

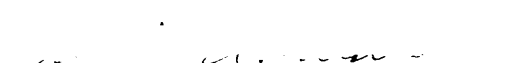
THE ELECTROCHEMICAL PRODUCTION  
OF BORON

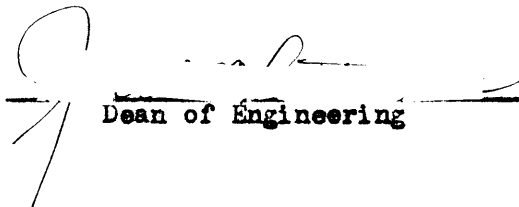
by

Richard S. Tinsley

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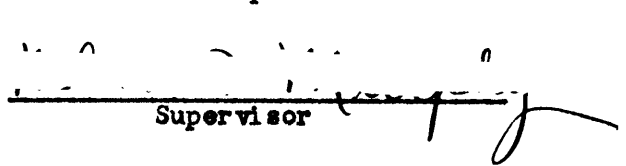
APPROVED:

  
\_\_\_\_\_  
Director of Graduate Studies

  
\_\_\_\_\_  
Dean of Engineering

APPROVED:

  
\_\_\_\_\_  
Head of Department

  
\_\_\_\_\_  
Supervisor

1953

Blacksburg, Virginia

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## I. INTRODUCTION

Boron does not exist in a free state in nature. Like silicon, boron is always found in nature combined with oxygen, usually in borate ions, which are associated with cations of the more active and common metals. Though practically insoluble in acids and almost as hard as silicon carbide, the free element has been put to no practical use prior to the last decade and is still used only in small quantities.

Elemental boron has a number of properties that make it potentially of great value in many fields. For example, its exceptionally high specific resistance at room temperature drops rapidly as the temperature increases, a characteristic that lends itself to extensive use in various types of electrical apparatus. Boron is a powerful deoxidizer and has a high affinity for various gases. This makes it highly useful in metallurgical fields, as a degassing agent in the production of dense castings. It is also practically insoluble in copper, being quite a unique metal in this respect, and is therefore probably the best agent known for the treatment of molten copper to remove occluded gases.

Although it is stated in the literature that boron oxide may be reduced by heating in the presence of magnesium to produce magnesium oxide and free boron, the reaction generally carries the boron only to a suboxide,  $B_2O$ . Where aluminum is employed in place of magnesium, a boride of aluminum is the result. The only method of producing

boron, of sufficient purity to be suitable for direct use in the production of boron compounds, involves the reduction of boron trichloride with hydrogen in a high voltage arc.

Many electrolytic processes, that have proved successful in producing other metals from their salts, have been applied to the production of boron from its salts. They have either failed to operate at all for their intended purpose, have yielded a product too impure for practical use, or have involved such serious operating difficulties as to be entirely impractical as commercial processes. The only methods reported commercially successful are the electrolysis of a fused mixture of potassium chloride-potassium fluoborate or a fused mixture of potassium chloride-potassium fluoborate-boric oxide.

The purpose of this investigation is to study electrolytic methods of producing boron from molten mixtures containing boric oxide.

## II. LITERATURE REVIEW

It is the purpose of this literature review to survey the previous work performed in electro-metallurgy and particularly to electrolytic methods of producing elemental boron. In addition, the literature concerning the history, uses, physical and chemical properties of boron has been surveyed.

### History of Boron

Boron does not exist in a free state in nature<sup>(42)</sup>. Like silicon, boron is always found in nature combined with oxygen, usually in borate ions, which are associated with cations of the more active and common metals. Records show that as long ago as the 16th century, borates, as a source of boron compounds, were exported to Europe from Central Asia through Constantinople and Venice.

Discovery. The element boron was isolated in 1808 by Gay-Lussac and Thenard<sup>(22)</sup>, who reduced boron oxide,  $B_2O_3$ , with potassium by heating in an iron tube. Sir Humphry Davy<sup>(15)</sup> in the preceding year, had independently obtained a dark-colored, combustible mass from the electrolysis of moist boric acid. Later, in a manner analogous to that of Gay-Lussac and Thenard, he obtained the same product. Davy named this new element "boron."

Occurance. Boron does not occur abundantly on the earth. F. W. Clarke and H. S. Washington<sup>(11)</sup> estimated that boron makes up 0.001 per cent of the earth's crust. This element occurs in the form of

boric acid and borates. Deposits of boron compounds are principally found where the salt-laden waters of lakes and inland seas have dried up.

Sources. Today the most important sources of boron are the minerals kernite,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$  and borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . These minerals<sup>(30)</sup> are found mainly in the Mojave Desert in California, from which, 50 per cent of the world's supply of boron minerals are produced. Countries having smaller deposits of boron minerals are Tibet, Italy, Russia, Turkey, Canada, and Germany.

#### Physical Properties of Boron

Boron<sup>(27)</sup>, atomic number 5, atomic weight 10.82, belongs to Group III in the periodic table. Boron is the only element in Group III that is nonmetallic in behavior. It has three valence electrons, and is the only element with less than four electrons in its outermost shell that is not a metal. This is due to the very small size of its atoms. Boron occurs in two forms. The crystalline form is a shiny, brittle, black solid that is extraordinarily hard. The crystal structure has not been determined but it is likely that it involves a compact giant, three-dimensional network of boron atoms strongly bonded together. A second form is a greenish-yellow powder. Boron is tasteless and odorless. It is a mixture of at least two isotopes with mass numbers of 10 and 11.

Physical Constants. Due to the difficulty in obtaining pure elemental boron and the wide disagreement of the literature the

following physical constants<sup>(27,38)</sup> can be considered only approximate: melting point 2300 °C; boiling point 2550 °C; specific gravity 2.3 (crystalline), 1.73 (amorphous); hardness 9 1/2 Mohs' (crystalline); specific heat 0.254 at 0 °C; heat of combustion 14.42 calories per gram.

Electrical Conductivity. The electrical conductivity of fused boron is one of its most interesting properties. At ordinary temperatures boron is a very poor conductor, but its conductivity rises with increase in temperature. Between 23 °C and dull red, the conductivity<sup>(38)</sup> of fused boron increases 2,000,000 times, a rate of increase unknown in any other element. Above dull red the conductivity still continues to increase and at bright red heat boron is a relatively good conductor. Moisson<sup>(39)</sup> found the electrical conductivity of powdered boron to be  $0.125 \times 10^{-6}$  mhos per cubic centimeter at 0 °C.

Electrical Resistance. Weintraub<sup>(43)</sup> found that the electrical resistance of boron dropped from 5,620,000 ohms at 27 °C to 5 ohms at 560 °C and was about  $10^{12}$  times that of copper at 23 °C. In this respect, boron resembles carbon, but unlike carbon, boron has an abnormally high negative temperature coefficient. Boron behaves, however, as a relatively good conductor when moderately high voltages are applied, on account of the change in resistance which takes place automatically and rapidly due to the heating of the boron by the current passing through it.

### Chemical Properties of Boron

Boron<sup>(38)</sup> is insoluble in water, alcohols, ethers, and solutions of caustic alkalis. It is soluble in nitric and sulfuric acids, and in most molten metals, such as aluminum, calcium, and magnesium. It is unaffected by air at ordinary temperatures and does not react with hydrogen, even when heated to red heat.

Effect of Temperature. The chemical activity of boron is greatly increased by heating (27, 38). Air attacks boron at 300 °C and the nitride, BN, and the oxide B<sub>2</sub>O<sub>3</sub> are formed. It reacts with nitrogen, iron, aluminum, bromine, sulfur, sodium carbonate, potassium carbonate, and platinum at higher temperatures. Boron reduces sulfur dioxide to sulfur at 600 °C, carbon dioxide to carbon at 1200 °C, silica to silicon, phosphorous pentoxide to phosphorus and antimony oxide to antimony at high temperatures. Carbon does not combine directly with boron unless heated in an electric arc. At electric furnace temperatures boron is insoluble in copper, tin, and silver. There is no reaction when boron is heated with mercury.

### Uses of Boron

Though practically insoluble in acids, and almost as hard as silicon carbide, the free element has been put to no practical use prior to the last decade. Boron is used today mainly in the metal industry. Due to new developments in the use of boron as a powerful

constituent of engineering and mechanical steels, the demand has increased for this element five-fold in a period of two years.

Hardenability of Steel. Boron increases the hardenability of steels<sup>(24)</sup> when used in small amounts. The term "hardenability" refers to the depth to which a steel will harden when quenched. While a small section of steel may be hardened throughout, the interior of a large section remains comparatively soft after quenching. The effect of boron is to lower the rate of cooling necessary to harden the steel, thereby increasing the depth of hardening. Addition of as little as 0.0004 to 0.0014 per cent boron has given as much as a 75 per cent increase in the hardenability of the steel.

Effect on Alloying Elements. The use of boron amplifies the effect of alloying elements used in steels. It lessens the amount of the element needed to give required results. Not only does this ease the shortage of alloying elements, but the equivalent boron steel<sup>(2)</sup> is very often cheaper than the conventional types of steel.

Production of Copper. Boron<sup>(27)</sup> is extremely reactive at high temperatures, particularly with the elements oxygen and nitrogen; it is used as a deoxidizer and degasifier in metallurgical reactions. Boron is insoluble in copper<sup>(12, 13)</sup>, being quite a unique metal in this respect and is therefore the best agent known for the removal of occluded gases from molten copper during the manufacturing of copper products.

Other Metallurgical Uses. Certain alloys<sup>(2)</sup> used for cutting tools and hard-facings contain boron in substantial percentages.

Boron acts as an accelerator<sup>(14)</sup> of the annealing time of malleable iron castings. Boron<sup>(27)</sup> permits the malleabilization of irons containing an amount of stray chromium otherwise making them unannealable. Boron is also used to refine the grain of aluminum castings.

### Preparations of Boron

Many attempts have been made to prepare boron since Gay-Lussac and Thenard first isolated it in 1808. Investigators have used many different methods and materials. Methods used vary from electrolysis to chemical replacement and raw materials from boric oxide to potassium fluoborate.

Reduction of Boron Oxide. The reduction of boron oxide has been the primary objective of most investigators up to the present time. This is due largely to the cheapness and ease in obtaining this raw material.

Potassium Reduction. The element, boron, was first isolated in 1808 by Gay-Lussac and Thenard<sup>(22)</sup>. They reduced boron oxide,  $B_2O_3$ , with potassium in an iron tube. Sir Humphry Davy<sup>(15)</sup> in the preceding year in a manner analogous to that of Gay-Lussac and Thenard, obtained the same product.

Sodium Reduction. Wohler and Deville<sup>(43)</sup> were among the earliest workers who isolated elemental boron. They reduced boric anhydride by heating it with metallic sodium and extracting the cold mass with hydrochloric acid. Boron prepared by this method is impure for it contains sodium and oxygen as well



as impurities from the crucible in which the reaction took place. The product is amorphous in nature and has the characteristic light brown color.

Magnesium Reduction. In 1895 Moissan<sup>(39)</sup> reduced boric anhydride by heating it with finely divided magnesium, the cold mass being extracted several times with hot, concentrated hydrochloric acid. The product thus obtained was a brown amorphous powder, which was quite impure. Weintraub<sup>(43)</sup> investigated this reaction thoroughly and concluded that pure boron could not be prepared in this way. He gave the formula  $B_7O$  to the product formed in this reaction. Kahlenberg<sup>(26)</sup> in 1924 proved that  $B_7O$  was not the formula for this product but it was actually a mixture of  $B_3O$  and Boron.

Carbon and Aluminum Reduction. Wohler and Deville<sup>(44)</sup> in 1857 prepared crystalline boron by heating an intimate mixture of pulverized boric anhydride, carbon and aluminum in a fireclay crucible to at least 1500 °C. On dissolving out the aluminum with hydrochloric acid, they obtained crystals which were reddish and transparent when reviewed in transmitted light, but they contained notable amounts of carbon and aluminum. Their investigations also succeeded in preparing boron crystals by fusing aluminum and amorphous boron together at a temperature of at least 1500 °C, and removing the aluminum from the mass by means of hydrochloric acid. The crystals thus obtained cannot properly be called crystalline boron, for they contain much

aluminum which cannot be removed with hydrochloric acid. The crystals are, in fact, more likely to be aluminum borides, such as  $AlB_{12}$ <sup>(26)</sup>.

Sulfur and Aluminum Reduction. Blits<sup>(4)</sup> in 1907 prepared a mixture of 250 grams of boric anhydride, 250 grams of flowers of sulfur and 600 grams of aluminum powder. He ignited this mixture and a violent reaction took place. After extracting the cold mass with water and hydrochloric acid, he obtained an impure boride which was high in boron content. The product was crystalline in character.

Reduction of Boron Trichloride. Dumas<sup>(17)</sup> in 1825 claimed to have reduced boron trichloride with hydrogen at a red heat, but Weintraub<sup>(43)</sup> proved in 1908 that at the low temperatures Dumas used, boron was not the product obtained. Weintraub passed a mixture of boron trichloride and hydrogen through a high voltage arc, formed between water-cooled copper electrodes. At the high temperatures thus obtained, the boron trichloride is reduced by hydrogen, boron being formed as a black powder, and also as little trees which branch out from the electrodes, so that the arc melts them into small globules of well fused boron. In this manner Weintraub was the first investigator to prepare boron in a perfectly pure as well as fused condition. Goss<sup>(23)</sup> in 1947 obtained a patent to produce boron by the reduction of boron trichloride with hydrogen in a rotary electric furnace.

Reduction of Boron Suboxide. Weintraub<sup>(43)</sup> prepared boron by heating boron suboxide,  $B_2O_3$ , to high temperatures in the electric arc. The boron suboxide was prepared by Moissan's method and decomposed to yield boron and oxygen. In this manner Weintraub made his largest quantities of boron. Kahlenberg<sup>(26)</sup> repeated his experiments, and also obtained boron of high purity.

Reduction of Boron Fluoride. Rawson<sup>(40)</sup> formed boron by passing boron fluoride over heated metallic potassium. He used a glass apparatus in preparing boron fluoride, and so his final product was contaminated with silicon as well as with potassium, which he could not remove.

Reduction of Boron Hydride. Formstecher and Ryskevich<sup>(21)</sup> in 1945 produced boron by passing a mixture of hydrogen and boron hydride,  $BH_3$ , over a filament of molybdenum at temperatures of 1250 to 1400 °C in a quartz tube. The molybdenum was removed chemically and the product proved to be better than 99 per cent pure boron.

#### Preparation of Boron by Electrolysis

Many electrolytic processes, that have proved successful in producing other metals from their salts, have been applied to the production of boron from its salts. They have either failed to operate at all for their intended purpose, have yielded a product too impure for practical use, or have involved such serious operating difficulties as to be entirely impractical as commercial processes. The following paragraphs are a review of the electrolytic methods that have been attempted:

Electrolysis of Borax. Kahlenberg<sup>(26)</sup> in 1924 performed the electrolysis of fused borax in a porcelain crucible, using a copper cathode and a carbon anode. The product obtained was a dark brown deposit. The formation of this boron deposit was evidently secondary in character, sodium being first formed, and boron being deposited by the action of the sodium upon the electrolyte. Boron produced in this manner always contained sodium, which could not be removed by boiling with concentrated hydrochloric acid. The resistance of the fusion was so high as to make the electrolysis impractical for commercial production.

Electrolysis of Boric Anhydride. Boric anhydride<sup>(26)</sup>, fused in a porcelain crucible, was electrolyzed, using a copper cathode and a carbon anode. It was found, however, that the resistance of the fusion was so high as to make electrolysis impracticable.

Electrolysis of Potassium Chloride-Boric Anhydride Mixture. Kahlenberg<sup>(26)</sup> attempted the electrolysis of potassium chloride and boric anhydride using a porcelain crucible. The two molten compounds however, did not mix at all. The same was true when sodium chloride was used in place of potassium chloride. It was found however, that boric anhydride dissolves readily in fused sodium metaphosphate, but on electrolysis of such a fusion, only phosphorus was deposited, which united with the cathode, whether the latter was of copper or nickel.

Electrolysis of Potassium Chloride-Calcium Chloride-Boric

Anhydride Mixture. On adding boric anhydride to a fusion of equal parts of potassium chloride and calcium chloride, a precipitate was formed, which was skimmed off. On electrolyzing the remaining fusion with a carbon anode and a copper cathode, boron powder was formed, but it proved to contain a large amount of calcium<sup>(26)</sup>.

Electrolysis of Potassium Chloride-Potassium Carbonate-Boric

Anhydride Mixture. A fusion of 25 grams potassium chloride, 20 grams potassium carbonate, and 20 grams of boric anhydride was made in a porcelain crucible, carbon dioxide being evolved during the process. This fusion was electrolyzed with a carbon anode and a nickel cathode. The voltage was 3.5 volts and the current was 5.5 amperes. Boron was deposited and alloyed at once with the nickel cathode, lowering its melting point so that a fused alloy<sup>(26)</sup> resulted. This alloy proved to contain about 7 per cent boron, but it was also contaminated with silicon from the porcelain crucible. In approximately two hours the fusion had eaten its way through the crucible. A similar experiment was conducted, using a copper cathode. A copper alloy was thus obtained which melted about 900 °C. It was white and hard but an analysis showed it contained relatively large amounts of silicon and only traces of boron.

Effect of Lower Voltage. By electrolyzing a fusion of 50 grams potassium chloride and 20 grams potassium carbonate, with as much boric anhydride added as the fusion would dissolve, some

pure boron was obtained as a fine black powder upon the copper cathode. The anode consisted of carbon, and the voltage was not allowed to exceed 2.0 volts, so as to avoid the deposition of potassium. This process of producing boron was very slow, since the fusion was a poor conductor, and an impressed electromotive force of 2.0 volts would only maintain a current of approximately 0.5 amperes. This process of preparing boron is so slow that it is of no real practical value.

Electrolysis of Potassium Chloride-Potassium Carbonate-Potassium Sulfate-Boric Anhydride Mixture. A fusion, using the following ingredients, was made in a porcelain crucible; 19 grams boric anhydride, 6.7 grams potassium carbonate, 4 grams potassium chloride and 2 grams potassium sulfate. This fusion was electrolyzed using a copper cathode and a carbon anode. The impressed electromotive force was 3 volts and the current was 0.9 amperes. A thin, smooth, black deposit was formed on the cathode. It did not appear to alloy with the copper, and quantitative tests showed that it consisted of pure boron.

Electrolysis of Potassium Fluoborate. Kahlenberg<sup>(26)</sup> electrolyzed potassium fluoborate,  $\text{KBF}_4$ , using a copper crucible, and a carbon anode, the crucible serving as the cathode. Black boron powder was deposited on the cathode, but it was always contaminated with copper which came from the crucible above the surface of the fusion, where the copper became oxidized and fell into the bath. The conductance of this fusion was good, and Kahlenberg claims that pure boron could be obtained by using a gold crucible as cathode.

Electrolysis of Potassium Chloride-Potassium Fluoborate.

Cooper<sup>(12)</sup> electrolyzed a fused mixture of potassium chloride and potassium fluoborate at temperatures in the range of 650 to 1000 °C. Potassium chloride was first charged into a graphite crucible and potassium fluoborate in the proportion of about 1 to 5 parts of the potassium chloride was added with continued heating to bring the bath to the operating temperature. An operating temperature of about 800 to 850 °C is preferred, though this temperature is not critical. A copper cathode was employed as the cathode. The product, purified by washing with water and hydrochloric acid, proved to be 99 per cent pure boron. The use of potassium as the positive radical, both in the chloride electrolyte and in the double fluoride compound of boron, appears to be essential. If sodium chloride is substituted, even in part, the results are adversely affected. Complete substitution of sodium for potassium is said to render the process commercially impractical, if not totally inoperative.

Electrolysis of Potassium Chloride-Potassium Fluoborate-Boric

Anhydride Mixture. Cooper<sup>(13)</sup> obtained a patent in 1951 for the production of boron by electrolyzing a fused bath containing 8 parts of potassium chloride or fluoride, 5 parts of potassium fluoborate and 1 part of boric anhydride at temperatures in the range of 650 to 1000 °C. He used an externally heated crucible of graphite, which served as his anode and a low carbon iron cathode. The boron deposited on the cathode in a fine granular form, together with

predominantly water and acid soluble impurities, which were readily removed by washing in water and hydrochloric acid. The product was 96 per cent pure boron with traces of iron, silicon and carbon present.

### Boron Compounds

Boron resembles carbon and especially silicon in many respects. It usually forms covalent bonds and its best known compounds either are molecular or contain complex ions in which the boron is covalently bonded to other atoms. Boron always uses all three of its valence electrons for bonding purposes and its usual oxidation states are +3 and -3.

Borides. Boron forms borides<sup>(3)</sup> of the metals at high temperatures by heating the metals to 1500 - 1700 °C. The compounds are obtained as powder, and then purified and compacted by sintering. Many of the borides are very hard and refractory, and hard alloys containing them are used for cutting tools. Borides have much in common with true metals. They have a high electrical conductivity and a negative temperature coefficient showing that true metallic conductivity is involved.

Borides are not usually attacked by water. Dilute acids decompose some of the borides. The borides of the alkaline earth metals and aluminum are not attacked by acids, but the richer the compounds are in metal the more easily acid attacks them. Thus CrB is not

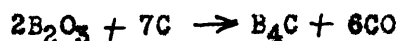


attacked by acid but  $\text{Cr}_3\text{B}_2$  is attacked to some extent. Examples of metal borides are:  $\text{Ni}_2\text{B}$  and  $\text{NiB}_2$ ,  $\text{CaB}_6$ ,  $\text{BaB}_6$ ,  $\text{MnB}$  and  $\text{MnB}_2$ .

Boron Carbide. Boron carbide<sup>(34)</sup>,  $\text{B}_4\text{C}$ , formula weight 55.29, is a black crystalline substance. Its special interest, scientific and commercial is due to its remarkable hardness, which lies on the Mohs scale between that of silicon carbide and that of diamond.

Physical and Chemical Properties. Boron carbide is non-metallic and does not warp or creep. It is nonmagnetic and non-electrostatic, although when compressed, cut, and polished it resembles a metal greatly. Its electrical conductivity is intermediate between graphite and silicon carbide. Commercial boron carbide<sup>(31)</sup> melts sharply at about  $2375^\circ\text{C}$  and shows little or no plasticity on approaching the melting point. Its vapor pressure is extremely low even at high temperatures. Its specific gravity (crystal) is 2.52. Boron carbide resists attack by acids or alkalies in solution (even fuming nitric acid) but is oxidized on alkaline fusion to borate and carbonate.

Method of Manufacture. Anhydrous boric oxide,  $\text{B}_2\text{O}_3$ , is pulverized and mixed with petroleum coke in accordance with the formula:



together with enough kerosene to hold the mass together and provide a reducing atmosphere at the higher furnace temperature.

The mixture is heated in a gastight, graphite resistance furnace to around 2500 °C, the furnace temperature being pretty well controllable through the power input. According to Ridgway<sup>(41)</sup> the furnace is made gastight to keep out nitrogen during the heating, and oxygen during the cooling. Firebricks are not practicable, because they flux too easily, so a wood lining is employed. The wood turns to charcoal and serves as insulation for heat and electricity. The central zone of the furnace melts, forming a 97 - 99 per cent pure boron compound, ordinarily found to be boron carbide, B<sub>4</sub>C. The product resembles fully glazed black clinkers with numerous spots of high light. Unreacted and insufficiently crystallized portions are reprocessed.

Boron Trifluoride. Boron trifluoride<sup>(33)</sup>, BF<sub>3</sub>, formula weight 67.82, is a colorless gas in a dry atmosphere but it fumes in the presence of moisture, producing a dense white smoke. Upon hydrolysis, it yields an acidic pungent odor that is irritating but not appreciably toxic. It is used widely as an acidic catalyst for many types of organic reactions, most common of which are polymerizations, esterifications and alkylations.

Physical Properties. Some of the physical constants<sup>(33)</sup> of boron trifluoride are: melting point, -127.1 °C; boiling point, -100.3 °C; apparent density, 3.076 grams per liter; critical temperature, -12.25 °C; and critical pressure, 49.2 atmospheres. It dissolves in water to the extent of 322 grams

per 100 grams of water at 0 °C and 762 mm of mercury. One volume of boron trifluoride is soluble in 50 volumes of sulfuric acid. It is also soluble in concentrated nitric acid. It dissolves in ethane, propane, pentane, kerosene, carbon disulfide, benzene and carbon tetrachloride.

Chemical Properties. Boron trifluoride<sup>(33)</sup> reacts with incandescence when heated with alkali or alkaline earth metals. Molten magnesium and its alloys, however, do not react. Neither gaseous nor liquid boron trifluoride, at room temperature or below reacts with mercury or chromium plate, even when subjected to pressure for a considerable length of time. Boron trifluoride is reported not to react with red-hot iron. When reduced with hydrogen gas in a tungsten arc, crystalline boron is obtained. Alkali and alkaline earth metal oxides react with boron trifluoride to form the borate and fluoborates.

Metal Fluoborates. The fluoborates have been found in nature only in trace amounts, among the products of volcanic activity. They were first synthesized by Gay-Lussac and Thenard, but the major part of the early work on these salts were done by Berzelius (33, 38). The potassium, rubidium and cesium salts are sparingly soluble in water and are precipitated when fluoboric acid is treated with a salt of the appropriate metal. The lithium, sodium, ammonium, alkaline earth, and heavy metal salts are soluble and in the majority of cases may be crystallized from solutions obtained by neutralizing

fluoboric acid with the appropriate hydroxide or carbonate. Ammonium, sodium, and potassium fluoborate are available commercially as white crystalline solids.

Potassium Fluoborate. Potassium fluoborate<sup>(33)</sup> is made by treating fluoboric acid with potassium carbonate, hydroxide, nitrate, chloride, or sulfate. It melts without decomposition, but dissociates into potassium fluoride and boron trifluoride before reaching its boiling point. It is decomposed by sulfuric acid into potassium sulfate, hydrogen fluoride, boric acid, and boron trifluoride. It has a melting point of 530 °C and specific gravity of 2.50.

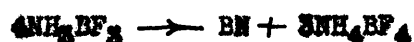
Boron Halides. The trihalides<sup>(29)</sup> of boron are colorless, volatile, molecular substances. The fluoride and chloride are gases, the bromide is a liquid, and the iodide is a solid. They can be made by heating the halogens with elementary boron or borides, except for the iodide, which can be prepared only indirectly, for example, by heating a mixture of boron trichloride and hydriodic acid. Boron trifluoride can be obtained by heating boron oxide with calcium fluoride and sulfuric acid. These halides of boron hydrolyze vigorously and fume in the air. Boron trifluoride and boron trichloride are valuable catalysts.

Boron Hydrides. The so-called hydrides of boron<sup>(3, 29)</sup>, boranes, constitute a group of compounds whose composition can be represented by two generic formulas:  $B_nH_{n+4}$  and  $B_nH_{n+6}$ . Those with  $n = 2, 5, 6$

and 10 for the first series, with  $n = 4$  and 5 for the second have been isolated and studied.

The term "borines" has been reserved for the hypothetical hydrogen compounds of boron in which the latter is bonded to three atoms,  $BH_3$ ,  $B_2H_4$ , etc. An interesting group of complex compounds having the general formula  $M(BH_4)_p$  (in which  $p$  may vary from 1 to 4 depending on the metal atom  $M$ ) are called borohydrides, although a more correct name might be "hydroborates."

Boron Nitride. Boron nitride<sup>(7, 30)</sup>,  $BN$ , can be made by heating borax with ammonium chloride or by the thermal decomposition of  $NH_3BF_3$



Boron nitride has a graphite structure and is highly refractory compound, which is an excellent electrical insulator even at high temperatures.

Boron Oxides. Several oxides of boron<sup>(30)</sup> are known, but only the trioxide,  $B_2O_3$  is well known and hence is often called simply "boron oxide." Some suboxides have been described, the most definite of which are  $B_2O_2$  and  $B_4O_5$  corresponding to the acids  $H_4B_2O_4$  and  $H_2B_4O_8$  respectively.

Physical Properties. Boron oxide,  $B_2O_3$  formula weight 69.64 is a colorless, transparent, very hard, very adhesive, but brittle glasslike solid, entirely odorless, of a slightly bitter

taste, and very hygroscopic. Some of its physical constants are: melting point, 450 °C; boiling point, 1500 °C; specific gravity, 1.8; electrical conductivity,  $0.06 \times 10^{-4}$  ohm per cm at 777 °C.

Solubility Determinations. Foex<sup>(20)</sup> used the following method for the determination of the solubility of oxides in molten boron oxide. The finely powdered oxide was agitated with boron oxide at 1200 °C until a constant composition was obtained. For oxides of the type  $X_2O$ , where X is lithium, sodium or potassium proved soluble in all proportions; silver oxide only up to 61 moles per 100 moles boron oxide. For oxides of the type  $XO$ , where X is manganese, calcium, magnesium, cobalt, nickel or cadmium form two layers, the lower containing much  $XO$  and frequently yielding borates on cooling, leaving the boron oxide solution of the oxide. Lead oxide does not give two layers, but is soluble in all proportions of boron oxide.

For oxides of the type  $X_2O_3$ , aluminum oxide is soluble to the extent of 0.72 mole per 100 moles boron oxide; those where X is arsenic, antimony or bismuth are soluble in all proportions. For the type  $XO_2$ , where X is silicon, tin, zirconium or thulium the solubility decreases from 39 moles per 100 moles boron oxide for silicon oxide to 0.15 for thulium oxide, as the molecular weight increases. For the types  $X_2O_5$  and  $XO_5$ , vanadium oxide and molybdenum oxide are soluble in all proportions.

Boric Acids. Of the free boric acids, orthoboric is the only important one. In 1702 W. Homberg<sup>(30)</sup> made boric acid from borax and called the acid "sol sedativum." After Lavoisier's work on acids the term "boracic acid" was substituted for "sol sedativum" and boracic acid was later abbreviated to boric acid. Several other acids are known (at least in the form of salts) all derived from boric oxide,  $B_2O_3$ , with varying amounts of water. When orthoboric acid,  $H_3BO_3$ , is heated above  $100^\circ C$  it gradually loses water, changing to metaboric acid,  $HBO_2$ , and at  $140^\circ C$  to tetraboric acid,  $H_2B_4O_7$ . On continued heating all water is lost and the anhydrous oxide,  $B_2O_3$ , is formed.

Borates. In this group, sodium tetraborate (borax) is by far the most important commercially. Certain other borates are also commercial products, but they are obtained mainly from borax.

Sodium Tetraborate. Sodium tetraborate<sup>(30)</sup>,  $Na_2B_4O_7 \cdot 10H_2O$  or  $Na_2O \cdot 2B_2O_3 \cdot 10H_2O$ , formula weight 281.44, melting point  $75.0^\circ C$ , specific gravity 1.715, hydrolyzes in aqueous solutions to give a weakly alkaline solution. One mole of borax can neutralize two moles of acid, and two moles of strong alkali can also be essentially neutralized by one mole of borax.

When borax is heated, it melts in its own water of crystallization, swells up to a frothy mass, loses its water of crystallization, and then fuses to a clear glass. These properties are used in the borax-bead test for various elements.

It loses some water of crystallization on exposure to air. Prolonged contact with a dry atmosphere alters the decahydrate to the pentahydrate,  $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ .

#### Analysis of Boron Compounds

The particular method employed in the quantitative or qualitative estimation of boron will depend upon the nature of the material containing the boron. Unless the boron compound is reasonably pure, it is usually necessary to separate the boron from foreign substances.

Quantitative Determination. Most quantitative<sup>(28)</sup> determinations of boron involve distillation of the boron as methyl borate followed by its hydrolysis to boric acid, which can be titrated in the presence of a polyhydric alcohol or estimated gravimetrically as its calcium salt, although the latter method appears less satisfactory. The methyl borate distillation may be omitted in the case of pure compounds readily hydrolyzable to boric acid and containing no interfering substances. The direct titration of free boric acid is unsatisfactory because the end point occurs at about a pH of eleven, where there would be considerable self-buffering by water and where most available indicators give poor end points. In the presence of polyhydric alcohols, boric acid forms acids that are considerable stronger than free boric acid and thus an end point at a more satisfactory pH can be achieved.



Fusion Method. Hildebrand and Lindell<sup>(25)</sup> found the following method satisfactory for analysis of boron in minerals and other insoluble materials. A quantity of sample equivalent to about 100 milligrams of boron oxide is fused with its sixfold weight of potassium carbonate-sodium carbonate, and after fusion the residue is taken up in one to one hydrochloric acid without boiling. Pure methanol is added and the methylborate distilled from a water bath. Excess acid is neutralized to the p-nitrophenol end point by sodium hydroxide, followed by addition of sodium hydroxide to the phenolphthalein end point, which will not be sharp. The difference between the two end points give a rough estimate of the amount of boron. Twice as much sodium hydroxide as used between these two end points is added and the methanol distilled off, the boron not being volatile in the presence of excess base. The color of both indicators is discharged with hydrochloric acid, and carbon dioxide is evolved by refluxing under reduce pressure. This is necessary to prevent high results. The solution is then carefully neutralized to the p-nitrophenol end point with sodium hydroxide, and one gram of mannite is added. This solution is titrated carefully with sodium hydroxide to the phenolphtholein end point, the amount of sodium hydroxide required corresponding to the boron present as metaboric acid,  $H_3BO_3$ .

Qualitative Determination. Boron may be identified by spectroscopic methods. Brode<sup>(6)</sup> states that there are at least two lines in emission which can be used for detecting the presence of boron in compounds. Feigl<sup>(18, 19)</sup> describes in detail very sensitive spot tests using turmeric test paper of hydroxyanthroquinones such as Alizarin Reel S or quinalizarin. Feigl also devised a spot test for boron in the presence of oxidizing agents or fluorides, which involves the decomposition of methyl borate with an alkali fluoride.

#### Molten Salt Electrolysis

The high electrode potentials and other characteristics of a number of metals make it difficult to isolate them by ordinary reduction methods or by electrodeposition from aqueous solutions of their salts. The metallurgy of these metals has been made possible by the electrolysis of their fused salts. Among the more common metals obtained in this manner may be mentioned aluminum, magnesium, sodium, and potassium. The electrochemical behavior of fused salts has been studied particularly by Lorenz and Blitz<sup>(4, 36, 37)</sup> and are discussed in the following paragraphs.

Electrical Conductivity. The conductance of fused electrolytes is ionic and the electrode deposits are the same as those obtained in aqueous solutions with proper allowance for secondary reactions that may occur<sup>(32)</sup>. The value of the conductance of fused salts is generally very much higher than that of their aqueous solutions. It

increases linearly with temperature, as a rule, and coincides essentially with the simultaneous decrease in viscosity of the liquid. The conductivity is usually less than would be calculated from the mixture law, and sometimes falls below the conductivity of any of the pure components<sup>(35)</sup>. Impurities in the salt however may give an abnormally large conductance.

General Rules of Conductance. Blitz and coworkers<sup>(5)</sup> have found some general rules for the conductance of fused salts. In the case of halides of different valence types with a given cation, the salt which has the cation with the lowest valence number has at the melting point the highest equivalent conductance. Halides with very low conductance values have as a rule low melting points, while good conductors melt at relatively high temperatures.

Conductivity Measurements. The measurement of the conductivity of fused salts usually offers no particular difficulties. The arrangement used is essentially that for aqueous solutions. Unplatinized platinum electrodes must be employed, as platinum black at high temperatures quickly changes its structure. With salt of particularly high conductivity, the electrodes must be separate by a capillary tube in order to increase the resistance to a convenient amount.

Current Efficiency. The causes which lower the current efficiencies at room temperature are far more active at high temperatures. Velocity of chemical reaction and velocity of diffusion are

both much greater. Hence, unless anodic and cathodic products are carefully kept separated from one another and from the action of the electrolyte and the air, the yields obtained will be less than those calculated from Faraday's law<sup>(37)</sup>. The chief factors causing low cathodic efficiency in the electrolysis of molten salts are volatility, diffusion of anode products to cathode, formation of "metal fog," composition of the melt and the temperature of electrolysis.

Effect of Current Density. The relations for the deposition of ions hold also for the electrolysis of melts. The deposition potential depends on the reversible electrode potential and on the over potential, which depends on the current density. The effect of increased current density on current efficiency depends on the fact that, while the absolute losses of cathodic product do increase to a certain degree owing to increased diffusion from the anode, yet the quantity produced in unit time increases still more quickly, and the current efficiency rises. At very low current densities the quantities of product formed in a given time may not exceed the amount absorbed by different losses, and the current efficiency may consequently fall to zero. The amount of increase of current density is only limited by considerations of voltage and of joule heat near the electrodes, and by the initiation of an "anode effect," which results in a large rise in voltage.

Anode Effect. A phenomenon that often causes considerable trouble during electrolysis of fused salts is the so-called "anode effect"<sup>(1, 32)</sup>. The voltage suddenly starts to increase while the current decreases and the anode appears to glow due to the formation of innumerable tiny arcs. The effect is most likely to occur at high current densities and disappears by stirring the melt, by momentarily raising the anode out of the liquid, or by reversing the current.

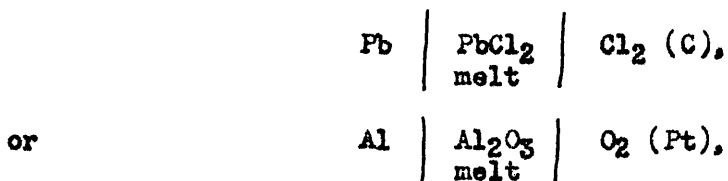
Effect of Diffusion. A frequent cause of low current efficiency<sup>(35)</sup> is that the cathodically deposited metals dissolve in the melt, diffuse to the anode and react there with the anodically deposited gases to reform salts. Depending therefore on the solubility of the metal in the melt, the temperature, the current density, the distance apart of the electrodes, the current yields deviate from the theoretical value. Through investigations of the electrolysis of lead chloride, for example, have shown that the current yield decreases with increase of temperature, decreasing cathodic current density and decreasing distance between the electrodes, because changing these factors in the direction indicated favours the dissolution of the deposited metal and its transport to the anode. At the boiling point of lead (956 °C) and at less than a critical current density depending on the experimental conditions, a point is reached where no more lead deposits.

Composition Effect. The current yield is dependent on the composition of the melt. Addition of potassium chloride, sodium chloride or barium chloride raises the current yield of the electrolysis of lead chloride, other conditions being unchanged. This finds explanation in the fact that the solubility of lead in these foreign salts is small and falls sharply as the melt becomes increasingly rich in them. Addition of ferric chloride on the other hand decreases the current yield for lead deposition considerably because the reduction of ferric to ferrous ions takes place in preference to the deposition of lead.

Metal Fog. When a metal such as zinc or lead is melted under one of its own fused salts (for example, zinc chloride or lead chloride) the molten salt will remain unaffected if the temperature is kept low. But if it is raised, dark clouds rise up from the metal and apparently dissolve in the melt. When the temperature falls, the clouds settle down slowly, and finally re-enter the metal. Essentially the same phenomena must occur during the electrolysis of molten salts, and will adversely affect the yield, since the metal in that form is far more readily attacked chemically than the massive metal. Lorenz and Eitel<sup>(36)</sup> have proven that these metal fogs are colloidal in nature and may be largely prevented by the addition of certain neutral salts to the original melt.

Effect of Temperature. The losses<sup>(35)</sup> in current yield due to "metal fog" formation can be reduced by electrolyzing at the lowest possible temperature. This can be achieved in practice by working with salt mixtures which melt below the melting point of the pure salt and by so choosing the added salts that the solubility of the cathodically deposited metal is depressed.

Single Potentials in Melts. In contrast to aqueous solutions the reversible single potential in melts<sup>(35)</sup>, measured against an arbitrary zero of potential, is not accurately determinable. It is only possible to measure the electromotive force of cells such as

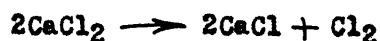


which cannot be separated into single potentials. Here the electromotive force is a measure of the maximum useful work of the formation of the salt from its elements under given conditions of temperature and pressure. As all the reactants are pure they have an activity of one and hence the electrode potentials are standard potentials. It is important to consider the effect of thermal electromotive forces on single potential measurements. If cathode and anode are of different materials and a large temperature gradient exists between them, the thermal electromotive force may constitute a considerable part of the measured electromotive force.

Deposition Potentials in Melts. Since the reversible single potentials of metals in their salt melts are ambiguous, it is evident that the corresponding deposition potentials are also uncertain. Current-voltage curves are however obtainable for electrolysis of melts and the decomposition potentials can be obtained from these by extrapolation to zero current. Special attention must be paid in such measurements<sup>(16)</sup> to the fact that no depolarisation arises as a result of the deposited metal in the melt and the diffusion of metal to the anode. Another difficulty arises due to the water content of the melt which may cause an inflection in the current-potential curve due to the decomposition of water. The potential applied to the cell then only reaches the value for the decomposition of the salt after the limiting current density for water has been attained. Finally, beside the simple decomposition of the salt, other electrode processes may occur. Thus in the electrolysis of molten stannous chloride, stannic chloride and not chlorine is deposited at the anode. The decomposition potential corresponds to the overall reaction:



Conversely, reduction of the metal to a lower valence state and complete discharge of metal ions may occur. An example of this is the case of calcium chloride where the decomposition corresponds to the net reaction



Special reactions of this kind can be detected by determining the cathodic and anodic current yields.



### III. EXPERIMENTAL

The experimental section includes a statement of the purpose of investigation and an outline of the plan of experimentation. The materials and apparatus used are described. The methods of procedure used in the experimental work, the data obtained in the experiments, the calculated results, and sample calculations are presented.

#### Purpose of Investigation

The purpose of this investigation was to study electrolytic methods of producing boron from molten mixtures containing boric oxide.

#### Plan of Experimentation

The plan of experimentation which was followed in this investigation included a review of the literature, assembly of equipment, preliminary operation, and experimental operation.

Literature Review. The literature was reviewed, covering the following items: the principal papers dealing with the preparations of boron, the literature covering the physical and chemical properties of boron, electrolysis of molten salts and information on experimental techniques and apparatus.

Assembly of Equipment. The first step in this investigation was to assemble the electrical circuit for the electrolysis of the molten salt mixtures. Next the electrical circuit for the thermocouple and potentiometer was assembled. These circuits are shown in Figure 1.

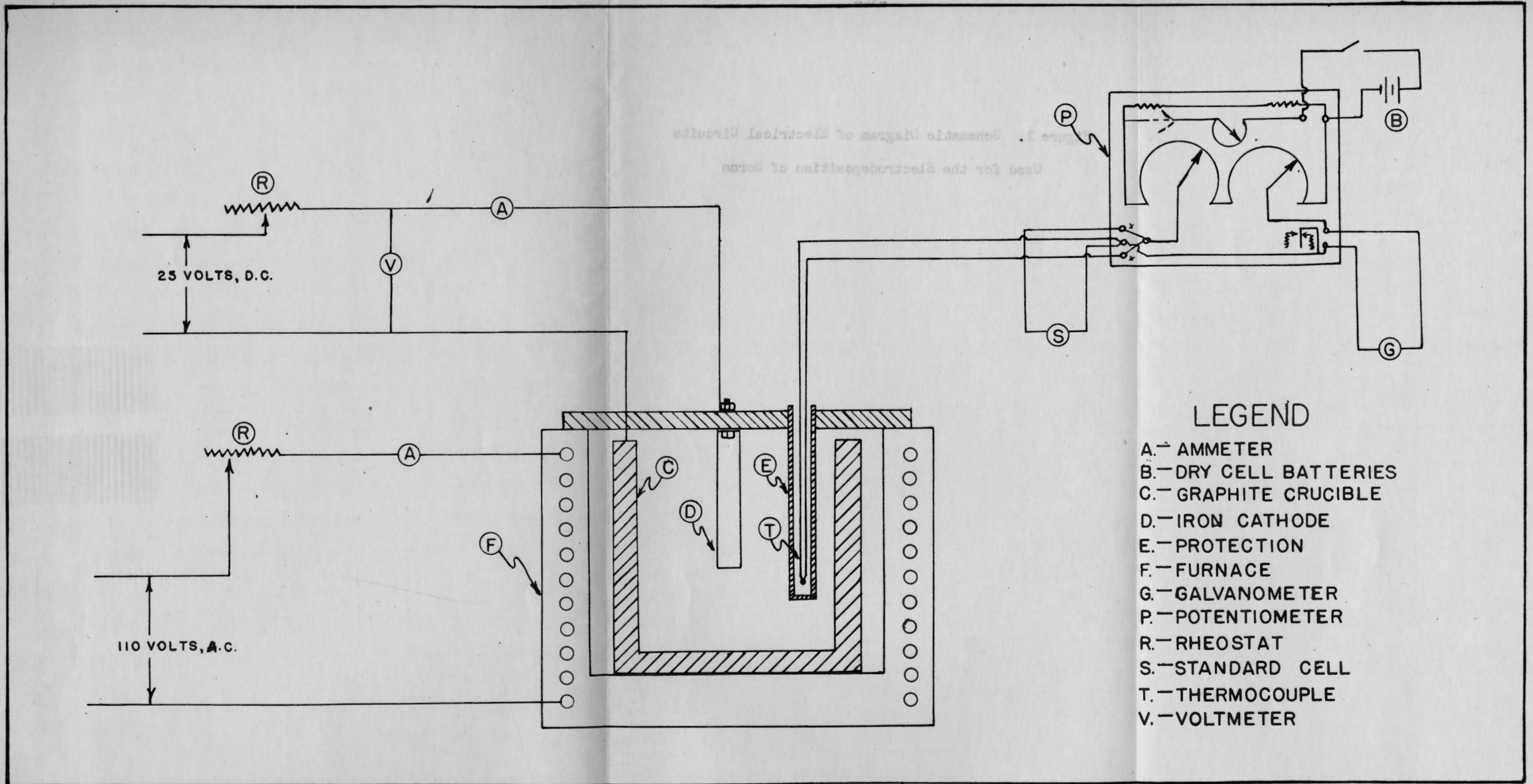


FIGURE 1. SCHEMATIC DIAGRAM OF ELECTRICAL CIRCUITS USED FOR THE ELECTRODEPOSITION OF BORON

Preliminary Operations. The following operations were performed prior to making any experimental tests: (1) baking of graphite crucible at 1000 °C for 8 hours, (2) calibration of thermocouples, and (3) testing furnace by heating to required temperature.

Experimental Operation. The plan of operation for the experimental tests consisted of: (1) charging the required amount of chemicals into the electrolytic cell, (2) start electrolysis by placing cathode in molten bath and connecting to source of direct current, (3) adjust temperature of electrolysis by adjusting voltage regulator, (4) measurement of current, voltage, and temperature every 15 minutes, (5) washing of product with water and hydrochloric acid, and (6) analysis of product for carbon and boron content.

#### Materials

Information relating to the source and description of all materials used in this investigation is presented in the following paragraphs:

Acid, Boric Anhydride. C. P., lot No B361J; obtained from General Chemical Co., New York, N. Y. Used for preparing electrolytes.

Acid, Hydrochloric. C. P., lot No 10921J; distributed by Fisher Scientific Co., Silver Spring, Md. Used in purification of electro-deposited boron.

Acid, Nitric. C. P., lot No E45005; obtained from General Chemical Co., New York, N. Y. Used for analysis.

Acid, Sulfuric. C. P., lot No E501030; obtained from General Chemical Co., New York, N. Y. For miscellaneous use.

Boron Carbide. Powder; obtained from Electrometallurgical Division of Union Carbide and Carbon Corp., Niagara Falls, N. Y. Used in nitric acid digestion tests.

Calcium Boron. Lump; obtained from Electrometallurgical Division of Union Carbide and Carbon Corp., Niagara Falls, N. Y. Used in nitric acid digestion tests.

Copper Metal. Strip, commercial grade, 3.2 mm thick; distributed by Fisher Scientific Co., Silver Spring, Md. Used to make copper cathodes.

Copper Wire. B & S gauge No 18; distributed by Fisher Scientific Co., Silver Spring, Md. Used for electrical connections.

Ferro-Boron. Powder; obtained from Electrometallurgical Division of Union Carbide and Carbon Corp., Niagara Falls, N. Y. Used in nitric acid digestion tests.

Iron Metal. Strip, commercial grade, low carbon, 3.2 mm thick; obtained from Virginia Bridge Co., Roanoke, Va. Used to make iron cathodes.

Lithium Carbonate. C. P., lot No C129J; obtained from General Chemical Co., New York, N. Y. Used for preparing electrolytes.

Manganese Boron. Lump; obtained from Electrometallurgical Division of Union Carbide and Carbon Corp., Niagara Falls, N. Y. Used in nitric acid digestion tests.

Mannite. Powder, tested purity, A. C. S.; obtained from Digestive Ferments Co., Detroit, Mich. Used in quantitative determination of boron.

Methyl Alcohol. C. P., lot No D201; distributed by Fisher Scientific Co., Silver Spring, Md. Used for analysis.

Nickel Boron. Lump; obtained from Electrometallurgical Division of Union Carbide and Carbon Corp., Niagara Falls, N. Y. Used in nitric acid digestion tests.

Nitrogen. Oil pumped; obtained from Southern Oxygen Co., Roanoke, Va. Used as protective atmosphere during electrolysis.

Potassium Carbonate. C. P., lot No 0098J; obtained from General Chemical Co., New York, N. Y. Used for preparing electrolytes.

Potassium Chloride. C. P., lot No H092; obtained from General Chemical Co., New York, N. Y. Used for preparing electrolytes.

Potassium Fluoborate. C. P., lot No H021; obtained from General Chemical Co., New York, N. Y. Used for preparing electrolytes.

Sodium Carbonate. C. P., lot No 474804; distributed by Fisher Scientific Co., Silver Spring, Md. Used for preparing electrolytes.

Sodium Chloride. C. P., lot No 514018; distributed by Fisher Scientific Co., Silver Spring, Md. For miscellaneous use.

Apparatus

This section contains detailed descriptions of all equipment used in the course of this investigation.

Ammeter. Direct current, 0 - 1.5, 0 - 3, 0 - 30 ampere ranges, model 489, serial number 62894, manufactured by Weston Electric Instrument Co., Newark, N. J. Used to measure the current in electrolysis circuit.

Balance, Analytical. Capacity 200 grams, sensitivity 0.1 gram, manufactured by Seoderer-Kohlbrach Co., Inc., Jersey City, N. J. Used to weigh products from electrolysis.

Balance, Beam. Capacity 1600 grams, obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for weighing chemicals for electrolytes.

Batteries, Dry Cell. Eveready, number 6, National Carbon Division of Union Carbide and Carbon Co., Atlanta, Ga. Used for potentiometer.

Crucible, Graphite. Self-made from 'LG plain acheson graphite', 50.8 mm inside diameter, by National Carbon Division of Union Carbide and Carbon Co., Atlanta, Ga. Used as the electrolytic cell.

Crucible, Plumbago. Diameter at top, 60 mm and height, 75 mm, obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as the electrolytic cell.

Furnace, Crucible, F. D. 104, diameter of heating chamber, 127 mm, depth of heating chamber, 127 mm, 1200 watts, for 110 volts,

manufactured by Hoskins Manufacturing Co., Detroit, Mich. Used for heating electrolytes.

Furnace, Muffle. Type FD 204C, serial No 34928, 110 volts, 30.9 amperes; manufactured by Hoskins Electric Co., Detroit, Mich. Used for baking graphite crucibles.

Galvanometer, Point Type. Catalog number 570-201, manufactured by G. M. Laboratories, Inc., Chicago, Ill. Used for potentiometer.

Generator. Model No 1198, 25 volts, direct current, 80 amperes, 2400 rpm, 2 K. W., manufactured by Burke Electric Co., Erie, Pa. Used as source for direct current.

Heater, Autemp. Variable temperature, 110 volts, alternating current, distributed by Fisher Scientific Co., Silver Spring, Md. Used for miscellaneous heating purposes.

Miscellaneous, Laboratory, Glassware and Equipment. Supplied by Fisher Scientific Co., Silver Spring, Md.

Motor, Induction. Serial No 4207, 220 volts, alternating current, 8 amperes, 1720 rpm, 3 phase, 3 cycles, obtained from Mechanical Appliance Co., Milwaukee, Wisc. Used to drive generator.

Oven, Electric Utility. Model number OV-8, serial number 8-270, 110 volts, 5 amperes, alternating current, manufactured by Modern Electric Laboratory, Chicago, Ill. Used to dry apparatus and chemicals.

pH Meter, Glass Electrode. 0 - 14 pH range, model H2, serial No 36147; manufactured by Beckman Instruments, Inc., South Pasadena, Cal. Used in quantitative analysis for boron.

Potentiometer, Type S. Two range: 0 - 0.017 and 0 - 1.70 volts; supplied by Fisher Scientific Co., Silver Spring, Md. Used to measure the millivolts generated by the thermocouple.

Protection Tube, Graphite. Inside diameter, 3.2 mm, length, 14 mm, self-made from .95 mm diameter LG plain acheson graphite rod; supplied by National Carbon Division of Union Carbide and Carbon Co., Atlanta, Ga. Used to protect the platinum-rhodium thermocouple.

Regulator, Voltage. Serial No 465196, 9 amperes, 0 - 110 volts; manufactured by American Transformer Co., Newark, N. J. Used to regulate temperature of Hoskins crucible furnace.

Rheostat. Variable, capacity, .13 amperes, 25 ohms; manufactured by Rex Rheostat Co., Long Island, N. Y. Used to control the voltage and current in electrolysis circuit.

Rheostat. High resistance, capacity 30 amperes; manufactured by Leonard Electric Co., Mount Vernon, N. Y. Used to control the Hoskins furnace and the current in the electrolysis circuit.

Standard Cell, Eppley. Cadmium, unsaturated, internal resistance less than 500 ohms; manufactured by Eppley Laboratory, Inc., Newport, R. I. Used to standardize the potentiometer.

Stirrer, Magnetic. Variable type, 110 volts, 50 cycles; manufactured by Laboratory Industries, Inc., Chicago, Ill. Used in analysis for boron.

Thermometer. General Laboratory, engraved stem, mercury filled, 350 mm long, 75 mm immersion, range: -5 to 200 °C, subdivisions 1 °C;



supplied by Fisher Scientific Co., Silver Spring, Md. Used to measure temperature of methyl borate distillation.

Thermocouple, Platinum-13 Per Cent Rhodium Platinum. B & S gauge 24, 457 mm long; obtained from Wheelco Instrument Co., Chicago, Ill. Used to measure the temperature of the electrolyte.

Thermocouple Insulators, Porcelain. Oval type, bore diameter, 0-71 mm, thickness, 218 mm, width, 3.56 mm and length, 76.2 mm; supplied by Brown Instrument Division, Minneapolis-Honeywell Regulator Co., Washington, D. C. Used for the insulation of thermocouple.

Voltmeter. Model 489, direct current, 0-3, 0-7.5, 0-150 voltage ranges; manufactured by Weston Electric Instrument Co., Newark, N. J. Used to control voltage in electrolysis circuit.

Voltmeter. Model 525, alternating current 0-5, 0-15 voltage ranges; manufactured by Weston Electric Instrument Co., Newark, N. J. Used to control voltage to Hoskins crucible furnace.

#### Method of Procedure

The method of procedure used in this investigation was as follows:

Calibration of Thermocouple. A chromel-alumel thermocouple was first used for measuring the temperature of the melts. Before this thermocouple was used, it was calibrated against the melting points of tin, lead and antimony. A standard temperature-millivolt curve

was drawn from published data<sup>(45)</sup>. On the same graph the experimental points were located, then a curve passing through these points was drawn parallel to the standard curve. Due to the corrosive action of the melts, a graphite protection tube was used to protect the thermocouples. A platinum, 13 per cent rhodium platinum thermocouple was also used for measuring the temperature of the melts. This thermocouple was also standardized against the chromel-alumel thermocouple.

Preparation of Graphite Crucibles. Before the graphite crucibles were used they were baked in the Hoskins muffle furnace. The crucibles were placed in the furnace and allowed to heat slowly to a temperature of 1000 °C. This was accomplished by adjusting the rheostat used to control the current to the furnace. The crucibles were baked at 1000 °C for a period of eight hours. The source of current to the furnace was then disconnected and the crucibles were allowed to cool inside the furnace.

Operational Procedure for Potassium Chloride-Potassium Fluoborate-Boron Oxide System. In a prebaked graphite crucible, 200 grams of potassium chloride and 75 grams of potassium fluoborate were melted together and the temperature of the bath was brought to 800 °C. To this fused melt was added 25 grams of boron oxide which quickly dissolved in the bath. A low-carbon iron cathode was lowered into the bath and the current was turned on to place the cell in operation. The temperature of the melt was regulated at 850 °C by

adjusting the current to the crucible furnace. The average voltage was 7.2 volts with an average current of 16.5 amperes that remained substantially constant throughout the two hour test.

At the end of two hours operation the current was shut off, and the cathode was withdrawn and quickly covered with dry sodium chloride to protect the boron deposit from oxidation. When the cathode had cooled to below a visible red glow, the cathode was immersed in water for a period of three hours. During this three hour period, most of the cathode deposit fell off and the remainder was readily scraped off. The deposit was then digested in water for a period of four hours and then with strong hydrochloric acid. The residue was finally washed with water, filtered and allowed to dry. The residue was then weighed and the weight recorded as the weight of product from this system during a two hour test.

For this system, four tests were made at  $850 \pm 5$  °C and one test at  $810 \pm 5$  °C. Nitrogen was passed over the melt in tests 3, 4 and 5 to aid in protecting the graphite crucible and iron cathode from oxidation.

#### Operational Procedure for Potassium Chloride-Potassium

Fluoborate System. In a prebaked graphite crucible, 200 grams of potassium chloride was first charged and melted. To this melt 40 grams of potassium fluoborate was added with continued heating to the operating temperature of 825 °C. When the desired operation temperature had been reached a copper cathode was lowered into the

bath and the current was applied to begin the electrolysis. The electrolysis was carried out for a period of two hours. After 1 hour of operation 100 grams of potassium chloride and 25 grams of potassium fluoborate was added to replace the amount that were consumed by the electrolysis. Nitrogen was passed over the melt during electrolysis to cut down the oxidation of the crucible and cathode. The current remained approximately constant at 12 amperes with an average voltage of 5 volts.

At the end of two hours operation the current was shut off, and the cathode was withdrawn and quickly covered with dry sodium chloride to protect the boron deposit from oxidation. When the cathode had cooled to below a visibly red glow, the cathode was immersed in water for a period of three hours. During this three hour period most of the cathode deposit fell off and the remainder was readily scraped off. The deposit was then digested in water for a period of four hours and then with strong hydrochloric acid. The residue was finally washed with water, filtered and allowed to dry. The residue was then weighed and the weight recorded as the weight of product from this system during a two hour test.

Two tests were made at the above conditions using a copper cathode. Three additional tests were made using the potassium chloride-potassium fluoborate system but the current was increased to 20 amperes with an average of 8 volts. A low-carbon, iron cathode was employed due to excess oxidation of the copper cathode during the two previous tests.

Operation Procedure for Sodium Oxide-Lithium Oxide-Boron Oxide

System. A prebaked graphite crucible was employed as the electrolytic cell for this system. A mixture of 53 grams of sodium carbonate, 42 grams of boron oxide, and 74 grams of lithium carbonate was fused at 900 °C for three hours. The bath was cooled to 650 °C and a low-carbon, iron cathode was lowered into the bath and the current was applied to begin the electrolysis. The current was maintained constant at 15 amperes with a range of 3.8 to 4.7 volts during the two hour test. The current was shut off at the end of the test and the same procedure used in the two previous systems was repeated.

Operational Procedure for Potassium Oxide-Potassium Fluoborate-

Boron Oxide System. A mixture of 138 grams of potassium carbonate, 41 grams of potassium fluoborate and 24 grams of boron oxide was fused at 900 °C for three hours. The bath was cooled to 850 °C and a low-carbon, iron cathode was lowered into the bath and the current was applied to begin the electrolysis. The current was maintained approximately constant at 15 amperes with an average of 7.2 volts. The current was shut off at the end of the test and the same procedure as used in the previous tests was repeated.

Due to the corrosive action of the bath on the graphite crucible, no further tests were made using the above mixture. In an attempt to decrease the alkalinity of the bath a mixture of two moles potassium carbonate to one mole of boron oxide instead of the three to one mole ratio used in the above test was tried. Two moles of potassium fluoborate was added which aided in decreasing the viscosity of the bath.

For this new mixture, 138 grams of potassium carbonate, 125 grams of potassium fluoborate and 35 grams of boron oxide were fused at 900 °C. The same procedure as used for the above mixture was employed. Three tests were made on this mixture. Two tests were performed at 850 °C and the other at 800 °C. Nitrogen was passed over the melt during one of the tests at 850 °C in order to determine the effect of nitrogen in decreasing the oxidation of the graphite crucible binder and iron cathode in this system.

Analytical Procedure. The cathode deposits were analyzed for boron and carbon content. A sample weighing approximately two grams was weighed on the analytical balance. This sample was then refluxed with 250 milliliters of 25 per cent by volume nitric acid. The sample was refluxed for one hour after all visible trace of nitrogen dioxide was evolved. The residue was filtered off and weighed. This weight being recorded as the weight of carbon in the sample.

The filtrate was analyzed for boron. The volume of filtrate was increased to 500 milliliters by adding distilled water. A 100 milliliter sample of the filtrate and 100 milliliters of methyl alcohol were distilled from a flask in a water bath. The methyl borate was distilled off and collected in distilled water where it immediately decomposed to form boric acid and methyl alcohol. An excess of mannite was added to the distillate which was then titrated with 0.789 normal sodium hydroxide. A Beckmen pH meter was employed and pH readings were recorded for every one milliliter of sodium hydroxide used. The pH values were then plotted against the volume

of sodium hydroxide used to titrate the distillate. From the changes in slope of the curve the volume of sodium hydroxide used to titrate the boric acid in the distillate was obtained. From this value the per cent boron in the original sample was calculated.

Digestion Tests. In order to furnish information as to the behavior of boron alloys, nitric acid digestion of boron carbide, manganese boron, nickel boron, calcium boron and ferro boron were performed. Samples weighing approximately two grams were refluxed with two to one nitric acid. Observations relating to the rate of reaction, effect of heating, and evolution of gas were recorded.

#### Data and Results

The experimental data and results obtained during this investigation have been converted to tabular form.

Experimental Data and Calculated Results. The experimental data and calculated results of this investigation are presented in Table I.

Analytical Data. The data obtained during the analysis of the products for boron and carbon content are presented in Table II.

Digestion Tests. Observations obtained from nitric acid digestion tests performed on boron alloys are presented in Table III.

TABLE I

Experimental Conditions, Data and Results  
for Electrolysis of Systems  
Containing Boron Oxide

Test No	Electrolyte	Electrolysis				Cathode C.D amps/sq cm	Product Wt. of Crude gm	Analysis of Product		Current Efficiency <sup>c</sup> %
		Time hrs	Temp. °C	Current amps	E.M.F. volts			Carbon %	Boron %	
1	4.5KCl-KBF <sub>4</sub> ·.6B <sub>2</sub> O <sub>3</sub> <sup>a</sup>	2	850	16.5	7.2	0.57	2.76	5.2	84.9	52.6
2	4.5KCl-KBF <sub>4</sub> ·.8B <sub>2</sub> O <sub>3</sub>	3	850	22.0	6.5	0.77	5.22	5.4	83.0	48.6
3	4.5KCl-KBF <sub>4</sub> ·.6B <sub>2</sub> O <sub>3</sub>	3	855	12.0	5.3	0.83	3.45	4.5	82.7	58.8
4	4.5KCl-KBF <sub>4</sub> ·.6B <sub>2</sub> O <sub>3</sub>	4	855	12.0	5.3	0.83	4.75	6.5	87.2	62.9
5	4.5KCl-KBF <sub>4</sub> ·.6B <sub>2</sub> O <sub>3</sub>	3	810	12.0	5.3	0.83	4.23	3.9	91.2	79.6
6	8.5KCl-KBF <sub>4</sub> <sup>b</sup>	2	825	12.0	4.9	0.41	2.68	0.9	78.2	65.0
7	8.5KCl-KBF <sub>4</sub>	2	825	12.0	5.0	0.41	2.82	0.7	63.4	55.4
8	8.5KCl-KBF <sub>4</sub>	2	835	20.0	8.0	1.38	4.82	0.9	95.6	85.4
9	8.5KCl-KBF <sub>4</sub>	2	835	19.0	8.0	1.31	4.31	0.9	94.6	79.8
10	8.5KCl-KBF <sub>4</sub>	2	825	20.5	7.5	1.41	4.56	0.9	96.8	82.5
11	5Na <sub>2</sub> O·10Li <sub>2</sub> O·6B <sub>2</sub> O <sub>3</sub>	2	650	15.0	4.5	1.04	1.52	68.4	11.1	4.2
12	3K <sub>2</sub> O-KBF <sub>4</sub> ·B <sub>2</sub> O <sub>3</sub>	2	845	14.5	7.1	1.02	2.16	13.0	78.2	43.4
13	2K <sub>2</sub> O·2KBF <sub>4</sub> ·B <sub>2</sub> O <sub>3</sub>	2	850	15.0	4.7	1.04	2.68	6.1	84.8	56.5
14	2K <sub>2</sub> O·2KBF <sub>4</sub> ·B <sub>2</sub> O <sub>3</sub>	2	850	15.0	5.0	1.04	2.84	5.8	85.1	60.1
15	2K <sub>2</sub> O·2KBF <sub>4</sub> ·B <sub>2</sub> O <sub>3</sub>	2	800	15.0	5.7	1.04	1.61	5.9	71.1	28.2

<sup>a</sup>Cooper, H. S.: Electrolytic Production of Elemental Boron, U. S. Patent 2,572,249 (Oct. 23, 1951)

<sup>b</sup>Cooper, H. S.: Electrolytic Method of Making Boron, U. S. Patent 2,572,248 (Oct. 23, 1951)

<sup>c</sup>Current efficiency based on 3.6 grams of pure boron per 26.8 ampere hours



TABLE II

Analytical Data for Product of Electrolysis  
of Systems Containing Boron Oxides

Test No	Electrolyte	Carbon Analysis			Boron Analysis			
		Weight of Sample gm	Carbon in Sample gm	Composition % C	Weight of Sample gm	Volume of 0.789 N NaOH ml	Boron in Sample gm	Composition % B
1	4.5KCl-KBF <sub>4</sub> -6B <sub>2</sub> O <sub>3</sub>	1.543	0.081	5.2	0.309	9.2	0.262	84.9
2	4.5KCl-KBF <sub>4</sub> -6B <sub>2</sub> O <sub>3</sub>	1.906	0.123	5.4	0.381	11.1	0.316	83.0
3	4.5KCl-KBF <sub>4</sub> -6B <sub>2</sub> O <sub>3</sub>	1.885	0.084	4.5	0.377	10.9	0.312	82.7
4	4.5KCl-KBF <sub>4</sub> -6B <sub>2</sub> O <sub>3</sub>	1.553	0.101	6.6	0.310	9.5	0.221	87.2
5	4.5KCl-KBF <sub>4</sub> -6B <sub>2</sub> O <sub>3</sub>	1.863	0.074	3.9	0.373	9.7	0.340	91.2
6	8.5KCl-KBF <sub>4</sub>	2.083	0.019	0.9	0.417	11.4	0.325	78.2
7	8.5KCl-KBF <sub>4</sub>	1.954	0.014	0.7	0.391	8.7	0.248	63.4
8	8.5KCl-KBF <sub>4</sub>	1.442	0.013	0.9	0.288	9.7	0.276	95.6
9	8.5KCl-KBF <sub>4</sub>	1.538	0.014	0.9	0.308	10.2	0.291	94.6
10	8.5KCl-KBF <sub>4</sub>	1.415	0.013	0.9	0.283	9.6	0.274	96.8
11	5Na <sub>2</sub> O-10Li <sub>2</sub> O-6B <sub>2</sub> O <sub>3</sub>	1.498	1.023	68.4	0.498	1.2	0.033	11.1
12	3K <sub>2</sub> O-KBF <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	1.992	0.258	13.0	0.398	10.9	0.311	78.2
13	2K <sub>2</sub> O-2KBF <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	1.532	0.094	6.1	0.306	9.1	0.306	84.8
14	2K <sub>2</sub> O-2KBF <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	1.576	0.091	5.8	0.315	9.5	0.271	85.1
15	2K <sub>2</sub> O-2KBF <sub>4</sub> -B <sub>2</sub> O <sub>3</sub>	1.238	0.073	5.9	0.248	6.2	0.177	71.1

TABLE III

Digestion Tests<sup>a</sup> of Boron Alloys  
in Nitric Acid

Alloy	Observations
Boron Carbide:	No reaction (even when concentrated HNO <sub>3</sub> was used).
Ferro-Boron:	Violent reaction, NO <sub>2</sub> given off, solution was pale yellow in color. Sample completely dissolved.
Manganese Boron:	Violent reaction, NO <sub>2</sub> given off, solution was yellow in color with a small amount of black residue present after refluxing.
Nickel Boron:	Slow reaction, greatly increased by heating, NO <sub>2</sub> given off, solution was green in color. Sample completely dissolved.
Calcium Boron:	Violent reaction, imparting a permanent dark red color to the solutions, NO <sub>2</sub> given off. Sample completely dissolved.

<sup>a</sup>Two gram samples were refluxed in 2:1 Nitric acid for 1 hour.

Sample Calculations

The calculations involved in this investigation were of the following types: calculation of the cathode current density, current efficiency, boron and carbon content of the product. This section contains all the calculations relating to test number 3. The same methods were employed for all other tests made in the attempt to produce boron by electrolysis.

Cathode Current Density. The current density was determined by dividing the average current, during the four hour test, by the surface area of the cathode below the level of the melt as follows:

$$D = \frac{C_a}{A}$$

where

D = current density, amps/sq cm

C<sub>a</sub> = average current, amps

A = surface area of cathode, sq cm

$$D = \frac{12.0}{14.5}$$

$$D = 0.83 \text{ amps/sq cm.}$$

Boron Analysis. The per cent boron in the product was determined by dividing the weight of boron in the sample by the total weight of the sample.

Weight of Boron. The boron in the sample was found by titrating the methyl borate distillate with sodium hydroxide using a pH meter. The volume of sodium hydroxide used to titrate the same was plotted against the pH values. The volume of sodium hydroxide required to titrate the sample, as boric acid, was found by the changes in slope of the curve as shown in Figure 2. The weight of boron was determined as follows:

$$W_b = V \times N \times E$$

where

- $W_b$  = weight of boron in sample, gm
- $V$  = volume of sodium hydroxide, ml
- $N$  = normality of sodium hydroxide
- $E$  = milliequivalents of boron, 0.0361

$$W_b = 10.9 \times 0.789 \times 0.0361$$

$$W_b = 0.312 \text{ gm.}$$

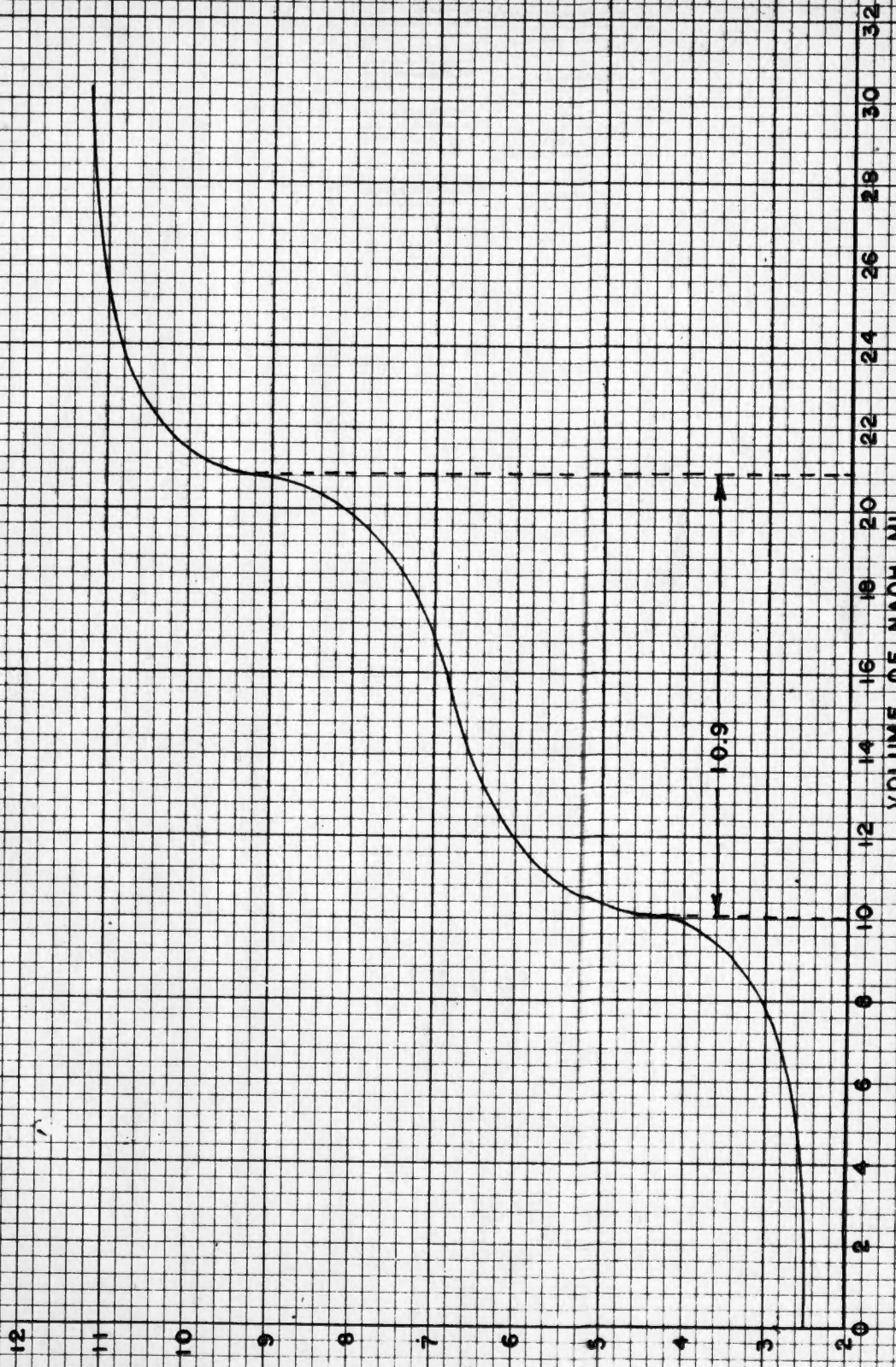


FIGURE 2. VOLUME-PH CURVE FOR BORON ANALYSIS USING 0.789 NORMAL SODIUM HYDROXIDE.

Per Cent Boron in Sample. The per cent boron in the product was determined as follows:

$$B = 100 \times \frac{W_b}{W_s}$$

where

B = boron in product, per cent

$W_b$  = boron in sample, gm

$W_s$  = weight of sample, gm

$$B = 100 \times \frac{0.512}{0.377}$$

$$B = 82.7 \text{ per cent.}$$

Carbon Analysis. The residue from the nitric acid digestion was expressed as the weight of carbon in the sample. The per cent carbon in the product was determined by dividing the weight of residue by the total weight of the sample as follows:

$$C = 100 \times \frac{W_c}{W_s}$$

where

C = carbon in product, per cent

$W_c$  = carbon in sample, gm

$W_s$  = total weight of sample, gm

$$C = 100 \times \frac{0.0841}{1.8853}$$

$$C = 4.5 \text{ per cent.}$$

Cathode Current Efficiency. The current efficiency was determined by dividing the actual weight of boron deposited on the cathode by the theoretical weight.

Theoretical Weight of Boron. The weight of boron that could be deposited, theoretically, was determined as follows:

$$W_t = \frac{C_a \times t \times E_q}{E_r}$$

where

$W_t$  = theoretical weight of boron, gm

$C_a$  = average current, amps

$t$  = time of test, hrs

$E_q$  = gram equivalent weight of boron,  
 $\frac{10.82}{3} = 3.61$

$E_r$  = ampere hours per equivalent, 26.8

$$W_t = \frac{12 \times 3 \times 3.61}{26.8}$$

$$W_t = 4.85 \text{ gm.}$$

Actual Weight of Boron. The weight of pure boron in the product was determined as follows:

$$W_b = W_p \times \frac{B}{100}$$

where

$W_b$  = boron in product, gm

$W_p$  = weight of product, gm

$B$  = boron in product, per cent

$$W_b = 3.45 \times \frac{82.7}{100}$$

$$W_b = 2.86 \text{ gm.}$$

Current Efficiency. The current efficiency was determined as follows:

$$C_e = 100 \times \frac{W_b}{W_t}$$

where

$C_e$  = current efficiency, per cent

$W_t$  = theoretical weight of boron, gm

$W_b$  = boron in product, gm

$$C_e = 100 \times \frac{2.86}{4.85}$$

$$C_e = 58.8 \text{ per cent.}$$



#### IV. DISCUSSION

The work performed in the investigation pertaining to the production of boron from systems containing boron oxide will be reviewed and analyzed under the general headings of discussion of results, recommendations and limitations.

##### Discussion of Results

The following discussion is presented in an attempt to interpret and clarify the experimental data and results of the investigation.

##### Potassium Chloride-Potassium Fluoborate-Boron Oxide System.

This system was studied in an attempt to duplicate the work performed by Cooper<sup>(13)</sup>. This was one of the first electrolytic processes reported as commercially practical as a means of producing elemental boron. A number of difficulties were encountered during the investigation and are worthy of mention in that they affected the operation of the system and experimental data.

Action of the Melt on Plumbago Crucibles. The first type of crucible used as the electrolytic cell in the study of the potassium chloride-potassium fluoborate-boron oxide system was a plumbago crucible. The plumbago crucible was made from "natural graphite" mixed with a clay binder and baked at 450 °C. The melt attacked the clay binder and penetrated the walls of the crucible in approximately two hours.

In an attempt to improve the resistance of the binder, a plumbago crucible was then baked at 1000 °C for a period of eight hours. Some of the graphite on the outside of the crucible was oxidized during the baking leaving the binder more exposed to the action of the melt. When the melt was heated to 850 °C in the prebaked crucible it penetrated the walls in less than 15 minutes.

Action of the Melt on Artificial Graphite Crucibles. An artificial graphite crucible was next used in an attempt to find a suitable electrolytic cell for the melt. The binder used in this type of crucible was presumed to be a coal tar pitch. The melt attacked the binder but not as fast as it attacked the clay binder in the plumbago crucibles.

Prebaking an artificial graphite crucible at 1000 °C for eight hours was tried in an attempt to improve the resistance of the crucible to the action of the melt. This proved very successful in that the same crucible was used for 7 hours of continuous operation with no noticeable attack by the melt.

Attack on the Graphite Crucible's Binder. During the electrolysis of the system potassium chloride-potassium fluoride-boron oxide, oxygen was evolved at the graphite crucible which served as the anode. Attack on the crucible's binder was observed around the top edge of the crucible.

A black scum was also observed on the surface of the melt, that had the appearance of finely divided carbon. This scum

was removed by Cooper<sup>(13)</sup> during larger scale operations and analyzed. It proved to be carbon, presumably from attack on the crucible's binder above the level of the melt and from erosive action of the hot bath. The bath was in a constant state of agitation due to the high current employed.

Cooper found that the carbon content of the product could be decreased from four per cent to less than one per cent by removing this black scum every ten or fifteen minutes during the electrolysis. The small scale operation used in this investigation made the removal of the black scum impractical. A protective atmosphere of nitrogen, however, was used in an attempt to decrease the attack on the crucible. By visual observation the action on the crucible was decreased considerably by the protective atmosphere. The carbon content of the product was decreased from 5.4 per cent in test 2 to 4.5 per cent in test 3 in a protective atmosphere.

Low-Carbon Iron Cathodes. It was found by Cooper<sup>(13)</sup> and confirmed by this investigation that low-carbon iron can be used satisfactorily as a cathode material. When cathodes of this material were removed from the cell, quickly coated with sodium chloride and allowed to cool, the bulk of the boron deposit was found to strip off easily. A thin adherent coating of boron remained on the cathode. This coating was not removed and proved helpful in reducing iron contamination of the product.

Further advantages of low-carbon iron cathodes are their excellent resistance to warping, low cost, and availability in any desired shape and size. The desired thickness of the cathode was found to be 3.2 millimeters or greater since the thinner electrodes tended to burn off above the bath.

Continuous Operation of the System. The same bath was used in test 3 and 4 in an attempt to check Cooper's<sup>(13)</sup> claim that the system could be operated on a continuous basis. The combined times of these two tests were 7 hours and boron oxide was added periodically as it was consumed in the electrolysis. Nitrogen was passed over the bath during the entire period of operation. After 3 hours of operation the cathode was removed and a new cathode was placed in the cell. This was done in order to find out if the carbon content of the product changed during long periods of operation.

The black scum accumulated as the time of electrolysis increased. The product from test 4 proved to contain 6.6 per cent carbon while the product from test 3 contained only 4.5 per cent carbon. This increase in carbon content was probably the result of the accumulation of finely divided carbon from the erosion of the graphite crucible.

Effect of Temperature. In this investigation of the system potassium chloride-potassium fluoborate-boron oxide, tests were made at  $850 \pm 5$  °C and  $810 \pm 5$  °C. Operation of the system at

$810 \pm 5$  °C proved to be more efficient than operating at  $850 \pm 5$  °C. The current efficiency increased from 62.9 to 79.6 per cent when the operating temperature was decreased 40 °C. This increase was presumably caused by a decrease in the diffusion of the cathode product to the anode. When the cathode was removed at the end of tests performed at  $850 \pm 5$  °C the cathode deposit appeared to be dissolving in the bath. The cathode deposit from the test performed at  $810 \pm 5$  °C was more uniform and attached more strongly to the cathode.

The amount of carbon in the product also decreased from 4.5 per cent for the test performed at  $810 \pm 5$  °C to 3.9 per cent for the test performed at  $850 \pm 5$  °C. These tests were performed under the same conditions except the temperature was varied 40 °C. The crucible used for the three hour test at  $810 \pm 5$  °C showed a sharp decrease in the attack on the crucible compared with the attack on the crucibles used at  $850 \pm 5$  °C.

The boron content of the product from the test performed at  $810 \pm 5$  °C increased 9.5 per cent over the tests performed at  $850 \pm 5$  °C.

Potassium Chloride-Potassium Fluoborate System. This system was also studied by Cooper<sup>(12)</sup>. In this system it appears that the potassium chloride is electrolytically decomposed to release chlorine at the anode. The potassium may be liberated and react with the boron salt to liberate boron at the cathode and produce potassium fluoride in the bath or boron may be liberated by direct electrode reaction.

Oxidation of Copper Cathodes. Cooper<sup>(12)</sup> stated that copper cathodes proved very successful in his investigation of this system at temperatures ranging between 800 and 850 °C. In this investigation copper cathodes were used in tests 6 and 7. It was found that the chlorine gas given off at the anode attacked the cathode even when nitrogen was used as a protective atmosphere. The tests were made at  $825 \pm 5$  °C and the product was contaminated by the copper from the cathode which oxidized above the level of the bath, fell in and dissolved, and was plated out along with the boron.

Since the copper cathodes, in tests 6 and 7 oxidized, low-carbon iron cathodes were used in tests 8, 9 and 10. The low-carbon iron was attacked by the chlorine gas but not to the same extent as was the copper. An oxidized layer formed on the iron cathodes but did not chip off and fall into the bath, as was the case when copper was used.

Oxidation of the Graphite Crucible's Binder. Oxidation of the binder around the top edge of the graphite crucibles was observed. This attack was not to the same extent as was observed when the system potassium chloride-potassium fluoborate-boron oxide was investigated. No black scum formed during this investigation although a small amount of finely divided carbon was noted floating in the bath. The products obtained in the five tests performed on this system contained less than one per cent carbon.

Continuous Operation of the System. In tests 6 and 7 the same bath was used. As the potassium chloride and potassium fluoborate were consumed, during the electrolysis, more was added. By adding more potassium chloride and potassium fluoborate the desired bath level was maintained.

The use of the same bath in both tests 6 and 7 explains the decrease in boron content and current efficiency of test 7. The boron content decreased from 78.2 per cent in test 6 to 63.3 per cent in test 7. This was caused by the accumulation of copper contamination from both tests. After test 7 was completed the bath was a brick color. The current efficiency decreased from 65 per cent in test 6 to 55.4 per cent in test 7. This current efficiency was based on the production of pure boron therefore it decreased as the boron content of the product decreased.

Tests 8, 9 and 10 were operated continuously in that the composition of the bath was maintained approximately constant by adding potassium chloride and potassium fluoborate as they were consumed. The products obtained during these tests, where a low-carbon iron cathode was used, proved to be rich in boron. The boron content in tests 8, 9 and 10 were 95.6, 94.8 and 96.8 per cent respectively. This system proved to give the purest product of the four systems investigated. Current efficiencies of 85.4, 79.8 and 82.5 per cent also proved the highest of any of the four systems investigated.

Sodium Oxide-Lithium Oxide-Boron Oxide System. This system was studied by Chao<sup>(8)</sup> in an attempt to find a suitable system for use in electrodeposition of aluminum. It was planned to investigate this system both under ordinary conditions and in an inert atmosphere to see if it could be used for electrolytic production of boron. Due to the operational difficulties and the poor results obtained from the one test performed on this system, work was discontinued.

Action of Melt on Graphite Crucible. The crucible used in this investigation was made of artificial graphite prebaked at 1000 °C for eight hours. The melt attacked the binder on the crucible to such an extent that the crucible fell apart. A two hour test was performed but the product proved to be 68 per cent carbon with only 11 per cent boron.

The current efficiency was only 39 per cent based on the total weight of product and only 4 per cent based on the production of pure boron. It was observed during the electrolysis at 650 °C that sodium was also deposited at the cathode and reacted with the atmosphere. During the first 15 minutes of the electrolysis the sodium was observed burning at the cathode. Due to the low current efficiency, low boron yield and the action of the melt on the crucible, work on this system was discontinued.



Potassium Oxide-Potassium Fluoborate-Boron Oxide System. This system was suggested by the work of Kahlenberg<sup>(26)</sup> and Cooper<sup>(13)</sup> although neither investigated this particular system. The mixtures  $3K_2O-KBF_4-B_2O_3$  and  $2K_2O-2KBF_4-B_2O_3$  were investigated.

Action of the Melt on Graphite Crucibles. The mixture  $3K_2O-KBF_4-B_2O_3$  proved to be too alkaline for the binder used in the graphite crucibles. The melt did not attack the binder to such an extent that the electrolysis could not be performed, but the product proved to contain 13 per cent carbon. A heavy black scum was noted on the surface of the bath as was the case when the potassium chloride-potassium fluoborate-boron oxide mixture was investigated. As the electrolysis proceeded the black scum accumulated rapidly. At the end of the two hour test the crucible was allowed to cool in order to observe the action of the melt on the crucible. The crucible was still solid but some crumbling was observed due to the action of the melt on the crucible binder.

The mixture  $2K_2O-2KBF_4-B_2O_3$  was next investigated in order to find out whether a decrease in potassium oxide would decrease the action of the melt on the crucible binder. This proved successful in that the carbon content of the product decreased from 13 to 6 per cent when this mixture was used. The crucible was attacked to some extent with formation of a black scum on the surface of the melt. This scum accumulated slowly and did not interfere with the electrolysis.

Nitrogen was passed over the melt in one test in order to see if this would decrease the black scum formation and therefore decrease the carbon content of the product. The binder at the top edge of the crucible was not oxidized to the same extent as during the test where nitrogen was not used. This however did not decrease the carbon content of the product enough to warrant its use. The carbon content decreased only from 6.1 to 5.8 per cent. From this it may be concluded that most of the black scum in this melt is caused by the erosive action of the melt on the crucible walls.

Effect of Temperature. Tests were made at 800 and 850 °C on the system  $2K_2O-2KBF_4-B_2O_3$ . The test performed at 800 °C proved unsatisfactory due to increase in viscosity of the melt. The viscosity increases very rapidly when the temperature was decreased 50 °C. When the cathode was removed from the bath at the end of the test at 800 °C it was observed that the melt stuck to the cathode. This increase in viscosity explains the low boron content of the product and the low current efficiency. The boron content decreased from 85 per cent for the tests performed at 850 °C to 71 per cent for the test at 800 °C. The current efficiency also decreased from 57 per cent to 28 per cent.

This decrease in temperature seemed to have little effect on the carbon of the product. The carbon content decreased only from 6.1 per cent to 5.9 per cent.

Digestion Tests on Boron Alloys. Nitric acid digestion tests were performed on various boron alloys. The observations recorded during these tests are given in Table III, page 50. Due to the possible formation of boron carbide and ferro-boron during this investigation, these tests are of interest.

Even when concentrated nitric acid was used, boron carbide failed to react. Since the boron carbide was not a desirable product, the use of this acid to dissolve the product did not introduce an error in the analysis for elemental boron. Any boron carbide present was included in the carbon content, for the undissolved residue was expressed as the carbon content of the product. The formation of boron carbide during electrolysis was very doubtful, because a temperature in the range of 2500 °C is necessary for its manufacture.

Ferro-boron reacted readily with nitric acid. If any ferro-boron was formed during the electrolysis it would cause an error in the boron analysis. To decrease this error a thin adherent coating of the product, which was probably ferro-boron, was allowed to remain on the cathode.

#### Recommendations

A number of improvements in both experimental apparatus and technique, suggested themselves during the course of the investigation. The following paragraphs contain recommendations to be considered in future investigations:

Effect of Concentration. The effect of varying the ratio of components in the system potassium oxide-potassium fluoborate-boron oxide should be studied. This investigation was limited to the two mixtures  $5K_2O-KBF_4-B_2O_3$  and  $2K_2O-2KBF_4-B_2O_3$ . Other mixtures should be studied in order to determine the optimum mixture to use in the production of elemental boron.

Effect of Potassium Fluoborate. The effect of potassium fluoborate on the production of elemental boron from the system potassium oxide-potassium fluoborate-boron oxide should be studied. Potassium fluoborate appears to decrease the viscosity of the mixture and a study of its effect may lead to a mixture that can be used efficiently to produce boron at operating temperature below  $800^\circ C$ .

Alkaline Resistant Crucibles. Due to the attack of the potassium oxide-potassium fluoborate-boron oxide mixture on the graphite crucible's binder an alkaline resistant crucible such as magnesia was desired. The use of an alkaline resistant crucible would eliminate most of the carbon in the product.

Graphite Rod Anodes. In this investigation the graphite crucible was used as the anode. The use of a graphite rod as the anode would make possible the use of some other material for the crucible that may prove more resistant to the alkaline attack on the crucible's binder.

Screen Analysis of Product. The use of screens for separating the product may prove valuable in decreasing the carbon content of the product. The carbon in the product is very finely divided and may possibly be removed by screening.

#### Limitations

This investigation was limited to the following: potassium chloride-potassium fluoborate-boron oxide, potassium chloride-potassium fluoborate, sodium oxide-lithium oxide-boron oxide and potassium oxide-potassium fluoborate-boron oxide.

Type of Apparatus. The crucibles used in this investigation were artificial graphite, 75 millimeters high with an inside diameter of 50.8 millimeters. The crucibles were prebaked at 1000 °C for a period of 8 hours.

The limitations placed on the investigation of the potassium chloride-potassium fluoborate-boron oxide system are given in the following paragraphs:

Melt Composition. The melt consisted of the following components: 4.5 moles potassium chloride, 1.0 mole potassium fluoborate, and 0.6 mole boron oxide.

Experimental Conditions. Five tests were performed during the investigation of this system. Four tests were made at  $850 \pm 5$  °C with current densities of 0.57, 0.77, 0.83 and 0.83 amperes per square centimeters, respectively. The times of the tests were 2, 3,

3 and 4 hours respectively. A three hour test was performed at  $810 \pm 5$  °C with a current density of 0.83 amperes per square centimeter. The crucibles studied were plumbago and artificial graphite which served as the anode as well as the electrolytic cell. Low-carbon iron was used as the material for the cathodes and a protective atmosphere of nitrogen was used in tests 3, 4 and 5.

The limitations placed on the investigation of the potassium chloride-potassium fluoborate system are given in the following paragraphs:

Melt Composition. The melt consisted of the following components: 8.5 moles potassium chloride and 1.0 mole of potassium fluoborate.

Experimental Conditions. Five 2 hour tests were performed during this investigation at  $825 \pm 5$  °C. Artificial graphite crucibles were used as the electrolytic cells as well as the anodes. Copper cathodes were used in two tests with a current density of 0.41 amperes per square centimeter. Low-carbon iron cathodes were used in three tests with current densities of 1.38, 1.31 and 1.41 amperes per square centimeter.

The limitations placed on the investigation of the system sodium oxide-lithium oxide-boron oxide are given in the following paragraphs:

Melt Composition. The melt consisted of the following components: 5 moles sodium oxide, 10 moles lithium oxide and 6 moles boron oxide.

Experimental Conditions. A two hour test at  $850 \pm 5$  °C, with a current density of 1.04 amperes per square centimeter was performed during this investigation. The cathode was low-carbon iron and the graphite crucible served as the anode as well as the electrolytic cell.

The limitations placed on the investigation of the system potassium oxide-potassium fluoborate-boron oxide are given in the following paragraphs:

Melt Composition. The two mixtures used in this investigation were  $3K_2O-KBF_4-B_2O_3$  and  $2K_2O-2KBF_4-B_2O_3$ .

Experimental Conditions. The investigation of the mixture  $3K_2O-KBF_4-B_2O_3$  was performed at  $845 \pm 5$  °C with a current density of 1.02 amperes per square centimeter. Three tests were performed on the mixture  $2K_2O-2KBF_4-B_2O_3$  with a current density of 1.04 amperes per square centimeter. The operating temperatures studied during these tests were  $850 \pm 5$  °C and  $800 \pm 5$  °C. Low-carbon iron cathodes and artificial graphite crucibles were used for this investigation.

## V. CONCLUSIONS

An investigation of the possibility of using a fused mixture of  $4.5\text{KCl-KBF}_4\text{-}.6\text{B}_2\text{O}_3$  for the electrodeposition of boron at  $810 \pm 5^\circ\text{C}$  and  $850 \pm 5^\circ\text{C}$ , led to the following conclusions:

(1) Boron, 91.2 per cent pure, can be electrodeposited from the fused mixture at a cathode current density of 0.83 amperes per square centimeter.

(2) A decrease in the operating temperature from  $850 \pm 5^\circ\text{C}$  to  $810 \pm 5^\circ\text{C}$  increased the boron content of the product by 8.5 per cent.

(3) The current efficiency increased by 20.8 per cent when the operating temperature was decreased  $50^\circ\text{C}$ .

(4) The carbon content of the product decreased by 0.6 per cent when a protective atmosphere of nitrogen was employed.

(5) The products contained a minimum of 3.9 per cent carbon from the erosive action of the melt on the graphite crucibles.

(6) Low-carbon iron can be used satisfactorily as a cathode material.

(7) Plumbago crucibles can not be used as the electrolytic cell.

(8) Artificial graphite crucibles, prebaked at  $1000^\circ\text{C}$  for 8 hours, can be used satisfactorily as the electrolytic cell.

An investigation of the possibility of using a fused mixture of  $8.5\text{KCl-KBF}_4$  for the electrodeposition of boron at  $825 \pm 5^\circ\text{C}$  led to the following conclusions:



(1) Boron, 96.8 per cent pure, can be electrodeposited from a fused mixture of  $8.5\text{KCl-KBF}_4$  at a cathode current density of 1.41 amperes per square centimeter.

(2) Low-carbon iron can be used satisfactorily as a cathode material.

(3) Copper can not be used satisfactorily as a cathode material since it oxidizes above the level of the melt.

(4) The purity of the boron product increased by 18.6 per cent when low-carbon iron was used in place of a copper cathode.

(5) The current efficiency increased by 17.5 per cent when the cathode current density was increased from 0.41 to 1.41 amperes per square centimeter and low-carbon iron was used instead of a copper cathode.

An exploratory investigation of the possibility of using a fused mixture of  $5\text{Na}_2\text{O-10Li}_2\text{O-6B}_2\text{O}_3$  for the electrodeposition of boron at  $650 \pm 5$  °C led to the following conclusions:

(1) Boron can not be electrodeposited from a fused mixture of  $5\text{Na}_2\text{O-10Li}_2\text{O-6B}_2\text{O}_3$  at a cathode current density of 1.04 amperes per square centimeter.

(2) Artificial graphite crucibles, prebaked at 1000 °C for 8 hours, can not be used satisfactorily as the electrolytic cell.

(3) Low-carbon iron can be used satisfactorily as a cathode material.

An exploratory investigation of the possibility of using a fused mixture of  $3K_2O-KBF_4-B_2O_3$  for the electrodeposition of boron at  $845 \pm 5$  °C, led to the following conclusions:

(1) Boron, 78.2 per cent pure, can be electrodeposited from a fused mixture of  $3K_2O-KBF_4-B_2O_3$  at a cathode current density of 1.00 amperes per square centimeter.

(2) Artificial graphite crucibles, prebaked at 1000 °C for 8 hours, can not be used satisfactorily as the electrolytic cell for the product will be contaminated with carbon.

(3) Low-carbon iron can be used satisfactorily as a cathode material.

An exploratory investigation of the possibility of using a fused mixture of  $2K_2O-2KBF_4-B_2O_3$  for the electrodeposition of boron at  $800 \pm 5$  °C and  $850 \pm 5$  °C, led to the following conclusions:

(1) Boron, 85 per cent pure, can be electrodeposited from a fused mixture of  $2K_2O-2KBF_4-B_2O_3$  at  $850 \pm 5$  °C with a cathode current density of 1.04 amperes per square centimeter.

(2) A 14 per cent decrease in boron content results when the operating temperature is decreased 50 °C.

(3) The melt is too viscous for efficient operation at  $800 \pm 5$  °C.

(4) The current efficiency decreases 32 per cent when the operating temperature is decreased 50 °C.

(5) A protective atmosphere of nitrogen decreased the carbon content of the product 0.3 per cent.

(6) Artificial graphite crucibles, prebaked at 1000 °C for 8 hours, can not be used satisfactorily as the electrolytic cell.

VI. SUMMARY

This investigation was conducted to attempt to find an electrolyte that would be suitable for the electrodeposition of boron and to duplicate work performed by previous investigators.

Methods for the electrochemical production of boron previously investigated have either yield a product too impure for practical use, or have involved such serious operating difficulties as to be entirely impractical as commercial processes.

In the present investigation, the systems  $4.5\text{KCl-KBF}_4\text{-}.6\text{B}_2\text{O}_3$  and  $8.5\text{KCl-KBF}_4$  were investigated at 800-850 °C in an attempt to duplicate the methods reported in the literature as suitable for use as commercial processes. When the electrolyte  $4.5\text{KCl-KBF}_4\text{-}.6\text{B}_2\text{O}_3$  was used, boron, 91.2 per cent pure, was electrodeposited at a cathode current density of 0.83 amperes per square centimeter. When the electrolyte  $8.5\text{KCl-KBF}_4$  was used, boron, 98 per cent pure, was electrodeposited at a cathode current density of 1.41 amperes per square centimeter.

The system  $5\text{Na}_2\text{O-}10\text{Li}_2\text{O-}6\text{B}_2\text{O}_3$  was investigated at  $650 \pm 5$  °C. The deposit obtained proved to contain 68 per cent carbon and only a trace of boron when a cathode current density of 1.04 amperes per square centimeter was employed. The melt attacked the graphite crucible's binder and in no way showed any promise as an electrolyte for commercial use in the production of elemental boron.

The systems  $3K_2O-KBF_4-B_2O_3$  and  $2K_2O-2KBF_4-B_2O_3$  were also investigated. The melts proved alkaline in nature and attacked the graphite crucible's binder. The product obtained when the  $3K_2O-KBF_4-B_2O_3$  system was investigated at  $850 \pm 5$  °C proved to contain 78 per cent boron and 13 per cent carbon. The system  $2K_2O-2KBF_4-B_2O_3$  was studied to determine the effect of decreasing the alkalinity of the bath. The product obtained when this mixture was studied at  $850 \pm 5$  °C proved to contain 85 per cent boron and 6 per cent carbon.

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