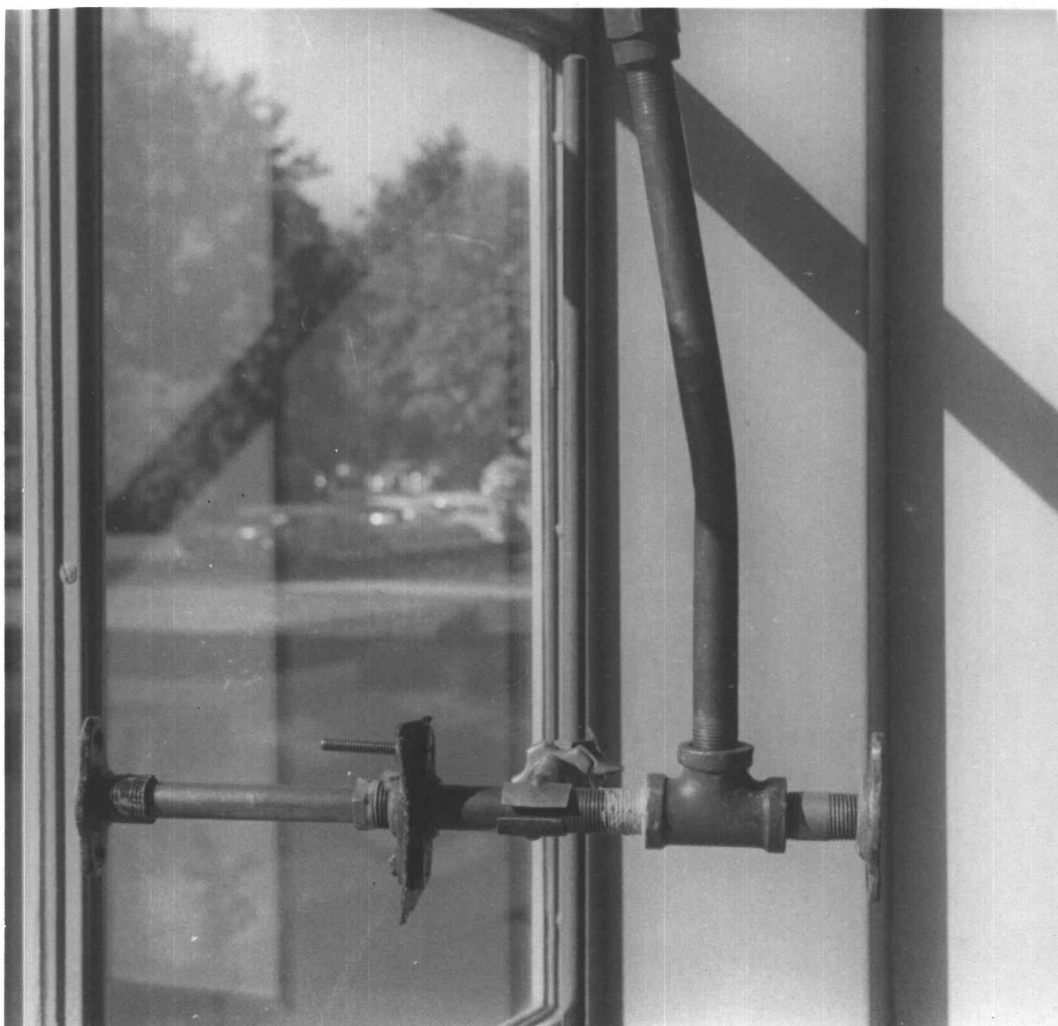


Figure 16 - Feeder for feeding when furnace was in a vertical position.



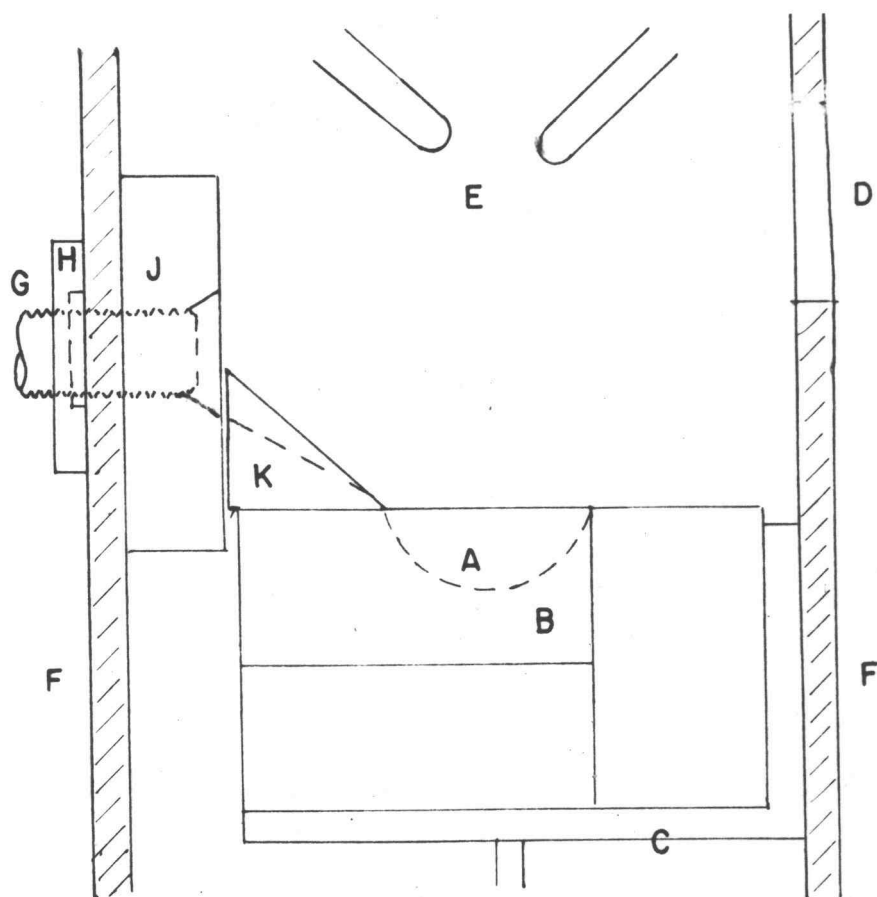


Figure 17. Brick arrangement for feeding with furnace in a vertical position. A- cup; B- boron bricks; C- adjustable, copper stand; D- sight hole; E- electrodes; F- furnace walls; G- feeder tube; H- stuffing box; J- boron brick with hole in center; K- boron slide.

feeder except during feeding. Water-cooling of the feeder was not required. A crude packing gland was built for the push rod to prevent leaking. The feeding process was slow because not many pellets could be fed at one time and still maintain even feeding.

Another method to obtain larger melts was found by heating the brick in the arc and then withdrawing one electrode, using the boron brick as the other electrode. Electrical connection was insured by pressing the brick on a five pronged copper plate. This method was not extensively explored as it could better be studied in a furnace of a different design.

#### CHEMICAL ANALYSIS

Tungsten was determined gravimetrically by precipitation with cinchonine. Magnesium was determined gravimetrically by precipitation with disodium phosphate. It was quite difficult to get complete fusion of the boron sample. The boron had to be ground exceedingly fine and a large excess of sodium carbonate used. The steps employed in these analyses are listed in the appendix.

Determination of boron was conducted by the Pacific Coast Borax Company of Los Angeles volumetrically by neutralization of boric acid formed by sodium carbonate fusion. Their method was similar to that outlined by Scott (14, p. 164 and 168).

Analysis of the deposits on the furnace walls was conducted by ordinary qualitative methods (14, pp. 1110-11).

## BULK DENSITY

The density of the fused layer was determined by measuring the volume displaced by a weighed sample. A pyknometer was used for this determination. Air bubbles adhering to the sample were removed by agitation before completely filling the pyknometer.

## ELECTRICAL CONDUCTIVITY

Electrical conductivity versus temperature relationships were obtained to determine if the presence of impurities could be detected. No attempt was made to measure the values of activation energies or the true resistance of the boron for several reasons. The material used was polycrystalline and contained impurities. Its composition was not completely homogenous: the electrical conductivity of the boron nearest the arc was higher than at the outer edge of the fused layer. A perfect electrical connection was not obtained since boron was not wetted by any of the materials tried (mercury, molten lead, molten copper, and electrical solder). Therefore, a true cross section could not be measured.

Figure 18 shows the equipment employed. The boron sample was cleaned, sanded with carborundum paper, washed and dried. It was then placed between lead plates and pressed by means of a small clamp. Too much pressure would break the sample. The arrangement of the sample in the clamp is shown in figure 19.

Power was supplied by dry cell batteries furnishing up to ten volts. Voltage was controlled by means of the potentiometer and



measured by a direct current voltmeter. Heat was supplied by a sun lamp and was varied by changing its distance from the sample. Current was measured by a microammeter, and temperature was measured by a mercury thermometer. Though this method was far from exact, duplication of results was good and values agreed fairly well during both the rise and decline in temperature.

#### CALCULATIONS

1. Power input to the arc was determined from the voltage-current data given in the appendix. The resistance other than that of the arc between the points of voltage measurement was negligible. In a direct current circuit:

$$\text{power (kilowatts)} = 0.001 \times \text{voltage drop (volts)} \times \text{current (amperes)}.$$

When an arc had a potential drop of 100 volts and was carrying 25 amperes current, power input was:

$$(0.001) (100) (25) = 2.5 \text{ kilowatts.}$$

2. Electrical resistance of the boron was determined from voltage-current measurements. It was assumed that circuit resistance was negligible compared to the high resistance of the boron. In direct current:

$$\text{resistance (ohms)} = \text{voltage drop (volts)} / \text{current (amps)}.$$

When a current of 42 microamps was observed to flow where the voltage drop was 10.1 volts, the electrical resistance of the boron was:

$$(10.1) / (42 \times 10^{-6}) = 2.4 \times 10^5 \text{ ohms.}$$

3. Determination of b in formulae 5 was accomplished by measuring the slope of the line obtained by plotting the log of the electrical resistance as the ordinate and the reciprocal of absolute temperature as the abscissa. Between points  $1000/T = 3.24$ ,  $\log R = 5.23$  and  $1000/T = 3.00$ ,  $\log k = 4.75$ .  $\Delta 1/T = 0.00024$  and  $\Delta \log R = 0.47$  and  $b = (0.47) (0.00024) = 1,950$ .

4. Bulk density was computed as follows:

The weight of pyknometer filled with water ( $W_{pw}$ ) plus the weight of the sample ( $W_s$ ) minus the weight of the pyknometer containing the sample and filled with water ( $W_{pws}$ ) equals the weight of the water displaced ( $W_d$ ). This was divided by the density of the water ( $D_w$ ) to give the volume of the sample ( $V_s$ ). The weight of the sample divided by its volume gave the density ( $D_s$ ).

$$D_s = \frac{W_s}{(W_{wb} + W_s - W_{wbs}) D_w}$$

For run 15:

$$W_s = 0.2388$$

$$W_{wb} = 48.0400$$

$$W_{wbs} = 48.1728$$

$$D_w = 0.997$$

$$D_s = (0.2388) / (48.0400 + 0.2388 - 48.1728) (0.997)$$

$$= 2.26 \text{ gm/cc}$$

5. Tungsten was precipitated as  $WO_3$  and was determined gravimetrically in this form. Correction of the weight of the residue for the



ash of the filter paper was necessary. Letting:

$W_r$  = weight of residue

$W_a$  = weight of the filter paper ash

$W_s$  = weight of the sample

$A_w$  = the atomic weight of tungsten = 183.92

$M$  = the molecular weight of tungsten oxide = 231.92.

then:

$$\begin{aligned} \% W &= (W_r - W_a) (A) (100) / W_s M \\ &= (79.31) (W_r - W_a) / W_s. \end{aligned}$$

For run 8:

$W_r$  = 0.0022

$W_a$  = 0.0005

$W_s$  = 0.5071

$$\% W = (79.31) (0.0022 - 0.0005) / 0.5071 = 0.26\%.$$

Magnesium was obtained by identical methods except the atomic weight of magnesium (24.32) and the equivalent weight  $Mg_2P_2O_7$  (222.68/2) were used.



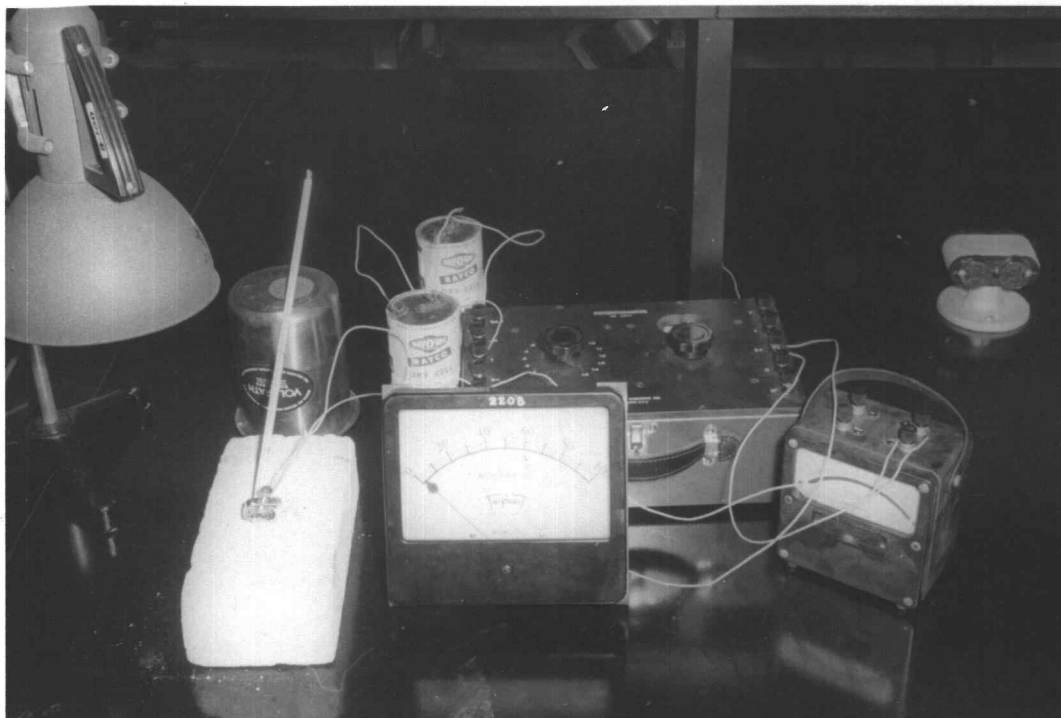


Figure 18 - Equipment employed for electrical conductivity experiments. From left to right is heating lamp, clamp, thermometer, microammeter, potentiometer, and voltmeter.

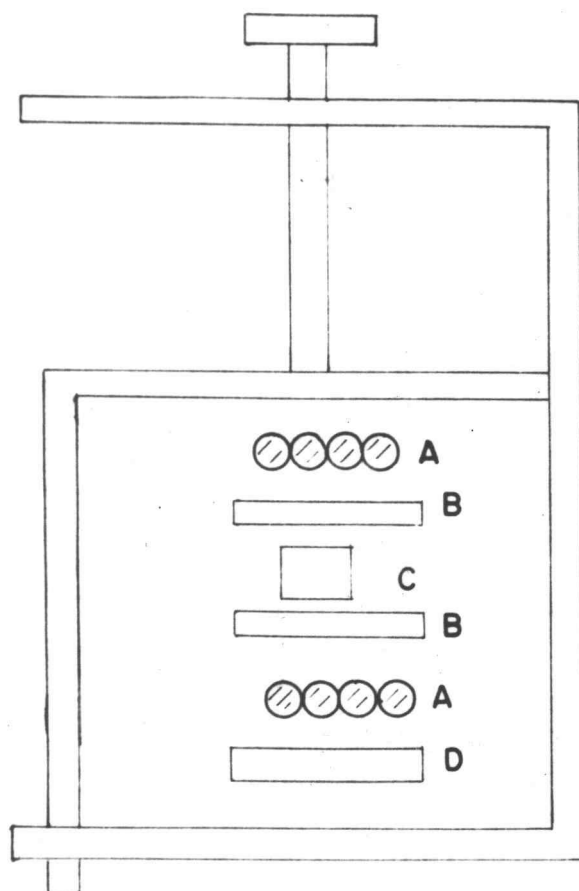


Figure 19. Arrangement of sample in clamp for temperature resistance measurements. A- coiled copper wire; B- lead sheet; C- boron sample; D- fiber insulator.

## RESULTS

## PURIFICATION

When the atomic hydrogen flame impinged upon the boron brick, the boron fused and an indentation or cup of fused boron was formed. The purity and amount of fused products obtained during this investigation is given in table 1.

TABLE 1  
Fused Boron Formation

<u>Run No</u>	<u>Time under flame(min)</u>	<u>Wt of fused product(gm)</u>	<u>% boron in fused product</u>
1	20	2.2	96.3
4	15	1.2	86.2
5	5	11.8	96.5
6	5	8.2	96.2
7*	6	3.2	96.4
8*	4	6.2	97.4
11	22	13.0	96.9
15	15	24.0	97.4
19	45	14.5	96.9
23	17	—	67.7
24	15	18.6	95.6 and 97.3
26	18	8.4	97.0
28	35	11.0	86.7 and 96.9
29	40	23.9	96.3
30	60	28.8	96.4
31*	18	11.0	97.3
32	15	—	97.3

\* 96.3% boron starting material

The highest purity obtained was 97.4% for both the 91.4% and the 96.3% starting materials. The downgrading in run four was probably due to an air leak in the furnace diaphragm. The low boron percentage in run twenty-three was caused by contact with the tungsten electrodes.



Several products were checked for tungsten and magnesium content and the results are included in table 2, which gives the percentage of constituents in the starting and final materials.

TABLE 2  
Initial and Final Composition  
of the Fused Layer

<u>Run No</u>	<u>8</u>	<u>15</u>	<u>19</u>	<u>24</u>	<u>29</u>
Initial B%	96.3	91.4	91.4	91.4	91.4
Initial Mg%	1.6	6.2	6.2	6.2	6.2
Initial % other	2.1	2.6	2.6	2.6	2.6
Final B%	97.4	97.4	96.9	97.3	96.3
Final W%	0.26	0.13	0.16	<0.1	0.19
Final Mg%	0.10	<0.1	0.11	0.13	0.38
Final % other	2.3	2.4	2.8	2.5	3.0

A better comparison can be made by a material balance. The material balance is tabulated in table 3, computed on a basis of 100 gms of starting material.

TABLE 3  
Material Balance

<u>Run No</u>	<u>8</u>	<u>15</u>	<u>19</u>	<u>24</u>	<u>29</u>
Final grams B	96.2	91.4	91.0	91.4	90.2
Final grams W	0.26	0.12	0.15	<0.1	0.18
Final grams Mg	0.1	<0.1	0.1	0.1	0.4
Final grams of other	2.3	2.2	2.6	2.4	2.8
Change in B	-0.1	0	-0.4	-0.3	-0.8
Change in W	0.26	0.12	0.15	<0.1	0.19
Change in Mg	-1.5	-6.1	-6.1	-6.0	-5.8
Change in other	0.2	-0.4	0	-0.1	0.2

Run eight was conducted with gas-cooled electrodes, furnace in the vertical position, and using 96.2% starting material. The brick was under the arc for only four minutes.

Run fifteen was conducted using the water-cooled anode, the furnace in the horizontal position, and the 91.4% boron starting material. Arc time was fifteen minutes. There was no fogging of the glass and only slight furnace coating on this run.

Run nineteen was made using the water-cooled anode and the furnace hole in a horizontal position. The heat was vented out of a pre-formed hole and feeding unsuccessfully attempted. The brick was 91.4% boron.

Run twenty-four consisted of melting of the boron brick by electrical resistance.

Run twenty-nine was conducted with the water-cooled anode, the furnace in the vertical position, and pellets fed into the cup. The cup was exposed to the arc for forty-five minutes.

The loss of boron was undoubtedly due to vaporization of boron during the run. The relatively high magnesium content of run twenty-nine was unexpected considering the long melting time. Apparently, feeding tended to cause some impurities to enter the cup.

The tungsten and magnesium analyses were not very accurate because of their small concentrations. Larger samples could not be used because of the difficulty in obtaining complete fusion. The thiocyanate spot test was negative for all the samples tested except for run eight, which gave a slight bluish tint. The limit of the thiocyanate



test is 0.004 milligrams of tungsten in a concentration of 80 parts per million.

Analysis of the residue on the furnace walls indicated a large amount of magnesium, considerable boron, a small amount of tungsten, and a trace of copper. A blue layer was formed next to the copper, which appeared to be a tungsten-copper complex. Next was a white layer with a slight brownish tint. This tint was usually more noticeable on longer runs. The water soluble portion containing the magnesium had a ph of approximately eight, indicating that it was in the form of magnesium boride.

One disturbing result was an increase in weight of the brick during several runs. Experiments in which weight change was measured are listed in table 4.

TABLE 4  
Change in Weight During Heating

Run	Change of Wt(gms)	Electrode loss(gms)	Amount fused(gms)	% Boron
7	0	0.9	3.2	96.4
8	3.0	1.8	6.2	97.4
9	2.0	0.4	3.2	—
11	-1.1	—	13.0	96.9
14	0.8	0.4	6.7	—
15	-0.3	0	24.0	97.4
16	-1.5	0	15.1	—

Runs seven and eight were made using 96.3% brick. The change in weight was also affected by loss due to flaking during heating and handling. The gain was only found during short runs, where a small amount of material was made.



In the other cases, the gain was apparently offset by the loss of magnesium and boron. A gain or loss in weight had no correlation to the purity of the product. The electrode loss seemed to be a partial villain, but it could not account for a large part of the gain.

The slight gain shown in table 2 for runs eight and twenty-nine indicate that another material besides tungsten was causing downgrading of the product. Air and water vapor were probably responsible. A small amount of air and water vapor is in the brick, but the quantities are insignificant. The asbestos gaskets, residue from previous runs, the copper wall, and the hydrogen and helium supplies could have all contributed moisture. The scrubber for the exit gases also presented a potential source of water if gas flow through the scrubber became too low. The pressure in the furnace usually would not drop to over twenty-four inches of vacuum during initial air removal, and the remaining air had to be removed by dilution with helium. A small amount of air was probably present at the start of the heating operation.

Bricks not directly heated by the arc, had a negligible weight change. On the hot areas of the brick being heated, but not in the cup, a black glassy layer, characteristic of  $B_2O_3$ , was formed. The edge of this layer adjacent to the cup analyzed 93.5% boron compared to 96.2% for the cup in run six. In a few runs a scum was formed over the cup which separated from the rest of the brick while cooling. The amount was too small for analysis, however.

Inside the heated brick, next to the cup, a black layer of sintered material was formed. This was analyzed for some earlier runs

and tabulated in table 5.

TABLE 5  
Comparison of Sintered and Fused Layers

Run	Sintered (% B)	Fused (% B)	Start (% B)	gms sintered	gms fused
4	82.8	86.8	91.4	1.7	1.2
6	93.5	96.2	91.4	2.5	8.2
7	95.5	96.4	96.3	5.4	3.2
8	95.8	97.4	96.3	4.7	6.2

It was expected that some magnesium would be distilled from this area and the sintered appearance seemed to indicate that this was so. However, only in run six did this appear to be the case. Examination of the cup did not show any indication of precipitation of oxides or other impurities from the melt. The poor results of run four were attributed to a small air leak.

Some of the fused product from run fifteen was remelted, but the purity dropped from 97.4% to 97.3% boron.

#### INCREASED PRODUCTION

In early experiments the highest yield of crystalline boron was not over 11.8 grams of boron per run. Separation of the cup from the rest of the brick was difficult and time consuming. The need for a continuous or large batch method was clearly indicated. The following approaches were tried:

1. Increasing the area heated.
2. Increasing the depth of penetration.

3. Removal of the boron while still in the molten state.

4. Addition of raw material to the cup during the run.

To increase the area of the brick that could be heated it was necessary to move either the electrodes or the brick. Coordinated movement of the electrodes and the gas supply was eliminated by initial furnace design. The movement of the sample was easily accomplished, however, by rotating the sample on an off-centered stand. Thirteen grams and a purity of 96.9% were obtained by this method. Considerable splattering was caused by reheating of the crystalline material. The boron melted fairly rapidly, but penetration was poor and separation was difficult for the amount of boron that was obtained. Penetration could have been increased by slower rotation.

Bigger electrodes and a higher power source would be used in a larger furnace, but they would not overcome the basic problem of the high heat insulating properties of the boron brick. By heating the brick to a temperature at which it became a fair conductor of electricity and then passing a current through it, melting of the boron was obtained. When two tungsten electrodes were used to make the electrical contact, a great deal of contamination resulted. The product analyzed 67.7% boron. When electrical connection was made by a single copper rod at the bottom of the brick, the rod melted and the sample fell apart.

When the brick was pressed on a five pronged copper stand and heated by the usual method until a cup was formed, one electrode could be withdrawn and electrical connection made between the brick and vertical feeding positions. Pellets did not melt to any great



and the copper jacket of the water-cooled electrode. A small greenish arc could briefly be maintained between the copper jacket and the brick. The bottom part of the brick melted next to the stand, especially around the prongs. The prongs melted slightly also, but the copper did not contaminate the boron. The melt at the bottom analyzed 97.3% boron. The top of the brick had copper on the surface. After cleaning off the copper with nitric acid, the top section was found to be 95.6% boron. Narrow streaks of crystalline boron connected the bottom and top sections. The brick was  $1\frac{1}{2}$  inches thick and an average current of fifty amperes was drawn. The prong stuck into the brick about  $\frac{3}{8}$  of an inch and were made of  $\frac{3}{16}$  inch copper tubing. The actual electrical conduction phase of the run was only about four minutes long.

Various arrangements of holes in the brick were tried in order to get the molten boron to collect in one area and to remove it from the melting area. This method was unsuccessful because the boron could not be heated hot enough for reasonable flow. Flow was observed only during the feeding runs where some of the pellets near the top of the cup overcame their surface tension and flowed to the bottom of the cup.

Cylinders from  $\frac{1}{4}$  to 1 inch in diameter were tried in an effort to determine whether the boron would run down the sides of the cylinder when melted. Here again, the boron stayed in place and did not flow.

Feeding pellets into the cup was accomplished in both horizontal and vertical feeding positions. Pellets did not melt to any great

extent because the heat vented out of the feed hole at the top of the cup. With a boron lid on the hole, except during feeding, this trouble could have been eliminated. There was not sufficient room in the furnace to try this. Vertical feeding was quite satisfactory. However, it was rather slow and the brick had to stay out of the arc flame while loading the cup. Only a small number of pellets could be fed at one time because of the small penetration power of the arc. About twenty-eight grams were prepared by feeding, though this could be increased by a longer run.

One disadvantage to the feeding process was that the purity obtained was not as good as other methods. For run twenty-nine table 3 shows that a considerable amount of boron was lost and that there was contamination by the entering pellets. For run twenty-eight the cup analyzed 96.7% boron and the pellets 96.9% boron.

#### THE ATOMIC HYDROGEN FURNACE

Power up to three kilowatts could be supplied to the arc, but a steady flame was obtained only in a region below two kilowatts. The power-voltage relationships have already been given in figure 10. The lower power limitations at low voltage were caused by a limitation of seventy amperes of current flow to prevent melting of the electrodes.

Electrode loss is tabulated in table 6.



TABLE 6

## Electrode Losses

<u>Run No</u>	<u>Time (min)</u>	<u>Anode (gms)</u>	<u>Cathode (gms)</u>	<u>Total (gms)</u>
A. Air-cooled				
4	15	1.8	0	1.8
5	5	0.9	0	0.9
6	5	0.4	0.4	0.8
7	6	0.9	0	0.9
8	4	1.0	0.8	1.8
9	4	1.3	0	1.3
B. Water-cooled				
14	5	0.1	0.3	0.4
25	15	0	0.1	0.1
26	18	0.1	0.2	0.3
27	60	0.1	0.1	0.2
28	35	0.1	0.3	0.4
29	40	0.1	0.5	0.6
30	60	0.1	0.3	0.4

Electrode loss is obviously reduced by water-cooling. In general, the loss increased with arc time, but was greatly influenced by other factors, such as type of flame and spattering. The water-cooled electrode jacket condensed the furnace vapors and was coated with a glossy layer which tended to drop off the end of the jacket.

Condensation of furnace vapors upon the observation window caused considerable trouble. A watch glass between the furnace and the window did little to prevent fogging. A copper plate attached to the slide was effective in blocking vapors, but naturally reduced the area of visibility. During horizontal operations, fogging was not a problem. Most condensation occurred in the furnace above the bricks.



The possible contribution of water vapor by the asbestos gaskets has previously been discussed.

Run twenty-six used only a helium atmosphere. Crystalline boron was formed and cup size was slightly larger in area than hydrogen runs. However, penetration was poor and there was little visible melting. The purity obtained was 97.0% boron.

#### PHYSICAL PROPERTIES

The bulk density of the fused layer was determined for a number of runs and these densities are tabulated in table 7.

TABLE 7

Bulk Density at 26°C

<u>Run</u>	<u>Density</u>
15	2.25 gm./cc.
23	2.25
24	2.40
26	2.35
28	2.25
29	2.20
31	1.95
32	2.05

Runs thirty-one and thirty-two were made from 96.3% starting material. Apparently, the purer material had a higher melting point and did not become completely molten.

#### ELECTRICAL CONDUCTIVITY

The results of the electrical conductivity temperature experiments are plotted in figure 20. The lines appear to be too straight

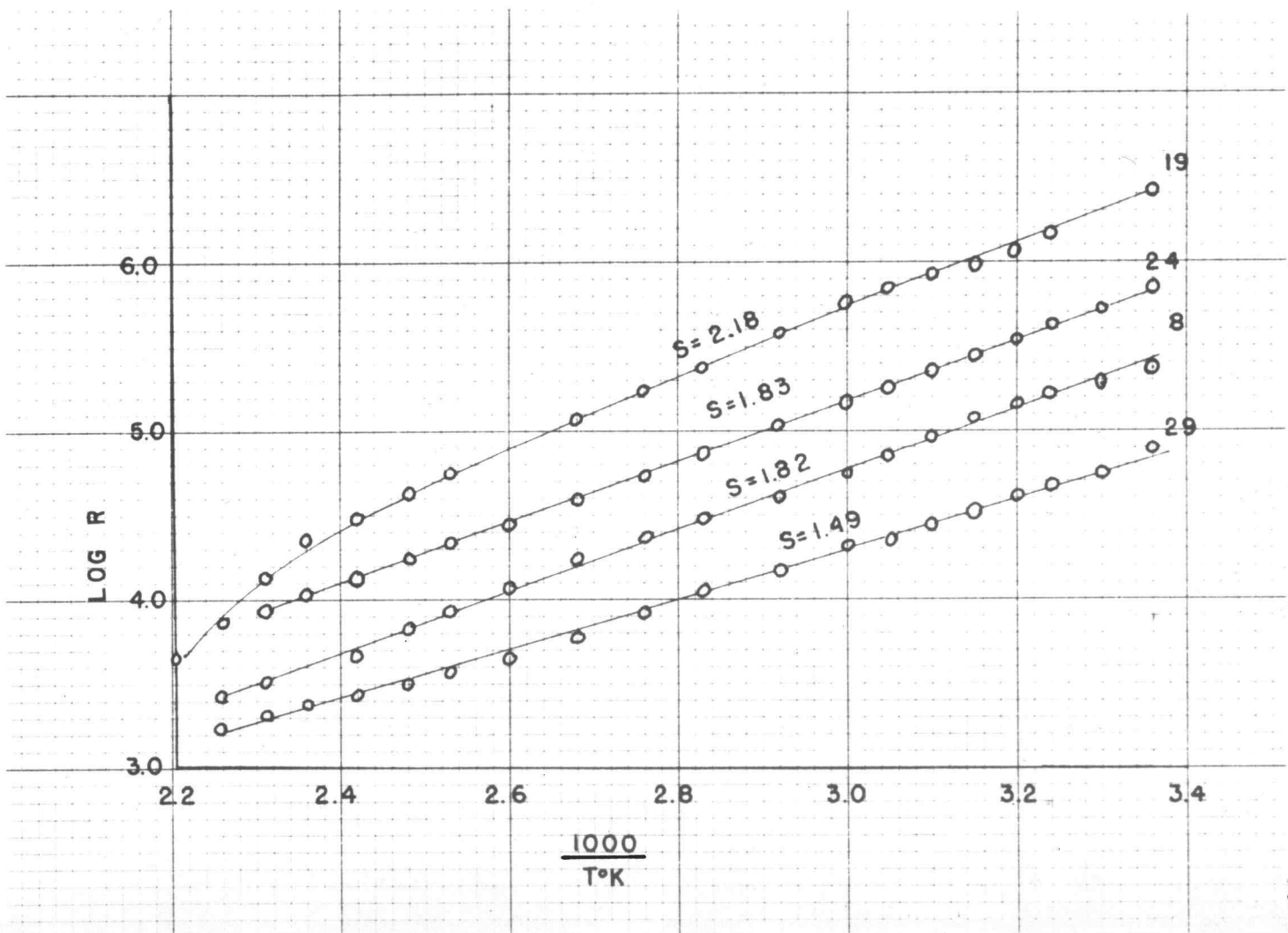


Figure 20. Plot of the log of resistance versus the reciprocal of temperature for samples 8, 19, 24, and 29.

to compare favorably with those of other observers as shown in figure 1. There is fair agreement with these observers up to 100°C., but at 165°C. there is little agreement with anyone. Table 8 compares the values of  $b$  of equation 11.

TABLE 8  
Values of  $b$  from  
Figures 1 and 20

<u>No.</u>	<u>30°C.</u>	<u>100°C.</u>	<u>160°C.</u>
A		0.0018	0.0026
B	<u>0.0016</u>	0.0017	0.0029
C		?	0.0028
D	<u>0.0015</u>	0.0022	
8	0.0018	0.0018	<u>0.0018</u>
19	0.0019	0.0022	0.0038
24	0.0018	0.0018	0.0018
29	0.0015	0.0015	0.0014

There seems to be no simple correlation between  $b$  values and the percentage of impurities in the runs selected. The failure to get a greater slope might be caused by failure to reach temperature equilibrium in the sample before measurements were taken.

#### CRYSTALS

The fused layer had a very high metallic luster, and in the bulk form appeared to be silver colored. When ground to a powder, it became quite black. No x-ray diffraction studies have been made of the fused layer. However, its properties seemed consistent with those reported for crystalline boron. Needle shaped formations with distinct plains of cleavage were observed in some of the later runs. These



were obtained in one case by slowly reducing the power input to the arc. Examination of these formations failed to show a definite crystal form.

#### ERRORS

The method used for determining boron percentages is considered the best available by the Pacific Coast Borax Company. They did not give the limits of error for their analysis but the volumetric method employed gives an error of less than 0.1%. They took great care to exclude carbon dioxide from their solutions, a probable source of error in many older claims of 100% boron. Weintraub reported obtaining 100.4% pure boron (19, p. 165), for example.

The tungsten and magnesium determinations were not extremely accurate because of the low concentrations involved. It is estimated that the residues from the ignitions were accurate to .0005 milligrams. In the determination of 0.20% tungsten, the error would be approximately 38%. For magnesium it would be considerably less than that.

Errors in bulk density measurements were introduced by tiny air bubbles adhering to the sample. Values were reproducible within 1% using the same samples. The cup is not uniform in density and the most dense portions were chosen for this determination.

The errors inherent in the electrical conductivity experiments have already been discussed.

## SUMMARY OF RESULTS

The heating of amorphous boron in the atomic hydrogen furnace produced the following changes:

1. Almost complete removal of magnesium.
2. Very little removal of the "other" impurities, such as oxygen.
3. Vaporization of a small amount of boron.
4. Contamination by a slight amount of tungsten.
5. Conversion of amorphous boron to the crystalline state.

There was no advantage in heating the brick for more than a few minutes as removal of magnesium was almost instantaneous once the proper temperature was reached. Continued heating of the sample resulted in a decrease in purity. The furnace atmosphere had some oxygen or water vapor present, but this seemed to form products away from the area of the cup. There was no advantage to starting with the higher grade material as a more dense product of equal purity was obtained with boron that was initially 91.4% pure.

The bricks could be heated by the tungsten arc without the aid of hydrogen. The temperatures were not as high as with the atomic hydrogen arc, but comparable purity was obtained using helium only.

The amount of crystalline boron was small, but this could be increased by feeding pellets into the cup. The experiments indicated that the feeding could be most satisfactorily done in a cup when the furnace was in a horizontal position. Feeding with the furnace in a vertical position was accomplished also. The horizontal method seemed



to have the advantage of higher temperatures, caused by better insulation and absence of up-draft. There were negligible boron losses in this position.

Boron was melted by its resistance to electric current. Magnesium could be distilled off by this method, but the other impurities were not affected. Tungsten electrodes were found unsatisfactory for effecting electrical connections because it severely contaminated the melt. Copper caused no contamination, but melted slightly.

Power output was limited by the electrode size and the voltage available. It appeared that the experiments were conducted at the lower end of the liquid range; and if greater power was available, the melted boron would be considerably more mobile.

Electrical conductivity versus temperature relationships showed no direct correlation with the concentration of impurities.



## SUGGESTIONS FOR FURTHER WORK

The use of an atomic hydrogen furnace for the purification of boron has little commercial potential unless higher temperatures can be obtained. Experiments indicate that the liquid range of boron goes at least to the  $2800^{\circ}\text{C}$ . recorded by Quill (12, p. 59) and possibly to the  $3500^{\circ}\text{C}$ . recorded by Scott (14, p. 162). At such temperatures, decomposition of some of the "other" impurities is probably or could be removed by slag. It is suggested that a larger furnace be built incorporating such refinements as two water-cooled electrodes, "o" rings, mercury seals, and a non-aqueous scrubbing system.

Results indicate that a large quantity of fused material could be obtained by passing an electric current through amorphous boron. This is similar to Weintraub's single electrode method, (19, pp. 110-15) except that electrical conduction through the brick instead of through the arc would be the major concern. This operation would have to be conducted in a water-cooled, copper container in an inert atmosphere. Since temperatures would be limited, elimination of impurities other than magnesium would have to be made by other means.

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## APPENDIX

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TABLE 9

Temperature versus Resistance  
Data for Figure 1

1. Shaw (15, p. 115) for crystal 13.

$T^{\circ}\text{K}$	$\frac{1000}{T_k}$	$R_{16}$	$\log R$
345	2.90	$9.43 \times 10^7$	7.97
385	2.60	$1.81 \times 10^7$	7.26
469	2.13	$9.50 \times 10^5$	5.98
532	1.88	$1.76 \times 10^5$	5.25

2. Freymann (3, p. 1109). Sample 5 mm. long, 1.5 mm. in diameter.

$T^{\circ}\text{K}$	$\frac{1000}{T_k}$	$R$	$\log R$
278	3.60	$1.20 \times 10^5$	5.08
288	3.47	$9.60 \times 10^4$	4.98
298	3.36	$7.12 \times 10^4$	4.85
308	3.24	$5.03 \times 10^4$	4.70
318	3.14	$3.46 \times 10^4$	4.53
328	3.05	$2.33 \times 10^4$	4.37
338	2.96	$1.66 \times 10^4$	4.22
348	2.87	$1.10 \times 10^4$	4.04
358	2.79	$7.2 \times 10^3$	3.86
368	2.72	$5.2 \times 10^3$	3.72
378	2.64	$3.3 \times 10^3$	3.52

3. Weintraub - crystal 1 (19, pp. 165-184).

298	3.36	$7.7 \times 10^5$	5.89
308	3.24	$5.0 \times 10^5$	5.70
318	3.14	$3.4 \times 10^5$	5.53
328	3.05	$2.3 \times 10^5$	5.36
338	2.96	$1.90 \times 10^5$	5.28
348	2.87	$1.26 \times 10^5$	5.10
358	2.79	$9.4 \times 10^4$	4.97
368	2.72	$7.2 \times 10^4$	4.86
378	2.64	$5.4 \times 10^4$	4.73
388	2.58	$4.4 \times 10^4$	4.64
398	2.51	$3.4 \times 10^4$	4.53
408	2.45	$2.6 \times 10^4$	4.41
418	2.39	$1.98 \times 10^4$	4.30

TABLE 9 (Cont'd.)

428	2.34	$1.60 \times 10^4$	4.20
438	2.28	$1.25 \times 10^4$	4.10
448	2.23	$9.9 \times 10^3$	3.00
458	2.18	$7.0 \times 10^3$	3.84
468	2.13	$4.5 \times 10^3$	3.65
478	2.09	$3.3 \times 10^3$	3.52
488	2.05	$2.3 \times 10^3$	3.36
498	2.01	$1.7 \times 10^3$	3.23

## 4. Weintraub - crystal 2 (19, pp. 165-184).

308	3.24	$3.3 \times 10^5$	5.52
318	3.14	$1.91 \times 10^5$	5.28
328	3.05	$1.04 \times 10^5$	5.02
338	2.96	$8.2 \times 10^4$	4.91
348	2.87	$5.0 \times 10^4$	4.70
358	2.79	$3.8 \times 10^4$	4.58
368	2.72	$2.9 \times 10^4$	4.46
378	2.64	$2.2 \times 10^4$	4.34
388	2.58	$1.71 \times 10^4$	4.23
398	2.51	$1.35 \times 10^4$	4.13
408	2.45	$1.04 \times 10^4$	4.02
418	2.39	$8.4 \times 10^3$	3.92
428	2.34	$6.9 \times 10^3$	3.84
438	2.28	$5.4 \times 10^3$	3.73
448	2.23	$3.8 \times 10^3$	3.58
458	2.18	$2.7 \times 10^3$	3.43
468	2.13	$1.80 \times 10^3$	3.25
478	2.09	$1.47 \times 10^3$	3.17
488	2.05	$1.16 \times 10^3$	3.06
498	2.01	$8.5 \times 10^2$	2.93

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TABLE 10

Temperature versus Resistance  
Data for Figure 19

## 1. Sample 8

<u>1000</u> T°K	T°K	$\mu$ Amp Up	$\mu$ Amp down	Volt	R	Log R
3.36	298	42	—	10.1	$2.4 \times 10^5$	5.38
3.30	303	51	39	10.1	$1.96 \times 10^5$	5.29
3.24	308	58	49	10.1	1.72	5.23
3.20	313	67	58	10.1	1.49	5.17
3.15	318	37	31	4.5	1.22	5.09
3.10	323	48	40	4.5	$9.4 \times 10^4$	4.97
3.05	328	65	48	4.5	6.9	4.84
3.00	333	81	62	4.5	5.6	4.75
2.92	343	40	35	1.6	4.0	4.60
2.83	353	52	45	1.6	3.1	4.49
2.76	363	66	63	1.6	2.4	4.38
2.68	373	94	92	1.6	1.70	4.23
2.61	383	42	42	0.50	1.19	4.08
2.55	393	58	60	0.50	$8.6 \times 10^3$	3.93
2.48	403	75	77	0.50	6.7	3.83
2.42	413	38	37	0.18	4.7	3.67
2.36	423	—	42	0.18	—	—
2.31	433	54	51	0.18	3.3	3.52
2.26	443	67	65	0.18	2.7	3.43

## 2. Sample 29

298	19	—	1.5	$7.9 \times 10^4$	4.90
303	26	25	1.5	5.8	4.76
308	31	30	1.5	4.8	4.68
313	37	36	1.5	4.1	4.61
318	43	40	1.5	3.5	4.51
323	53	49	1.5	2.8	4.45
328	65	59	1.5	2.3	4.36
333	72	68	1.5	2.1	4.32
343	38	35	0.56	1.47	4.17
353	51	45	0.56	1.10	4.04
363	22	19	0.18	$8.2 \times 10^3$	3.91
373	30	26	0.18	6.0	3.78
383	39	35	0.18	4.6	3.66
393	47	44	0.18	3.8	3.58
403	57	53	0.18	3.2	3.50
413	67	60	0.18	2.7	3.43
423	75	70	0.18	2.4	3.38

TABLE 10 (Cont'd.)

433	86	83	0.18	2.09	3.32
443	100	97	0.18	1.80	3.25

## 3. Sample 24

298	14	—	10	$7.2 \times 10^5$	5.86
303	19	18	10	5.3	5.72
308	23	22	10	4.3	5.63
313	29	27	10	3.5	5.54
318	35	32	10	2.8	5.45
323	43	39	10	2.3	5.36
328	54	48	10	1.85	5.27
333	65	60	10	1.54	5.19
343	15	13	1.6	1.07	5.03
353	21	18	1.6	$7.6 \times 10^4$	4.87
363	30	26	1.6	5.3	4.72
373	41	35	1.6	3.9	4.59
383	56	50	1.6	2.9	4.46
393	72	63	1.6	2.2	4.34
403	90	80	1.6	1.78	4.25
413	46	40	0.6	1.30	4.11
423	54	49	0.6	1.11	4.04
433	69	68	0.6	$8.6 \times 10^3$	3.93

## 4. Sample 19

298	3.7	10	$2.7 \times 10^6$	6.43
303	—	10	—	—
308	6.8	10	1.47	6.17
313	8.8	10	1.14	6.06
318	10.2	10	$9.8 \times 10^5$	5.99
323	11.8	10	8.5	5.93
328	14	10	7.1	5.85
333	17	10	5.9	5.77
343	26	10	3.8	5.58
353	41	10	2.4	5.38
363	58	10	1.7	5.23
373	83	10	1.2	5.08
393	86	5	$5.8 \times 10^4$	4.76
403	68	2.8	4.3	4.63
413	49	1.5	3.1	4.49
423	66	1.5	2.3	4.36
433	74	1.0	1.35	4.13
443	53	0.5	$9.4 \times 10^3$	3.97
453	22	0.1	$4.5 \times 10^2$	3.65



## PROCEDURE USED FOR TUNGSTEN DETERMINATION

1. Approximately 0.5 grams of the boron sample was ground to a fine powder in an iron crucible.
2. The powder was dried at  $120^{\circ}\text{C}$ . for 30 minutes.
3. 8 grams of sodium carbonate and 2 grams of sodium peroxide were mixed with a weighed amount of boron powder.
4. The mixture was placed in a nickle crucible and covered with a layer of sodium carbonate.
5. The crucible was placed over a gas blow torch; the temperature was slowly increased until fusion occurred; and then this temperature maintained for about an hour.
6. After the crucible had cooled, the cake was removed, washed, and made acid with concentrated hydrochloric acid.
7. The mixture was boiled, digested in cinchonine and filter paper, and then filtered.
8. The filtrate was treated with hydrogen sulfide and ammonium hydroxide and the filtrate from that used for the magnesium determination.
9. The residue from number 7 was treated with ammonia and again filtered and the filtrate boiled down to 10 milliliters.
10. After being boiled with nitric and hydrochloric acids, it was digested with cinchonine and filtered.
11. The residue and filter paper were ignited in a platinum crucible, and treated with hydrofloric acid.



12. 79.31 times the weight of the residue divided by the weight of the sample gave the percentage of tungsten. Correction for the weight of the filter paper ash was necessary (0.0005 gms).
13. This method was based on that of Scott (14, pp. 1005-10).

#### PROCEDURE USED FOR MAGNESIUM DETERMINATION

1. To the filtrate from number 8 of the tungsten determination, 2 milliliters of disodium phosphate solution was added and the mixture allowed to stand.
2. The solution was then filtered, washed, and the residue dissolved in hydrochloric acid.
3. The dissolved residue was made basic by adding ammonia and disodium phosphate was again added.
4. After it was allowed to stand for several hours, the mixture was filtered and the filter paper and residue ignited. The weight of the residue times 21.84 divided by the weight of the sample gave the percentage of magnesium.
5. This method was based on that of Scott (14, pp. 532-4).

## OPERATING PROCEDURE

## I. Preparation of sample

- A. Weigh out desired amount of amorphous boron. 62 gms makes a brick  $2 \times 2 \times 1$  inches.
- B. Press to the desired shape in the hydraulic press.
- C. Place brick in vacuum oven and heat in a vacuum at  $200^{\circ}\text{C}$ . for several hours.
- D. Cool in a dessicator.

## II. Preparing for run

- A. Weigh electrodes and install.
- B. Place sample in furnace with electrodes withdrawn.
- C. Position electrodes and brick.
- D. Place top flange on furnace and position hydrogen tube.
- E. Bolt flange.
- F. Fill drying bulbs.
- G. Take suction with vacuum and obtain vacuum of 20 inches or better.
- H. Fill with helium, shut off vacuum pump and return pressure to slightly above atmospheric with He.
- I. Flush with He for about 5 minutes.
- J. Turn on water supply to water-cooled electrode.
- K. Check electrical connection. Welders should be set on minimum current and low voltage.
- L. Check position of electrodes, tube, and sample

### III. Run

- A. Open windows in room.
- B. With electrodes separated, start welders together.
- C. Check voltage to make sure that welders are correctly alined.  
Shut off immediately if there is any current flow.
- D. Touch electrodes and draw arc.
- E. Adjust hydrogen regulator to give about one pound pressure at a non-flow condition.
- F. Emit hydrogen and slowly bring up voltage, trying to keep current below 50 amperes.
- G. During the run, constantly check pressure, balloon size, water tubes, and bubblers for signs of irregular behavior.
- H. When a steady spark is maintained, slowly bring bricks into position, avoiding spattering.
- I. When desired melting is accomplished, slowly reduce the voltage until the arc goes out.
- J. Turn off hydrogen feed and exhaust line. Fill helium reservoir and keep a positive pressure in the furnace during cooling. Keep a partial flow of water going through the electrode.
- K. When cooling is complete, shut off helium balloon and open furnace and remove bricks and electrodes, if desired.

### IV. Cleaning

- A. Normally the furnace can be cleaned by scraping the sides and pulling the material out with a vacuum cleaner.



- B. The window can be cleaned with a damp cloth.
- C. The electrodes can be wiped off with a damp cloth or acetone.
- D. Extensive cleaning is occasionally necessary and involves a complete washing.

# ADDITIONAL DATA

Run	Sum of Arc times (min)	Longest continous arc	Electrode Loss (grams) Anode Cathode		Sample weight change (grams)	Grams of fused product	% boron in fused product	Key
1	20	5	--	--	--	2.2	96.3	1,3,5
2	5	3	--	--	--	0.7	--	1,3,5,8
3	4	4	--	--	--	0.1	--	1,3,5,8
4	15	10	1.8	0	--	1.2	86.2	1,3,5,7,8
5	5	4	0.9	0	--	11.8	96.5	1,3,5
6	5	5	0.4	0.4	--	8.2	96.2	1,3,5,9
7	6	5	0.9	0	0	3.2	96.4	2,3,5
8	4	4	1.0	0.8	3.0	6.2	97.4	2,3,5
9	4	2	1.3	0	2.0	3.2	--	1,3,5
10	45	30	--	--	--	--	--	1,3,5,8
11	22	15	--	--	1.1	13.0	96.9	1,3,5,11
12	4	2	--	--	--	--	--	1,3,5,12
13	10	10	--	0.2	--	4.4	--	1,4,5
14	5	5	0.1	0.3	0.8	6.7	--	1,4,6,13
15	15	15	0.0	0.0	0.3	24.0	97.4	1,4,6
16	15	12	0.0	0.0	1.5	15.1	--	1,4,6,10
17	35	12	0.0	0.4	--	--	--	1,4,6
18	35	10	0.0	0.2	--	1.5	--	1,4,6,14
19	45	45	0.1	0.2	--	14.5	96.9	1,4,6,14
20	20	5	0.1	0.6	--	--	--	1,4,6,14
21	45	10	0.0	0.3	--	13.5	--	1,4,6,14
22	40	15	0.0	0.0	--	5.5	--	1,4,6,14
23	17	10	0.2	0.1	--	--	67.7	1,4,5,10
24	15	10	0.3	0.2	--	18.6	95.6 97.3	1,4,5,12
25	15	15	0	0.1	--	4.8	--	1,4,5,15
26	18	15	0.1	0.2	--	8.4	97.0	1,4,5,15
27	60	20	0.1	0.1	--	4.0	--	1,4,5,15



# ADDITIONAL DATA (Cont'd.)

28	35	10	0.1	0.3	--	11.0	86.7	96.9	1,4,5,15
29	40	25	0.1	0.5	--	23.9	96.3		1,4,5,15
30	60	35	0.1	0.3	--	28.8	96.4		1,4,5,15
31	18	15	0.1	0.3	--	11.0	97.3		2,4,5,15
32	15	15	--	--	--	--	97.3		4,5,15

## KEY

1. 91.4% boron
2. 97.4% boron
3. air-cooled electrode
4. water-cooled electrode
5. vertical furnace
6. horizontal furnace
7. air leak
8. little fusion
9. cathode fell on brick
10. cylindrical shapes and taps
11. brick rotated
12. electrical conduction through boron
13. feeder (figure 13)
14. feeder (figure 15)
15. feeder (figures 16 & 17)