

ELECTROCHEMISTRY OF SYSTEMS CONTAINING
ALUMINUM PHOSPHATE DISSOLVED IN
FUSED BORATE AND PHOSPHATE
MIXTURES

by

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I. INTRODUCTION

Aluminum coated metal has the merits of good appearance and high resistance to oxidation at all temperatures. Thus aluminum coated metals combine the desirable mechanical properties of the base metal and the chemical resistance of aluminum.

Various methods proposed for the production of these aluminum coatings are: electrodeposition of aluminum on the base metal, rolling the sheet of the base metal and sheet of aluminum together and thereby welding together, casting the base metal in an aluminum-lined mold and rolling the product, calorizing, spraying, dipping, thermal evaporation and cathode sputtering.

However, there are deficiencies in all these methods, with the exception of electrodeposition method. It is very difficult to obtain a good bond between the metals when the base is an aluminum alloy, a bond which will have satisfactory mechanical properties under bending, and stresses. A further disadvantage of these methods is that, in the case of an object of complex form, it is difficult to obtain a uniform coating. Evaporation and cathode sputtering, because of the high vacuum required, are only used for coating special mirrors.

On the other hand, electroplating method possesses

the advantage of giving a more mechanically stable coating of even and easily controlled thickness. Also, owing to the high purity and regularity of electrodeposited metal, its resistance against corrosion is excellent.

The reason it is difficult to electroplate with aluminum from aqueous solution is that aluminum has a much lower molar electrode potential than that of hydrogen, and aluminum compounds are amphoteric in character. When an aqueous solution of aluminum salt is electrolyzed, hydrogen gas is evolved, without deposition of aluminum.

All methods proposed for deposition of aluminum have not been commercially successful. Aluminum halides, especially aluminum chloride, are the most frequently used solutes. Aluminum chloride is one of the strongest peptizing agents for aluminum oxide and its hydrate. The decisive factor in the corrosion of aluminum is the behavior of the system of aluminum and aluminum oxide which is always present as a surface film. The articles plated from the bath containing aluminum chloride always have aluminum chloride occluded on their surfaces. Therefore, severe corrosion of the articles plated from the bath containing aluminum chloride is expected.

Furthermore, because of the moisture-absorbing property of aluminum halides, all processes containing them require special precautions to exclude moisture in order

to maintain the life of the electrolytic bath.

For these reasons, investigation of the use of aluminum salts other than halides as solute for the preparing the electrolytic bath appears to offer advantages.

The purpose of this investigation was to study the possibility of using, as the electrolyte for the deposition of aluminum, systems containing aluminum phosphate dissolved in fused borate and phosphate mixtures.

II. LITERATURE REVIEW

It is proposed to review the literature with the following objectives: the principal papers dealing with the evaluation of various methods of electrodeposition of aluminum will be reviewed. The literature on the phase relations of aluminum salts with other salts, electrochemical studies of the nonaqueous solutions of aluminum salts and the properties of electrodeposited aluminum coating will be surveyed and information on experimental techniques and apparatus pertinent to the problem will be examined.

History of Electrochemistry of Aluminum

To trace the story of aluminum it is not necessary to go back very far, since aluminum is a recent development.

It was 1809 that an attempt to separate it from its oxide was made by Sir Humphry Davy⁽⁴²⁾. This attempt was made by passing an electric current from a voltaic pile through a fused bath of iron and aluminum oxide. The product was an alloy of aluminum alloy which could not be separated. This is the earliest report of an experiment using electricity to produce aluminum.

Oersted⁽¹⁴⁸⁾ produced the first aluminum in 1824 by gently heating potassium amalgam with aluminum chloride

and then distilling off the mercury. Wohler⁽²¹²⁾ changed Oersted's method by using metallic potassium instead of potassium amalgam in 1827. Deville⁽⁴⁸⁾ further improved Wohler's method by using metallic sodium instead of potassium as a reducing agent in 1854. The successful preparation of aluminum by electricity was also accomplished in 1854. Bunsen and Deville^(34,44) obtained the aluminum independently by the electrolysis of fused aluminum chloride and sodium chloride mixture. The present process of commercial production of aluminum was developed simultaneously and independently by Charles M. Hall and C. S. Bradley^(79,31) in the United States and by Paul Heroult in France.⁽⁸²⁾ The essential of the process was the use of the cryolite as the electrolyte in which pure aluminum oxide was dissolved. An electric current of low voltage, high amperage was passed through the fused bath.

Despite its apparent simplicity of operation and other advantages, Hall's process has the following serious drawbacks: use of the comparatively high temperature (1000 °C), high purification cost of the bauxite ore, very rapid rate of consumption of specially prepared high grade carbon anodes (0.6 to 0.8 pound carbon per pound aluminum produced), high corrosive nature of molten cryolite and impure nature of primary metal and its subsequent costly refining to obtain a high purity product. For these reasons, Bunsen and

Deville's method was varied by Plotnikov and co-workers,⁽¹⁶⁴⁾ Yntema and co-workers,^(217, 218, 219) Wasilewski and co-workers⁽²⁰¹⁾. Fink and Solanki⁽⁶⁷⁾ claimed success in producing 100 per cent pure aluminum crystals from a fused bath of 1 to 1 molar ratio of aluminum chloride and sodium chloride at 400 °C with a cell voltage 5 to 8 volts, and current density 10 amperes per square decimeter. Johannes Brode and co-workers⁽³²⁾ were successful in producing aluminum by using a rotating cathode in a low melting point fused mixture of aluminum chloride and less than equimolecular amount of a chloride of alkali or alkaline earth metal.

Another attempt to solve the production of metallic aluminum was the electrolysis of aluminum subsulfide. Paul Rontgen and Heins Brochers⁽¹⁷⁸⁾ showed that it seemed best to use a mixture of 60 per cent aluminum subsulfide and 40 per cent sodium chloride which had good fluidity at 700 °C. Preliminary experiments disclosed that the electrolysis of this system should be cheaper than that of aluminum oxide-cryolite, because the decomposition potential of aluminum subsulfide was one volt lower, the current efficiency was 25 per cent higher, the attack on carbon anode was less and the operating temperature was lower. According to Khazanov and Belyaev,⁽⁹⁹⁾ the current efficiency for electrolyzing a fused mixture of aluminum subsulfide dissolved in 70 per cent sodium chloride and 30 per cent cryolite at

800 °C was 55 per cent. Addition of alumina did not influence the current efficiency, but the addition of ferrous sulfide reduced the efficiency sharply.

Another way of producing aluminum was patented by G. L. Williams⁽²¹⁰⁾. He used an "oleum" comprising sulfuric acid containing 85 per cent of sulfuric anhydride as electrolyte to dissolve aluminum sulfate. The anode was graphite and the cathode was aluminum. When current was passed, aluminum was deposited at the cathode and the sulfuric anhydride was generated at the anode. The latter dissolved in the "oleum" electrolyte vehicle. As "oleum vehicle" became depleted of aluminum by its deposition through its electrolysis, aluminum hydroxide or hydrated oxide was added to the "oleum".

Aluminum produced by Hall's process seldom has a purity higher than 99.7 per cent. Hoopes⁽⁸⁶⁾ developed a process for refining aluminum electrolytically to produce a product that is 99.99 per cent pure. The aluminum to be refined is alloyed with copper and silicon and rests in the bottom of the cell under a layer of fused mixture of cryolite, aluminum fluoride, barium fluoride, and alumina. Floating on this is a layer of molten refined aluminum, serving as cathode. The operating temperature of the cell is between 900 to 1000 °C. A thick crust that is rich in alumina solidifies on the walls of the cell, insulating

it electrically and thermally. The cell operates at 5 to 7 volts and about 20,000 amperes.

Physical Properties of Aluminum

Physical properties of aluminum are reviewed under the topics of color, density, freezing point, electrical resistivity and mechanical properties.

Color. The pure metal is silvery white in color, but the aluminum of commercial purity has a bluish tinge resulting from the presence of iron and silicon constituents.

Density. With the exception of magnesium and beryllium, aluminum is the lightest metal used structurally. The density of a sample of aluminum of 99.971 per cent purity was 2.6989 grams per cubic centimeter at 20 °C when in the rolled condition and 2.6996 grams per cubic centimeter after annealing. (55)

Freezing Point. The freezing point⁽⁵⁵⁾ for a sample of metal having 99.60 per cent purity is 653 °C. The purest metal tested (99.97 per cent aluminum) had a freezing point of 659.8 °C. By extrapolation from the available data, the freezing point of substantially pure aluminum would be close to 660 °C. Commercial aluminum having a purity of about 99.2 per cent has a freezing point of 657 °C.

Electrical Resistivity. Measurements at the Bureau of Standards⁽¹¹⁶⁾ on wire made from electrolytically refined

aluminum (99.968 per cent) showed a resistivity at 20 °C of 2.688 and 2.674 microhms per centimeter cube for hard drawn and annealed wire, respectively. The temperature coefficient of resistance at 20 °C was 0.00421 per degree Centigrade for the hard drawn wire and was 0.00423 for the annealed wire.

The resistivity of liquid aluminum at the freezing point, 658 °C was 20.13⁽¹⁴⁷⁾, 25.5⁽¹²⁹⁾, and 27.1⁽²⁹⁾, microhms per centimeter cube according to different workers.

For commercial aluminum conductors of 99.5 per cent purity, hard drawn samples are specified at an electrical resistivity of 2.828 microhms-centimeters at 20 °C with a resistance temperature coefficient of 0.00403 per degree Centigrade⁽¹²⁾.

Mechanical Properties. Electrolytically refined aluminum of high purity possesses mechanical properties appreciably different from those usually associated with commercial grades of the metal⁽⁵⁸⁾. The values of mechanical properties of refined grade of the metal were obtained by extrapolation of curves obtained from tests of 99.98 per cent pure metal and other samples of less purity. Commercial aluminum always has higher tensile strength, shearing strength and Brinell hardness than the corresponding properties of the refined aluminum.

Chemical Properties of Aluminum

Chemical properties are reviewed under the topics of composition of commercial aluminum, electrolytic solution potential, behavior toward oxygen and water, actions toward acids and alkalies, actions toward fused alkalies and fused salts, and miscellaneous reactions.

Electrolytic Solution Potential. Generally, aluminum⁽⁵⁷⁾ is considered to be electropositive to magnesium and electronegative to such metals as manganese, zinc, cadmium, iron, nickel, and copper. Some writers, however, speak of aluminum as being "electropositive" to such elements as nickel and copper.

The determination of solution potential of aluminum by different observers shows considerable variation. The erratic behavior of aluminum is usually ascribed to the formation of a film of oxide on the surface of aluminum.⁽⁵⁷⁾ The classic results are those of Neumann,⁽¹⁴⁶⁾ who measured the potential of aluminum immersed in normal solutions of aluminum sulfate, aluminum chloride and aluminum nitrate; when referred to the normal hydrogen electrode as zero of reference, Neumann's values are -1.31, -1.29 and -1.05 volts respectively.

Latimer and Greenfelder⁽¹¹⁴⁾ have calculated the electrode potential of aluminum from appropriate thermal data to be -1.69 ± 0.01 volts at 25 °C.

In most natural waters, in dilute, neutral salt solutions and in weak acid solutions, zinc is anodic to aluminum, whereas in strong alkaline solutions, the reverse is true ⁽¹⁰¹⁾. However, the heavy metals, particularly, copper and nickel, have much lower solution potentials than aluminum, and their contact in presence of an electrolyte usually results in definite electrolytic attack on aluminum. The fact that zinc is anodic to aluminum can be used in the protection of aluminum.

Attack on aluminum ⁽⁸⁾ occurs only when in direct contact for appreciable length of time with metals that are considerably more cathodic, with an electrolyte present. Thus galvanic attack can be prevented by separating the adjoining surfaces by use of bituminous paint, by keeping the contacting surface dry, by electroplating, or by painting the contacting surfaces with aluminum paint to cut the difference in solution potentials of the adjoining metal surfaces.

Another type of attack ⁽¹⁰²⁾ may result from contact of aluminum with solutions containing salts of heavy metals such as copper, nickel, cobalt and mercury. For example, copper in solution may deposit on aluminum by replacement, an equivalent amount of aluminum going into solution. The precipitated copper acts as the cathode in a short circuit electrolytic cell, so that the aluminum anode continues to

dissolve and pitting results. The action can be minimized by regular cleaning of the surface with an abrasive cleaner, which removes the heavy metal deposits.

Behavior Toward Oxygen and Water. Although aluminum stands high in the electrolytic potential series with an electronegative potential, it is resistant to atmospheric attack and water (102). A freshly exposed surface of aluminum does oxidize instantaneously in air, but the oxide film which is formed is highly protective and stable, so that oxidation ceases under ordinary conditions as soon as the protective film is formed.

The film of aluminum oxide is so compact and non-porous⁽⁵⁹⁾ that it can prevent the aluminum from oxidation with dry oxygen even at 600 °C. Even molten aluminum is protected by the oxide film. This is the reason why molten aluminum can be tapped from the reduction cell without any evidence of burning. It is impossible to ignite sheet aluminum, even with an oxyhydrogen flame; the metal melts but does not burn.

When aluminum is in contact with pure water, the oxide film on aluminum becomes completely protective, so that no appreciable corrosion or solution of aluminum occurs. The action of water containing dissolved salts may or may not be corrosive, depending on the quantity and character of the dissolved material⁽⁵⁹⁾.

Salts composed of strong acid radicals, except the halides, and weak base radicals have very little effect on aluminum⁽¹³⁷⁾. The halogen bearing salts, such as ammonium chloride, are very corrosive unless used in connection with an inhibitor. Ammonium nitrate and ammonium sulfate are used satisfactorily with aluminum.⁽¹³⁷⁾

Salts composed of weak acid radicals and strong base radicals, which on hydrolysis form pseudo-alkaline solutions, should not be used with aluminum unless suitable corrosion inhibitors, such as sodium or potassium chromate, are employed⁽¹³⁷⁾.

Neutral salts have little effect on aluminum if heavy metal salts are absent.⁽¹³⁷⁾

Action Toward Acids and Alkalies. In general, aluminum is more resistant to attack by acids rather than by alkalies⁽⁶²⁾.

All dilute mineral acids attack aluminum at an appreciable rate. Generally speaking, the attack increases with the concentration of the acid and with the temperature.⁽¹⁰⁰⁾

Mitchell⁽¹³⁷⁾ has given a qualitative description of the action of different acids and alkalies on aluminum and its alloys:

"Concentrated nitric acid, 95 per cent by weight, does not attack high purity aluminum. The rate of attack is very slow for concentrations above 80 per cent or below

5 per cent, but the attack is considered excessive for concentrations between 5 to 70 per cent by weight. Fuming nitric acid is commonly handled in aluminum tanks and drums.

"The attack by sulfuric acid is greater than that by nitric acid, but high purity aluminum can be used with solutions containing up to 5 per cent sulfuric acid. High purity alloys have been used with solutions up to 15 per cent sulfuric acid. Fuming sulfuric acid has a low rate of attack, but any appreciable amounts of water or water vapor cause serious attack.

"Hydrochloric acid, hydrofluoric acid and hydrobromic acid solutions readily attack the aluminum alloys. Perchloric acid is decidedly corrosive to aluminum alloys. Phosphoric acid solutions are usually used to clean and etch aluminum surfaces, and therefore, should not be used in lengthy contact with aluminum.

"All strengths of boric acid solutions have very limited effects on aluminum. Weak solutions, less than 5 per cent, of chromic acid have little effect on aluminum; the rate of attack is excessive for concentration above 10 per cent.

"Dilute acetic acid has a very low rate of attack on aluminum and glacial acetic acid has negligible rate, either hot or cold. Most of the other organic acids,

except formic acid, have little action on aluminum at room temperature, although the rate increases somewhat at high temperatures. The presence of a few tenths per cent water in organic acids will inhibit the action because of the film formation."

Edwards⁽⁶¹⁾ showed that aluminum dissolves energetically in caustic alkali solution and is attacked with less rapidity by hot solutions of sodium carbonate. The presence of sodium silicate largely inhibits the action of sodium carbonate upon aluminum but is hardly effective with sodium and potassium hydroxide unless the solution is very dilute. Ammonium hydroxide, however, appears to form a protective coating on aluminum so that it becomes relatively insoluble.

Actions Toward Fused Alkalies and Fused Salts.

Deville⁽⁴⁵⁾ showed that fused sodium hydroxide did not attack aluminum. Beketoff⁽¹⁹⁾ showed aluminum reacted with fused potassium hydroxide at high temperature, some potassium was formed and volatilized.

According to Mallet⁽¹²²⁾, calcium, strontium and barium oxides are partially reduced at high temperature by aluminum and the reduced metals are volatilized. Weston and Ellis⁽²⁰⁶⁾ found that aluminum reduced lime when heat was applied, but it did not reduce magnesia.

According to Goldschmidt⁽⁷²⁾, practically all metal

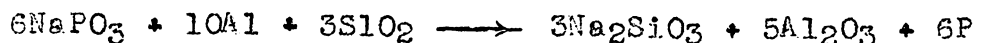
oxides other than those discussed above are reduced by heating them with aluminum powder. The metal sulfides are more easily reduced than the oxides. The metal sulfates react more vigorously than sulfides. Violent explosion may occur when sulfates and aluminum are melted together. Metal chlorides are not suitable for high temperature reduction by aluminum on account of their volatility. Deville⁽⁴⁷⁾ said that aluminum could be fused with potassium nitrate without the least change, even at red heat. If the temperature be high enough to decompose the nitre, the metal forms potassium aluminate with the liberated potassium oxide, and the reaction is sometimes accompanied by deflagration.

Potassium carbonate⁽¹⁹⁵⁾ is less vigorously reduced by aluminum than the sulfate, some carbon and aluminate being formed. There is no deflagration. If a mixture of aluminum and dry sodium carbonate be heated in a carbon and lime crucible, or in graphite crucible lined with lamp black, sodium is formed and volatilized, and there remains a regulus of aluminum, crystal of alumina, aluminum nitride and carbon.

According to Richards⁽¹⁷⁶⁾, when fluorspar is melted, it gives a little hydrogen fluoride vapor, produced by a reaction with hygroscopic moisture, thus forms a little aluminum fluoride; otherwise, the molten fluoride has no

action on aluminum. Cryolite attacks finely divided aluminum at a temperature exceeding 1,000 °C, but the metal en masse is not attacked.

Tissier⁽¹⁹⁵⁾ observed no change when a mixture of calcium phosphate and aluminum foil was heated to whiteness. Rossel and Frank⁽¹⁷⁹⁾ found that many phosphates, for example, ammonium sodium hydrophosphate, sodium metaphosphate, bone meal, phosphorite and magnesium pyrophosphate, when heated with aluminum, aluminum phosphide, alumina and aluminate were formed, and phosphorus was volatilized. If silica was simultaneously present, whole phosphorus in the compound was volatilized as shown by the following reaction:



Miscellaneous Reactions. Pure nitrogen⁽⁶⁰⁾ does not appear to react with aluminum below its melting point. It can be bubbled through molten aluminum at a temperature as high as 800 °C with very little reaction taking place. However, finely divided aluminum, such as aluminum powder, will react energetically with nitrogen, once the reaction is started by heating.

Sulfur⁽⁶⁰⁾ has very little reaction upon aluminum, even in the molten state. A salient characteristic of aluminum, which makes it quite useful in many industries, is its resistance to sulfur, sulfur fumes and hydrogen sulfide.

Aluminum powder can be safely stirred into molten sulfur somewhat above the melting point of sulfur; such a mixture has an appearance of cast aluminum, and has been used to patch defects of aluminum castings. But if sulfur and aluminum mixture is burned with magnesium ribbon, the reaction is "lively but harmless". If it is ignited with a mixture of magnesium and barium peroxide, however, it reacts explosively.

According to Mellor⁽¹³²⁾, silicon does not unite with aluminum when the two elements are heated together, but if a third element is present, mixed silicides are formed. Aluminum vapor attacks porcelain liberating silicon, which is absorbed by the molten aluminum. Molten aluminum was found by Smith⁽¹⁹⁰⁾ to blacken glass. If the metal be melted in a fireclay crucible, there is a risk of contamination. Magnesia lined crucible or furnace beds can be used satisfactorily for melting aluminum.

"Deville"⁽⁴⁴⁾ made an alloy of aluminum with boron by melting the metal with borax, boric acid or potassium fluoborate. Wohler and Deville⁽²¹³⁾ further showed that the so-called "graphitforming Bors" was really AlB_2 or Al_2B_4 , and they made it by heating a mixture of boron and aluminum, or of boric oxide and aluminum for a short time at not too high temperature; by passing boron chloride over heated aluminum; or by heating a mixture of potassium fluoborate (8 parts), potassium and sodium chloride

(16 parts) and aluminum (5 parts) at the melting point of silver. The excess of aluminum was removed by treatment with hydrochloric acid, sodium hydroxide and hydrofluoric acid. Weston and Ellis⁽²⁰⁶⁾ reduced boron trioxide with aluminum powder by the thermite reaction, and boiled the product with hydrochloric or hydrofluoric acid, or fused it with borax and extracted with water. A residue said to contain aluminum boride and alumina remained. Hampe⁽⁸⁰⁾ said that the crystals of the diboride looked as red copper plates, and he showed that the crystalline boron by Wohler and Deville was really a mixture of AlB_{12} or Al_2B_{24} and aluminum borocarbide. He made it by fusing aluminum with boric oxide and cryolite or fluospar and by passing boron fluoride over heated aluminum. The first process gave the best results, the most important condition for the success being the absence of carbon; the temperature of melting iron maintained for two to three hours was sufficient to produce the crystals, but the yield was larger at high temperatures. According to Blitz⁽²²⁾, the black crystals, being specifically lighter, could be separated from those of aluminum borocarbide by flotation in a mixture of CH_2I_2 and C_6H_6 . Hampe⁽⁸⁰⁾ stated that the crystals were black or in very thin laminae dark red, and yielded a borwnish red powder; they belonged to the monoclinic system. The hardness is

greater than that of corundum, and less than that of diamond. The crystals become steel-blue when heated in air, and do not change when heated in oxygen at the temperature at which the diamond burns; they are not attacked by aqueous solution of potassium hydroxide, or boiling concentrated sulfuric acid; gradually dissolved completely by hot concentrated nitric acid, with the production of some aluminum hydroxide; oxidized with incandescence by molten potassium hydroxide or lead chromate; not attacked by molten potassium nitrate; and slowly dissolved by molten pyrosulfate. This boride forms a fusible alloy with platinum."

Electrochemistry of Molten Electrolytes

The electrolysis of fused salts is of considerable importance technically. The chief work in this field has been that of Lorenz and his pupils. (118,119,120,121) Hall-Heroult's process (79,80) of manufacturing aluminum is a good example of its application to industry.

Electrical Conductivity. Molten salts are good conductors of electricity, and their conductivity is electrolytic. At anode and cathode are liberated the products as expected. Thus lead chloride gives lead and chlorine, sodium nitrate gives sodium together with oxygen and nitrous gases. The specific conductance of the most con-

centrated aqueous solutions, but the equivalent conductance is comparatively small on account of the high concentration of the electrolyte. As with aqueous solutions, the conductance increases considerably with rise of temperature, indeed for moderate temperatures almost linearly. At high temperatures the increase of conductivity falls behind the rise of temperature. In most cases, the effect of temperature can essentially be accounted for by the decrease thereby produced in the viscosity of the melt.

The conductivity of a fused salt mixture is usually rather less than what would be calculated from the mixture law, and sometimes falls below the conductivity of any of the pure components⁽¹⁸⁵⁾. Impurities in the salt, however, sometimes give an abnormally large conductance.

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 salts of particularly high conductivity, the electrodes must be separated 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.

"Thus Lorenz and Helfenstein⁽¹²¹⁾, in the electrolysis of lead chloride, obtained the following figures for the cathodic current efficiency at 520 °C: anode protected from electrolyte, 97.95 per cent; cathode protected from electrolyte, 99.46 per cent; both electrodes protected from electrolyte, 99.98 per cent" as cited by Allmand and Ellingham⁽³⁾.

The chief factors in low cathodic efficiency in the electrolysis of molten salts are volatility, diffusion of anode products to cathode, formation of "metal fog" and action of atmospheric oxygen. With increase in temperature, the yield must therefore fall rapidly. 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

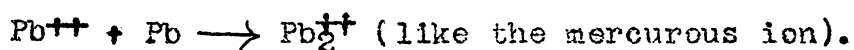
may consequently fall to zero. The amount of increase of current density is only limited by considerations of voltage and development of Joule heat near the electrodes, and by the entrance of an "anode effect", which results in large rise in voltage. Occasionally, losses may occur because of the formation of a subsalt between the precipitated metal and the melt. This can happen under certain conditions in the electrolysis of calcium chloride where red crystals of calcium subchloride are produced, or, again, the melt may actually dissolve the metal, forming a true solution, as occurs during electrolysis of molten sodium hydroxide. However, such cases are rare.

Metal Fog. If a metal such as zinc or lead be melted under one of its own fused salts (for example, zinc chloride or lead chloride), the molten salt will remain unaffected if the temperature be kept low. But if it is raised, dark clouds rise up from the metal and apparently dissolve in the melt, and this continues until a state of equilibrium is reached. When the temperature falls, the clouds settle down slowly, and finally re-enter the metal. If the excess of the massive metal be removed and air excluded, then the colored melt appears stable, but if the oxygen be admitted, or a trace of oxidizing agent added, the color disappears.

On the other hand, metal fog can be produced in the

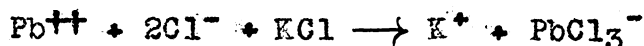
absence of the massive metal by the addition of a small quantity of a reducing agent. Essentially the same phenomena must occur during the electrolysis of molten salts, and will adversely affect the yield, since the metal present in that form is far more readily attacked chemically than the massive metal.

That these metal fogs are colloidal in nature would naturally be conjectured, and has been proven by the work of Lorenz and Eitel⁽¹²⁰⁾. It is not, however, precisely certain what forces regulate their density and stability.⁽¹¹⁹⁾ In this connection, it is interesting to notice the effect on the metal fog formation of addition of certain neutral salts to the original melt. These largely prevent fog formation, just as the addition of electrolytes to an aqueous colloidal solution may precipitate the colloid. The mode of action in the two cases can hardly be the same, however, It has been suggested that when fused metal and fused salt come into contact, a certain amount of complex cation is produced, thus:



The metal fog would then represent metal dissociated from this complex and in equilibrium with it. The effect of added salts is explained by assuming that they remove the cation of the first salt from the melt as complex

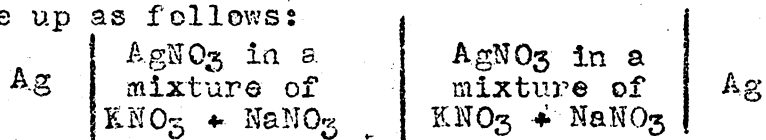
anion, thus perhaps:



The concentration of the complex cation, and hence the metal fog, must decrease.

The effect of this addition of neutral electrolytes can be studied by measuring its effect on the cathodic current efficiency during electrolysis. As the fog formation is one of the chief sources of loss in the preparation of metal, the two effects will run more or less parallel. In other cases, where the electrolysis losses under normal conditions are greater, the effects produced are even more marked. But not every addition to the electrolyte increases the current efficiency.

Voltage Relations. With pure fused salts, the reversible electromotive force of a primary cell depends simply on the nature of the electrodes and the electrolyte and on the temperature, as does the corresponding decomposition voltage. With mixtures of salts, however, it can be shown that the electromotive forces depend upon the concentration of the salt corresponding to the metal used as electrode. Thus Gordon⁽⁷⁴⁾ measured the voltage of cells made up as follows:



the concentration of silver nitrate in the melts surrounding the two electrodes being different. He found that the

electromotive force of such cells could be expressed by the well-known formula for concentration cells,

$$E = \frac{0.0002T}{n} \ln \frac{C_1}{C_2}$$

where n is, of course, one in this case, and C_1 and C_2 are the molecular concentrations of the silver nitrate.

Irreversible voltage effects⁽⁴⁾, are far less important with molten salts than with aqueous solutions. Such effects ultimately depend upon the low velocity of some stage of electrode process, and, in view of the known effect of temperature on reaction velocity, it is natural that at high temperatures they should be in general very slight. But nevertheless, when the current density becomes excessive, they make their appearance; and particularly what is known as the "anode effect" is observed at the carbon anodes in fused metallic halides. The electrodes became covered with a film of gas, chlorine, fluorine, bromine or iodine, through which the current can only pass as an arc discharge. The voltage rises very considerably and the anode appears to glow, as a consequence of the number of tiny arcs which are passing. It is most pronounced with fluorides, least so with iodides. Stirring, raising the anode from the melt for a moment, or reversing the current--in other words, removal of the gas layer--cause the effect to disappear.

The only other appreciable irreversible effect is the concentration polarization which occurs at high current densities⁽⁴⁾. Apart from the formation of a gas layer on the electrode, the voltage of the working cell increases with increasing current density, just as in aqueous electrolytes. In the latter case, the cause of increasing voltage is the exhaustion of the ions near the electrode, and if the presence of ions in the molten salts is assumed, the same cause can be assumed to be active in the case of molten salts.

The reversible electromotive force of a cell can be determined by either the decomposition voltage or the polarization discharge method⁽⁴⁾. In the latter case, the curve obtained falls far more rapidly than a similar curve obtained with an aqueous electrolyte, because of the high temperature and rapid rate of diffusion of products away from the electrodes.

Through the differences in decomposition potential shown by different salts⁽⁴⁾, a separation of the several metallic constituents from a mixture is possible in a molten state, just as in aqueous solution. The relations, of course, may be rendered rather complex by the varying tendencies of the metals to alloy among themselves, and thus to depolarize one another's discharge.

Hall-Heroult's Process. The connection between the exact composition of the electrolyte and its freezing point

in the process has been studied by several workers, whose results are not very concordant. Cryolite is reported to have a melting point of 977⁽¹⁵⁰⁾, 1000⁽⁶⁵⁾, and 1023⁽¹⁷⁵⁾ °C. Its melting point is lowered by the addition of either sodium fluoride or aluminum fluoride as shown in Figure 1⁽¹⁷⁵⁾. On the addition of sodium fluoride, the melting points of the eutectic are reported to be at: 885 °C, 14 mole per cent aluminum fluoride and 86 mole per cent sodium fluoride⁽⁶⁵⁾; 886 °C, 13.6 mole per cent aluminum fluoride and 86.4 mole per cent sodium fluoride⁽¹¹⁸⁾; or 935 °C, 16.5 mole per cent aluminum fluoride and 83.5 mole per cent sodium fluoride⁽¹⁷⁵⁾. The formation of a compound in which the content of aluminum fluoride is richer than that in cryolite, commences to solidify at 740⁽¹⁷⁵⁾, 725⁽⁶⁵⁾, and complete solidification takes place at 685 °C with a composition 46.4 mole per cent aluminum fluoride and 53.6 mole per cent sodium fluoride.

The solubility of alumina in cryolite is shown in Figure 2 as determined by Fedotieff and Iljinsky⁽⁶⁵⁾. The lowest freezing point, 935 °C, is obtained at an alumina content of about 15.5 per cent. Excess of sodium fluoride increases the solubility of alumina, while excess of aluminum fluoride diminishes it.

Pascal and Jouniaux⁽¹⁵⁰⁾ have studied the effects of addition of fluorspar to the eutectic mixture of cryolite

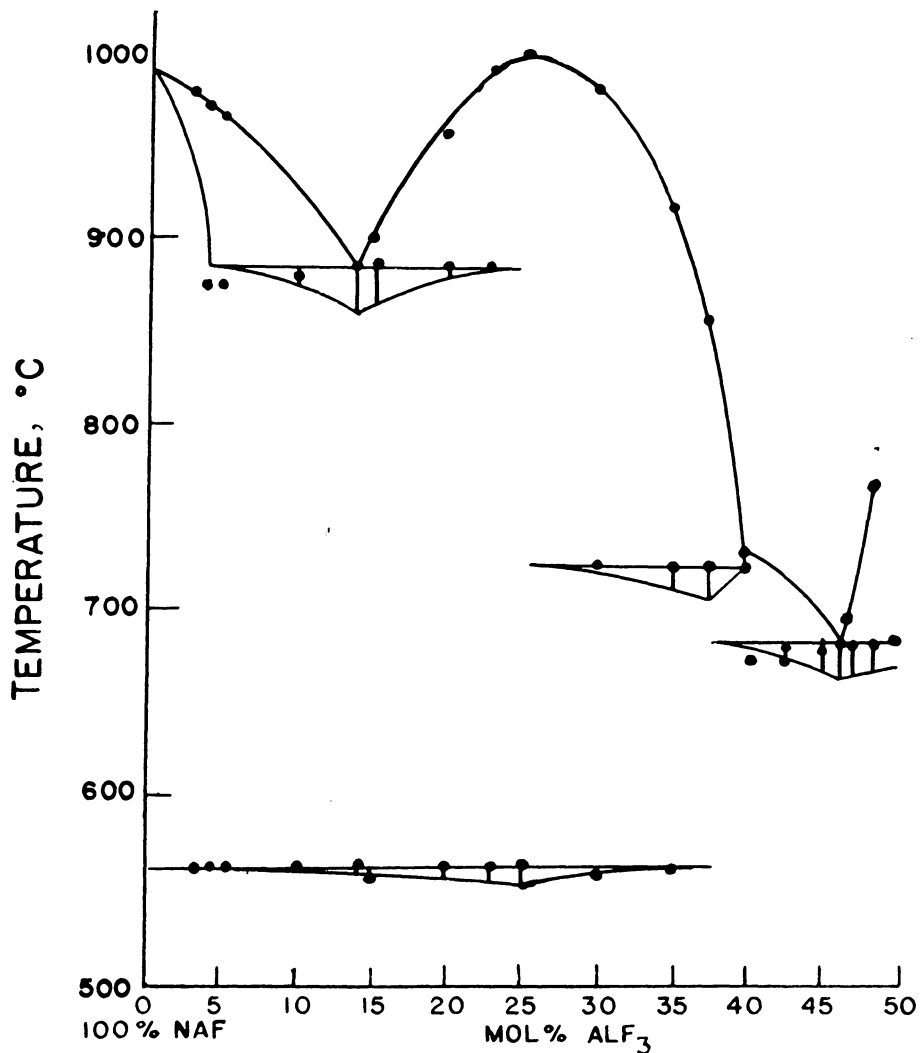


FIGURE 1. TEMPERATURE—CONCENTRATION
DIAGRAM OF ALUMINUM FLUORIDE
AND SODIUM FLUORIDE

PUSCHIN, N. A. AND A. V. BASKOV: EQUILI-
BRIUM IN BINARY SYSTEMS OF FLUORIDES
ZEITSCH. ANORG. CHEM. 81, 347 (1913)

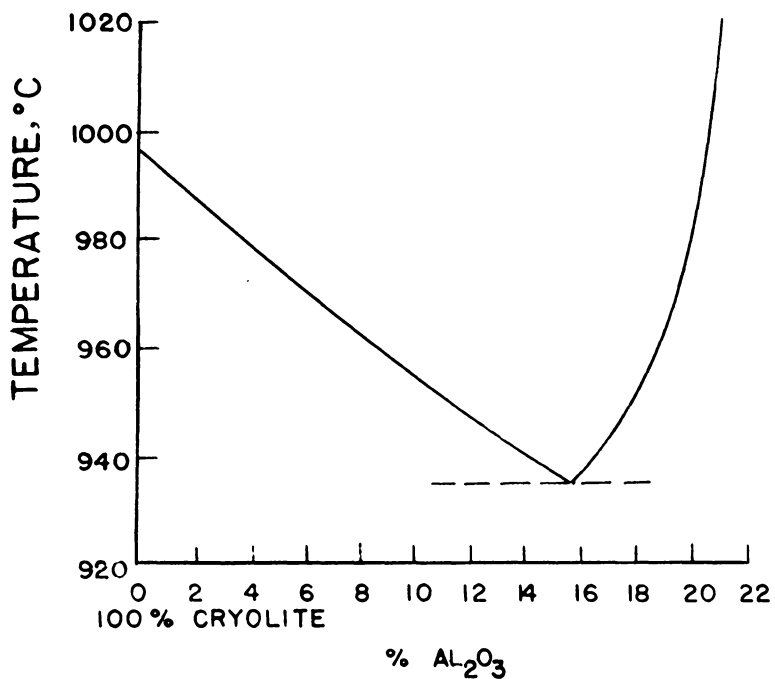


FIGURE 2. FREEZING POINT CURVE FOR ALUMINA-CRYOLITE SYSTEM

FEDOTIEFF, P. P. AND D. V. ILJINSKII
ELECTROMETALLURGY OF ALUMINUM,
ZEITSCH. ANORG. CHEM. 80, 113 (1913)

and aluminum oxide, and have shown that it is possible, by addition of one part of fluospar per three parts of cryolite, to reduce the solidifying point of a melt containing 20 to 25 per cent aluminum oxide and 75 to 80 per cent cryolite by another 30 to 40 °C. In practice, the temperature of the bath is almost invariably kept at 900 to 950 °C.

The specific conductivity of the technical bath has been given as 5 reciprocal ohms per inch-cube, or about 1.9 reciprocal ohms per centimeter-cube⁽¹¹⁸⁾. Addition of an excess of sodium fluoride raised the specific conductivity. The conductivity decreases linearly as the alumina content increases. It is clear therefore that the voltage rise across the technical cell when its aluminum content becomes low is caused by electrode polarization phenomena, and not by resistance change in the electrolyte.

The decomposition voltage of solutions of alumina in fused cryolite lies at 2.1 to 2.2 volts⁽⁶⁵⁾. If calculated by Helmholtz-Thomson rule, the result is shown by Allmand and Ellingham⁽⁷⁾ as: sodium fluoride, 4.7 volts; aluminum fluoride, 4.0 volts; and alumina, 2.8 volts. These values, though far from being absolutely correct, will stand in the right order, and aluminum oxide will most easily undergo decomposition. When a very high current density is used at the cathode, the liberation of sodium has been observed.

Fluorine can be formed anodically if the aluminum oxide content of the electrolyte has become very low, or if the current density used is too high. In that case, there is a marked "anode effect" and the voltage rises considerably.

When the anode effect takes place, the voltage across the cell rises suddenly from 6 to 7 volts up to 40 or 60 volts, and the carbon anodes are surrounded by a gaseous envelope. The liquid electrolyte does not seem actually to touch or "wet" the anodes so that current passes from the anodes to the electrolytes as a multitude of tiny sparks or arcs. The gas evolved at the anodes during this time is carbon monoxide, whereas during normal operation the anode gas contains well above 50 per cent carbon dioxide (105).

The formation of metal fog or cloud is a common phenomenon. Metallic aluminum in extremely fine particles becomes suspended in the electrolyte. Because of the circulation of the electrolyte caused by the electromagnetic forces acting on it, some of the metallic fog comes in contact with anode where it is reoxidized to alumina, resulting in low current efficiency (105).

During normal operation the voltage drop per cell including that of connections varies between 5 to 7 volts. Forty to one hundred cells are connected in series requiring

a line electromotive force from 200 to 600 volts, and each line of cells will take from 8,000 to 30,000 amperes⁽¹⁰⁵⁾.

The power required per pound of aluminum produced is generally between 10 to 12 kilowatt-hours, and there is anode carbon consumption of 0.6 to 0.8 pound per pound of aluminum. The current efficiency varies between 75 to 90 per cent⁽¹⁰⁶⁾.

The study of the production of aluminum has been the subject of several laboratory investigations.^(78,193,145,177) The results of these investigations confirm the advisability of using low anodic current densities. Not only is "anodic effect" thereby excluded, but both voltage and anode consumption are decreased in the regular course of work. The excessive anode losses observed by Harber and Gerpert⁽⁷⁸⁾ are directly attributable to their very high current densities. There can be little doubt that the anode effect which occasionally appears is not due to a layer of oxygen or oxides of carbon but to one of fluorine gas, which is formed because electrolyte has become depleted of alumina. High anodic current density thus falls into line with all other anode effects attributed to evolved halogens, particularly with that noticed by Muthmann, Hoffer and Weiss⁽¹⁴⁴⁾, in the electrolysis of pure molten cryolite, which was very marked at a current density of 4 to 5 amperes per square centimeter.

Survey of Literature on Deposition of Aluminum

Attempts to deposit aluminum from aqueous solutions were first made by Wohler⁽²¹²⁾ and Deville⁽⁴⁵⁾ in 1854. Since then, numerous other trials have been made⁽¹³¹⁾. These include the electrolysis of freshly precipitated alumina or alum in a solution of potassium cyanide, a mixed solution of alum or aluminum sulfate and calcium or sodium chloride, warm dilute solution of aluminum hydroxide in hydrochloric acid, saturated aqueous solution of ammonium aluminum chloride. Several of these processes have been challenged by Wohler and Deville. Though there were many claims of success, deposition of aluminum was not achieved. Doubt was also thrown on Tucker and Thomssen's deposit⁽¹⁹⁶⁾ which they claimed to be obtained by carrying out electrolysis in an aqueous aluminum chloride paste with a rotating cathode at the rate of 20,000 rotations per minute. After 1915, P. Marino⁽¹²⁴⁾ obtained a patent covering an electrolyte of strong solution of pyrophosphate to which has been added 10 per cent phosphoric acid and 5 to 10 per cent sulfanilic acid; Quintin Marino and Darlington Wire Mill, Ltd.⁽¹²⁵⁾, claimed to get a deposit of aluminum from an aqueous solution of aluminum tartrate, paratartrate or oxalate; Tumanov⁽¹⁹⁷⁾ utilized a diaphragm over

the cathode on the bottom of liquids immiscible with water such as aniline or chloroform to prevent the resolution of the aluminum deposited from aqueous solution on the cathode.

Another attempt to deposit aluminum is from non-aqueous inorganic solvents. Thus, Taft and Harold Barham⁽¹⁹¹⁾ electrolyzed a solution of aluminum nitrate in liquid ammonia at a temperature range of -33.5° to -57°C . In no case was the slightest deposited aluminum obtained, but gasing always occurred at both electrodes.

Booth and Merlub-Sobel⁽²⁸⁾ electrolyzed aluminum iodide solution in liquid ammonia. With the various current densities tried, there was vigorous gasing and a blue-black film seemed to form on the cathode, but this deposit, if such it was, disappeared whenever the current was turned off.

Three other possible methods for solving the problem of depositing aluminum remain: to electroplate from a bath of fused inorganic mixture, fused onium salts, and from organic solvents. Most investigations were in these three fields. They will be discussed separately in some detail.

Electrochemistry of Solutions of Aluminum in Fused Inorganic Bath. Some aluminum salts and other salts fuse together to form a liquid bath of melting point below that

of aluminum. Many such liquid mixtures possess high electrical conductivity, and can be used to deposit aluminum. In the literature, the aluminum salts used are nearly always limited to aluminum halides, especially aluminum chloride.

Prediction of Solubility of Fused Inorganic Mixtures.

A good method for predicting the solubility of fused mixtures does not exist. James Kendall and co-workers⁽⁹⁶⁾ studied the solubility behavior, which is attributed to the following nine factors.

Diversity Factor. Solubility and formation of compounds depend primarily upon the diversity of the constituent radicals. For example, bromides of metals much more positive than aluminum provide the most complex and most stable compounds with aluminum bromide. Alkali bromides are all extremely soluble in aluminum bromide at a temperature only slightly above its melting point; at 130 °C, 30 to 40 mole per cent. With bromides of alkaline earth metals, the solubility is less than one mole per cent at the same temperature. The same low solubility is found for magnesium, manganese, cadmium and lead bromides, while silver bromide again shows a solubility of more than 30 per cent.

The Valence Factor. The salts of univalent metal, in general, give several compounds with

either aluminum chloride or aluminum bromide, the unimolecular type being particularly stable. Salts of divalent metals, for example: those of calcium, barium, magnesium, seldom furnish more than one compound with aluminum chloride or bromide and even that is sometimes unstable. Salts of trivalent metals give highly dissociate compounds in the liquid state. Antimony tribromide and bismuth tribromide are two examples. No formation of compounds at all was obtained for salts of quadrivalent radical, such as stannic chloride.

The Unsaturation Factor. The salt in which the radical is unsaturated shows far greater compound formation than the salt in which the maximum valence is exercised. For example: stannous chloride forms compounds with aluminum chloride, but stannic chloride does not form compound with aluminum chloride.

The Position Factor. The tendency towards the formation of compounds with aluminum halides in general decreases as one goes down the electrode-potential series.

The Temperature Factor. Many of the compounds in the aluminum bromide series crystallize at tempera-

tures far below the available experimental range for aluminum chloride mixture, and the failure to isolate compounds in the latter series must frequently be due to the impossibility of securing sufficiently low temperature for their separation as solid phase from solutions containing them.

Internal Pressure Difference. Hildebrand⁽⁸³⁾ showed that in nonpolar system, solubility or freezing point depression are dependent primarily upon the relative values of the internal pressures of the two compounds. The internal pressure is the force which, together with the external pressure, opposes the thermal pressure which is due to the kinetic energy of the molecules. Where internal pressures are equal, the course of the curves may be calculated directly from ideal solution theory. As internal pressures diverge, solubility diminishes and when the divergence is very large, two liquid layers may occur.

Molecular and Atomic Volumes. Holmes⁽⁸⁵⁾ showed that when the ratio of molecular radii exceeds 1.618 to 1, partial miscibility will occur; whereas a ratio higher than 2.414 to 1, will induce complete immiscibility. In none of the mixtures studied by Kendall and co-workers does the

molecular volume ratio of the components exceed the lower limiting value of the cube of 1.618 to 1, yet partial miscibility is very frequent.

In fused salt systems, indeed, where the polarity of at least one component is generally marked, to consider the action of atomic volume or radical volume as the factors that directly affect compound formation and solubility appears more logical.

The Atomic Number Factor. Abegg⁽¹⁾ has noted that addition compound formation, with a given group of positive radicals in the periodic system, increases with increasing atomic weight, for example; when aluminum bromide was used as the solvent, phosphorus tribromide and arsenic tribromide did not form complex compounds; the freezing point curve of antimony tribromide indicated an equimolecular compound, very highly dissociated into its components; with bismuth bromide, a much more stable complex was isolated. When antimony trichloride was used as the solvent, lithium chloride and sodium chloride were insoluble, but potassium chloride gave two different complex compounds. In general, however, the in-

fluence of highly polar compounds is sufficient to mask the effect entirely.

Association Factor. In systems consisting of two similar components, both associated, compound formation may occur by substitution instead by addition. When both components are highly polar, disintegration and recombination of various molecular and ionic types will be present.

Summary of Solubility Factors. As shown previously, many factors conflict with each other, hence these factors can only offer some help in prediction and are not very reliable.

Phase Diagrams of Fused Inorganic Bath. The phase diagrams reviewed in this section include aluminum fluoride series, aluminum chloride series, aluminum bromide series and miscellaneous.

Aluminum Fluoride Series. Fused mixtures of aluminum fluoride with sodium fluoride alone, and with sodium fluoride and aluminum oxide, and the effect of calcium fluoride on the melting point of latter mixtures was discussed previously in Hall-Heroult's process.

Puschin and Baskoff⁽¹⁷⁵⁾ made a thorough study of the melting point-composition curve of aluminum

fluoride with other alkali fluorides.

The melting point of mixtures of lithium fluoride and aluminum fluoride decreases from 870 °C to a eutectic at 706 °C as the composition varies from zero to 14.5 mole per cent of aluminum fluoride; then rises to a maximum of more than 783 °C, when the mixture corresponds with the formula $3\text{LiF} \cdot \text{AlF}_3$. The temperature then falls to the eutectic 691 °C at 37 mole per cent aluminum fluoride. The curve was not further explored.

For aluminum fluoride and potassium fluoride, there is a eutectic at 837 °C, 7.5 mole per cent aluminum fluoride. There is another eutectic at 568 °C at about 40 mole per cent aluminum fluoride. Between the eutectic points the curve rises to a maximum at 1030 °C with a composition approximating $3\text{KF} \cdot \text{AlF}_3$.

For aluminum fluoride and rubidium fluoride, an eutectic exists at 790 °C with 6.5 mole per cent of aluminum fluoride, a maximum at 985 °C corresponding to $3\text{RbF} \cdot \text{AlF}_3$ and a second eutectic at 570 °C.

For caesium fluoride and aluminum fluoride, an eutectic exists at 685 °C with 5.5 mole per cent aluminum fluoride; a maximum at 823 °C corresponding

with the melting point of $3\text{CsF}\cdot\text{AlF}_3$ and another eutectic at 490°C .

Fedotief and Timofeev⁽⁶⁴⁾ worked with the systems potassium fluoride-aluminum fluoride and lithium fluoride-aluminum fluoride. The data they obtained may be said to check with Puschin and Baskoff's work. The melting point of the cryolite type compound $3\text{KF}\cdot\text{AlF}_3$ and $3\text{LiF}\cdot\text{AlF}_3$ are 1025° and 790°C respectively. In the fused mixture of potassium fluoride and aluminum fluoride, there is probably an unstable compound $\text{KF}\cdot\text{AlF}_3$ with transition point at 575°C . There is no evidence of a similar compound of lithium fluoride and aluminum fluoride.

Aluminum Chloride Series. This series has been subjected to the most extensive study by many investigators: James Kendall and co-workers⁽⁹⁶⁾, André Chretien and Eskild Louis⁽³⁸⁾, Shvartsman⁽¹⁸⁸⁾ worked on two-component systems, whereas Wasilewski and co-workers⁽²⁰¹⁾ and Plotnikov and Shvartsman⁽¹⁷⁰⁾ worked on three-component systems. Slight differences exist among different reports. The melting points of bicomponent equimolar compounds $\text{LiCl}\cdot\text{AlCl}_3$, $\text{NaCl}\cdot\text{AlCl}_3$ and $\text{KCl}\cdot\text{AlCl}_3$ are 143.5° , 152° and 257°C . The eutectic points are: for lithium chloride

and aluminum chloride mixture, 114 °C and 40 mole per cent lithium chloride; for sodium chloride and aluminum chloride mixture, at 93, 108 or 123 °C and 34, 39 or 41 mole per cent sodium chloride; for potassium chloride and aluminum chloride mixture, at 114, 128 or 149 °C and 29, 33 or 34.5 mole per cent potassium chloride. The eutectic point of aluminum chloride, potassium chloride and sodium chloride mixture is reported to be: 70 °C with a composition: aluminum chloride 66 mole per cent, sodium chloride 20 mole per cent and potassium chloride 14 mole per cent by Wasilewski and co-workers⁽²⁰¹⁾; and 89 °C with a composition: aluminum chloride 63.5 mole per cent, sodium chloride 20 mole per cent and potassium chloride 16.5 mole per cent by Plotnikov and co-workers.⁽¹⁷⁰⁾ A comparison of bicomponent eutectic mixture and tricomponent eutectic mixtures shows that the latter have lower melting points than the former.

Aluminum Bromide Series. In this series, only bicomponent data can be found in the literature. The melting points of equimolar compounds are reported as: $\text{LiBr} \cdot \text{AlBr}_3$, 194⁽¹⁵⁴⁾ or 197⁽⁹⁶⁾ °C, $\text{NaBr} \cdot \text{AlBr}_3$, 201 °C⁽⁹⁶⁾, and $\text{KBr} \cdot \text{AlBr}_3$, 191.5⁽⁹⁶⁾

or 170 to 173 °C⁽¹⁷¹⁾. There are still other molecular compounds, such as: $\text{LiBr} \cdot 7\text{AlBr}_3$, $\text{NaBr} \cdot 7\text{AlBr}_3$ and $\text{KBr} \cdot 2\text{AlBr}_3$ with melting points of 114, 95.6 and 95.8 °C respectively, as given by Kendall and co-workers⁽⁹⁶⁾. The eutectic mixtures are reported to be for sodium bromide and aluminum bromide, 95 °C and 18 mole per cent sodium bromide, and for potassium bromide and aluminum bromide, 88 °C and 26 mole per cent potassium bromide⁽⁹⁶⁾.

A comparison of three halide series shows that fluoride series differs greatly from the remaining two as expected from the special property of fluorine compounds in the halogen family. Most fused fluorides without special modification cannot be used for electroplating aluminum, because of too high melting point of eutectics. The higher or lower temperature of the melting point of the eutectic mixture depends upon the positive radical of alkali salts used. For the same halide of the same type complex compound, the melting point is increased, with the exception of $\text{KBr} \cdot \text{AlBr}_3$, $\text{LiBr} \cdot 7\text{AlBr}_3$ and $\text{NaBr} \cdot 7\text{AlBr}_3$, as the atomic weight of alkali radical is increased. The more aluminum chloride in the complex molecule,

the lower the melting point of the complex salt.

A glance at phase diagrams of chloride series and bromide series shows that on the latter series, the melting point-composition curve is much flatter than on the former series. Henceforth, fused bromides may offer better regions for study than the fused chlorides do.

Miscellaneous. Aluminum chloride and phosphorus pentachloride fused mixtures have been studied by Fisher and Juberma⁽⁶⁸⁾. The compound formed at 1 to 1 ratio is unexpectedly stable. Its melting point, 380 °C is above the critical temperatures of both components. Between the range of 0 to 50 mole per cent phosphorus pentachloride, the melting point-composition diagram of the system shows eutectic formation with possibility of a solid solution region between 40 to 45 mole per cent phosphorus pentachloride. Between the range of 50 to 100 mole per cent phosphorus pentachloride, two immiscible phases appear. Apparently, the compound $AlPCl_3$ is composed of ionic aggregates.

The melting point of the mixture of aluminum chloride and aluminum bromide also have been subjected to study⁽¹⁹⁸⁾. The data cover the range

of aluminum chloride from 0 to 76.1 mole per cent. The eutectic point is 73.1 °C and 34.8 mole per cent aluminum chloride.

Electrochemistry of Fused Aluminum Salts. Electrochemistry of fused aluminum salts is studied under four topics: electrical conductivity, deposition potential of aluminum from fused liquid, effect on the structure of aluminum deposit in fused aluminum chloride-sodium chloride bath and electrodeposition of aluminum from inorganic fused mixtures.

Electrical Conductivity. The conductivities of the pure aluminum halides were measured by Biltz and Voigt⁽²³⁾. Of the molten halides, the aluminum iodide has the greatest conductance, aluminum chloride an intermediate, and aluminum bromide the least conductivity. The values at 230 °C are aluminum iodide, 4.1×10^{-6} ; aluminum chloride, 0.9×10^{-6} and aluminum bromide, 1.5×10^{-7} reciprocal ohms.

Dissolving alkali halide in aluminum halide, the conductivity of resulting liquid rises sharply. For the systems lithium chloride, sodium chloride and potassium chloride in fused aluminum bromide, the conductivity is greater, the greater the mobility of the alkali metal ion.

For the system aluminum chloride-sodium chloride, the molar conductivity⁽¹¹¹⁾ is directly proportional to the temperature. Maximum conductivity occurs at equal mole amounts of aluminum chloride and sodium chloride. For aluminum chloride within the range of 53 to 57 mole per cent, Bainakov and Shelomov⁽¹⁷⁾ showed that the current was carried by sodium ion; during the transfer of the current by the sodium ion, there was also some solvation of sodium chloride which was carried off to the cathode; aluminum chloride was in complex, and because of its small mobility, complexes did not act as a current carrier.

The conductivity of a ternary system is much greater than that of a binary system; for example: addition of a little calcium sulfate to aluminum chloride-sodium chloride system increases the conductivity 200 times⁽¹⁶⁷⁾.

Deposition Potential of Aluminum from Fused Salts. Aluminum has never been deposited satisfactorily from fused salts bath. Most of the literature is limited to the determinations of electromotive force of reversible cell made of aluminum electrodes immersed in the fused salts

bath^(153,54,189) and the decomposition potential of the cell^(217,218,219). Yntema and co-workers⁽²¹⁹⁾ have determined the deposition potentials of metals including aluminum from alkali chloride-aluminum chloride bath with reference to platinum electrode as zero potential. The order of the deposition is the same as that in the voltaic series in aqueous solution with the exception of copper in the experiment with the copper ion, nickel ion, ferric ion, zinc ion, manganous ion, aluminum ion and hydrogen ion. In another paper, Yntema and co-workers⁽²¹⁸⁾ showed that in aluminum bromide-alkali bromide bath, the order of deposition potentials of the metals: aluminum, zinc, lead, bismuth, silver, copper, mercury and hydrogen, is the same as the voltaic series for the aqueous sulfate solution of these metals, except for the interchanged positions of copper and silver and the location of hydrogen at the noble end of the series. All these investigations showed that only in the presence of alkali or alkaline earth metals does the fused aluminum salt bath favor deposition of pure aluminum. If other heavy metallic ions are present in the bath, heavy metals will deposit before aluminum.

The decomposition potential of aluminum chloride in fused alkali chloride-aluminum chloride bath is 2.02 volts as determined by Yutema and co-workers⁽²¹⁷⁾. At this potential value, smooth bright deposits on the platinum cathode were obtained. Dendritic or grey deposits were invariably obtained at somewhat high potentials. For aluminum bromide-alkali bromide bath, the decomposition potential of aluminum bromide is 1.61 volts⁽²¹⁸⁾. When chloride is substituted for the part of the bromide in the bromide bath, values of potentials that are intermediate between those for a chloride bath and those for a bromide bath only are obtained⁽²¹⁸⁾.

Effect on the Structure of Aluminum Deposit in Fused Aluminum Chloride-Sodium Chloride Bath.
As shown by Gorbunova and Adzhemyan⁽⁷³⁾, the electrolysis of three electrolytes with 19, 40 and 52 mole per cent sodium chloride in the mixture was carried out at temperatures from 130 ° to 210 °C with a current density from 0.002 to 0.2 ampere per square centimeter. Examination of the aluminum deposits indicates: the decrease of the current density produces fine crystals and lessens the

formation of dendritics; the optimum electrolyte is approximately the equimolar mixture of sodium chloride and aluminum chloride; anodic solution of the cathode facilitates the formation of a solid deposit; lowering the temperature favors a more compact deposit without dendritics; radiographic examination shows the absence of any special orientation in the crystal growth and the dimension of the crystal are within the limits 1×10^{-2} and 1×10^{-3} millimeter. A German patent (220) further shows that dense and adherent coatings are obtained by depositing on the cathode, simultaneously with aluminum, a small quantity of metal other than iron but less electropositive than aluminum, for example lead. Compounds of the less electropositive metal may be introduced into the electrolyte, or auxiliary anodes of that metal may be used. The cathode current density may be less than one ampere per square decimeter. This method can also be applied to a mixture of aluminum halides and alkali or alkaline earth halides.

Electrodeposition of Aluminum from Inorganic Fused Mixtures. According to Orlova and Lainer⁽¹⁴⁹⁾, best results were obtained with fused chlorides where the molar ratio of aluminum chloride to

sodium chloride is 1 to 3 at a current density of 0.2 to 0.5 ampere per square centimeter at 120 °C. The aluminum chloride is volatile. Results become poorer as the aluminum chloride concentration decreases. The addition of 0.2 per cent lead chloride improves the quality of coating.

Orlova and Lainer's result is somewhat different from the data of other workers. Plotnikov and his co-workers^(162,163) have previously obtained deposits of aluminum plated on copper and iron alloys with the electrolyte of a fused mixture of aluminum chloride and sodium chloride in the molar ratio of 3 to 2 or 2 to 1 at 200 to 250 °C at a current density of one ampere per square decimeter. Gratzian⁽⁷⁶⁾ showed that aluminum was plated on nickel by electro-deposition from a sodium chloride-aluminum chloride bath with a current density of one ampere per square decimeter at 250 °C.

Recently, a thorough investigation of the aluminum chloride-sodium chloride system was made at the Aluminum Research Laboratories⁽²²¹⁾. The bath for plating varies with the metal to be plated. In addition to aluminum chloride and

sodium chloride, a small amount of lithium chloride or a mixture of lithium chloride and potassium chloride is added. Current densities used range from 5 to 25 amperes per square foot, and the normal value is approximately 15 amperes per square foot. Lower current densities produce smooth deposits, but adherence is likely to be poor. The bath is kept homogenous by "sloshing" motion of the work. The brightening effect of the plating may be increased by the addition of the brightening agent lithium chloride or cryolite or by superimposing alternating current upon the direct current used for plating.

Chittum⁽³⁷⁾ obtained a patent on the use of a molten bath comprising aluminum chloride and lithium chloride for plating aluminum on copper. The composition of the electrolyte consisted of 40.1 mole per cent of lithium chloride and 59.9 mole per cent of aluminum chloride; the melting point of such mixture is approximately 115 °C. The cathode current density used is 0.2 ampere per square centimeter. After the bath was melted in the vessel, the aluminum piece, connected with anode, and object, connected with cathode, are lowered into the bath. The molten bath is an

excellent conductor so that a current density of 0.1 ampere per square centimeter may be obtained with a drop in the potential of less than 2 volts across the electrodes, if they are not more than 1.5 to 2 inches apart.

The composition of the bath may vary somewhat with the sublimation of the aluminum chloride, but the melting point of the mixture is below 130 °C over the range of composition from 37 to 44 mole per cent of lithium chloride. The maximum temperature desirable is 160 °C.

He further extended his patent to use aluminum bromide as a solvent with sodium chloride, lithium bromide and sodium bromide as solutes.

According to Kameyama and his co-workers⁽⁹³⁾, best results were obtained when the electrolysis was carried out with aluminum bromide plus 16 to 18 per cent potassium bromide at 110 to 130 °C with a current density less than 1 ampere per square decimeter. The anode was aluminum and the cathode most easily plated was lead; other metals plated with lead can be used as the cathode; copper, zinc, brass, tin, cadmium, iron, magnesium and aluminum cathodes are also suitable. Superposing alternating current on direct current gave good results. The

fused salt bath must be free from iron.

A process was developed for the deposition of aluminum from an ether solution of aluminum chloride and a metal hydride by Couch and Brenner⁽⁴¹⁾. The best deposits were obtained from an ethyl ether solution that was 2 to 3 molar in aluminum chloride and 0.5 to 1.0 molar in lithium hydride. The deposits were quite ductile and deposition rates of 0.025 to 0.05 millimeter per hour were possible. The bath is said to be not highly sensitive to moisture, but will have a longer life if protected from air.

Electrochemistry of Aluminum Salts in Organic Solutions.

Aluminum chloride is expected to be soluble in a great number of solvents as seen from the wide applications of Friedel-Craft reaction in many fields. Meerwein⁽¹³⁰⁾ has shown that many weak electrolytes are increased in strength by the formation of complex ions. The existence of conductivity has been attributed to the formation of solute-solvent complexes by Hein and Schramm⁽⁸¹⁾. Consideration of all these facts indicates a possible means of solving the problem of electroplating aluminum from organic solvents.

The literature reports studies of the electrochemistry of aluminum halides in many solvents; including: various alkyl halides such as: ethyl chloride⁽²⁵⁾, ethyl bromide^(94, 112, 135, 155, 172, 215, 216), ethyl iodide⁽⁹⁵⁾, and ethyl thio-

cyanate⁽²⁾; aromatic hydrocarbons, as: benzene^(153,156,157,158,215,227), toluene^(152,157,215), and xylene^(152,157,215); nitroderivatives of aromatic hydrocarbons, as: nitrobenzene^(133,159,160,161,165,166,173,183); heterocyclic compounds, as: pyridine^(141,142,143,169); ethers, as ethyl ether⁽⁹⁷⁾; polyhydric alcohols, as: cellosolve⁽¹⁸⁾, glycerin⁽¹³⁸⁾; aldehydes, as: valeraldehyde⁽²⁰⁵⁾, benzaldehyde⁽²⁰⁵⁾, crotonaldehyde⁽²⁰⁵⁾, cinnamaldehyde⁽²⁰⁵⁾; ketones, as: acetone⁽²⁰⁵⁾, methyl acetone⁽²⁰⁵⁾, acetophenone⁽²⁰⁵⁾; acids, as: acetic acid⁽⁴⁹⁾, formic acid⁽²⁰⁵⁾; amides, as: formamide⁽²⁴⁾. Of these, more detailed information can be found and will be summarized for ethyl bromide, ethyl iodide, ethyl thiocyanate, benzene, toluene, xylene, nitrobenzene and pyridine.

The study in this field is further complicated by adding another salt in company with aluminum halides and by using mixed solvents, such as: toluene-nitrobenzene, ethyl bromide-nitrobenzene and ethyl bromide-benzene-xylene.

Ethyl Bromide as a Solvent. For the aluminum bromide-ethyl bromide system, the specific conductivity of electricity increases with the concentration of the aluminum bromide within

the range of 46.3 to 72.3 per cent⁽⁹⁴⁾.

The maximum specific conductivity occurs at the molar ratio of 0.64 to 0.66 aluminum bromide to ethyl bromide⁽⁹⁴⁾.

The decomposition potential of aluminum bromide is 0.98 volt.⁽⁹⁴⁾ At various current densities, the lower constant value is 0.74 volt⁽¹¹²⁾, while the value calculated from the thermochemical data is 1.76 volts⁽¹¹²⁾. The upper decomposition potentials for 5, 30 and 55 per cent of aluminum bromide are 3.25, 2.10 and 2.05 volts respectively⁽¹¹²⁾.

For the ternary system, alkali halide-aluminum bromide-alkyl bromide, the specific conductivity is increased by the addition of metallic halides of lithium, sodium, potassium and silver, also bromide of rubidium^(135,155,172).

For the system metallic bromide-aluminum bromide-ethyl bromide⁽¹⁵⁵⁾, the conductivity increases with the concentration of metallic bromide in the first group in the periodic system and decreases with dilution. For different metallic salts, the conductivity decreases with the following order: silver, lithium, copper, potassium and rubidium.

For lithium bromide-aluminum bromide-ethyl bromide system⁽¹⁵⁵⁾, maximum specific conductivity is 12.78×10^{-3} reciprocal ohms at 18 °C for the ratio of 0.839 lithium bromide to aluminum bromide. This value was obtained by holding constant the molar ratio of aluminum bromide to ethyl bromide equal to 0.289, while the ratio of lithium bromide to aluminum bromide was varied between 0.017 and 0.905.

For the sodium bromide-aluminum bromide-ethyl bromide system⁽¹⁷²⁾, the specific conductivity of solution increases as the concentration of sodium bromide increases. The increase in conductivity is greater for solutions of greater aluminum chloride concentrations. Addition of 0.5 gram mole of sodium bromide per gram mole of aluminum bromide to a solution with a ratio of aluminum bromide to ethyl bromide of 0.27 raises the conductivity five times. The increase is tenfold for solutions containing less aluminum bromide.

For alkali chloride-aluminum bromide-ethyl bromide system⁽¹³⁵⁾, the increase in conductivity is more rapid for the metal of greater atomic weight. The increase in conductivity with temperature was

noted in the case of lithium chloride and sodium chloride only. During electrolysis with a platinum anode, a red yellow coloration was observed in the anode region. This coloration was absent when aluminum and silver anodes were used.

For the potassium iodide-aluminum bromide-ethyl bromide system⁽⁹⁴⁾, the increase in conductivity depends on the concentration of aluminum bromide in the solution to which potassium iodide is added. The conductivity, upon the addition of potassium iodide, increases with aluminum bromide up to a molar ratio of 0.3 for aluminum bromide to ethyl bromide. Beyond the ratio of 0.42, the conductivity upon the addition of potassium iodide decreases as aluminum bromide concentration increases.

In the ternary system, alkyl bromide-aluminum bromide-metallic halide⁽¹⁵⁵⁾, when the metallic chloride added is lithium, sodium, potassium or rubidium chloride, a deposit of aluminum forms on the cathode; but when it is silver chloride, silver is deposited on the cathode.

The decomposition potentials⁽¹⁵⁵⁾ for lithium bromide, rubidium bromide and silver bromide are 2.0, 1.66 and 1.3 volts, respectively. A decomposition potential of 1.88 volts is obtained for the following

two systems⁽¹⁷²⁾: 2.51 mole per cent sodium bromide, 28.49 mole per cent aluminum bromide and 68.97 mole per cent ethyl bromide; 6.9 mole per cent sodium bromide, 36.8 mole per cent aluminum bromide and 56.3 mole per cent ethyl bromide.

For the sodium chloride-aluminum bromide-ethyl bromide system⁽¹³⁵⁾, the addition of sodium chloride to the aluminum bromide-ethyl bromide system causes the disappearance of the lower decomposition potential. Addition in large amounts also causes an increase of upper decomposition potential to 4.05 to 4.25 volts for the molar ratio of 1 to 1 for sodium chloride to aluminum bromide.

Current-voltage curves⁽²¹⁵⁾ show a decomposition potential of 2.0 volts when "x" is 0.5 or less, a decomposition potential of 2.0 to 4.0 volts when "x" is 0.6 to 0.9, and a decomposition potential of 4.0 volts when "x" is 1; the symbol "x" represents the number of moles of sodium chloride in a solution of one mole of aluminum chloride and ten moles of ethyl bromide.

These data show that at small values of "x," only aluminum bromide is decomposed; at medium values of "x," both aluminum bromide and sodium chloride are decomposed; and at high values of "x," only the decom-

position of sodium chloride takes place.

For the systems aluminum bromide-sodium bromide-ethyl bromide and aluminum bromide-potassium bromide-ethyl bromide⁽²¹⁶⁾, only the alkali salt is decomposed at a 1 to 1 molar ratio of aluminum bromide to alkali bromide; only the aluminum bromide decomposes at molar ratios of alkali bromide to aluminum bromide that are much less than 1.

For the aluminum bromide-ethyl bromide-potassium iodide system⁽⁹⁴⁾, the decomposition potential is 1.28 volts.

Ethyl Iodide as a Solvent. Upon the investigation of the solubility of alkali halides in an aluminum bromide-ethyl iodide solution, Katsnel'son and Aizenberg⁽⁹⁵⁾ showed that the solubilities of alkali halides increase with the concentration of aluminum bromide in the solution. For a definite aluminum bromide concentration, the solubility of halides decreases in the following order: lithium, sodium and potassium halides.

Conductivity is affected by the addition of salts at different molar ratios of aluminum bromide to ethyl bromide. For a molar ratio of 0.23 to 0.24, the addition of halides decreases the conductivity. For a molar ratio of 0.44 to 0.46, the addition of

chlorides or bromides raises the conductivity, but the addition of iodides lowers it. For a molar ratio of 0.67 to 0.71, the conductivity rises in all cases except for the addition of potassium iodide.

The decomposition potential is 1.26 to 1.29 volts for the aluminum bromide-ethyl iodide-alkali halide system regardless of which halide is used. Electrolysis of these systems results in aluminum crystals that adhere to the electrode poorly.

Ethyl Thiocyanate as a Solvent.⁽²⁾ The specific conductivity of thiocyanate solutions is similar to the absolute values and in the character of curves to that of ethyl bromide and ethyl iodide for the systems: aluminum bromide-ethyl thiocyanate, potassium bromide-aluminum bromide-ethyl thiocyanate and potassium iodide-aluminum bromide-ethyl thiocyanate and potassium thiocyanate-aluminum bromide-ethyl thiocyanate. There is a closer similarity in the properties of ethyl thiocyanate and ethyl iodide than for those of ethyl thiocyanate and ethyl bromide.

Benzene as a Solvent. The specific conductivity⁽¹⁵⁶⁾ of aluminum bromide or aluminum chloride in benzene rises with dilution and with increasing alkali halide, but falls with increasing aluminum halide. Here alkali metal represents chlorine or

bromine.

When ammonium halides are added to the system of aluminum bromide-benzene⁽¹⁵⁸⁾, within a molar ratio of 0.15 to 0.36, several effects are obtained. Increase in the concentration of ammonium halides increases the specific conductivity; upon dilution, the specific conductivity decreases. The specific conductivity decreases in order of chloride, bromide, and iodide. Within the range of 18 to 50 °C, the conductivity increases proportionally with temperature. The maximum conductivity of all three systems occurs at the molar ratio of 1 mole of ammonium halide to 2 moles of aluminum bromide.

The maximum specific conductivity for the sodium iodide-aluminum bromide system occurs at 0.5 mole sodium iodide and 1 mole aluminum bromide⁽²²⁷⁾.

The maximum specific conductivity of lithium bromide in benzene solution of aluminum bromide is 5.72×10^{-3} reciprocal ohms⁽¹⁵⁷⁾.

The specific conductivity of the system of 51.5 per cent benzene, 41.5 per cent aluminum bromide and 7.0 per cent potassium bromide is 6.1×10^{-4} reciprocal ohms⁽¹⁵³⁾.

The decomposition potentials for the systems ammonium halide-aluminum bromide-benzene are 1.95

volts for chloride, 2.00 volts for bromide, but no constant value is obtained for iodide⁽¹⁵⁸⁾.

The decomposition potential for the system lithium bromide-aluminum bromide-benzene is 1.60 volts⁽¹⁵⁷⁾.

The decomposition potential for the system sodium iodide-aluminum bromide-benzene shows two discontinuities at 1.08 and 1.78 volts as determined by Plotnikov⁽²²⁷⁾. But Yakubson⁽²¹⁵⁾ gave two values at 1.1 to 1.2 and 1.9 to 2.0 volts. The former value corresponds to the decomposition potential of aluminum iodide, and the latter value corresponds to the decomposition potential of aluminum bromide.

Toluene and Xylene as Solvents. The maximum conductivity of the system lithium bromide-aluminum bromide-toluene is 5.28×10^{-3} reciprocal ohm⁽¹⁵⁷⁾. With the increase in concentration of bromide of lithium, copper and silver, the conductivity increases and changes abruptly when the molar ratio corresponds to complexes of the compositions: $\text{LiBr} \cdot 2\text{AlBr}_3$, $\text{CuBr} \cdot 2\text{AlBr}_3$ and $\text{AgBr} \cdot \text{AlBr}_3$ ⁽¹⁵⁷⁾.

The specific conductivity of aluminum bromide-xylene system and the ternary systems aluminum bromide-xylene with potassium bromide, sodium bromide, ammonium bromide, potassium chloride, sodium chlo-

ride, ammonium chloride and ammonium iodide vary with time⁽¹⁵²⁾.

The decomposition potential of aluminum bromide-xylene solution, as well as the ternary system aluminum bromide-xylene with alkali halides is 1.64 to 1.68 volts, which correspond with the value calculated by Thomson equation⁽¹⁵²⁾. Dense and shiny deposits of aluminum were obtained from xylene solution of aluminum bromide containing additions of potassium chloride, sodium chloride or ammonium iodide⁽¹⁵²⁾. During electrolysis of aluminum bromide-xylene with the addition of potassium chloride using an anode of silumin, pure metallic aluminum was deposited on a copper cathode⁽¹⁵²⁾.

The decomposition potentials of the system sodium iodide-aluminum bromide-toluene is 1.1 to 1.2 and 1.9 to 2.0 volts, corresponding to the decomposition potentials of aluminum iodide and aluminum bromide respectively⁽²¹⁵⁾.

Nitrobenzene as a Solvent. The specific conductivity of aluminum chloride in nitrobenzene increases with the concentration of aluminum chloride, with a maximum conductivity of 1.46×10^{-3} reciprocal ohm at 14 per cent aluminum chloride⁽¹⁶⁰⁾. There is a similar increase in conductivity with aluminum bro-

mide solution, with maximum specific conductivity at 18 per cent aluminum bromide⁽¹⁵⁹⁾.

The addition of metallic halides increases the specific conductivity of the solution of aluminum chloride or aluminum bromide in nitrobenzene to a maximum at a molar ratio 1 to 1 for aluminum chloride to metallic halide⁽¹³³⁾, where metal represents ammonium, potassium, rubidium and lithium; and halide represents chloride, bromide and iodide. Aluminum bromide may be substituted for aluminum chloride. Each specific conductivity-concentration curve of aluminum bromide in the nitrobenzene shows a maximum⁽¹⁶¹⁾. At 50 °C, the specific conductivity of 28.3 per cent aluminum bromide solution is 2.52×10^{-3} reciprocal ohm⁽¹⁶¹⁾.

The molar conductivity of aluminum chloride in nitrobenzene increases with dilution and reaches a limit of 4.5 reciprocal ohms⁽¹⁶⁰⁾.

Upon electrolysis of alkali halides mixed with aluminum halides in nitrobenzene solution, alkali metal is deposited at the cathode and halogen is deposited at the anode⁽²¹⁵⁾. The decomposition potential is 5 volts for potassium deposited at the copper cathode⁽¹⁶⁰⁾. For sodium deposits, the decomposition potential is 4.5 volts⁽¹⁸³⁾.

Upon electrolysis of an aluminum bromide-potassium chloride-nitrobenzene system with platinum electrodes, the metallic aluminum is deposited on the cathode and bromine on the anode⁽¹⁶⁰⁾. The decomposition potential is 2.12 volts⁽¹⁶⁰⁾.

All of the mixed solvents containing nitrobenzene forming solutions with alkali halides and aluminum halides gave alkali metal deposits upon electrolysis^(165,166,173).

Pyridine as a Solvent. The conductivities of aluminum bromide in pyridine and in benzonitrile were measured with high frequency bridge⁽¹⁴¹⁾. With pyridine, careful measurements were made at 25 °C for solutions from saturation (1 mole in 123 liters) to a dilution of 1×10^{-5} liters. The conductivity at infinite dilution is found by extrapolation to be 62.5 reciprocal ohms.

The potentials of pure aluminum and a 2 per cent aluminum amalgam in saturated solution of aluminum bromide in pyridine were measured at 25 °C against the electrode, Ag, AgNO₃, 0.1N C₅H₅N⁽¹⁴³⁾. The electromotive force of the latter was practically equal to that of a normal calomel electrode.

The values of the electrode potential referred to the normal calomel electrode are 0.827 volt for

pure aluminum and 1.16 volts for 2 per cent aluminum amalgam⁽¹⁴³⁾.

Muller and co-workers⁽¹⁴²⁾ were unable to deposit aluminum from a solution of aluminum bromide in anhydrous pyridine. However, Plotnikov and Balyasnuil⁽¹⁶⁹⁾ made a thermal analysis of the system: aluminum bromide-pyridine and found three eutectic points. Using a mixture which melted below 45 °C, they were able to separate aluminum.

Miscellaneous Solvents. Dirls and Briscoe⁽⁴⁹⁾ succeeded in depositing traces of aluminum from ethanoline solutions of aluminum salts, but were unsuccessful with acetamide, aniline, benzoyl chloride and glacial acetic acid solutions. Blue and Mather⁽²⁴⁾ found that pure aluminum could not be deposited from a solution of aluminum chloride in formamide, but that alloys of aluminum with iron and with zinc could be deposited, if the concentration of aluminum in alloy reaching 17 per cent. Beal and Mann⁽¹⁸⁾ failed to deposit aluminum perchlorate solutions in the monoethyl ether of ethylene glycol.

Comparative Study of Conductivity of Different Solvents. The conductivity of aluminum halide solutions made by dissolving it in different solvents depends on its reaction with solvents⁽²⁰⁵⁾. In the case of cro-

tonaldehyde, benzaldehyde and cinnamaldehyde, aluminum chloride solvates in these solutions are salt-like so that molar conductivity increases with dilution⁽²⁰⁵⁾. As the aluminum chloride addition products are not salt-like, the molar conductivity of aluminum chloride solutions in acetone, mesityl oxide and methyl acetone is small⁽²⁰⁵⁾.

The conductivity of aluminum halide solution in a solvent always increases with time⁽²⁰⁴⁾.

The addition of another solvent to an aluminum halide solution always increases the specific conductivity of the solution, because of the formation of addition compounds. For example, the conductivity of aluminum bromide in ethyl bromide is increased by the addition of benzene, the increase being greater with time⁽²⁰⁴⁾. The increase is because of the greater ability of the higher cyclic hydrocarbons to form additional compounds⁽²⁰⁴⁾. The behavior of naphthalene is similar, but the increased conductivity with 2-methyl butylene-2 can be attributed to polymerization.

The addition of polar compounds to the aluminum halide solution causes an increase in conductivity of the solution because of the formation of complex associated compounds. For example, the cryoscopic

investigation of $\text{LiBr} \cdot 2\text{AlBr}_3$, $\text{AgBr} \cdot 2\text{AlBr}_3$ and $\text{CuBr} \cdot \text{AlBr}_3$ in benzene shows that the complexes are very much associated and the degree of association increases with concentration⁽¹⁵⁷⁾.

The addition of nonpolar compounds to solutions of aluminum halide lowers the specific conductivity of the solutions⁽⁷⁵⁾. Compounds such as stannic bromide, stannic chloride, carbon tetrachloride and so forth, do not form complexes with aluminum salts and probably decompose the complexes already existing between the aluminum halide and the solvent⁽⁷⁵⁾. They also increase the viscosity of the solution. Even a slightly polar compound such as arsenious bromide causes a decrease in specific conductivity. For example, at the molar ratio of 5.8 for arsenious bromide to aluminum bromide and 0.19 for aluminum bromide to ethyl bromide, the specific conductivity is less than one-third of the conductivity for the same solution of aluminum bromide in ethyl bromide but in the absence of arsenious bromide⁽¹⁶⁸⁾.

Comparative Study of Decomposition Potential of Aluminum Salts in Different Solvents. The magnitude of electromotive force and order of deposition of metals is different for different solvents⁽¹⁵⁶⁾. Upon electrolysis of alkali halide-aluminum halide-

nitrobenzene system, the alkali metal deposits on the cathode⁽¹⁵⁶⁾. But upon electrolysis of alkali halide-aluminum halide-benzene system or alkali halide-aluminum halide-ethyl halide system, results in a metallic aluminum deposit on the cathode, provided the concentration of alkali salts is low as compared with that of aluminum salts.

Among three solvents; benzene, toluene and xylene, the best deposits of aluminum are obtained from the use of xylene⁽²⁵⁾.

Addition of a solvent to a solution of aluminum halide-alkali halide may influence the transference of aluminum⁽²⁰⁴⁾. Approximately equal amounts of aluminum are transferred to the anode and cathode in the electrolysis of solutions of aluminum bromide in ethyl bromide, but when in hexaethyl benzene, most of the aluminum goes to the anode and most of the hexaethyl benzene goes to the cathode⁽²⁰⁴⁾.

The magnitude of the decomposition potentials of different systems gives an insight into the strength of complexes and solvates in solution and it can be used as an analytical tool⁽²¹⁵⁾.

The electrodeposition of aluminum alloys from halide solutions in benzene is easier than from aqueous solutions because the deposition potentials of other

metals are nearer that of aluminum in benzene than in water solutions⁽²⁴⁾.

Except for the alkali metal salts, all other metal salts added to the aluminum halide gave the corresponding metal deposit on electrolysis but no aluminum deposit⁽²⁴⁾.

Most heavy metals can be codeposited with aluminum as alloy from aluminum halide organic bath, but the best-looking alloy deposits are generally high in aluminum⁽²⁴⁾.

Electrodeposition of Aluminum From Organic Solutions. Lalbin⁽¹¹³⁾ obtained a patent for the deposition of aluminum at low temperature from a solution of binary salt in a liquid containing no oxygen and preferably no element other than carbon, hydrogen and nitrogen, as toluene, xylene or acetonitrile. A 10 per cent solution of aluminum chloride in acetonitrile is suitable. To increase the conductivity of the electrolyte, a substance such as acid potassium fluoride, other alkali fluoride or bifluoride, or phosphorus trifluoride or phosphorus pentafluoride, was added to the amount of about 1 per cent. The temperature of the bath might vary from 0 to 100 °C and upwards but was preferably 110 °C. A cathode current density of 2 to 3 amperes

per square decimeter was suggested.

Keyes and co-workers⁽⁹⁸⁾ obtained a patent for the use of a mixture of tetraethyl ammonium bromide and aluminum bromide as electrolyte. The voltage was 22.6 volts and current density was 0.068 ampere per square centimeter of cathode surface. The process is suitable for plating steel economizer tubes. Keys and co-workers⁽⁹⁷⁾ also devised a method of electrodeposition of aluminum by the use of aluminum Grignard compounds in ether solution.

Moller⁽¹³⁸⁾ obtained a patent for the use of an electrolytic bath containing an alcohol with a boiling point considerably higher than 100 °C and an aluminum salt. The temperature of the bath during treatment was maintained above 100 °C; pH value was 5.8 to 6.0. The bath might contain glycerol and alcohols of the glycol group. Among different aluminum salts, aluminum chloride was preferred. An aluminum anode might be used instead of aluminum salt.

Gray and co-workers⁽⁷⁷⁾ obtained a patent for the use of an aluminum salt of an aminobenzenesulfonic acid as the electrolyte. A material to be coated was used as cathode and aluminum as anode.

According to Blue and Mather⁽²⁵⁾, aluminum of high purity can be deposited easily in bright finely

crystals in adherent form from a solution made by dissolving metallic aluminum in ethyl bromide and benzene. The best procedure for preparation of the bath is as follows: 2.5 grams of aluminum foil, 0.1 centimeter thick warmed with a few drops of bromine in a dry erlenmeyer flask equipped with a reflux condenser until all the bromine has reacted. After cooling to room temperature, 10 milliliters of ethyl bromide are added and the mixture is allowed to digest for approximately 5 minutes. Because of the reaction of aluminum with ethyl bromide is exothermic, no external heat is necessary to start or continue the reaction. Then 25 milliliters of benzene are added carefully over a period of 15 minutes. At first benzene is added a few drops at a time because of its vigorous reaction and the evolution of the hydrogen bromide gas. Then 15 milliliters of ethyl bromide are added in 5-milliliter portions at intervals of 3 to 5 minutes. Benzene and ethyl bromide can then be added in equal portions to make any desired volume of plating solution. No care is necessary in adding the benzene except for the initial additions as an excess benzene is used; but ethyl bromide has to be added carefully in each 5-milliliter portion.

As the digestion proceeds, the mixture separates into two layers; the lower containing the aluminum compounds is deep red, while the upper is a nearly colorless layer of benzene. The excess benzene upper layer protects the lower layer quite well from contact with the moisture in the air.

After electrolyzing solution for six hours, with an aluminum anode and a platinum cathode at a current density of 1.25 amperes per square decimeter, aluminum begins to deposit at the cathode. The deposits at first are dull, gray and finely crystalline. With continued electrolysis, the deposits improved, and after operating about 10 hours, the deposits are bright, adherent, white and finely crystalline. The deposit on copper, which is free from oxide, is very adherent and cannot be loosened or stripped off by bending back and forth. Any oxide film on the copper causes the deposits to peel easily. The aluminum deposits on platinum are very adherent and can be stripped only with difficulty. Greasing the cathode does not decrease the adherence of the deposits, because the grease is dissolved by the benzene layer on the bath. The aluminum adhered well to the steel; aluminum coated steel can be heated to redness without the deposits peeling. The aluminum can also be adhered well to cast iron, but not to magnesium and aluminum.

The bath has a current efficiency of 60 per cent and more at both electrodes and a throwing power as high as 28. The bath does not deteriorate and can be operated indefinitely if moisture is excluded.

Toluene, xylene, B-tetrahydronaphthalene and kerosene may be substituted for benzene under certain conditions as can ethyl chloride, methyl chloride and ethylene dichloride for ethyl bromide.

Wyllie⁽²¹⁴⁾ repeated Blue and Mather's experiment with a pure aluminum anode and a steel cathode. Using a current density of 1 ampere per square decimeter, at room temperature, he obtained good, adherent, bright deposits after the electrolyte has been worked some time. No perceptible stress, either expansive or contractive was observed on the coating. X-ray diffraction showed that the deposits were of grain size of 10^{-2} to 10^{-3} centimeter and were random in orientation.

Later, a new, cheaper and a more efficient bath was reported by Blue and Mather⁽²⁶⁾. This bath contained the condensation or reaction products formed when aluminum chloride and aluminum bromide are dissolved in ethyl bromide and benzene. Also, hydrogen bromide and hydrogen chloride yielded condensation products in benzene with aluminum bromide and alumi-

num chloride from which aluminum could be deposited electrolytically.

The procedure for preparing aluminum bromide bath was as follows: The anhydrous aluminum bromide was dissolved in dry benzene by gently heating. The solution was cooled to room temperature, and varying amounts of dry ethyl bromide were added; a deep red condensation product resulted. Any excess of aluminum from the preparation of aluminum bromide reacted with ethyl bromide and considerable hydrogen bromide was evolved. Approximately 1 milliliter of ethyl bromide for each gram of aluminum bromide formed the most efficient bath. No satisfactory aluminum chloride bath can be made. For mixed chloride and bromide bath, the best results were obtained with equal parts of two aluminum salts. If the bath was prepared by dissolving aluminum chloride and aluminum bromide in benzene, the resistance of the bath was very high, but it could be improved by first fusing together the aluminum chloride and aluminum bromide and then adding the fused salts to the benzene.

Toluene and xylene in the bath have a brightening effect. Xylene has more of a brightening action than an equivalent weight of toluene. The best composition

suggested results from dissolving 20 grams of aluminum chloride in 80 milliliters of benzene and adding 40 milliliters ethyl bromide and 40 milliliters of xylene. The average cathode efficiency is above 75 per cent and the anode efficiency is above 100 per cent. The conductivity of the baths varied considerably. With continued electrolysis there was a gradual decrease in the conductivity because of the decrease in the concentration of ethyl bromide, which was due to the reaction of ethyl bromide with aluminum anode. This decrease could be remedied by adding small amounts of ethyl bromide. The bath had a long life. One bath of 50 milliliters was operated 8 to 10 hours daily for three months with excellent results.

Deposition of Aluminum From "Onium" Salts. Audrieth and Schmidt⁽¹⁶⁾ showed that fused ammonium nitrate dissolved in aluminum nitrate, other nitrates and carbonates. The melt is a good conductor of electricity, but it is too strongly acid to permit the electrodeposition of metals. This is one of the examples to show that "onium" salts are acids, as set forth by Bronsted⁽³³⁾. The acid character of "onium" salts was further shown by the solubility of various metals, oxides and salts in the fused pyridine hydrochloride as expected by Audrieth, Long and Edwards⁽¹⁵⁾. They also found that many

of these melts conducted the electrical current readily. However, metallic deposits were obtained only in the following instances: melts prepared by dissolving lead oxide and antimonous oxide in fused pyridine hydrochloride; melts prepared by dissolving arsenious, bismuth, mercuric, plumbus and stannous chloride in fused pyridine hydrochlorides; and from the fused double salts $\text{AsCl}_3 \cdot (\text{C}_5\text{H}_5\text{N} \cdot \text{HCl})_3$, $\text{BiCl}_3 \cdot (\text{C}_5\text{H}_5\text{N} \cdot \text{HCl})_2$ and $\text{SbCl}_3 \cdot (\text{C}_5\text{H}_5\text{N} \cdot \text{HCl})_2$ and later ⁽¹⁴⁾ $\text{CoCl}_2 \cdot (\text{C}_5\text{H}_5\text{N} \cdot \text{HCl})_5$. The less active metals: arsenic, bismuth, and antimony could be readily discharged in the form of good crystalline deposits ⁽¹⁴⁾. Mercury collected on the cathode in the form of small globules. Cobalt gave a lustrous plate while tin deposited in the form of loose, metallic flakes. Attempts to deposit the more active metals, such as aluminum, etc., were unsuccessful ⁽¹⁴⁾. This difficulty may be solved if the hydrogen atom causing acidity in fused pyridinium compounds is replaced by some other group, such as an alkyl group.

Hurley's patent ⁽⁹²⁾ shows that a fused bath can be made of an N-alkyl pyridinium halide and an anhydrous fused aluminum halide, preferably in various anhydrous fused pyridinium compounds, particularly ethyl pyridinium bromide, ethyl pyridinium chloride, ethylene dipyridinium dibromide and ethylene dipyridinium dichloride. Generally, the bath composition should be such that the pyridinium cation is not

reduced at the cathode. In any case, if the aluminum chloride concentration is too low, the aforementioned reduction of pyridinium cation occurs at the cathode, while if the aluminum chloride concentration is too high, the plate will contain what appears to be occluded aluminum chloride. Two moles of aluminum chloride to one mole of halide or nitrogen atom in the pyridinium salt is the optimum ratio. In the case of the aluminum chloride and ethyl pyridinium bromide, the content of the latter compound may vary between 30 and 40 mole per cent.

The temperature of the bath was also subjected to investigation in connection with that patent. Too low a temperature results in low conductivity and produces spongy deposits. At high temperatures, aluminum chloride will distill from the bath and the decomposition of the electrolyte may occur. For ethyl pyridinium bromide and aluminum chloride, temperatures varied in the range from 40 to 150 °C, depending on the composition of the bath. The preferred temperature for a 2 to 1 molar ratio of aluminum chloride to ethyl pyridinium bromide is 125 °C.

The optimum cathode current density for baths of this type is approximately 0.5 ampere per square decimeter. Those obtained at current density much lower than 0.5 ampere per square decimeter are usually white and dull, whereas at current density somewhat higher than this value they are usually gray and dull. Only at this preferred value

are bright and shiny plates obtained. In cells in which the anode and the cathode are about 1.5 inches apart, two or three volts are employed. In general, the anode should be as large as, or larger than the cathode object.

Weir and co-workers⁽²⁰³⁾ obtained a patent for electroplating with aluminum at room temperature from a liquid mixture of N-substituted alkyl pyridinium chloride or bromide and aluminum chloride in the presence of an excess of benzene or its derivatives.

Good plates of aluminum can be obtained when the nitrogen substituted alkyl halide is the ethyl derivative. The proportion of aluminum chloride to ethyl pyridinium salt in the bath should be approximately two moles of aluminum chloride to one mole of either nitrogen or halide in the pyridinium salt.

Such a bath is employed in plating by providing an aluminum anode, and a cathode object which may be of iron, copper, brass, bronze, lead, nickel, tin or the like. Zinc should not be used because it usually reacts with the bath. When the current is passed between the electrodes, aluminum dissolves at the anode and is deposited upon the cathode.

For example, a mixture of 33.3 mole per cent ethyl pyridinium bromide and 66.7 mole per cent aluminum chloride is prepared and toluene is added until the mixture is saturated and excess toluene floats on top. The bottom layer

is the plating solution. Very bright and shiny plates can be obtained at current densities between 0.5 and 1.0 ampere per square decimeter.

Weir⁽²⁰²⁾ further showed that the plates secured by aluminum chloride and N-substituted pyridinium halide bath with or without benzene or its derivatives, with direct current alone are brittle and tend to crack, break or flake away from the base, particularly if the article is repeatedly flexed. With the same bath, if a suitable alternating current is superimposed on the direct current, adherence of the plate to the base metal is increased with the result that the articles can thereafter be worked and bent to shape. Furthermore, the plate secured is more uniform and, in addition, its thickness can be increased. At the same direct current density, the voltage required is lowered somewhat. In addition, higher cathode direct current densities can be used to obtain plates of the same general type as with direct current only.

X-ray examination of plates made in accordance with the present invention shows that when direct current alone is employed, the plates consist of partly oriented, small crystals, whereas when the alternating current is imposed in addition, the plate is composed of large crystals which are not oriented. Improved adherence and other properties of the plates are probably accounted for in this way.

The best results are obtained when the root-mean-square value of the alternating current is 2 to 3 times the value of the direct current. At lower ratios, the improvement in adherence diminishes until, at a ratio of about 1 to 1, the effect is very small. If, however, the ratio is too high, the plates become burned. The most desirable ratio of alternating current to direct current depends somewhat on the design of the cell, the direct current density employed, and the type of the plate desired. When high current densities are desired, the ratio of alternating current to direct current should be increased. Likewise, when thick, nonbrittle deposits are to be obtained, the ratio should be increased. The exact value of the ratio is usually not highly critical and can readily be determined for a given set of conditions. The direct current and alternating current voltages employed are usually low (of the order of few volts, usually less than 10) and depend upon several factors mentioned previously.

The platings obtained under these conditions were brighter, more adherent, and it was possible to increase the thickness to 0.030 millimeter without lowering the ductility. The usual thickness of the deposit for direct current only was 0.006 millimeter, although plates of 0.025 millimeter could be obtained. High current densities, as

much as 100 per cent greater, could be used with the superimposed alternating current.

In a report by Sefranek, Schickner and Faust⁽¹⁸⁴⁾ on electroforming methods for manufacture of wave guides, an account is given of further investigation of the system aluminum chloride, ethyl pyridinium bromide and toluene.

The principal bath used for the electroforming of wave guides was composed of 36 parts of the ethyl pyridinium bromide-aluminum chloride fusion product dissolved in 64 parts, by volume, of toluene, corresponding to 49 parts, by weight, of toluene. Baths that were operated continuously for more than 40 days, without replenishing, deteriorated so that the electroforms produced were defective in density and outer surface smoothness. To prevent this deterioration, the specific gravity of the bath was maintained at 1.11 to 1.13 and the weight fraction of toluene at 0.47 to 0.48. These conditions were held constant by the replacement of 1.8 per cent of volume with fresh bath every three days. The new bath added contained 1.2 per cent methyl tertiary butyl ether which resulted in a long-lasting smoothening of the deposits.

The substitution of the following addition agents for methyl tertiary butyl ether also resulted in smooth deposits: diethylaniline, di-o-tolylurea, diphenyl oxide,

di-o-tolylthiourea, dichloroethylene, pyridine, quinoline, butyraldehyde and ethyl ether. Of these additives, only ethyl ether could be used without some slight degrading of the deposit such as treeing, porosity, nodularity, or cracking.

When electroforming was accomplished with the use of direct current only, the plates were ductile and smooth but so high stressed that they usually cracked in a short time.

The superimposition of alternating current on the direct current decreased the dislodgement of sludge particles from the plates, and this decrease resulted in smoother, less nodular aluminum plates. The best ranges for the cathode current density were found to be 8 to 12 amperes per square foot for the alternating current. For the anode, the best ranges of current densities were 1 to 3 amperes per square foot for the direct current and 10 to 12 amperes per square foot for the alternating current. The potential differences between the cathode and the anode were 1.5 to 2.0 volts direct current and 1.5 to 2.5 volts alternating current. The bath temperature was maintained at 83 to 87 °F. Nitrogen, employed for the agitation of the bath, was used at the rate of 6.5 to 8 cubic feet per hour.

General attempts were made to reduce the cost of operation of the bath containing ethyl pyridinium bromide, aluminum chloride and toluene. Commercial toluene, which had been dried over calcium sulfate, was used satisfactorily in place of chemical pure toluene. The substitution of commercial aluminum chloride for the resublimed compound was not satisfactory for making thick-walled electroforms, but it is expected to be usable for thinner coatings.

It was found that recycling of the nitrogen gas, used for the agitation of the bath, might be feasible if all the hydrogen halide vapors would be removed. An acid-absorbing tower containing sodium hydroxide pellets removed all but 0.0002 gram of hydrogen chloride per cubic foot of nitrogen gas. It was not certain whether this small amount of hydrogen halide vapors or other impurities were the cause of nodularity on the electroforms. The substitution of carbon dioxide gas for nitrogen as the agitating medium resulted in powdery deposit of aluminum. Mechanical agitation did not prove satisfactory, since the action of the propeller tended to loosen sludge particles from the anodes; the sludge particles made the deposits less ductile and not as smooth as those obtained with agitation by nitrogen gas.

III. EXPERIMENTAL

The experimental section includes a statement of the plan 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 of calculations are presented.

Purpose of Investigation

The purpose of this investigation was to study the possibility of using, as the electrolyte for the deposition of aluminum, systems containing aluminum phosphate dissolved in fused borate and phosphate mixtures.

Plan of Experimentation

Literature Review. The literature was reviewed, covering the following items: the principal papers dealing with the evaluation of various methods of electrodeposition of aluminum were reviewed; the literature on phase relations of aluminum salts with other salts, electrochemical studies of the nonaqueous solutions of aluminum salts and the properties of the electrodeposited aluminum coating were surveyed and information on experimental techniques and apparatus was examined.

Experimental Work. For the system, the first step in the investigation was to obtain the chemicals necessary either by purchase or by synthesis.

The second step was to find the suitable, working, "fluid range" of the system under study.

The third step was to study the corrosive properties of the electrolytes chosen, in order to find the suitable containers.

The fourth step was the determination of the electrochemical properties of the electrolyte which included electrical conductivity, decomposition potential, and electrodeposition work.

The last step in the investigation was to study the properties of the deposits. Mechanisms of the electrochemical reactions were then proposed.

The results obtained from the studies were evaluated by tabulation, graphical interpretation (where suitable), and by discussion.

Materials

The following materials were used in the investigation for the electrodeposition of aluminum:

Acid, Boric. U. S. P., lot No. 11, produced by Pacific Borax Co., New York, N. Y. Used for preparing electrolytes.

Acid, Hydrochloric. C. P., lot No. E407014, obtained from General Chemical Co., New York, N. Y. For miscellaneous use.

Acid, Hydrochloric. Specific gravity 1.19, tested purity, A. C. S., distributed by Fisher Scientific Co., Silver Spring, Md. Used for analysis.

Acid, Nitric. C. P., obtained from General Chemical Co., New York, N. Y. For miscellaneous use.

Acid, Sulfuric. C. P., lot No. E406026, obtained from General Chemical Co., New York, N. Y. For miscellaneous use.

Aluminum, Metal Foil. Thickness 0.13 mm, width 152.4 mm. Distributed by Fisher Scientific Co., Silver Spring, Md. Used for preparation of the black powder.

Aluminum, Sheet. Alloy 3SH14, containing 1.2 per cent manganese, obtained from Reynolds Metal Co., Louisville, Ky. Used as material to prepare anode.

Aluminum, Wire. B. & S. gauge No. 14, distributed by

Fisher Scientific Co., Pittsburgh, Pa.

Aluminum Phosphate. Powders, purified, obtained from Fisher Scientific Co., Silver Spring, Md. Used in the electrolyte.

Ascarite. Lot No. 2246, 20-30 mesh, supplied by Arthur H. Thomas Co., Philadelphia, Pa. Used for quantitative determination of carbon dioxide.

Barium Hydroxide. Anhydrous powder, tested purity, distributed by Fisher Scientific Co., Silver Spring, Md. Used in the qualitative test for the carbon in the black powder.

Copper Metal. Strip, commercial grade, .8 mm thick, distributed by Fisher Scientific Co., Pittsburgh, Pa. Used to make the copper cathode.

Copper, Wire. B. & S. gauge No. 18, distributed by Fisher Scientific Co., Pittsburgh, Pa. Used for electrical connections.

Lithium Carbonate. Commercial powder, supplied by Foote Mineral Co., Philadelphia, Pa. Used to prepare electrolyte.

Magnesium Oxide. Heavy powder, U. S. P. grade, supplied by Merck & Co., Inc., Rahway, N. J. Used to line the plumbago crucible.

Magnesium Perchlorate. Anhydrous, manufactured by G. Frederick Smith Chemical Co., Columbus, Ohio. Used in

the quantitative determination of carbon dioxide in the fused electrolyte.

Platinum, Foil. Thickness 0.076 mm and width 152.4 mm, distributed by Fisher Scientific Co., Pittsburgh, Pa.

Used to prepare electrodes.

Platinum, Wire. B. & S. gauge No. 24, distributed by Fisher Scientific Co., Pittsburgh, Pa. Used to connect platinum electrodes to the source of electricity.

Potassium Acid Sulfate. Fused powder, tested purity, A. C. S., supplied by Fisher Scientific Co., Silver Spring, Md. Used to fuse black powder.

Sodium Carbonate. Anhydrous powder, C. P., distributed by Fisher Scientific Co., Silver Spring, Md. For miscellaneous use.

Sodium Metaphosphate. C. P. grade, obtained from General Chemical Co., New York, N. Y. Used to prepare the fused electrolyte.

Sodium Peroxide. Powder, tested purity, A. C. S., obtained from General Chemical Co., New York, N. Y. Used to fuse black powder.

Sodium Pyrophosphate. Crystal, tested purity, A. C. S., distributed by Fisher Scientific Co., Pittsburgh, Pa. Used to prepare the fused electrolyte.

Apparatus

The following apparatus was used in the borate investigation of the electrodeposition of aluminum:

Ammeter. Direct current, 0-3, 0-15 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 Seederer-Kohlbusch Co., Inc., Jersey City, N. J. Used to weigh samples and electrodes.

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.

Batteries, storage. Model 1724AN, 24 volts, manufactured by Delco-Remy Division, General Motors Corp., Anderson, Ind. Used as source of direct current.

Crucible, alundum, melting. Number C, 70 mm diameter of rim and 120 mm high, available from Fisher Scientific Co., Pittsburgh, Pa. Used to fuse boric acid with metallic aluminum.

Crucible, ampco. Self-made from 'ampco metal, grade 15, extruded rod', 76.2 mm diameter and 127 mm long. The composition of the metal: copper, 87 per cent; aluminum, 9 per cent and iron, 3 per cent, supplied by the Ampco Metal Co., Milwaukee, Wis. Used for determination of the corrosion of the electrolyte.

Crucible, armco iron. Extra heavy, 54 mm diameter and 36 mm high, supplied by Fisher Scientific Co., Pittsburgh, Pa. Used for the corrosion test for the electrolyte.

Crucible, graphite. Self-made from 'LG plain acheson graphite', 31.8 mm inside diameter, 101.6 mm high and 9.5 mm thick, supplied by National Carbon Division of Union Carbide and Carbon Co., Atlanta, Ga. Used for the determination of fluid range of the electrolyte.

Crucible, graphite. Self-made from 'LG plain acheson graphite', 50.8 mm inside diameter, 101.6 mm high and 19.1 mm thick, supplied by National Carbon Division of Union Carbide and Carbon Co., Atlanta, Ga. Used as the electrolytic cell.

Crucible, nickel. Diameter at top, 60 mm and height, 64 mm, supplied by Fisher Scientific Co., Pittsburgh, Pa. Used for corrosion test for the electrolyte.

Crucible, platinum. Capacity, 20 ml, supplied from J. Bishop & Co., Platinum Works, Malvern, Pa. Used for corrosion test for electrolyte and for analysis.

Crucible, plumbago. Diameter at top, 60 mm and height, 75 mm, obtained from Fisher Scientific Co., Pittsburgh, Pa. Used for the corrosion test for electrolyte.

Crucible, porcelain, coors. Wide form, number 4, 81 mm diameter at top and 52 mm high, supplied by Fisher Scientific Co., Pittsburgh, Pa. Used as the electrolytic cell.

Crucible, silica, opaque. Diameter of rim, 56 mm and height, 36 mm, supplied by Fisher Scientific Co., Pittsburgh, Pa. Used for fusing the black powders with potassium acid sulfate.

Dish, platinum. Capacity, 200 ml, supplied by J. Bishop & Co., Platinum Works, Malvern, Pa. Used as the electrolytic cell.

Furnace, crucible, Hoskins electric. FD 104, diameter of heating chamber, 127 mm, depth of heating chamber, 127 mm, 1200 watts, for 110 volts, supplied by Hoskins Manufacturing Co., Detroit, Mich. Used for heating electrolytes.

Furnace, muffle, Hoskins. Type FD 204C, serial 34928, 110 volts, 30.9 amperes, manufactured by Hoskins Electric Co., Detroit, Mich. Used for fusing metallic aluminum with boric acid, and for preparing aluminum-copper alloy.

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

Heater, autemp. Variable temperature, 110 volts, alternating current, manufactured by Fisher Scientific Co., Pittsburgh, Pa. Used for miscellaneous heating purposes.

Microscope. Dissecting, serial number 176465, manufactured by Spencer Lens Co., Buffalo, N. Y. Used to examine electrodeposits.

Milliammeter, Westinghouse. U. S. Navy type, CAY-22065, style 1160955A, range 0-250, supplied by Westinghouse Electric Corporation, Meter Division, Newark, N. J. Used for the measurement of the current in electrolysis circuit.

Milliammeter, Westinghouse. Direct current, U. S. Navy type, CAY-22059, style WG-41610-5, type NX-35, range 0-100, supplied by Westinghouse Electric Co., Meter Division, Newark, N. J. Used for the measurement of the current in the electrolysis circuit.

Miscellaneous, laboratory, glasswares and equipment.

Supplied by Fisher Scientific Co., Pittsburgh, Pa.

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

Potentiometer, Fisher type S. Two ranges: 0-0.017 and 0-1.70 volts, supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to measure the millivolts generated by the thermocouple.

Protection Tube, ampco. Inside diameter, 3.2 mm, outside diameter, .95 mm and length, 140 mm. Self-made from ampco metal grade 15, extruded rod, the composition of the metal: copper, 87 per cent, aluminum, 9 per cent, and iron, 3 per cent, supplied by the Ampco Metal Co., Milwaukee, Wis. Used to protect the iron-constantan thermocouple.

Protection Tube, graphite. Inside diameter, 3.2 mm, length, 140 mm. Self-made from .95 mm diameter IG plain acheson graphite rod, supplied by National Carbon Division of Union Carbide and Carbon Co., Atlanta, Ga. Used to protect the iron-constantan thermocouple.

Protection Tube, porcelain. Diameter, 6.4 mm, length, 305 mm, supplied by Wheelco Instrument Co., Chicago, Ill. Used to protect the iron-constantan thermocouple.

Rheostat. Variable, 110 volts, capacity, 11.8-5 amperes, alternating current, obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to control the Hoskins crucible furnace.

Rheostat. Sliding contact, resistance, 125 ohms, current capacity, 3 amperes, obtained from Phipps and Bird, Inc., Richmond, Va. Used to control the voltages and amperes in electrolysis circuit.

Rheostat. Variable, 110 volts, capacity, 30-15 amperes, alternating current, obtained from Fisher Scientific Co., Pittsburgh, Pa. Used to control the muffle furnace.

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

Thermometer. General laboratory, engraved stem, mercury filled, Centigrade, 75 mm immersion, range: -5 to 200 °C, subdivision 1 °C and 350 mm long, supplied by Fisher Scientific Co., Pittsburgh, Pa. Used to measure the temperature for miscellaneous purposes.

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, 2.18 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.

Thermocouple Wire, constantan. B. & S. gauge 22, Wheelco constantan wire, supplied by Wheelco Instrument Co., Chicago, Ill. Used to prepare the iron-constantan thermocouple.

Thermocouple Wire, iron. B. & S. gauge, 22, Wheelco iron wire, supplied by Wheelco Instrument Co., Chicago, Ill. Used to prepare the iron-constantan thermocouple.

Method of Procedure

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

Analysis of Raw Materials. The amount of the material insoluble in alcohol and "the material nonvolatile with methanol" in the boric acid used were determined strictly according to the methods recommended by "A. C. S. Analytical Reagents" (10).

The carbon dioxide content of lithium carbonate was determined by the direct method suggested by Kolthoff and Sandell. (108)

The phosphoric oxide content in the aluminum phosphate was determined by the method for phosphoric oxide in phosphate rock as suggested by Kolthoff and Sandell.

The Limiting Composition Curve, Boric Acid and Alkali Carbonate Mixture. The limit-composition as used here, means the maximum number of moles of alkali carbonates which are completely decomposed by one mole of boric acid.

When the platinum dish was used to fuse alkali carbonates with boric acid, its loss in weight was negligible as compared with the loss in weight of chemicals on fusion. One mole of boric acid and one and one-half moles of alkali carbonates were used for each determination. The composition of the alkali-carbonate mixture was 0, 20, 33.3, 50, 66.7, 80 and 100 mole per cent sodium carbonate in the sodium carbonate-lithium carbonate mixture.

The chemicals were weighed to an accuracy of 0.1 gram and thoroughly mixed on glazed paper. The platinum dish was weighed to an accuracy of 0.1 gram and was then put into the crucible furnace. The mixture of boric acid and alkali carbonates was then transferred to the platinum dish in the furnace with a spatula, until the dish was one-third full. The furnace was then heated and the rest of the mixture was gradually added to the platinum dish after the contents of the dish had been fused. In this way, the spattering loss of the fusion mixture is kept at a minimum. After all the mixture had been added to the crucible, the furnace was gradually heated to 600 °C. When the mixture was completely fused, the furnace was covered

and heated to 900 ± 20 °C and maintained at that temperature for three hours. The furnace was then cooled. As the temperature dropped below 60 °C, the platinum dish was taken out and cooled in a desiccator. After it had cooled, it was weighed with an accuracy of 0.1 gram. The platinum dish and its content was reheated to 900 ± 20 °C, cooled and reweighed. After a third heating, the platinum dish and its contents usually reached a constant weight.

After the undecomposed carbonates remaining in each batch were calculated from the loss in weight, a new mixture was prepared by quantitatively reducing the weight of excess carbonates used in the original mixture. The new mixture was then fused in the platinum dish, heated to 900 ± 20 °C, and weighed as before.

The temperature of the bath was measured with a platinum-rhodium thermocouple attached to a potentiometer. The schematic diagram of the thermocouple connections is shown in Figure 3.

Part of each fused mixture, after weighing, was removed, dissolved in water, and tested for the presence of carbon dioxide by addition of 3-normal hydrochloric acid.

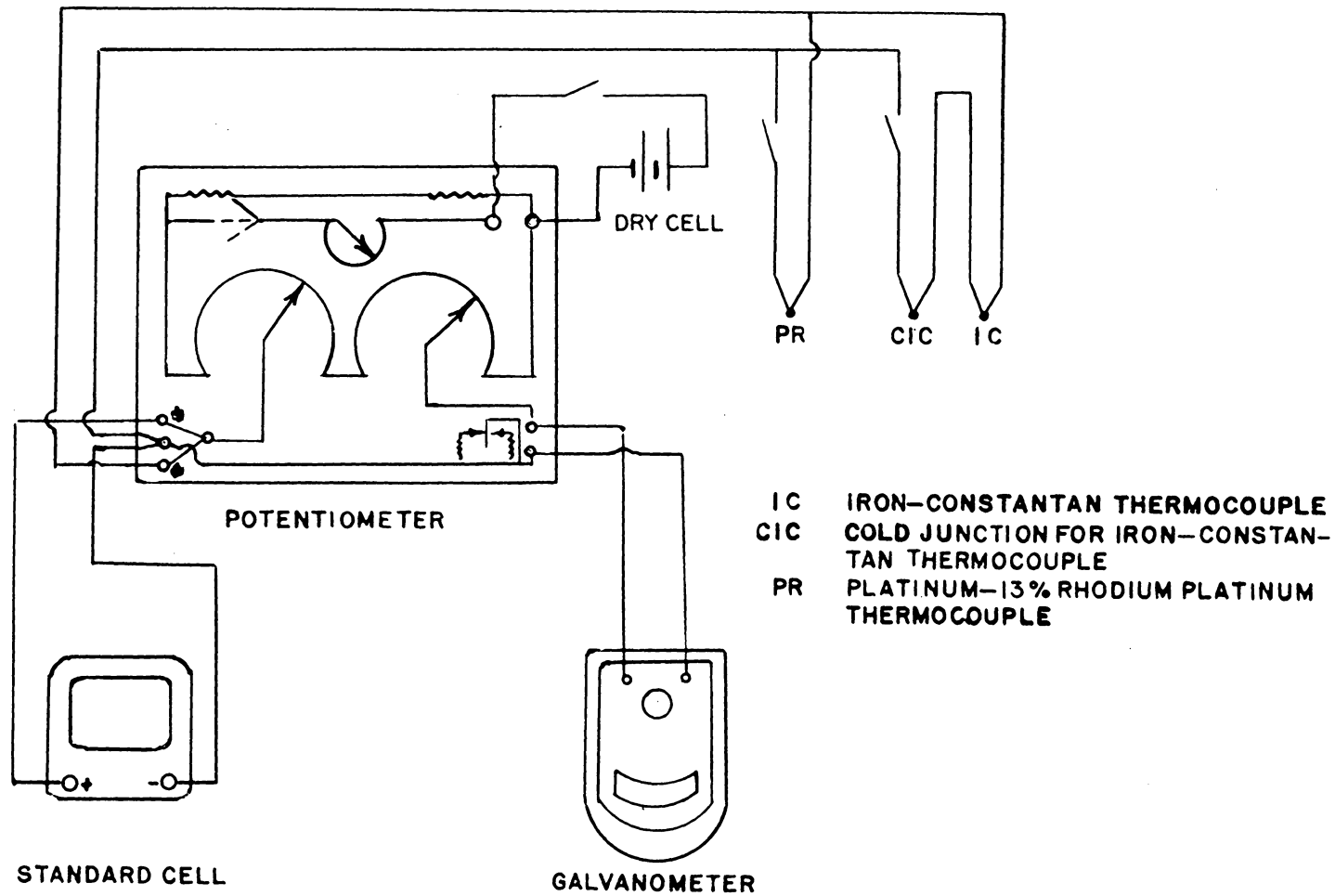


FIGURE 3. SCHEMATIC DIAGRAM OF THERMOCOUPLE AND POTENTIOMETER

Fluid Range of $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ System. The fluid range was determined by visual observation with the help of a cooling curve.

An iron-constantan thermocouple was used for measuring the temperature, in a graphite protection tube.

Before this thermocouple was used, it was calibrated against the boiling point of water, and the melting points of tin, lead and antimony. A standard temperature-millivolt curve was drawn from published data⁽²⁰⁷⁾. On the same graph the experimental points were located, then a curve passing through these four experimental points was drawn to parallel the standard curve. This newly drawn curve was used to determine the temperature from experimental millivolt readings.

Mixtures of various compositions within the limiting composition curve on the $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ triangular diagram, were prepared, and the fluid ranges of these mixtures were determined. For $\text{Na}_2\text{O-B}_2\text{O}_3$ system and $\text{Li}_2\text{O-B}_2\text{O}_3$ systems, most mixtures with boric oxide content greater than 50 mole per cent possess high melting points, and therefore were rejected. Some of them have a melting point below 660 °C, but they are in the viscous region, with a resulting fluid range higher than 660 °C. Therefore, no determinations were made for these two systems in the range of boric oxide content greater than 50 mole per cent.

For $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ system, in the region of boric oxide content greater than 50 mole per cent, two points with the Li_2O to Na_2O ratio equal to 2 to 1 were selected for fluid-range determination. Because the fluid ranges at these two points were high, no further mixtures with boric oxide content greater than 50 mole per cent were taken for determination of the fluid range.

For the $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ system, the mixtures used for fluid-range determinations, were made with fixed ratios of Li_2O to Na_2O of 1 to 0, 9 to 1, 4 to 1, 1.34 to 1, 2 to 1 and 1 to 1; but a varied content of boric oxide. For each set of such determinations, the mixture with an upper value of fluid range at 660 and at 600 °C was then determined by interpolation. On triangular coordinate paper, mixtures possessing the upper-fluid range at 660 and at 600 °C were then located. Two isothermal-composition curves were then plotted by connecting these two sets of isothermal points. The area encircled by the 660 °C upper-fluid range and the limiting composition curve on the $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ triangular diagram is a possible working region of the system from which mixtures were taken out for electrochemical study.

Effect on the Fluid Range of Adding Aluminum Phosphate to the Fused Borates. In a graphite crucible, 30.9 grams of boric acid and 79.5 grams of sodium carbonate were fused. After the content was thoroughly fused and heated to 900 °C for four hours, it was cooled to 600 °C. Aluminum phosphate was added to the fused liquid, heated and stirred, until a homogenous mass was formed. The resulting liquid was then used to measure the fluid range in the $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ system. Five different quantities of aluminum phosphate were added into the five fused mixtures and the fluid range of each mixture was determined.

In a graphite crucible, 30.9 grams of boric acid, 30.8 grams of lithium carbonate and 22.1 grams of sodium carbonate were fused. After the mixture was thoroughly fused and heated to 900 °C for four hours, it was cooled to around 600 °C and used to dissolve various quantities of aluminum phosphate. The resulting solutions were used to determine the fluid range as before. In this case, eight determinations were made.

Corrosion by the Fused Mixture, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$.

A preliminary test was made by fusing a mixture of 30.9 grams of boric acid, 30.8 grams of lithium carbonate and 22.1 grams of sodium carbonate in a graphite crucible. After the mixture was thoroughly fused and heated to 900 °C for four hours, it was cooled to about 650 to 700 °C.

Small pieces of porcelain, nickel and steel were immersed into the fused liquid one by one and the corrosion was observed.

As nickel was not attacked under this condition, a nickel crucible was then used to fuse a mixture of 61.8 grams of boric acid, 31.7 grams of lithium carbonate and 44.2 grams of sodium carbonate under exactly the same condition described above. Again corrosion was observed.

Because the result of this test was entirely different from that in the preliminary test, the experiment was repeated with crucibles made of ampco metal, armco iron, plumbago, porcelain, and platinum.

Decomposition Potential of the Fused Borates and Borate-Phosphate Mixture. A mixture of 123.6 grams of boric acid, 123.4 grams of lithium carbonate and 83.4 grams of sodium carbonate was thoroughly fused in a graphite crucible. The fused mixture was then cooled to 560 ± 10 °C and maintained at that temperature.

Wires directly connected to the aluminum anode and platinum cathode were sealed in 5 mm glass tubes. Such glass tubes were in turn fixed on a 15-millimeters glass tube with asbestos cloth and nichrome wire, so as to maintain a fixed distance of 2.5 to 3.5 mm between two electrodes. The distance between two electrodes can be slightly adjusted by moving the small glass tubes up and down along

the large glass tube.

Direct current was obtained from storage batteries. The electromotive force applied to the cell was adjusted with a rheostat. The schematic diagram of the whole circuit connection was shown in Figure 4.

Voltage applied to the cell was increased in steps, and the current readings were taken at each voltage after the reading became stable. Decomposition potential was obtained by plotting the voltage against the corresponding current reading and extrapolating the straight portion on the chart to zero current.

One experiment was made with a platinum cathode and an aluminum anode.

A second mixture was made by melting the same ingredients as before; then after this was thoroughly fused, 18.7 grams of aluminum phosphate were added gradually to the liquid with stirring. After the contents of the crucible had melted to a homogenous mass, it was kept at 600 ± 10 °C for the determination of decomposition potential.

Two other runs were made with platinum cathode and platinum anode.

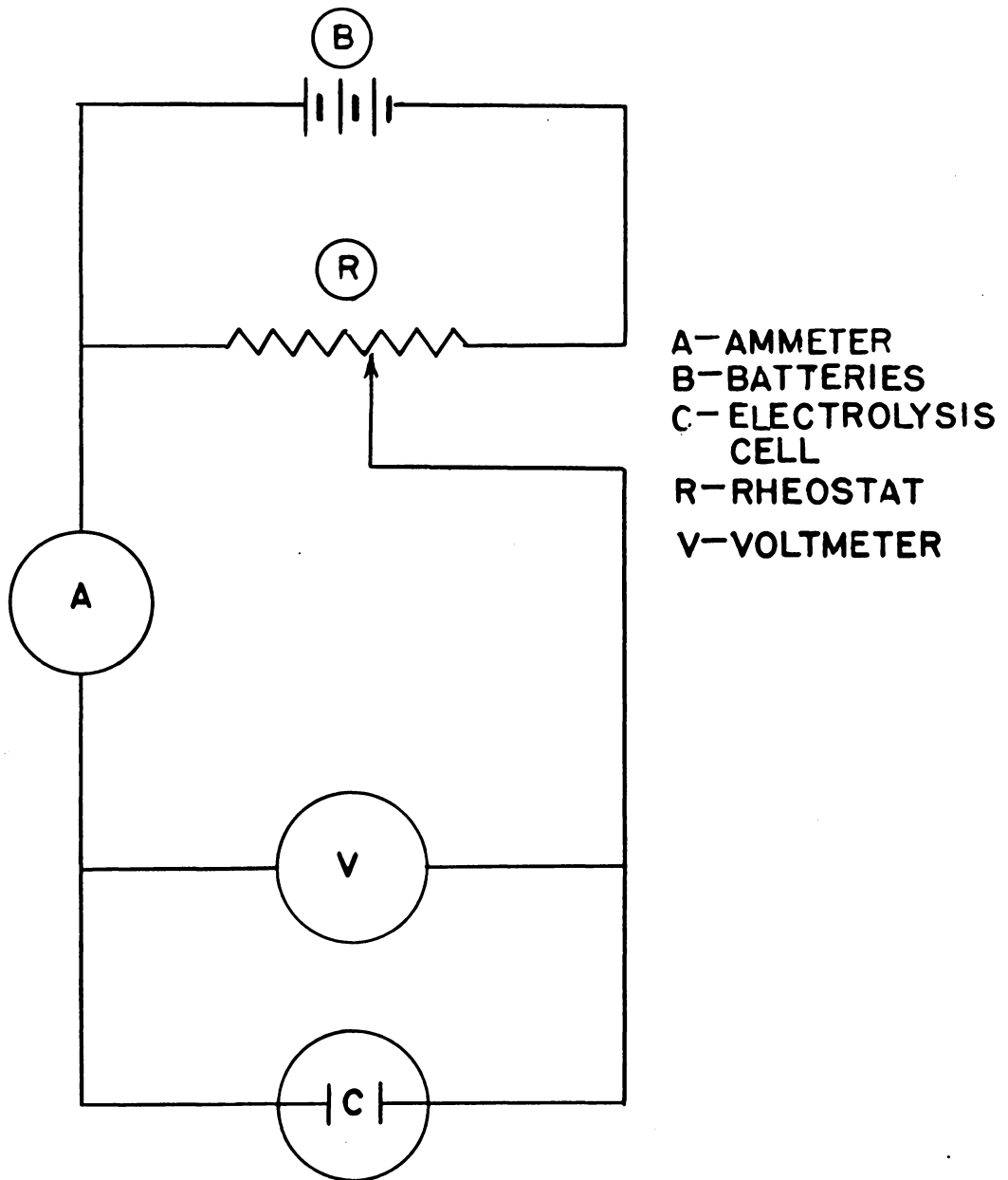


FIGURE 4. ELECTRICAL DIAGRAM OF CIRCUIT USED FOR THE ELECTRODEPOSITION OF ALUMINUM

Unsteady Electrolysis in Fused Borate-Phosphate and Borate Mixtures. Fluctuations of current at constant voltage when the melts were electrolyzed were observed and experiments were carried out to determine the cause. An electrolyte of 9.4 per cent aluminum phosphate and 90.6 per cent $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ was prepared by fusing a mixture of 185.4 grams of boric acid, 185.1 grams of lithium carbonate and 132.6 grams of sodium carbonate in a graphite crucible. After the mixture was thoroughly melted and tested free from carbon dioxide on treatment with 3 normal hydrochloric acid, 27.1 grams of aluminum phosphate were gradually added into the liquid with stirring. After the content in the crucible had melted into a homogenous mass, it was kept at 560 ± 10 °C. An aluminum anode and copper cathode, 2.0 by 3.0 cm were first connected to the direct-current source then inserted into the liquid. For each test, the voltage was kept constant and the current readings were recorded every five minutes or less. A total of six runs were made at 1.5, 2.0, 2.5, 3.5, 4.5 and 5.5 volts.

An identical mixture was made in a graphite crucible and the temperature of the bath was kept at 560 ± 10 °C. Both platinum electrodes, 2.5 by 2.5 cm were first connected to the direct current source, then inserted into the liquid. The voltage was kept at 1.5 and 2.5 volts, the electrolyte was stirred continually and the current readings

were recorded every five minutes or less.

To determine the effect of moisture on the electrolysis, water was added to the bath. Before electrodes and electrolyte were moistened with water, they had to cool below 100 °C in order to avoid explosion. They were then moistened, reheated to 560 ± 10 °C and maintained at that temperature during electrolysis. Current readings were taken at five-minute intervals at constant potential of 1.5 volts.

At the constant temperature, 560 ± 10 °C, and under a constant voltage of 1.5, the electrodes were repeatedly taken out and reinserted into the fused electrolyte to determine the effect of alternating exposure of electrodes to air. The current readings were taken at five-minute intervals. The time when the electrodes were taken out and immersed into the electrolyte was recorded.

To determine if the current fluctuations were as bad as in the absence of aluminum phosphate, an electrolyte of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ was prepared as before in a platinum dish. After the electrolytes were thoroughly fused, it was heated to 900 °C for four hours, then cooled to 560 ± 10 °C and maintained at that temperature during the whole period of electrolysis. Aluminum anode and platinum cathode, first connected to the direct current source, were then inserted into the liquid. The voltage was kept constant at 1.5 volts

during the whole electrolysis and current readings were taken at intervals of five minutes or less. Two runs were made.

Electrodeposition Test in Phosphates Bath. Morey and Ingerson's⁽¹³⁹⁾ eutectic mixture of sodium metaphosphate and sodium pyrophosphate was prepared by melting together 138 grams of sodium metaphosphate and 62 grams of sodium pyrophosphate in a porcelain crucible. When the mixture was thoroughly melted, 20 grams of aluminum phosphate were added to the liquid. After this mixture was melted and mixed to a homogenous mass, the temperature of the bath was maintained at 580 ± 10 °C and prepared for electrolysis.

An aluminum anode and copper cathode, connected to the direct-current source, were inserted into the liquid, and the electrolysis observed. The electrolysis was then repeated with new electrodes.

An aluminum alloy of 75 per cent of aluminum and 25 per cent of copper was made by melting together 15 grams of aluminum and 5 grams of copper in a magnesia-lined plumbago crucible in an electric furnace. This alloy was then used to substitute for pure aluminum as the anode for electrolysis with copper cathode. The electrolysis was repeated with platinum anode and copper cathode.

Analysis of Black Coating from Phosphates Bath.

The black coats deposited on the copper cathode were ignited over the bunsen flame. After this ignition, they were treated with 3-normal hydrochloric acid and then with 15-normal ammonia solution.

Electrodeposition Test in Borates Bath. The elec-

trolyte, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, was prepared by fusing 92.7 grams of boric acid, 92.6 grams of lithium carbonate and 66.3 grams of sodium carbonate in a platinum crucible. The mixture was thoroughly fused, and then heated to 900 ± 10 °C for five hours. After a sample of the fused liquid was cooled down to 600 ± 10 °C and maintained at that temperature, the electrodes were accurately weighed, connected to electric source before being immersed in the fused electrolyte. After electrodeposition, the electrodes were taken out before the current was cut off. The current was kept constant by varying the applied voltage during the run. From the duration of the run and the current passing, the theoretical loss in weight for the anode and gain in weight for the cathode were calculated as aluminum.

The electrodes were then repeatedly washed in boiling distilled water to remove the adhering salt. They were then dried in an oven at 110 °C, and accurately weighed again. From the differences in the weight before and after electrodeposition test, the actual gain and loss in weight were determined. Anode efficiency and cathode efficiency were then calculated.

Electrodeposition Test in Borate-Phosphate Bath.

The selected mixture, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, was prepared by fusing 30.9 grams of boric acid, 30.8 grams of lithium carbonate and 22.1 grams of sodium carbonate in a graphite crucible. After the contents were thoroughly fused, heated to 900°C for four hours, the mixture was found free of carbon dioxide with 3-normal hydrochloric acid. Then 4.53 grams of aluminum phosphate were added to the liquid and heated to a homogenous mass. The temperature was then lowered to $560 \pm 10^\circ\text{C}$ and maintained at that point for the deposition test.

An aluminum anode and copper cathode, connected to the direct current source, were inserted into the liquid. During the electrolysis, the applied voltage was kept constant. Because the current was erratic, the average of the current readings in the whole period of electrolysis was taken for the calculation of the current density. After electrolysis, the electrodes were taken out before the current was cut off, in order to avoid redissolving of any deposits.

An identical mixture was prepared for quantitative electrodeposition test. The temperature of the bath was kept at $600 \pm 10^\circ\text{C}$. Quantitative electrodeposition tests for this electrolyte were made by means of the same procedure as that described for the tests in borates bath.

Preparation and Analysis of Black Powder from Borate

Mixture. Two batches were made for the preparation of black powder by reacting fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ with aluminum. In the first batch, a mixture of 61.8 grams of boric acid, 61.7 grams of lithium carbonate and 44.2 grams of sodium carbonate was fused in a platinum dish. After the mixture was thoroughly fused, it was heated to 900 ± 10 °C for four hours, a sample of the fused liquid was taken out, cooled and tested for carbon dioxide with 3-normal hydrochloric acid. It was then cooled to 560 ± 10 °C and held at that temperature. Chopped pieces of aluminum foil were added to the fused liquid. After the reaction stopped, the whole mass was cooled to room temperature. The contents of the platinum crucible were first extracted with water, then with 3-normal hydrochloric acid and finally washed with distilled water. It was then dried in the oven at 110 °C.

In the second batch, the fused bath was prepared in the same way as above, but 8.4 grams of aluminum foil was used. The black powder was extracted, washed and dried in the same way as above.

The temperature in the bath was measured with a calibrated platinum-13 per cent rhodium, platinum thermocouple.

Samples of black powder prepared above were separately treated with 3-normal hydrochloric acid, nitric acid and

3-molar sulfuric acid both hot and cold.

A sample of the black powder was treated with hydrofluoric acid and volatilized in a platinum crucible.

Another sample was treated with a mixture of hydrofluoric acid and strong sulfuric acid in a platinum crucible, and then volatilized the hydrofluoric acid by heating.

Two samples of black powder in porcelain crucibles were ignited over the bunsen flame and the loss on ignition determined.

One sample was fused with potassium acid sulfate in a silica crucible. One was fused with sodium hydroxide and the other was fused with sodium peroxide in an iron crucible.

A sample of black powder was put in the bottom of a pyrex tube $1\frac{1}{2}$ inches in diameter by 14 inches long. The tube was fitted with a two-hole rubber stopper. A tube, inserted in one hole, projecting almost to the bottom of the tube, was connected to an oxygen cylinder. Another hole in the stopper was fitted with a tube projecting just through the stopper. The other end of this tube was inserted into a clear solution of barium hydroxide. Before the bottom of the pyrex tube was heated, oxygen gas was passed through the tube to be sure that no precipitate was formed in the barium hydroxide solution. The pyrex tube was then heated until all the black powder was consumed.

A sample was sent to Micro Laboratory, 800 Lincoln Avenue, Skokie, Ill. for quantitative determination of hydrogen and carbon⁽¹³⁶⁾.

For a spectrographic analysis of the black powder, the instrument was properly positioned to photograph the spectrum in the range of 2230 to 3550 angstrom.

A sample was also sent to Material Laboratory, Air Material Command, Dayton, O., for spectrographic analysis and X-ray diffraction analysis⁽¹²⁶⁾.

Analysis for Carbon Dioxide in the Fused

5Na₂O.10Li₂O.6B₂O₃. A quantitative analysis for carbon dioxide in the fused electrolyte 5Na₂O.10Li₂O.6B₂O₃ was made. The method used for it is the direct method for carbon dioxide as suggested by Kolthoff and Sandell⁽¹⁰⁸⁾.

Because of the slight solubility of the fused salt in water, a large volume of water had to be used. Therefore, the decomposition vessel used was a 500-milliliter erlenmeyer flask. Another modification was to use both sulfuric acid and hydrochloric acid in different batches to test the reliability of this method.

A mixture of 3.09 grams of boric acid, 3.08 grams of lithium carbonate and 2.21 grams of sodium carbonate was fused in a platinum crucible. After the sample was thoroughly fused, it was heated to 900 °C and maintained at that temperature for at least two hours. It was then cooled to 200 °C and plunged into 200 milliliters of boiling

water. The water was kept boiling until all fused salts were dissolved. The solution was then quickly transferred into the decomposition vessel and analyzed in the usual way.

Chemistry of Formation of Black Powder. A fused mixture of the composition $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 7.5 \text{B}_2\text{O}_3$ was prepared by fusing 106 grams of sodium carbonate, 148 grams of lithium carbonate and 185.7 grams of boric acid in a platinum dish. The fused mixture was thoroughly fused and then heated at 900 ± 10 °C for five hours. A sample of the fused mixture was taken out, cooled, dissolved in water and treated with 3-normal hydrochloric acid. After such test showed no gas bubbles, an aluminum sheet was immersed into the fused salt at a temperature around 500 to 600 °C.

The black deposit formed on the aluminum surface was tested for carbon by the combustion method as described in the preparation and analysis of black powders.

The reaction of aluminum with boric acid was studied by fusing 45 grams of boric acid and 60 grams of metallic aluminum in an aluminum crucible to 1000 °C and maintaining at that temperature five hours. It was then cooled and the fused mass was repeatedly extracted with concentrated hydrochloric acid. A fritted, pyrex buchner-type funnel was used to separate the undissolved solids from the liquid.

After thoroughly washing with water and being dried, the appearance of the residue was noted. An analysis was made for the identification of carbon in the residue by the combustion method. Spectrographic analysis and X-ray diffraction analysis⁽¹²⁷⁾ were made by Material Laboratory, Air Material Command, Dayton, O.

The residue from the reaction of aluminum on boric acid was sprinkled into a fused mixture of 0.1 gram mole of lithium carbonate with 0.1 gram mole of sodium carbonate in a platinum crucible. After any reaction of the residue and fused carbonates was complete, the mass was cooled and dissolved in water. The insoluble residue was filtered on a fritted pyrex, buchner-type funnel. After this residue was thoroughly washed with distilled water and dried, analysis was made for the presence of carbon by the combustion method.

To determine if aluminum would reduce pure, molten carbonates, an aluminum sheet was then dipped into a fused, freshly prepared, equal-molar-mixture of sodium carbonate and lithium carbonate. The behavior was carefully observed as the temperature was gradually raised from the melting point of the mixture to the melting point of aluminum.

To determine the effect of content of boric acid on the action of alkali carbonates on aluminum at 600 °C, another mixture of 2 to 1 molar ratio of lithium carbonate

to sodium carbonate was made by fusing 74 grams of lithium carbonate and 53 grams of sodium carbonate in a platinum dish. An aluminum sheet was then dipped into the fused mixture and observed. The aluminum sheet was removed from the fused liquid, 3.09 grams of boric acid (0.05 mole) was added to the fused liquid and the mixture was thoroughly fused. Another aluminum sheet was dipped into this fused liquid, and the behavior was observed. The addition of boric acid (3.09 grams) and fusion were repeated, and the action of the resulting liquid on aluminum was observed. The process was repeated until finally a black deposit was formed on the surface of the metallic aluminum.

A fresh mixture of 148 grams of lithium carbonate and 106 grams of sodium carbonate was prepared by fusing in a platinum dish. An aluminum anode and platinum cathode, both being 2.0 by 3.0 cm and 2.0 cm apart, connected to the direct current source, were inserted into the fused liquid, so as to maintain a current of one ampere. The behavior was observed.

Thermodynamic Study of the Reactions of Fused Electrolyte $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ on Aluminum. Various possible reactions for $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ with aluminum were further studied by means of thermodynamic methods. According to Dodge⁽⁵³⁾, for the purpose of ascertaining quickly, but only approximately, if any reaction is promising at a

given temperature, the following guide may be useful:

$\Delta F_T^0 < 0$. Reaction is promising.

$\Delta F_T^0 > 0$, but $\leq 10,000$. Reaction is of doubtful promise but warrants further study.

$\Delta F_T^0 > 10,000$. Very unfavorable. Would be feasible only under unusual circumstances.

Where ΔF_T = Free energy change of the reaction at absolute temperature "T"

Superscript "0" refers to standard state of low pressure where gases are ideal.

The free energy of the reaction at absolute temperature T can be calculated from the enthalpy, entropy and the absolute temperature "T", as shown by the following equation: (50)

$$\Delta F = H_2 - H_1 - T (S_2 - S_1) \quad (1)$$

Where H_2 = Enthalpy of the products of the reaction at the absolute temperature "T".

H_1 = Enthalpy of the reactants of the reaction at the absolute temperature "T".

S_2 = Entropy of the products of the reaction at the absolute temperature "T".

S_1 = Entropy of the reactants of the reaction at the absolute temperature "T".

Let $(\Delta H_f)_T$ represent the heat of reaction at absolute temperature "T" and S_T represent the entropy change of the reaction at the absolute temperature "T", reaction (1) can be

simplified to:

$$\Delta F_T = (\Delta H_f)_{T-T} \Delta S_T \quad (2)$$

The heat of reaction at temperature "T" can be calculated from the heat of reaction at some base temperature "T₀", by the following formula: (52)

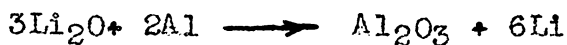
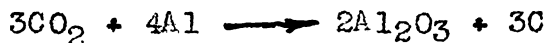
$$(\Delta H_f)_T = (\Delta H_f)_{T_0} + \int_{T_0}^T C_p dT \quad (3)$$

The enthalpy and entropy of a substance at absolute temperature "T" can be calculated from the enthalpy and entropy at some base temperature by the following formulae: (51)

$$H_T = H_0 + \int_{T_0}^T C_p dT \quad (4)$$

$$S_T = S_0 + \int_{T_0}^T C_p dT/T \quad (5)$$

The possible reactions studied in this way were:



The possibility of the formation of aluminum boride said to have the formula AlB_{12} (80) by the following equation was also considered:



Data and Results

Analysis of the Raw Materials. No analysis was made of the sodium carbonate. It was labeled chemical pure.

For boric acid, the material insoluble in alcohol passed A. C. S. test. "The nonvolatile with methanol" was found to be 0.0023 gram in a 2-gram sample, corresponding to 0.115 per cent which is more than A. C. S. standard limit of 0.05 per cent, but it is good enough to use to prepare the fused bath.

For lithium carbonate, the carbon dioxide content was determined to check the purity. The carbon dioxide content was 59.5 per cent by weight which is identical with the theoretical percentage of carbon dioxide in pure, anhydrous lithium carbonate.

The aluminum phosphate was a technical grade, obtained from Fisher Scientific Co., and was known to be impure. The phosphorus pentoxide content was found to be 33.8 per cent by weight, while the theoretical content of phosphorus pentoxide is 58.1 per cent by weight for aluminum phosphate. This would indicate an aluminum phosphate content of 58.3 per cent by weight, the remainder probably consisting of aluminum oxide. For exploratory experiments, it was not thought necessary to use a more pure grade of aluminum phosphate, as would have been secured if experiments had been of sufficient promise to warrant further development.

The Limiting Composition of Boric Acid and Alkali Carbonate Mixture. The "Limiting Composition" is expressed as the minimum content of boric oxide which will eliminate all carbon dioxide from the sodium oxide-lithium oxide-boric oxide mixture. The absence of carbonate in the mixture was proved by taking a sample of the fused mixture, cooling, dissolving it in water and adding 3-normal hydrochloric acid in excess. This test was assumed to show the absence of carbonate if a sample gave no gas bubbles when so treated. The results are summarized in Table I. The points were plotted on triangular paper in Figure 5.

Fluid Range of Various Mixtures of $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ System. The fluid range data of various mixtures is summarized in Table II and Figure 5. From the experimental, fluid-range data, interpolations were made to obtain the mixtures which have an upper value at 660 and 600 °C as shown in Tables III and IV. Two curves were plotted on the triangular diagram by connecting isothermal, fluid-range points of 660 and 600 °C respectively, as shown in Figure 6. The area enclosed between the limiting composition line and the curve of 660 °C fluid range represents the possible working region from which selected mixtures were used for electrodeposition.

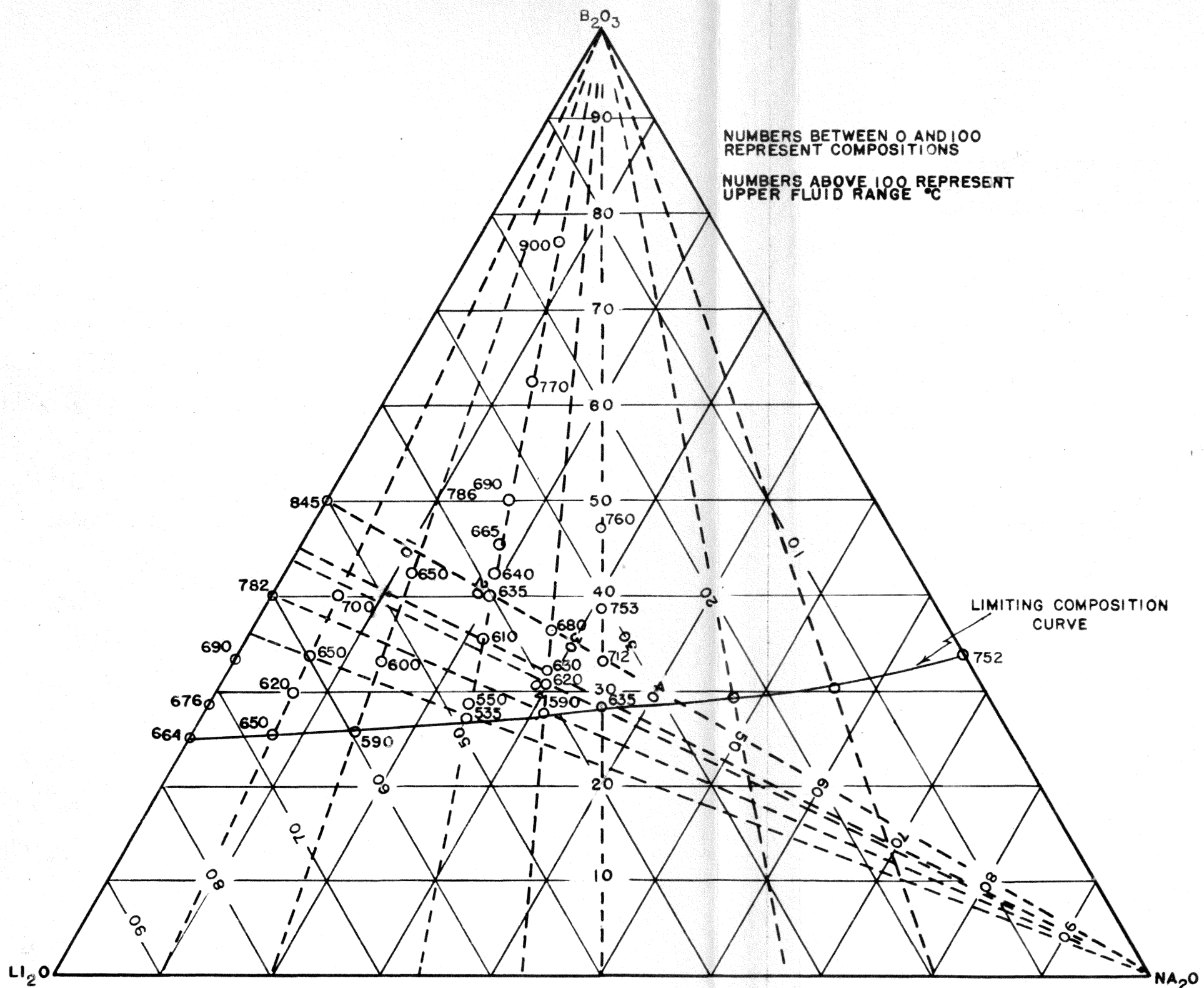
TABLE I

Limiting Composition in System Na₂O-Li₂O-B₂O₃ from Fusing Boric Acid
and Alkali Carbonate Mixture

Limiting composition is the minimum amount
of B₂O₃ which will eliminate all CO₂ from
Na₂CO₃-Li₂CO₃ mixture, melted to 900 °C
for three hours.

Weight of Materials Used				Net Weight After Fusion	Weight Less	Composition of Mixture					Limiting Composition		
Li ₂ CO ₃	Na ₂ CO ₃	H ₃ BO ₃	Total			Li ₂ CO ₃	Na ₂ CO ₃	Li ₂ O	Na ₂ O	B ₂ O ₃	Li ₂ O	Na ₂ O	B ₂ O ₃
gm	gm	gm	gm	gm	gm	mole	mole	mole	mole	mole	mole%	mole%	mole%
111.0	0.0	61.8	172.8	78.9	93.9	0.000	0.000	1.500	0.000	0.500	75.0	0.0	25.0
111.0	40.5	77.3	228.8	116.4	112.4	0.068	0.017	1.432	0.358	0.625	59.4	14.8	25.8
53.0	74.0	61.8	188.8	103.6	85.2	0.118	0.059	0.882	0.441	0.500	48.4	24.1	27.5
55.0	79.5	61.8	196.3	113.5	82.8	0.115	0.115	0.635	0.635	0.500	35.9	35.9	28.2
37.0	106.2	61.8	204.8	124.3	80.5	0.095	0.190	0.405	0.810	0.500	23.5	47.3	29.2
22.2	127.2	61.8	211.2	133.8	77.4	0.071	0.285	0.229	0.915	0.500	13.9	55.6	30.5
0.0	159.0	61.8	220.8	151.1	69.7	0.000	0.530	0.000	0.970	0.500	0.0	66.0	34.0

Figure 5. UPPER FLUID RANGE-COMPOSITION
DIAGRAM FOR SODIUM OXIDE-
LITHIUM OXIDE-BORIC OXIDE
SYSTEM



NUMBERS BETWEEN 0 AND 100 REPRESENT COMPOSITIONS
 NUMBERS ABOVE 100 REPRESENT UPPER FLUID RANGE °C

LIMITING COMPOSITION CURVE

FIGURE 5. UPPER FLUID RANGE—COMPOSITION DIAGRAM FOR SODIUM OXIDE—LITHIUM OXIDE—BORIC OXIDE SYSTEM

TABLE II

Fluid Range of Various Mixtures in
System Na₂O-Li₂O-B₂O₃

Molar Ratio Na ₂ O:Li ₂ O	Composition			Fluid Range	
	Na ₂ O	Li ₂ O	B ₂ O ₃	Upper	Lower
	Mol %	Mol %	Mol %	°C	°C
0:1	0.0	50.0	50.0	845	825
	0.0	60.0	40.0	782	760
	0.0	66.7	33.3	690	670
	0.0	71.4	28.6	676	662
	0.0	75.0	25.0	664	661
1:9	6.0	54.0	40.0	700	695
	6.6	59.7	33.7	650	645
	7.0	63.0	30.0	620	615
	7.5	67.2	25.3	650	645
1:4	10.0	40.0	50.0	786	754
	11.4	45.7	42.8	650	640
	13.3	53.4	33.3	600	590
	14.8	59.4	25.8	590	580
1:1.54	27.0	36.5	36.5	620	616
	28.8	39.0	32.2	630	620
	29.5	39.5	31.0	620	615
	30.9	41.3	27.8	590	560
1:2	7.7	15.4	76.9	--	900
	12.8	25.7	62.5	770	732
	16.7	33.3	50.0	690	680
	18.2	36.5	45.5	665	640
	19.1	38.4	42.5	640	630
	20.0	40.0	40.0	635	630
	21.4	42.8	35.7	610	600
	23.8	47.6	28.6	550	540
	24.1	48.4	27.5	535	535
1:1	27.2	27.2	45.5	760	753
	30.8	30.8	38.5	753	746
	33.3	33.3	33.3	712	700
	35.9	35.9	28.2	635	620
1:0	66.0	0.0	34.0	752	752

TABLE III
Compositions in System Na₂O-Li₂O-B₂O₃
with Upper Fluid Range of 660 °C

Test No.	Components		
	Na ₂ O Mol %	Li ₂ O Mol %	B ₂ O ₃ Mol %
1	35.3	35.3	29.5
2	2.0	68.0	30.0
3	5.3	60.0	34.1
4	6.4	58.6	35.0
5	27.6	37.4	35.0
6	5.5	56.7	37.8
7	24.0	38.0	38.0
8	24.5	34.5	40.0
9	9.0	51.0	40.0
10	7.0	52.3	40.7
11	8.5	50.2	41.3
12	12.2	43.9	43.9
13	11.0	45.0	44.0
14	17.7	35.7	46.6

TABLE IV
Compositions in System Na₂O-Li₂O-B₂O₃
with Upper Fluid Range of 600 °C

Test No.	Compositions		
	Na ₂ O Mol %	Li ₂ O Mol %	B ₂ O ₃ Mol %
1	30.3	40.7	29.0
2	28.4	41.6	30.0
3	12.0	58.0	30.0
4	13.0	53.6	33.4
5	21.8	44.3	33.9
6	15.0	51.0	34.0

Figure 6. COMPOSITION-CONSTANT FLUID
RANGE CURVES FOR LITHIUM
OXIDE-SODIUM OXIDE-BORIC
OXIDE SYSTEM

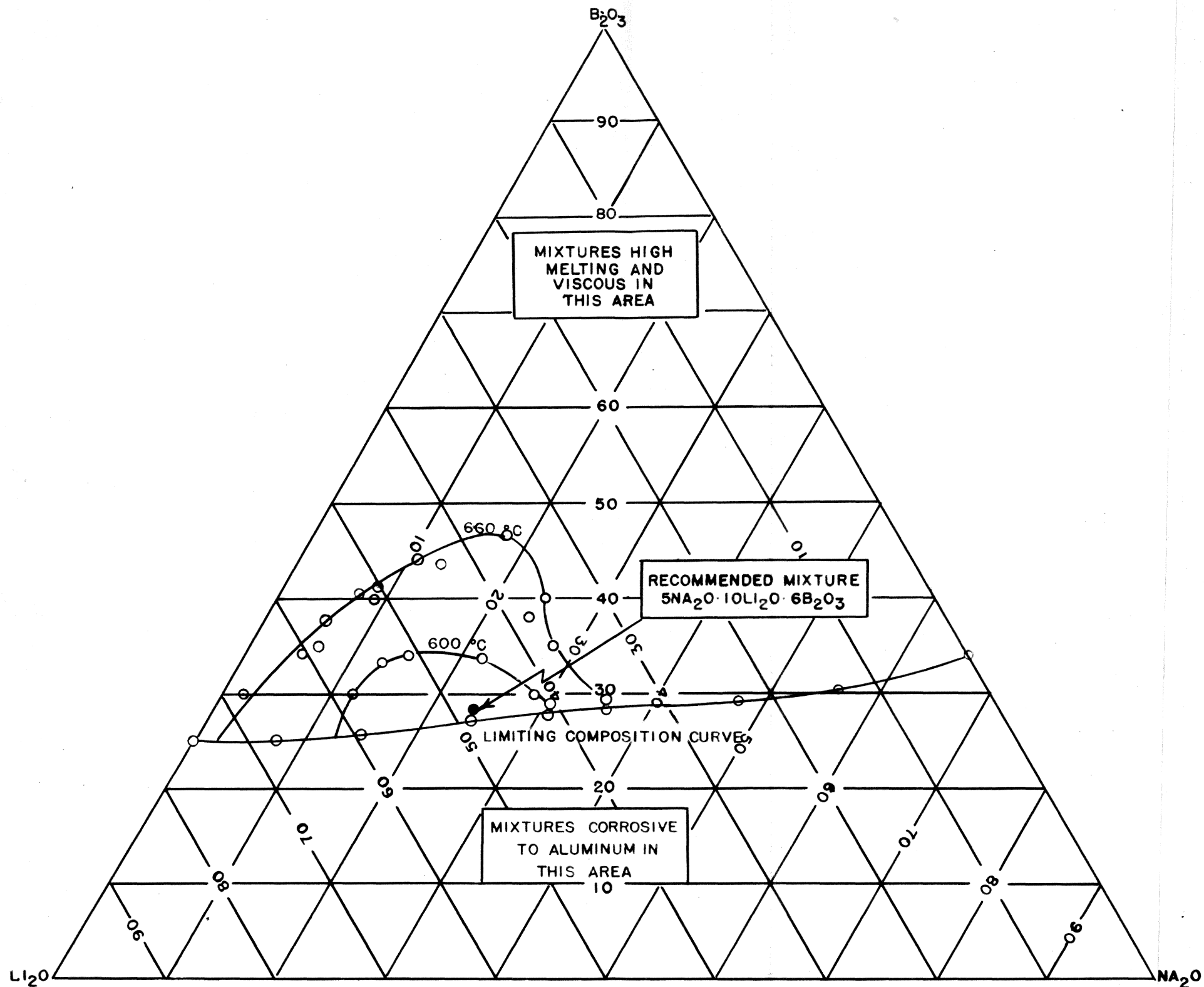


FIGURE 6. COMPOSITION-CONSTANT FLUID RANGE CURVES FOR LITHIUM OXIDE-SODIUM OXIDE-BORIC OXIDE SYSTEM

Effect on the Fluid Range of Adding Aluminum Phosphate to the Fused Borates. The fluid range of $B_2O_3 \cdot 1.94Na_2O + 1.06Na_2CO_3$ alone and its mixture with aluminum phosphate were shown in Table V. A plot of the weight per cent of aluminum phosphate in fused $B_2O_3 \cdot 1.94Na_2O + 1.06Na_2CO_3$ against the upper fluid range is shown in Figure 7.

The eutectic temperature derived from the plot is 688 °C, at a composition of 11.3 per cent by weight of aluminum phosphate in $B_2O_3 \cdot 1.94Na_2O + 1.06Na_2CO_3$.

The fluid ranges of the selected mixture, $5Na_2O \cdot 10Li_2O \cdot 6B_2O_3$, and the mixture of this with aluminum phosphate are summarized in Table VI. A plot of the fluid range against the weight per cent of aluminum phosphate in the chosen mixture $5Na_2O \cdot 10Li_2O \cdot 6B_2O_3$ is shown in Figure 8. It shows that the addition of aluminum phosphate has little effect on the fluid range to 18.68 per cent by weight of aluminum phosphate.

Corrosion by the Fused Mixture. The results of corrosion tests on seven materials is summarized in Table VII. Obviously, except for the graphite crucible and the platinum dish, no material was suitable for use as a container.

Decomposition Potentials of Fused Borates and Borates-Phosphate Mixture. The current-voltage relation data for the mixture $5Na_2O \cdot 10Li_2O \cdot 6B_2O_3$ at 560 ± 10 °C with aluminum anode and platinum cathode are shown in Table VIII and

TABLE V
Experimental Data for
Composition-Fluid Range of AlPO₄
in B₂O₃·1.94Na₂O+1.06Na₂CO₃

Composition, AlPO ₄	Fluid Range,
Weight %	°C
0	735-752
8.75	682-702
17.8	669-706
29.6	716-735
46.4	716-782
56.3	above 900

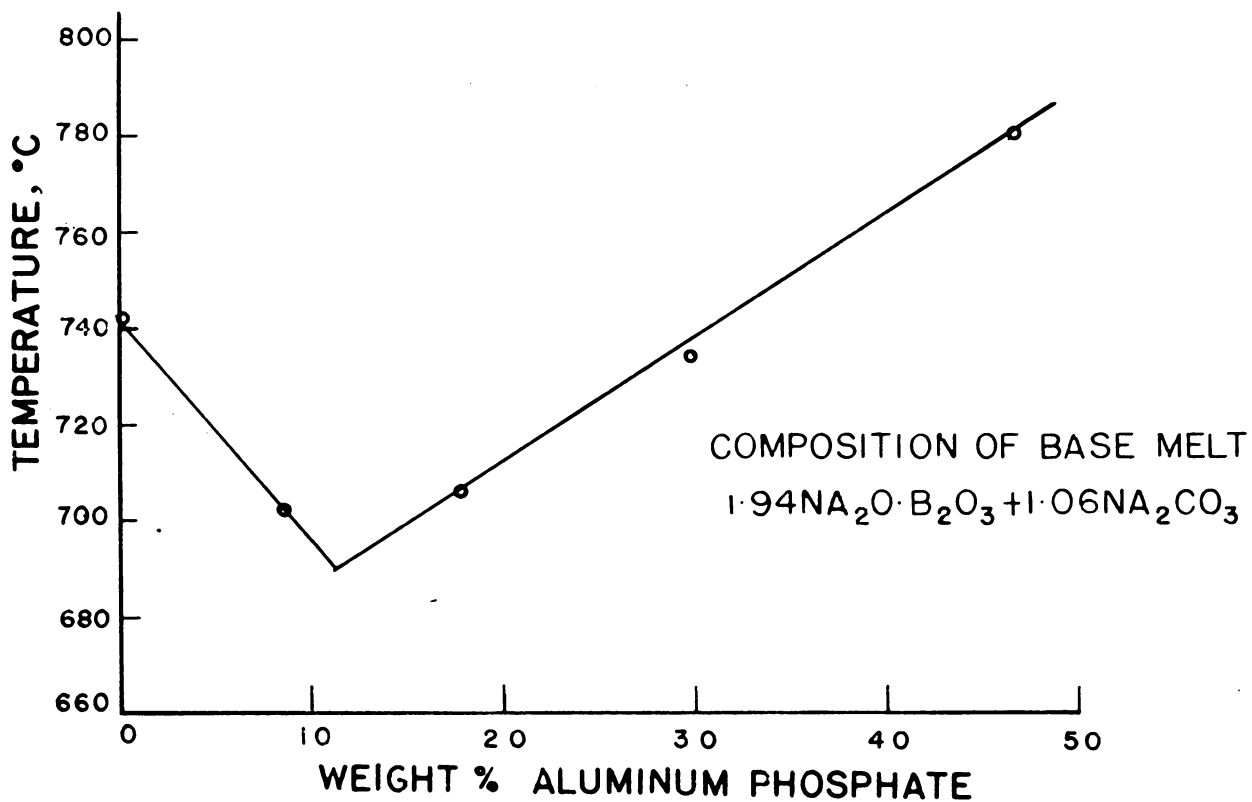


FIGURE 7. COMPOSITION-FLUID RANGE
OF ALUMINUM PHOSPHATE IN SODIUM
BORATE AND SODIUM CARBONATE

TABLE VI
Experimental Data for
Composition-Fluid Range of AlPO₄
in 5Na₂O.10Li₂O.6B₂O₃

Composition, AlPO ₄	Fluid Range
Weight %	°C
0	540-550
2.34	550-560
4.68	560-570
7.02	555-560
9.35	555-560
11.69	555-560
14.01	555-560
16.34	555-560
18.68	550-555

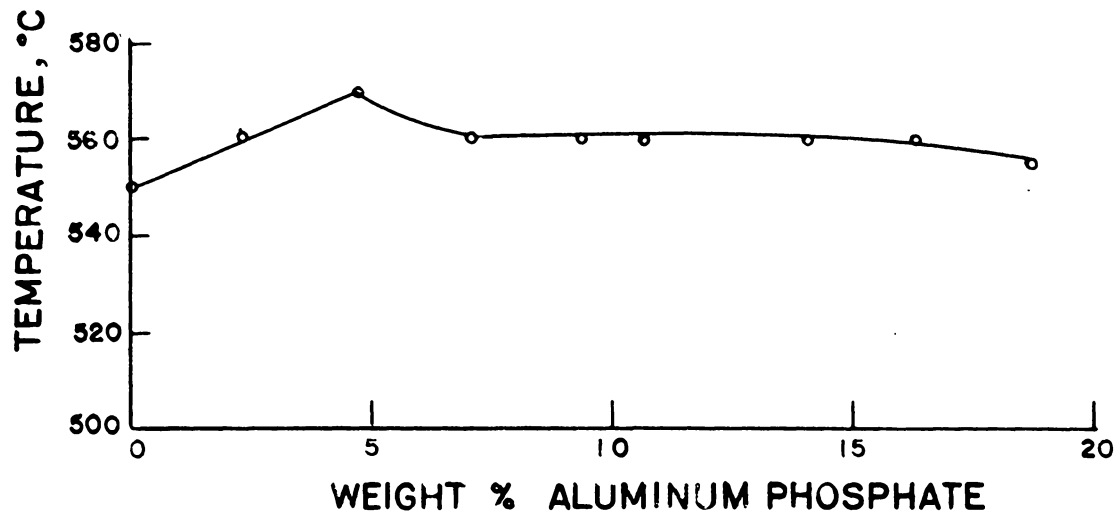


FIGURE 8. COMPOSITION—FLUID RANGE OF ALUMINUM PHOSPHATE IN THE MIXTURE $5\text{Na}_2\text{O}\cdot 10\text{Li}_2\text{O}\cdot 6\text{B}_2\text{O}_3$

TABLE VII

Corrosive Action of Fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$
at 650 to 700 °C. on Various Materials

Type of Crucible	Appearance of Fused Liquid	Description of Corrosion on Crucibles
Porcelain, Coors, wide form, No. 4.	Liquid was water white, clear, without any color change.	The lining of the crucible was first attacked. If the time of fusion was over four hours, the crucible cracked in the furnace. Even if the time of fusion was not too long, the crucible always cracked after the mixture had been cooled to room temperature.
Nickel, 100 ml. capacity, 60 mm. dia. and 64 mm. high.	The clear liquid turned opaque, then green to dark color.	The crucible wall was full of holes after a short fusion time.
Ampeco, 76.2 mm. dia., 127 mm. high.	Liquid was first clear white, but gradually turned to green and finally black.	The inner surface of the crucible under the surface of the liquid gradually changed to rubby color. Black scales were continually formed on the inner surface of the fusion liquid and dropped into the liquid.
Armco iron, extra heavy, 50 ml. capacity.	Liquid was discolored by brown iron oxide in suspension.	A brown stain was formed on the inner wall of the crucible. There was no severe solution of the crucible.
Plumbago, 95 mm. dia., on the top, 115 mm. high.	Liquid contained a black graphite suspension.	No obvious corrosive action on the crucible was observed. The crucible did not crack on cooling.
Graphite, 50.8 mm. inside dia., 76.2 mm. high and 19.1 mm. thickness of wall and bottom	Slight carbon suspension was observed in the liquid, but it was clear and transparent.	There was some combustion of the crucible. There was some loss of the liquid through the wall and bottom.
Platinum dish, 8.5 cm. dia., and 4.0 cm. high.	Liquid was clear and transparent during the whole experiment.	No perceptible corrosion was observed.

TABLE VIII

Decomposition Potential
of Fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$
with Aluminum Anode and Platinum Cathode

Composition of Electrolyte:

	Grams
H_3BO_3	123.6
Li_2CO_3	123.4
Na_2CO_3	88.4

Dimension of Electrodes:

Aluminum anode 2.5 by 2.5 cm
 Platinum cathode 2.5 by 2.5 cm

Temperature: 560 ± 10 °C

Agitation: None

Voltage,	Current	Voltage,	Current
volts	ma	volts	ma
0.1	190	1.3	650
0.2	225	1.4	700
0.3	275	1.5	738
0.4	300	1.6	775
0.5	350	1.7	825
0.6	388	1.8	875
0.7	412	1.9	900
0.8	450	2.0	950
0.9	488	2.2	1050
1.0	525	2.4	1150
1.1	588	2.6	1200*
1.2	625	-	-

* The current suddenly dropped from 1200 to 950 milliamperes, probably because of polarization.

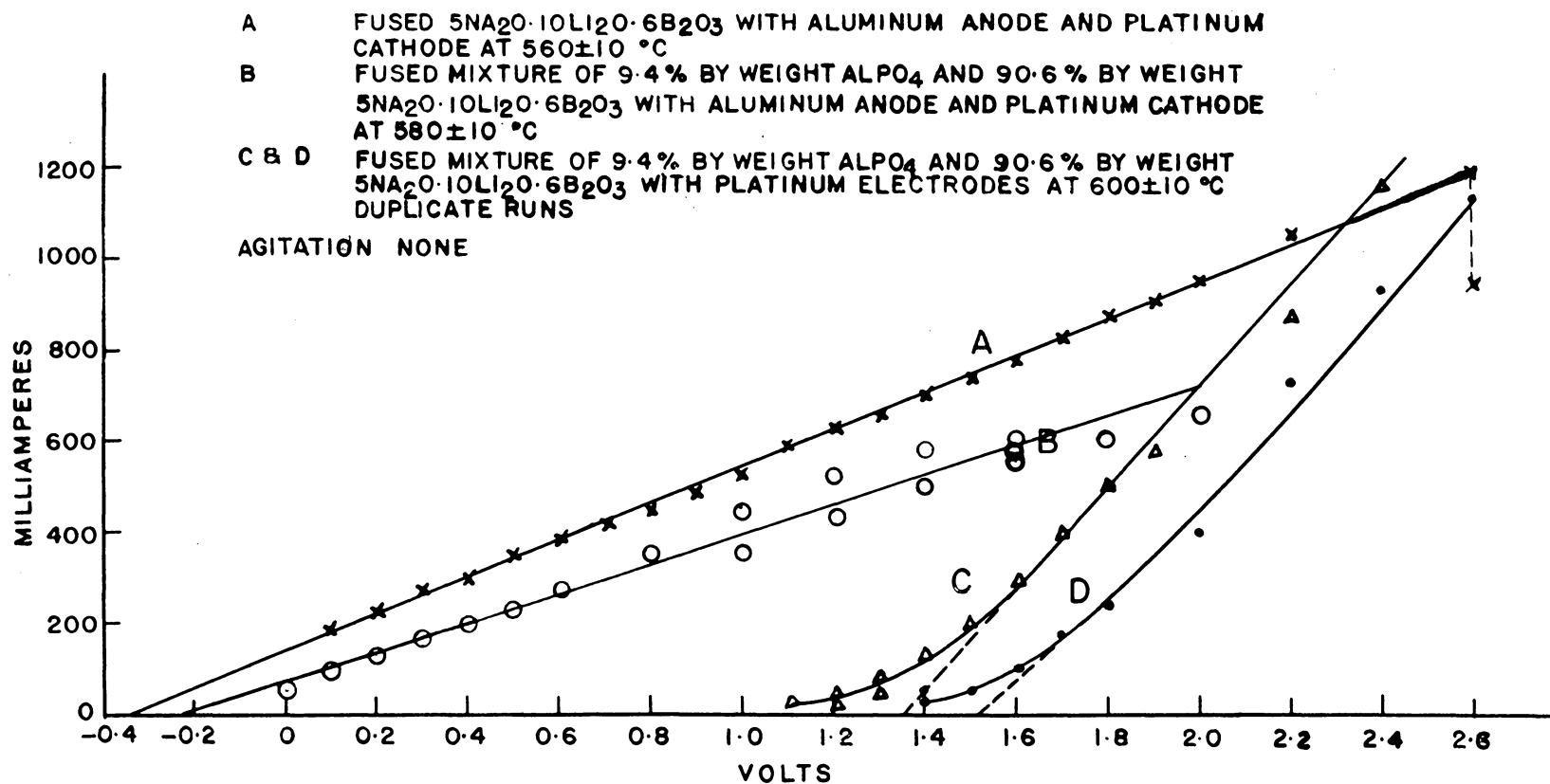


FIGURE 9. CURRENT-VOLTAGE CURVE FOR FUSED BORATES

curve A in Figure 9. The current was proportional to the applied voltage when the applied voltage was below the number of 1.6 volts, the current was increased out of direct proportion and then suddenly dropped to 0.75 of the original current at 2.6 volts. The cell potential extrapolated at zero current was found to be -0.36 volt.

After the current-voltage determination, the platinum cathode was coated black, and the aluminum anode was coated with a layer of yellow-brown substance which looks like an alloy. There was also few black particles adhering to the aluminum anode. In the fused electrolyte, aluminum can be detected qualitatively.

The data for the current-voltage relation for the fused liquid containing 9.4 per cent aluminum phosphate and 90.6 per cent $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ at 580 ± 10 °C, with aluminum anode and platinum cathode, are shown in Table IX and curve B in Figure 9. The current readings were not stable when the applied voltages were greater than 1.0. In each set of current readings for the same applied voltage, the lowest reading of the current fitted better in the current-voltage curve. The cell potential was -0.1 volt as extrapolated from the current-voltage curve. This experiment was not continued to the point where current fell off as in the previous case.

After the experiment, both electrodes were covered with the black film.

TABLE IX

Decomposition Potential
of Fused Mixture of 9.4 per cent of AlPO_4
and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$

Composition of Electrolyte:

	Grams
H_3BO_3	185.4
Li_2CO_3	185.1
Na_2CO_3	132.6
AlPO_4	27.1

Dimension of Electrodes:

Aluminum anode	2.5 by 2.5 cm.
Platinum cathode	2.5 by 3.0 cm.
Temperature	580 ± 10 °C
Agitation	None

Voltage,	Current,	Voltage,	Current,
volts	ma	volts	ma
0.0	55	0.8	350
0.1	100	1.0	350(450)*
0.2	130	1.2	425(525)*
0.3	165	1.4	500(575)*
0.4	200	1.6	550(600)*
0.5	230	1.8	600
0.6	280	2.0	650

* The value in parenthesis are not shown in the plot.

The current-voltage data for the fused liquid of 9.4 per cent aluminum phosphate and 90.6 per cent $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ at 600 ± 10 °C, with platinum electrodes, are shown in Table X and curve C and D in Figure 9.

The decomposition potentials, extrapolated from two duplicate tests, were 1.35 and 1.51 volts.

During the electrolysis, many small gas bubbles surrounded the anode, but there were only a few of them around the cathode. No color change was observed on the anode, but some black powders were deposited on the cathode.

Unsteady Electrolysis in Fused Borates-Phosphate and Borates Mixture. The data for the effect of time on current at constant voltage in a fused electrolyte consisting of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ with aluminum anode and copper cathode at 560 ± 10 °C are shown in Table XI and Figure 10. The relation is rather irregular and cannot be reproduced.

The data for the effect of stirring for the same electrolyte with platinum electrodes at a constant potential of 1.5 volts and at 560 ± 10 °C are shown in Table XII. The effect of moisture on electrodes and electrolyte is shown in Table XIII and Figure 11. In Figure 11, the data for the curve for current flow in system without

TABLE X

Decomposition Potential
of Fused Mixture of 9.4 per cent of AlPO_4
and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$

Composition of Electrolyte:

	Grams
H_3BO_3	185.4
Li_2CO_3	185.1
Na_2CO_3	132.4
AlPO_4	27.1

Dimension of Electrodes:

Platinum anode	2.5 by 2.5 cm.
Platinum cathode	2.5 by 2.5 cm.

Temperature: 600 \pm 10 $^\circ\text{C}$

Agitation: None

Test I		Test II	
Voltage,	Current,	Voltage,	Current,
volts	am	volts	am
0.6	0.0	1.0	0.0
0.8	0.0	1.1	0.0
1.0	0.0	1.2	10
1.1	20.0	1.3	40
1.2	37.5	1.4	50
1.3	65.0	1.5	50
1.4	120.0	1.6	100
1.5	192.5	1.7	175
1.6	288	1.8	240
1.7	400	2.0	400
1.8	500	2.2	725
1.9	575	2.4	925
2.0	650	2.6	1125
2.2	863	2.8	1300
2.4	1150	-	-

TABLE XI

Fluctuation of Current at Constant
Voltage in Fused Borates-Phosphate Bath

Composition of Electrolyte:

$5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ 90.6 %
 AlPO_4 9.4 %

Electrodes: Aluminum anode and copper cathode.

Temperature: 560 ± 10 °C.

Agitation: None.

Time, min.	Voltages,					
	1.5 amp.	2.0 amp.	2.5 amp.	3.5 amp.	4.5 amp.	5.5 amp.
0	0.400	0.175	0.350	1.500	1.250	0.400
5	--	--	0.350	1.400	1.375	0.350
8	--	--	--	--	1.250	--
10	0.100	0.100	0.250	1.250	1.250	0.350
15	--	0.100	0.225	1.250	0.500	0.325
18	--	--	--	--	0.400	--
20	0.075	0.100	0.200	1.250	0.350	0.300
23	--	--	--	0.375	0.325	0.200
25	0.075	0.100	0.200	0.375	0.350	0.200
26	--	--	0.150	--	--	0.250
28	--	--	--	--	--	--
30	0.075	0.500	0.150	0.375	0.350	0.300
35	0.075	0.500	0.125	0.325	0.350	0.100
40	0.075	0.175	0.125	0.275	0.350	0.225
45	0.075	0.175	0.125	0.250	0.500	0.075
48	--	--	--	--	0.625	--
50	0.075	0.175	0.125	0.250	0.850	0.175
55	0.075	0.175	0.125	0.250	0.850	0.350
58	--	--	--	--	--	0.300
60	0.075	0.175	0.125	0.200	0.850	0.300
65	0.075	0.175	0.125	0.175	1.100	0.225
70	0.075	0.175	0.125		1.100	0.225
75	0.075	0.500	0.125		1.100	0.225
80	0.075		0.125		1.200	0.200
85	0.075		0.125		1.275	0.200
90	0.075		0.125			0.150
120	0.075		0.125			

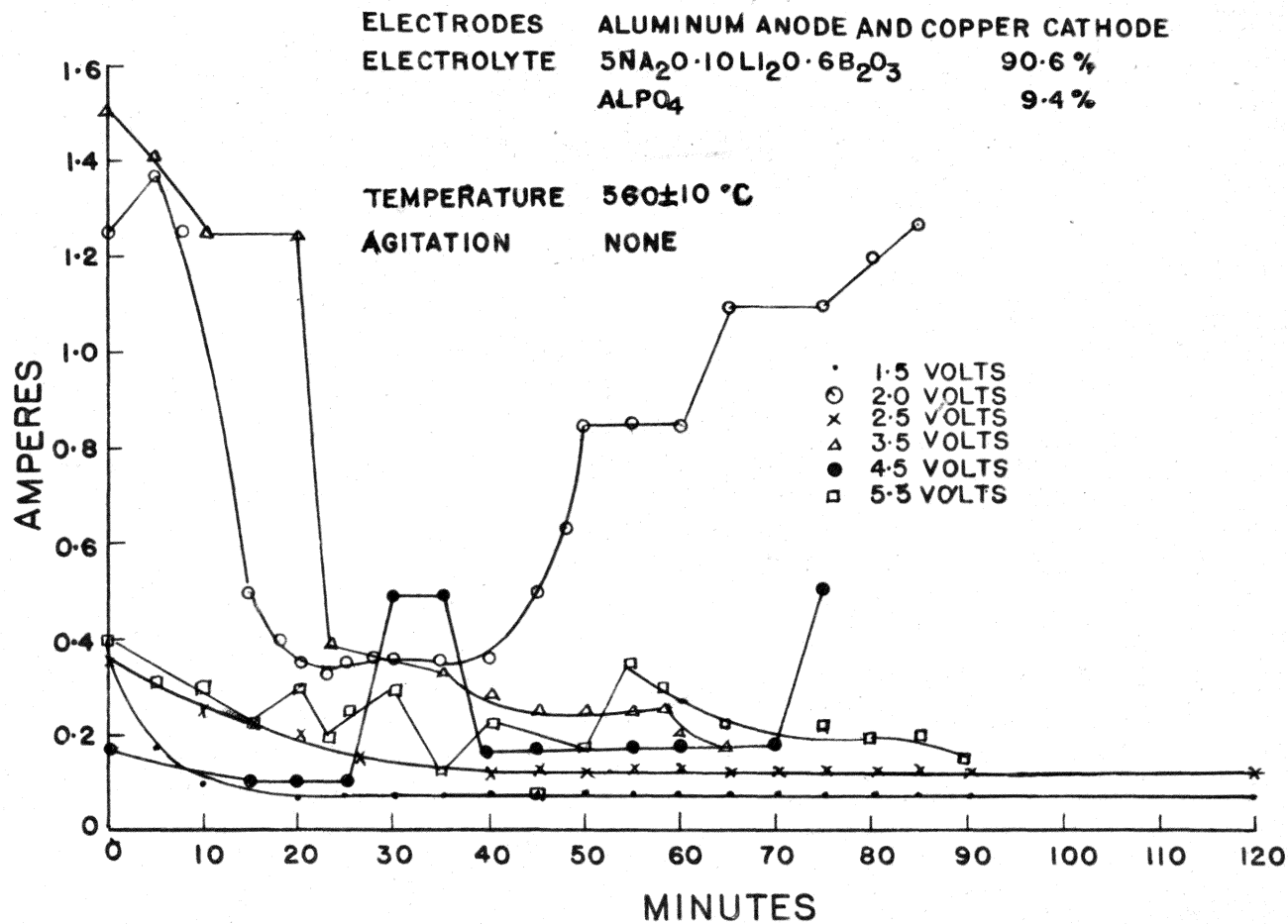


FIGURE 10. EFFECT OF TIME ON CURRENT AT
 CONSTANT VOLTS

TABLE XII

Effect of Stirring on
the Current-Time Relationship
in Fused Electrolyte 9.4 per cent $AlPO_4$ and
90.6 per cent $5Na_2O \cdot 0.10Li_2O \cdot 0.6B_2O_3$

Electrodes: Platinum anode and platinum cathode.
Temperature: 560 ± 10 °C.
Voltage: 1.5 volts.
Agitation: Using a chromel wire and stirred by hand.

Time, min.	Current, amp.	Description of Phenomena
0	0.250	
5	0.075	After stirring, the current dropped to 0.040 ampere.
10	0.075	The current was not changed by stirring.
15	0.075	ditto.
25	0.075	The current dropped to 0.050 ampere after stirring, but recovered to 0.075 ampere after resting.
35	0.075	The current was not changed on stirring.
40	0.075	ditto.
45	0.075	ditto.
55	0.075	ditto.
65	0.075	ditto.
75	0.075	ditto.
85	0.075	ditto.
95	0.075	ditto.
105	0.075	ditto.
115	0.075	ditto.

TABLE XIII

Effect of Moisture on
the Current-Time Relationship
in Fused Electrolyte 9.4 per cent AlPO_4 and
90.6 per cent $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$

Electrodes: Platinum anode and platinum cathode.
 Temperature: 560 ± 10 °C.
 Voltage: 1.5 volts.
 Agitation: None.
 Moisture: See note*.

Time, min.	Current, amp.	Time, min.	Current, amp.
0	0.40	55	0.45
5	0.45	60	0.45
10	0.45	65	0.45
15	0.45	70	0.45
20	0.45	75	0.45
25	0.45	80	0.45
30	0.45	85	0.45
35	0.45	95	0.45
40	0.45	105	0.45
45	0.45	115	0.45
50	0.45	-	-

* The electrodes and 259.2 grams of electrolyte were moistened with 0.5 grams of water and heated to 560 ± 10 °C before electrolysis.

ELECTRODES	PLATINUM	
ELECTROLYTE	5NA ₂ O·10LI ₂ O·6B ₂ O ₃	90.6 %
	ALPO ₄	9.4 %
POTENTIAL	1.5 VOLTS	
TEMPERATURE	560±10 °C	
AGITATION	NONE	

△ CURRENT WHEN THE ELECTRODES AND 259.2 GRAMS OF ELECTROLYTE MOISTENED WITH 0.5 GRAMS OF WATER AND HEATED TO 560±10 °C
X CURRENT WITH NO WATER PRESENT

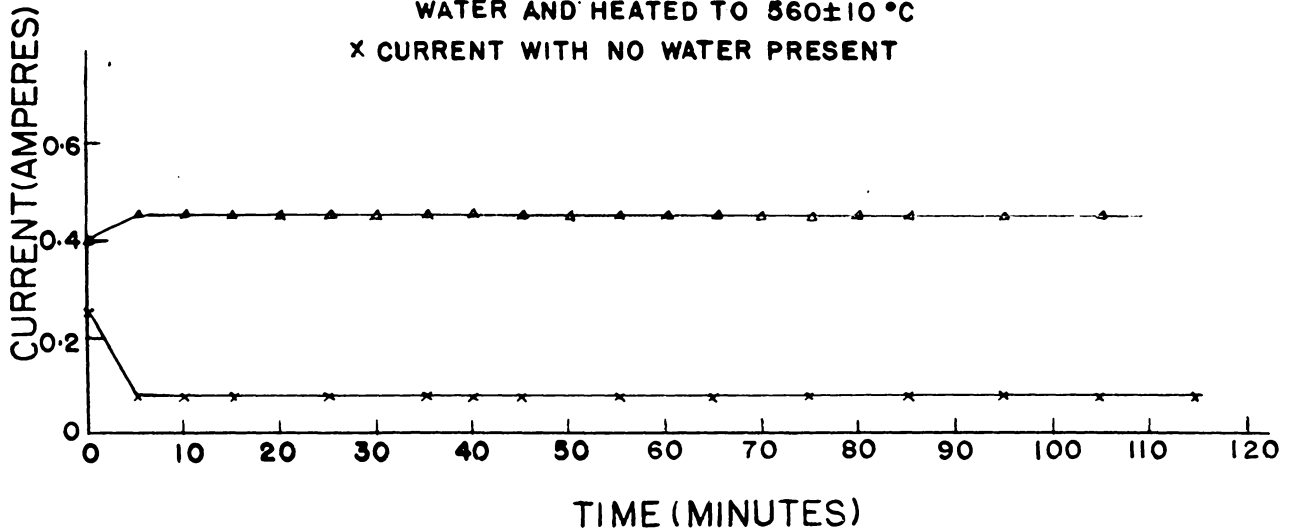


FIGURE II. EFFECT OF MOISTURE ON CURRENT DURING ELECTROLYSIS OF FUSED BORATE-PHOSPHATE ELECTROLYTE

water were taken from Table XII. The effect of periodic immersions is shown in Table XIV and Figure 12. The effect of temperature is shown in Table XV.

The result for the time-current relation for the same electrolyte at constant voltage 2.5 volts and 560 ± 10 °C with platinum electrodes is shown in Table XVI and Figure 13. Vigorous evolution of gas occurred during electrolysis. After electrolysis, the cathode was completely burnt off, but the anode was still in good condition with the shining white color of platinum. In the fused electrolyte around the cathode, a porous black mass was suspended. After this black mass was treated with 3-normal hydrochloric acid, ignited to white ash and then extracted with 3-normal hydrochloric acid again, fragments of platinum cathode were found. Such fragments were very brittle and grayish in color.

For the electrolyte, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, an aluminum anode and platinum cathode were used at 560 ± 10 °C and 1.5 volts. Duplicate runs were made. The first test lasted only two hours. Since the current readings dropped low as compared with readings at the start, the electrolysis was stopped. In the second test, the same electrolyte was used, but the aluminum anode was replaced with a new one. The current readings showed the same tendency of dropping to very low value. As the electrolysis continued, part of

TABLE XIV

Effect of Inserting and
Removing Electrodes from Fused Electrolyte

9.4 per cent AlPO_4

and 90.6 per cent $5\text{Na}_2\text{O} \cdot 0.10\text{Li}_2\text{O} \cdot 0.6\text{B}_2\text{O}_3$

Electrodes: Platinum anode and platinum cathode.
Temperature: 560 ± 10 °C.
Voltage: 1.5 volts.
Agitation: None.

Time, min.	Current, amp.	Description of Phenomena
0	0.45	Electrodes were removed from fused electrolyte.
20	0.40	When the electrodes were first put into the fused electrolyte, it was 0.40 ampere, then dropped, but rebuilt to 0.40 ampere gradually.
25	0.45	
35	0.45	
45	0.45	
55	0.45	The electrodes were taken from the electrolyte.
70	0.45	The electrodes were reinserted.
80	0.45	
90	0.45	
100	0.45	The electrodes were removed from the electrolyte. After the electrodes were inserted into the fused liquid, the current was gradually raised to 0.45 ampere.
145	0.45	The electrodes were taken from the electrolyte.
395	0.40	The electrodes were inserted into the liquid.
400	0.40	
410	0.40	
420	0.40	

ELECTRODES	PLATINUM	
ELECTROLYTE	$5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$	90.6%
	AlPO_4	9.4%
POTENTIAL	1.5 VOLTS	
TEMPERATURE	$560 \pm 10^\circ\text{C}$	
AGITATION	NONE	

* ELECTRODES TAKEN OUT FROM ELECTROLYTE
^ ELECTRODES PUT INTO ELECTROLYTE

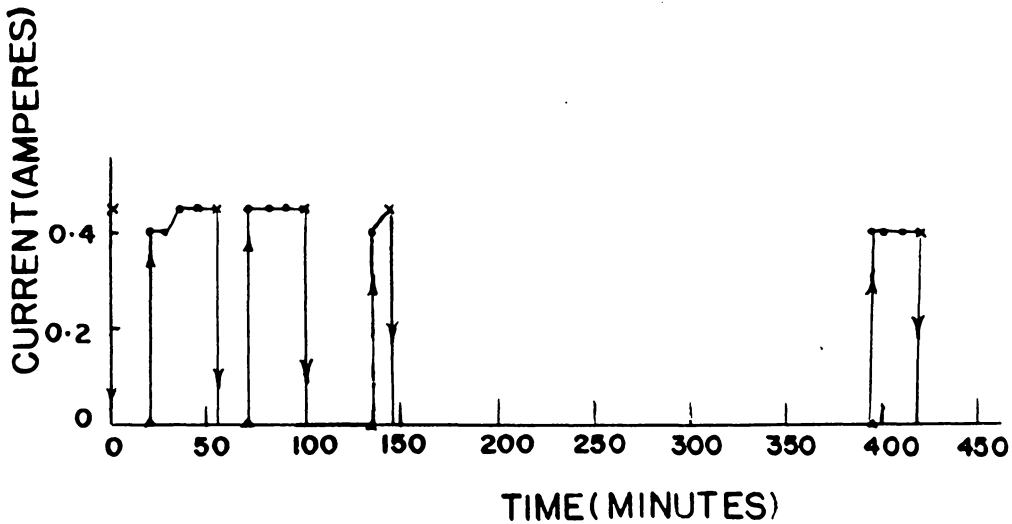


FIGURE 12. EFFECT OF ALTERNATING IMMERSIONS ON CURRENT DURING ELECTROLYSIS OF FUSED BORATE-PHOSPHATE

TABLE XV

Effect of Temperature on
the Current in Fused Electrolyte 9.4 per cent AlPO_4
90.6 per cent $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$

Electrodes: Platinum anode and platinum cathode.

Temperature: 560 ± 10 °C.

Voltage: 1.5 volts.

Agitation: None.

Temperature,	Current,
°C	amp.
524	0.375
560	0.400

TABLE XVI

Current-Time Relationships

in Fused Electrolyte 9.4 per cent AlPO_4

and 90.6 per cent $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$

Electrodes: Platinum anode and platinum cathode.
Temperature: 560 ± 10 °C.
Voltage: 2.5 volts.
Agitation: None.

Time,	Current,	Description of Phenomena
min.	amp.	
0	5.4	Vigorous gas bubbles around both electrodes.
5	5.0	ditto
8	4.8	Solid beginning to form around the anode.
9	4.6	ditto.
10	4.6	Anode completely covered with solid salt.
15	4.6	ditto.
20	4.6	ditto.
25	4.6	ditto.
30	4.6	ditto.
35	4.6	ditto.
40	4.6	ditto.
45	4.6	ditto.
48	4.6	ditto.

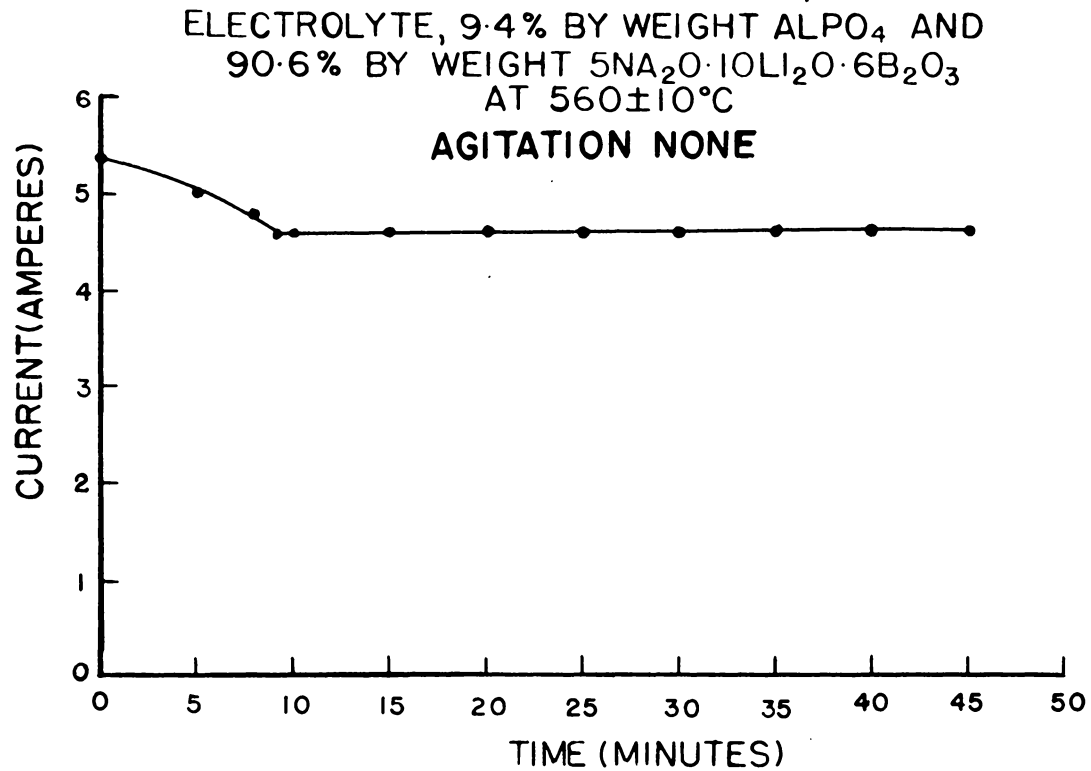


FIGURE 13. EFFECT OF TIME ON CURRENT AT 2.5 VOLTS
WITH PLATINUM ELECTRODES

the black deposit formed on the electrodes dispersed into the fused liquid and the current increased again. Soon after the increase in the current, the deposit on the electrodes built up, and the current dropped again. As the electrolysis went on, the high current existed for a shorter duration and the low current for a longer. The results are shown in Table XVII and Figure 14.

As the current dropped below 0.05 ampere, the evolution of gas bubbles around the platinum cathode stopped, but there were a few around the aluminum anode.

After the electrodes were taken from the bath, the platinum cathode were found to be covered with a thin black layer, and the aluminum anode, with a thick black mixture containing white aluminum oxide.

After the electrolysis, the fused electrolyte became turbid with both black and white particles.

Electrodeposition Test in Phosphate Mixture. A fused electrolyte of 69 per cent of sodium metaphosphate and 31 per cent of sodium pyrophosphate with 10 per cent of aluminum phosphate dissolved in it was a clear, colorless liquid. It was electrolyzed with copper cathode and three different anodes: aluminum, an alloy of 75 per cent aluminum and 25 per cent copper, and platinum at 600 ± 10 °C. In no case could aluminum be deposited on the cathode. The copper cathode were covered with a layer of black coating in all experiments. The results were summarized in Table XVIII.

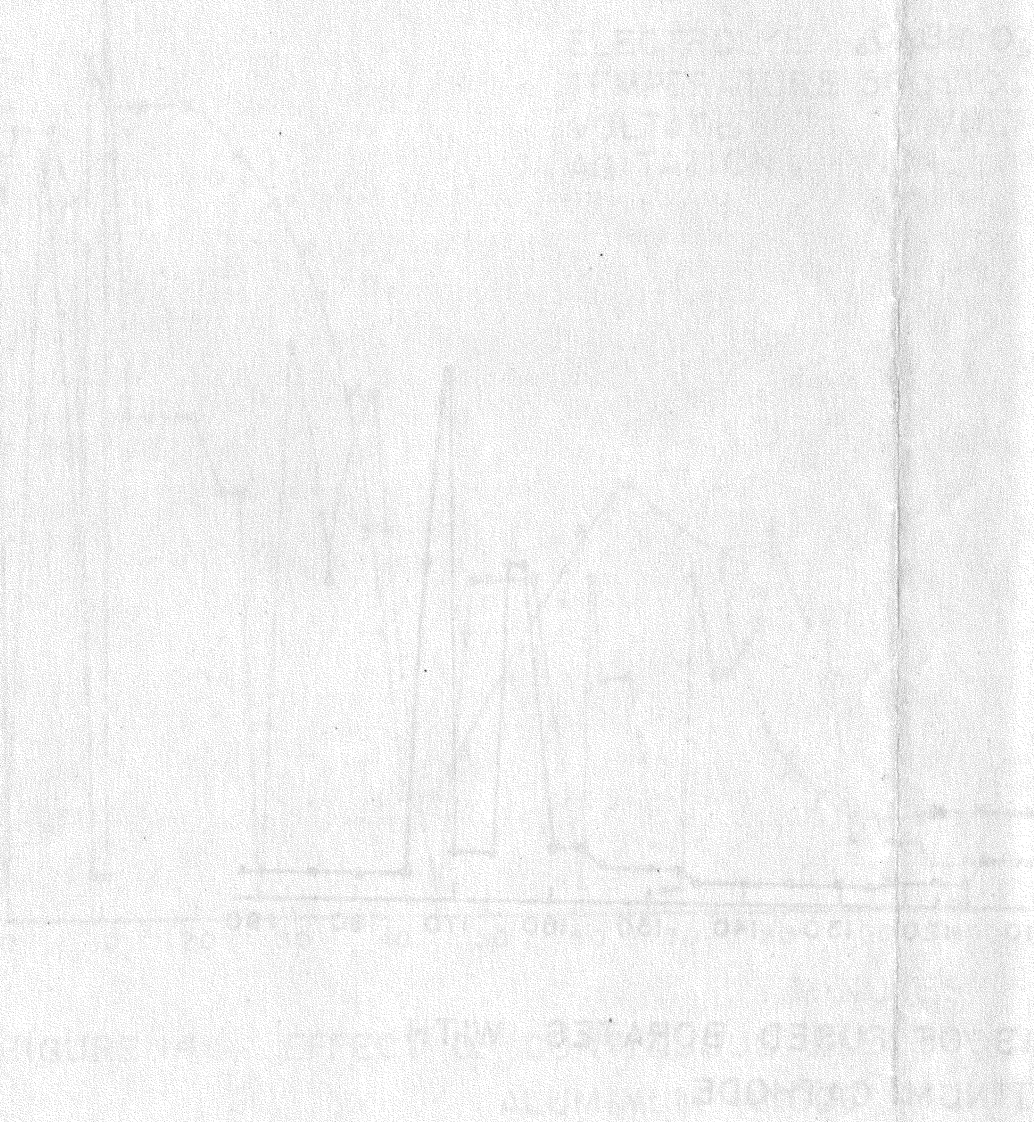
TABLE XVII

Effect of Continuous Electrolysis
of Fused Electrolyte $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$

Electrodes: Aluminum anode and platinum cathode.
Temperature: 560 ± 10 °C.
Voltage: 1.5 volts.
Agitation: None.

Test I		Test II			
Time,	Current,	Time,	Current,	Time,	Current,
min.	amp.	min.	amp.	min.	amp.
0	0.35	0	1.50	80	0.70
5	1.60	2	1.65	84	0.60
8	0.80	5	1.65	85	0.60
10	1.80	8	1.50	86	0.50
11	1.70	9	0.10	88	0.15
15	1.70	10	0.10	90	0.20
20	1.70	11	2.00	92	0.15
25	1.60	12	1.60	95	0.15
29	1.50	13	1.05	96	0.10
30	1.50	15	1.05	100	0.10
32	1.40	20	1.05	105	0.10
33	1.30	23	0.90	110	0.10
35	1.20	25	0.90	115	0.10
37	1.10	26	0.05	117	0.05
38	0.80	30	1.20	120	0.05
39	0.60	33	0.90	125	0.05
40	0.50	34	0.70	127	0.04
42	0.25	35	0.90	130	0.04
45	0.25	39	1.10	135	0.04
46	0.30	40	0.80	140	0.04
48	0.35	45	0.05	145	0.04
50	0.40	48	0.60	147	0.07
52	0.50	49	0.70	150	0.07
53	0.55	50	0.70	155	0.07
55	0.55	55	0.70	157	0.11
58	0.65	60	0.05	160	0.11
60	0.80	61	0.70	164	0.70
63	0.85	62	0.50	167	0.10
65	0.90	65	0.50	170	0.10
70	0.80	68	0.05	172	0.10
75	0.55	70	0.05	174	0.70
80	0.35	72	0.70	175	0.05
81	0.30	73	0.60	180	0.05
85	0.25	74	0.50	185	0.05
88	0.20	75	0.50	190	0.05
90	0.20	79	0.60	192	0.05
95	0.20				
100	0.20				
105	0.20				
110	0.20				
115	0.20				
120	0.20				

Figure 14. Effect of continuous electrolysis of fused borates with aluminum anode and platinum cathode.



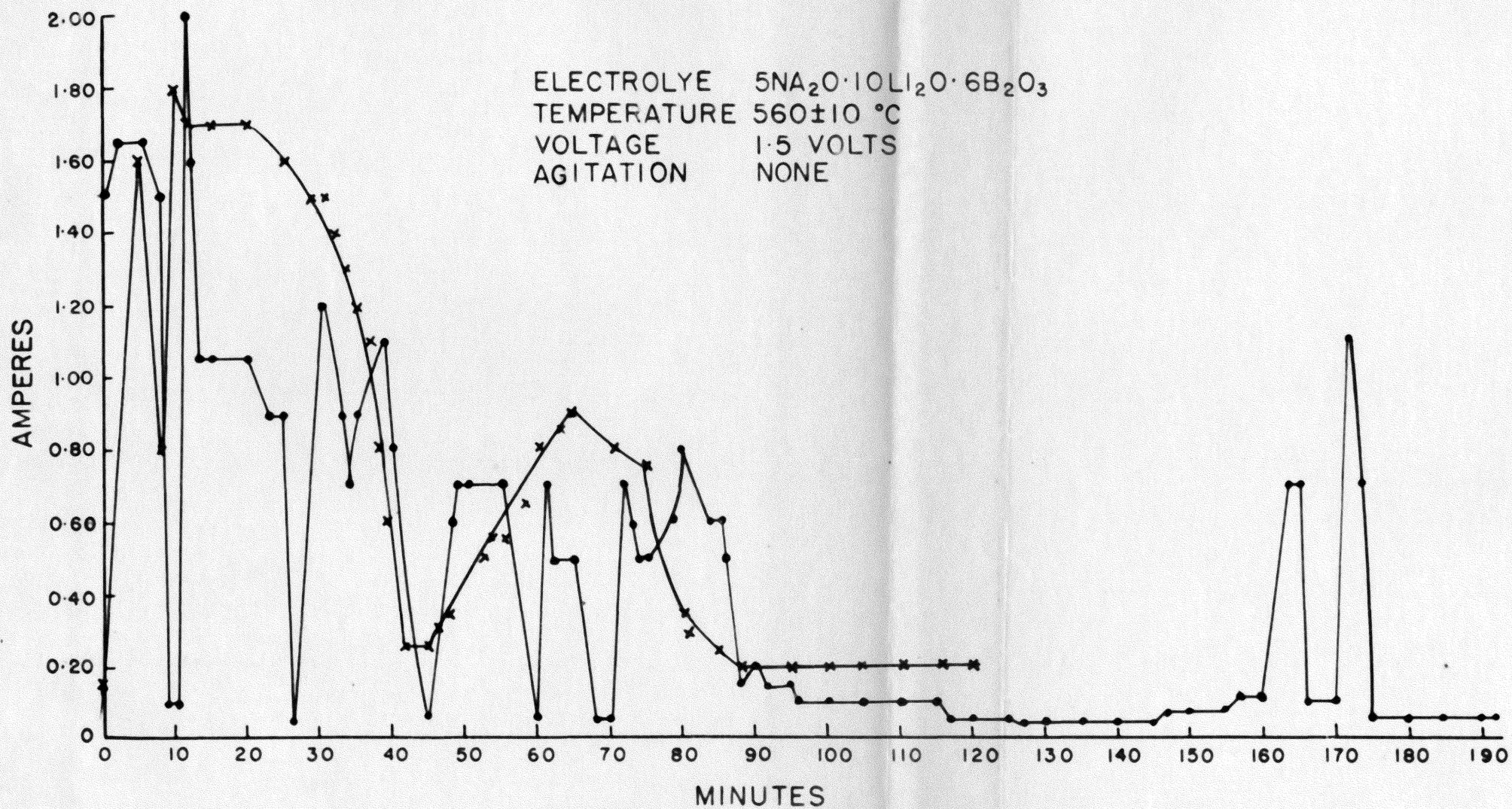


FIGURE 14. EFFECT OF CONTINUOUS ELECTROLYSIS OF FUSED BORATES WITH ALUMINUM ANODE AND PLATINUM CATHODE

TABLE XVIII

Electrodeposition Test

Electrolyte: Aluminum Phosphate 10%
 Eutectic Mixture of Phosphates 90%
 Composition of the eutectic:
 Sodium Pyrophosphate 31%
 Sodium Metaphosphate 69%

Temperature: 600 ± 10 °C.

Agitation: None.

Electrodes used		Description of Phenomena
Anode	Cathode	
Aluminum	Copper	1) Strong anode effect. 2) The electrical conductivity was good at start. The current readings were very unstable and quickly dropped to zero. 3) Aluminum anode was covered with a layer of aluminum oxide. 4) Black coating on cathode.
An alloy, 75 % aluminum and 25 % copper	Copper	1) No anode effect 2) The current was stable, 0.5 ampere at 3 volts. 3) Black coating on cathode.
Platinum	Copper	1) No anode effect. 2) The current was stable, 0.55 ampere at 3 volts. 3) Black coating on cathode.

Analysis of Black Coat from Phosphates Bath. The black coat from different tests using the eutectic mixture of sodium metaphosphate and sodium pyrophosphate, and aluminum phosphate were, separately, put in porcelain crucibles and ignited over a bunsen flame. It was not combustible. After ignition, the black powder was soluble in the concentrated hydrochloric acid. The solution, green in color, changed to deep blue when ammonia solution was added. Thus, the black coat was probably a copper compound.

Electrodeposition Test in Borates Bath. Quantitative electrodeposition tests were made using fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ with copper cathode and aluminum anode at 600 ± 10 °C. Both electrodes were immersed in water after electrolysis to remove the adhering salts. Both electrodes were coated with a black powder. In the first test, there was much loss of black coating on boiling the electrodes with distilled water to remove the adhering salts. The electrolyte, after electrolysis, turned a red color. The aluminum anode was covered with a layer of brass-yellow color and some parts had a red brown surface under the black coat. In the second test, cavities were observed on the surface of the aluminum anode.

The aluminum anode was slightly eroded by boiling with water. Particles of the black coat, on both electrodes, separated when immersed in boiling water. White aluminum

oxide was also found on the surface of the aluminum anode. The data are shown in Table XIX.

Electrodeposition Test in Borate-Phosphate Bath.

Qualitative electrodeposition tests were made in fused electrolyte of 9.4 per cent aluminum phosphate and 90.6 per cent $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ with aluminum anode and platinum cathode at 560 ± 10 °C. In no case could aluminum be deposited on the cathode. The aluminum anode was generally coated black. The surface of the copper cathode was stained with a red-brown deposit and sometimes it was coated black also.

During the electrolysis, an aluminum anode was surrounded by fine gas bubbles and the copper cathode was surrounded by larger gas bubbles. At the start of the electrolysis, only the anode was surrounded by the gas bubbles.

Two quantitative electrodeposition tests were made with the above electrolyte at 600 ± 10 °C. In the first test, the cathode was surrounded by a big porous bulk of solid which was lost when an attempt was made to remove the adhering salts. No calculation was made for the cathode efficiency.

The aluminum anode was slightly attacked by boiling with water, probably because of alkali present. Meanwhile, part of the black coating on both electrodes separated on boiling with water. White aluminum oxide was also found on the surface of the aluminum anode.

TABLE XIX

Determination of Current Efficiencies
for Electrode Reactions in Fused
Borates and Borates-Phosphate Systems

Electrodes: Aluminum anode and platinum cathode, both sizes were 2.5 by 2.5 cm, with a distance 2.5 cm between them.

Temperature: 600 ± 10 °C.

Agitation: None.

Voltage applied, volts	Current Density, amp/dm ²	Time of operation, hr.	Efficiency (calculated as aluminum) per cent of theory	
			Anode	Cathode
For Electrolyte 5Na ₂ O.10Li ₂ O.6B ₂ O ₃				
0.4-1.0	2.67	4	14.0	3.8
0.8-1.2	6.67	2	106.3	2.3
5.7-7.0	26.7	0.5	167.5	---
For Electrolyte 9.4% AlPO ₄ and 90.6 % 5Na ₂ O.10Li ₂ O.6B ₂ O ₃				
5.0-6.5	13.3	0.67	49.8	--
1.5-4.5	6.57	1.0	56.1	24.5

Data from qualitative electrodeposition test are shown in Table XX and those of the quantitative electrodeposition test are shown in Table XIX.

Preparation and Analysis of Black Powder from Borates Mixture. The total weight of fused liquid used in two batches for the preparation of black powder was 172.8 grams of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ and 10 grams of aluminum foil. The total amount of black powder prepared weighed one gram.

The black powder was insoluble in 3-normal hydrochloric acid, 3-normal nitric acid or 3-molar sulfuric acid. It was not attacked by hydrofluoric acid alone, a mixture of hydrofluoric acid and concentrated sulfuric acid, concentrated hydrochloric acid, and aqua regia. It was not dissolved when heated with sulfuric acid to fuming. Finally, it was not attacked by fusing with potassium bisulfate, sodium peroxide, or sodium hydroxide.

The ignition loss of the black powder was 83.6 per cent.

In the identification test for carbon in black powder by the combustion method, the clear barium hydroxide solution was suddenly turned to white as soon as the brilliant sparklings were observed on the black powder. The black color of the powder was then changed to a white color. The white precipitate in the barium hydroxide solution was dissolved with the evolution of gas bubbles after acidifying with

TABLE XX

Effect of Current Density on the
Electrode Reactions in the Fused
Borates-Phosphate System

Electrolyte: Aluminum phosphate 9.4 %
 $5Na_2O \cdot 10Li_2O \cdot 6B_2O_3$ 90.6 %

Electrodes: Aluminum anode and copper cathode

Temperature: 560 ± 10 °C.

Agitation: None.

Voltage applied, volts	Current Density, Max.		Time of Operation, hr.	Description of Phenomena
	Anode amp/dm ²	Cathode amp/dm ²		
1.5	1.0	1.0	2.0	Aluminum anode was coated black, but copper cathode had no change.
2.0	1.54	1.23	5.0	Both electrodes were coated black.
2.0	2.33	2.33	0.67	Aluminum anode was coated black; while copper cathode was stained unevenly brown.
2.5	1.1	0.73	4.0	Same as above.
2.5	2.1	2.1	0.33	Same as above.
3.5	10.4	10.4	0.33	Same as above.
4.5	10.4	10.4	0.5	Aluminum anode was coated black; copper cathode was stained unevenly brown and partly coated black.
5.5	2.9	2.9	1.5	Same as above

3-normal hydrochloric acid. It is, therefore, proved that the black powder really contains carbon.

A quantitative analysis for carbon in the black powders was made by Micro-Tech Laboratory⁽¹³⁶⁾, 8000 Lincoln Avenue, Skokie, Ill. The carbon content of the black powder was 80.85 per cent and hydrogen content was 0.86 per cent.

The elements which were found in the black powder by ordinary spectrographic analysis were aluminum, boron, and traces of sodium and lithium.

A spectrographic analysis, reported by Material Laboratory, Air Material Command⁽¹²⁶⁾, Dayton, Ohio, on the black powder, indicated the presence of major amounts of aluminum, boron, and sodium, minor amount of iron and copper, and traces of lead, silicon, titanium, nickel and chromium. Minor amounts and traces of materials may be introduced from the chromel-wire stirrer used for mixing the fused electrolyte.

A report of analysis of the black powder by X-ray from Material Laboratory, Air Material Command⁽¹²⁶⁾, Dayton, O., indicated that the crystalline material was principally aluminum oxide and very finely divided elementary aluminum. The black appearance of the material was attributed to large amounts of amorphous carbon. The results of X-ray diffraction analysis are shown in Table XXI.

TABLE XXI

Analysis of X-ray Diffraction Pattern
of Black Powder from Reaction of
Aluminum with $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$
at 560 ± 10 °C*

Line No.	Intensity	"d" value	Indicated Chemical Composition
1	Weak	2.88	$\text{Na}_2\text{B}_2\text{O}_4$
2	Faint	2.55	$\alpha\text{Al}_2\text{O}_3$
3	Medium	2.43	$\gamma\text{Al}_2\text{O}_3$
4	Strong	2.29	Al
5	Strong	2.11	$\alpha\text{Al}_2\text{O}_3$
6	Medium	2.00	$\text{Al} + \gamma\text{Al}_2\text{O}_3$
7	Weak	1.84	$\alpha\text{Al}_2\text{O}_3 + \text{H}_2\text{O}$
8	Very strong	1.41	$\text{Al} + \text{Al}_2\text{O}_3$
9	Faint	1.34	$\alpha\text{Al}_2\text{O}_3$
10	Faint	1.17	Al

* Material Laboratory, Air Material Command, Personal communication, April 2, 1951, Wright-Patterson Air Force Base, Dayton, Ohio.

Analysis for Carbon-Dioxide in the Fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot$

$6\text{B}_2\text{O}_3$. The results of determination of carbon dioxide in $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, formed by fusing 3.09 grams of boric acid, 3.08 grams of lithium carbonate and 2.21 grams of sodium carbonate at 900 °C for two hours are summarized in Table XXII.

Chemistry of Formation of Black Powder in Fused Borate.

The aluminum sheet was immediately covered with a black layer when the aluminum sheet was immersed in fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 7.5\text{B}_2\text{O}_3$. This black deposit was shown by the combustion method to contain carbon.

The reaction product from boric acid with aluminum constituted of two different kinds of substances. One is white powder, looks like aluminum oxide, while the other is shining purplish black flakes of unknown composition. This flaky product cannot be burnt. It did not contain carbon as shown by the combustion test.

Spectrographic analysis from Material Laboratory, Air Material Command⁽¹²⁷⁾, Dayton, O., indicated that principal elements were boron and aluminum with minor amounts of silicon and copper. X-ray diffraction analysis⁽¹²⁷⁾ from the same laboratory, indicated that the material was principally aluminum oxide and metallic aluminum, and small amount of iron oxide. The report⁽⁹⁾ from X-ray department of the Aluminum Research Laboratories in Aluminum Company of America

TABLE XXII

Analysis of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ for Carbon Dioxide

Composition of Reacting Mixture: Boric Acid 3.09 grams
 Lithium Carbonate 3.08 grams
 Sodium Carbonate 2.21 grams

Temperature of Fusing: 2 hours at 900 °C.

Test No.	Weight of Sample,	Water used to dissolve the sample,	Acid to decompose the Carbonates,	CO ₂ in the Sample,	
	gm.	ml.	Reagents	ml.	per cent
1.	4.32	200	1.16-N HCl, H ₂ O,	70 50	0.18
2.	4.32	200	1.16-N HCl,	90	2.57
3.	4.32	200	17.8-M H ₂ SO ₄ , H ₂ O,	50 150	0.22
4.	4.32	200	17.8-M H ₂ SO ₄ , H ₂ O,	100 150	0.37
5.	4.32	200	17.8-M H ₂ SO ₄ , H ₂ O,	100 150	0.27

stated that the sample contained a large amount of aluminum oxide with a small amount of unidentified phase. A spectrographic analysis of the material by the same laboratory showed aluminum and boron to be present. The material appears to consist of aluminum oxide mixed with some boron or boron compounds.

The insoluble residue, after treating the above product with a fused equimolar mixture of sodium carbonate and lithium carbonate and extracting with water, did not contain carbon, as shown by the combustion test.

Metallic aluminum was reacted with two carbonate mixtures whose molal ratios of sodium carbonate to lithium carbonate were one to one and one to two. They did not react with metallic aluminum, even when the temperature of the bath was raised to the melting point of aluminum.

The results of reaction of a fused mixture having a molal ratio of one sodium carbonate to two lithium carbonate and various amounts of boric acid added are shown in Table XXIII. Black powder was only formed when 0.25 mole boric acid was added to 1.5 moles mixed carbonates, or when there was 8.33 mole per cent of boric oxide in fused carbonates.

Though metallic aluminum was not acted upon by fused carbonates alone without boric acid, if an aluminum anode and a platinum cathode were immersed in an equimolar mixture

TABLE XXIII

Effect of Content of Boric Acid
on the Action of Alkali Carbonates on Aluminum at 600 °C

Quantity of Boric Acid in Mole Added to:	Phenomena Observed
1 Mole Li_2CO_3 0.5 Mole Na_2CO_3	
0	No action.
0.05	No action.
0.10	Slight gas bubbles, no black deposits.
0.15	Gas bubble, no black deposit.
0.20	More gas bubbles, no black deposit.
0.25	More gas bubbles and black deposits appearing on the surface of aluminum sheet.

of fused sodium and lithium carbonate, black deposits were formed on the surface of the aluminum anode. Gas bubbles were also observed around both electrodes. The platinum dish used to fuse the carbonates mixture was covered with a coat of green color on the portion not covered by the fused liquid.

Thermodynamic Study of the Reactions of Fused Electrolyte $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ on Aluminum. For the reaction:



$$(\Delta H_f)_{291} \text{ for } \text{CO}_2 = -92 \text{ Calories/mole}^{(87)}$$

$$(\Delta H_f)_{291} \text{ for } \text{Al}_2\text{O}_3 = -380 \text{ Calories/mole}^{(88)}$$

$$C_p \text{ for } \text{CO}_2 = 6.85 + 8.533 \times 10^{-3}T - 2.475 \times 10^{-6}T^2^{(87)}$$

$$C_p \text{ for graphite} = 0.314 \text{ Calories/gram, } ^\circ\text{C between } 40 \text{ and } 892 \text{ } ^\circ\text{C}^{(198)}$$

Heat capacity of aluminum⁽⁵⁶⁾, and aluminum oxide⁽²⁰⁰⁾ are shown in Tables XXIV and XXV.

Standard molar entropy of aluminum⁽⁹⁰⁾, carbon dioxide⁽⁹¹⁾, aluminum oxide⁽⁹¹⁾ and carbon⁽⁹¹⁾ are shown in Table XXVI.

The result of calculation of free energy of this reaction is shown in Table XXVII.

TABLE XXIV
Heat Capacity of Aluminum*

Temperature,		Heat Capacity,	
$^{\circ}\text{C}$	$^{\circ}\text{K}$	cal/gm, $^{\circ}\text{C}$	cal/gm, mol, $^{\circ}\text{C}$
0	273	0.2220	5.99
100	373	0.2297	6.20
200	473	0.2374	6.41
300	573	0.2451	6.61
400	673	0.2529	6.83
500	773	0.2609	7.05
600	873	0.2683	7.26
657	930	0.2727	7.36

* Edwards, J. D., F. C. Frary and Z. Jeffries:

"The Aluminum Industry, Aluminum Products
 and Their Fabrication", p. 33, McGraw-Hill
 Book Co., Inc., New York, N. Y., 1930, 1 ed.

TABLE XXV
Heat Capacity of Aluminum Oxide*

Temperature,		Heat Capacity,	
$^{\circ}\text{C}$	$^{\circ}\text{K}$	cal/gm, $^{\circ}\text{C}$	cal/gm. mol, $^{\circ}\text{C}$
0	273	0.73	17.8
50	323	0.83	20.2
100	373	0.89	21.7
200	473	0.97	23.6
400	673	1.07	26.0
600	873	1.12	27.2

* Washburn, E. W.: "International Critical Tables of Numerical Data, Physics, Chemistry and Technology", Vol V, p. 93, McGraw-Hill Book Co., Inc., New York, N. Y., 1929.

TABLE XXVI
Standard Molar Entropy at 25 °C
for Certain Substances

Material	Entropy, cal/gm mol, °C
Aluminum ^a	6.75
Carbon(Graphite) ^b	1.36
Carbon Dioxide ^b	51.08
Aluminum Oxide ^a	12.5

a. Heugen, O. A. and K. M. Watson: "Chemical Process Principles", Part II, p. 701, John Wiley & Sons, Inc., New York, N. Y., 1947, 1 ed.

b. *ibid*, p. 702.

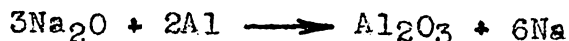
TABLE XXVII

Free Energy Calculations for Four Reactions at 870 °K

Reactions	Free Energy Change		Note
	Equation, calories	Per Mole Aluminum, calories	
$3\text{CO}_2 + 4\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 3\text{C}$	-579,690	-113,200	Promising
$3\text{Na}_2\text{O} + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 6\text{Na}$	-115,100	-57,500	Promising
$3\text{Li}_2\text{O} + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 6\text{Li}$	+18,919+1,716x	9640+858x	Unfavorable
$\text{B}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{B}$	-63,130	-31,570	Promising

x represents unknown molar entropy of Li_2O .

For the reaction:



$$(\Delta H_f)_{298} \text{ for Na}_2\text{O} = -99.4 \text{ Calories/mole}^{(182)}$$

$$\Delta S_{298} \text{ for the formation of Na}_2\text{O} = 17.4 \text{ Calories/mole, } ^\circ\text{C}^{(182)}$$

$$C_p \text{ for solid Na}_2\text{O} = 16.3 \text{ Calories/mole, } ^\circ\text{C}^{(182)}$$

$$S_{298} \text{ for solid Na} = 12.2 \text{ Calories/mole, } ^\circ\text{C}^{(182)}$$

$$C_p \text{ for solid Na} = 6.79 \text{ Calories/mole, } ^\circ\text{C}^{(182)}$$

$$\text{Fusion Point of Na} = 371 \text{ } ^\circ\text{K}^{(182)}$$

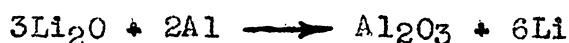
$$\text{Heat of Fusion at } 371 \text{ } ^\circ\text{K} = 630 \text{ Calories/mole}^{(182)}$$

$$\Delta S \text{ of Fusion for Na at } 371 \text{ } ^\circ\text{K} = 1.7 \text{ Calories/mole } ^\circ\text{C}^{(182)}$$

$$\Delta C_p \text{ of Fusion for Na at } 371 \text{ } ^\circ\text{K} = 0.51 \text{ Calories per mole, } ^\circ\text{C}^{(182)}$$

The result of calculation of free energy of this reaction is shown in Table XXVII.

For the reaction:



$$(\Delta H_f)_{298} \text{ for Li}_2\text{O} = -142.4 \text{ Calories/mole}^{(181)}$$

$$C_p \text{ for Li}_2\text{O} \text{ was estimated by Kopp's rule}^{(109)} \text{ to be } 15.30 \text{ Calories/mole Li}_2\text{O}.$$

$$S_{298} \text{ for Li} = 5.65 \text{ Calories/mole, } ^\circ\text{C}^{(181)}$$

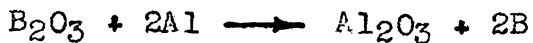
$$\text{Transition temperature for Li} = 353 \text{ } ^\circ\text{K}^{(181)}$$

$$\text{Heat of fusion for Li at } 353 \text{ } ^\circ\text{K} = 1000 \text{ Calories/mole}^{(181)}$$

$$\Delta S \text{ for Li at } 353 \text{ } ^\circ\text{K} = 5.65 \text{ Calories/mole, } ^\circ\text{C}^{(181)}$$

The result of calculation of the free energy of this reaction is shown in Table XXVII.

For the reaction:



$(\Delta H_f)_{298}$ for B_2O_3 in glass state = -297.6
Calories/mole⁽¹⁸⁰⁾

ΔS_{298} for the formation of B_2O_3 18.8
Calories/mole, °C⁽¹⁸⁰⁾

C_p for B_2O_3 in glass state = 14.6 Calories/mole, °C⁽¹⁸⁰⁾

S_{298} for B = 1.56 calories/mole °C⁽¹⁸⁰⁾

C_p for B = 2.86 Calories/mole °C⁽¹⁸⁰⁾

The result of calculation of free energy of this reaction is shown in Table XXVII.

Because of the lack of data on both the heat of formation and standard molar entropy of aluminum boride, no calculation can be made on the change of free energy of the reaction of boric oxide on aluminum to form aluminum boride.

Sample Calculations

The calculations involved in this investigation were of only two types: calculation of the limiting composition of borates, and calculation of the thermodynamic functions of the possible reactions of fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ on aluminum.

Limiting Composition of Borates. The limiting composition of the system $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ as given in Table I were calculated from the experimental results as follows:

For $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ System

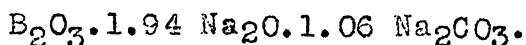
Weight of platinum dish	49.25 gm
Weight of H_3BO_3 (1 mole)	61.84 gm
Weight of Na_2CO_3 (1.5 moles)	159.00 gm
<hr/>	
Weight of platinum dish and its contents before fusion	270.1 gm
Weight of platinum dish and its contents after fusion to constant weight	200.4 gm
<hr/>	
Weight loss in fusion	69.7 gm
Weight loss due to water on the assumption of total expulsion (1.5 moles)	27.0 gm
<hr/>	
Weight loss assumed due to CO_2	42.7 gm
Theoretical loss of CO_2 for complete decomposition of Na_2CO_3 (1.5 moles)	66.0 gm
Per cent of Na_2CO_3 decomposed ($42.7 \times 100/66.0$)	64.7 gm
<hr/>	

Composition of the fused mixture may be calculated

as:

<u>Components</u>	<u>Mole</u>	<u>Mole Ratio</u>
B ₂ O ₃ (1 mole H ₃ BO ₃)	0.50	1.00
Na ₂ O (1.5 mole x 0.647)	0.97	1.94
Na ₂ CO ₃ (1.5 mole - 0.97 mole)	0.53	1.06

This may be represented by the empirical formula:



The limiting composition was calculated from the above mixture by excluding the undecomposed sodium carbonate, as follows:

<u>Components</u>	<u>Mole</u>	<u>Mole Per Cent</u>
B ₂ O ₃	0.50	34
Na ₂ O	0.97	66
<hr/>		
Total	1.47	100

For Na₂O-Li₂O-B₂O₃ System:

Weight of platinum dish	48.5 gm
Weight of H ₃ BO ₃ (1 mole)	61.8 gm
Weight of Li ₂ CO ₃ (1 mole)	74.0 gm
Weight of Na ₂ CO ₃ (0.5 mole)	53.0 gm
<hr/>	
Weight of platinum dish and its contents before fusion	237.3 gm
Weight of platinum dish and its contents after fusion	152.1 gm
<hr/>	
Weight loss in fusion	85.2 gm
Weight loss due to water on the assumption of total expulsion (1.5 moles)	27.0 gm
<hr/>	

Weight loss due to CO ₂	58.2 gm
Theoretical loss of CO ₂ for complete decomposition of carbonates (1.5 moles)	66.0 gm
Per cent of carbonates decomposed (58.2 x 100/66.0)	88.2 gm

Composition of the fused mixture on the basis of the same degree of decomposition of both carbonates may be calculated as:

<u>Components</u>	<u>Moles</u>
B ₂ O ₃ (1 mole H ₃ BO ₃)	0.500
Li ₂ O (1 mole x 0.882)	0.882
Na ₂ O (0.5 mole x 0.882)	0.441
Li ₂ CO ₃ (1 mole - 0.882 mole)	0.118
Na ₂ CO ₃ (0.5 mole - 0.441 mole)	0.059

The limiting composition can be calculated from the fused mixture by excluding both undecomposed carbonates, as follows:

<u>Components</u>	<u>Moles</u>	<u>Moles Per Cent</u>
B ₂ O ₃	0.500	27.4
Li ₂ O	0.882	48.4
Na ₂ O	0.441	24.2
<hr/>		
Total	1.823	100.0

Thermodynamic Study of the Reaction of Fused

5Na₂O.10Al₂O₃.6B₂O₃ on Aluminum. For a sample calculation of the thermodynamic functions, the case of the reaction,



was chosen. For this reaction,

$$(\Delta H_f)_{291} \text{ for CO}_2 = -92 \text{ Calories/mole}^{(89)}$$

$$(\Delta H_f)_{291} \text{ for Al}_2\text{O}_3 = -380 \text{ Calories/mole}^{(88)}$$

$$(\Delta H_f)_{291} \text{ for the reaction} = -380 \times 2 - (-92 \times 3)$$

$$= -478 \text{ Calories}$$

Where $(\Delta H_f)_{291}$ represents the heat of formation of compounds or heat of reaction at 291 °K.

The enthalpy of a substance " H_T " at absolute temperature " T " can be calculated from the enthalpy " H_0 " at some base temperature " T_0 " by the following formula⁽⁵¹⁾:

$$H_T - H_0 = \int_{T_0}^T C_p dT$$

$$C_p \text{ for CO}_2 = 6.85 + 8.533 \times 10^{-3}T - 2.475 \times 10^{-6}T^2 \text{ (87)}$$

$$H_{870} - H_{291} \text{ for CO}_2$$

$$= \int_{291}^{870} (6.85 + 8.533 \times 10^{-3}T - 2.475 \times 10^{-6}T^2) dT$$

$$= 6.85(870 - 291) + \frac{1}{2} \times 8.533(870^2 - 291^2) \times 10^{-3}$$

$$- 2.475(870^3 - 291^3) \times 10^{-6} / 3$$

$$= 6336 \text{ calories per mole}$$

" C_p " of aluminum was shown in Table XXIV. A plot of " C_p " versus absolute temperature shows that the " C_p " of aluminum is a linear function of the absolute temperature within the temperature limits 271 to 870 °K. Therefore,

$H_{870}-H_{291}$ for aluminum can be calculated by using an average " C_p " between two temperature limits multiplied by the temperature difference.

$$\begin{aligned} H_{870}-H_{291} &= \frac{1}{2}(6.09 + 7.26) \times (870-291) \\ &= 3860 \text{ calories per mole.} \end{aligned}$$

" C_p " for aluminum oxide was shown in Table XXV⁽³⁰⁰⁾, $H_{870}-H_{291}$ for aluminum oxide was calculated by the graphical integration as shown in Figure 15. The value obtained in this way is 13,109 calories per mole.

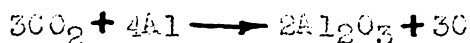
" C_p " for graphite = 0.314 calorie/gm, °C between 40 and 892 °C⁽¹⁹⁸⁾

$$\begin{aligned} H_{870}-H_{291} &= 0.314 \times 12 \times (870-291) \\ &= 2180 \text{ calories per mole} \end{aligned}$$

$(\Delta H_f)_{870}$ was then calculated from $(\Delta H_f)_{291}$ by the equation⁽⁵²⁾.

$$\begin{aligned} (\Delta H_f)_{870} &= (\Delta H_f)_{291} + \int_{291}^{870} C_p dT \\ (\Delta H_f)_{870} &= -478,000 + 2 \times 13,109 + 3 \times 2,180 - 3 \times 6,356 \\ &\quad - 4 \times 3860 = -579,690 \text{ calories} \end{aligned}$$

The heat of the reaction of the equation:



at 870 °K is -579,690 calories, or 144,920 calories per gram mole of aluminum.

Standard molar entropy of aluminum⁽⁹⁰⁾, carbon dioxide⁽⁹¹⁾, aluminum oxide⁽⁹⁰⁾ and carbon⁽⁹¹⁾ are shown

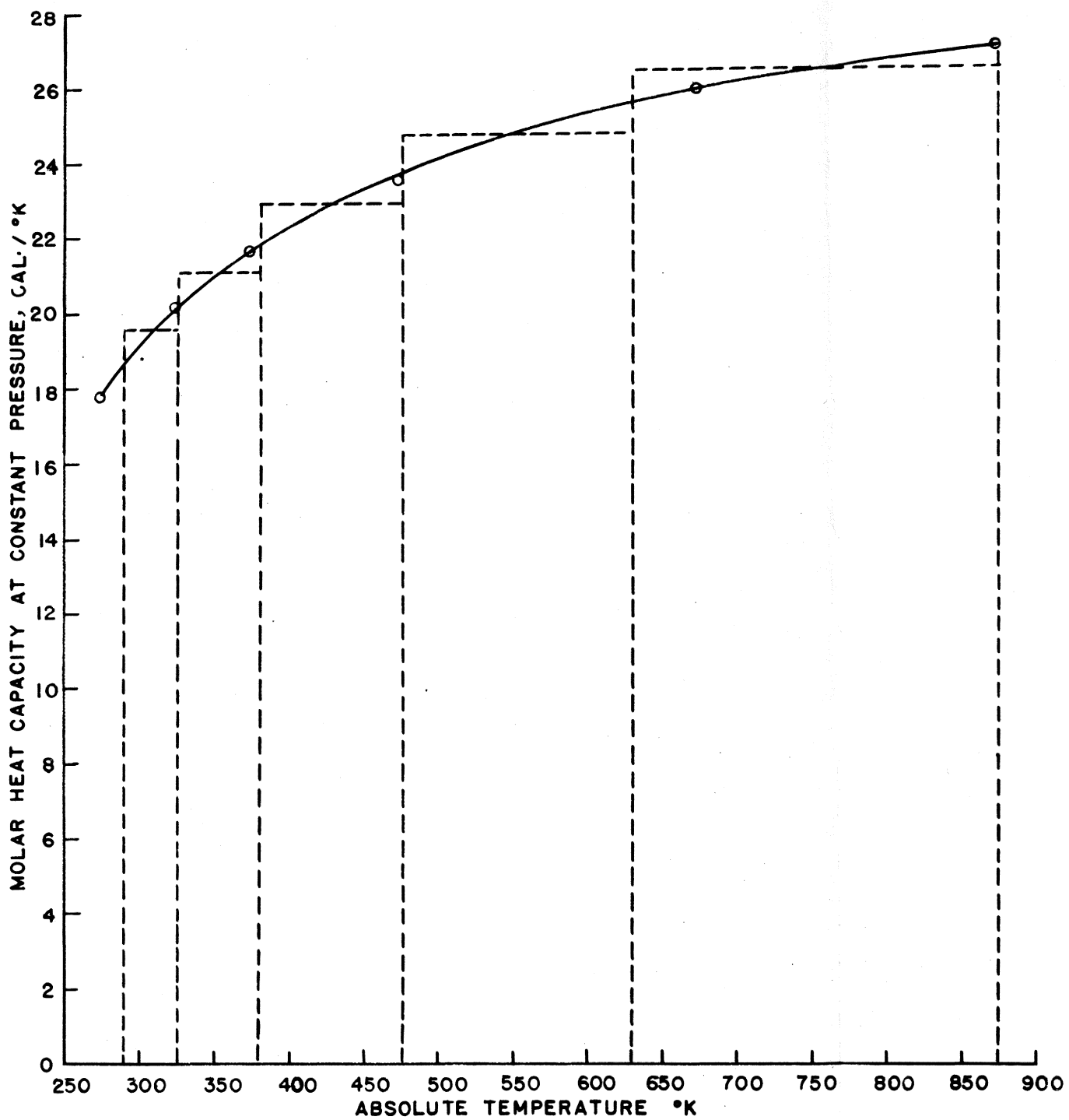


FIGURE 15. GRAPHICAL INTEGRATION OF ENTHALPY OF Al_2O_3

in Table XXVI.

The entropy of a substance " S_T " at absolute temperature " T ", can be calculated from the entropy " S_0 " of the same substance at some base temperature " T_0 " by the equation (51):

$$S_T - S_0 = \int_{T_0}^T C_p dT/T$$

For CO_2 ,

$$\begin{aligned} S_{870} - S_{291} &= \int_{291}^{870} (6.85 + 8.533 \times 10^{-3}T - 2.745 \times 10^{-6}T^2) dT/T \\ &= 6.85 \times 2.303 (\log 870 - \log 291) \\ &\quad + 8.533 \times 10^{-3} (870 - 291) - 1378 \times 10^{-6} (870^2 - 291^2) \\ &= 11.16 \text{ calories/gm mole, } ^\circ C. \end{aligned}$$

For aluminum, " C_p " can be roughly represented by the equation from the data given in Table XXIV and Figure 16:

$$\begin{aligned} C_p &= 2.96 \times 10^{-3}T + 5.18 \\ S_{870} - S_{291} &= \int_{291}^{870} (2.96 \times 10^{-3}T + 5.18) dT/T \\ &= 2.96 \times 10^{-3} (870 - 291) \\ &\quad + 5.18 \times 2.303 (\log 870 - \log 291) \\ &= 6.41 \text{ calories/gm mole, } ^\circ C \end{aligned}$$

For aluminum oxide, $S_{870} - S_{291}$ was calculated by graphical integration as shown in Table XXVIII and Figure 17.

The value obtained is 25.8 calories/gm mole, $^\circ C$

$$\begin{aligned} \text{For graphite, } S_{870} - S_{291} &= \int_{291}^{870} 0.314 \times 12 dT/T \\ &\quad + 0.314 \times 12 \times 2.303 (\log 870 - \log 291) \\ &= 4.11 \text{ calories/gm mole, } ^\circ C \end{aligned}$$

The entropy change for the given reaction at 298 $^\circ C$

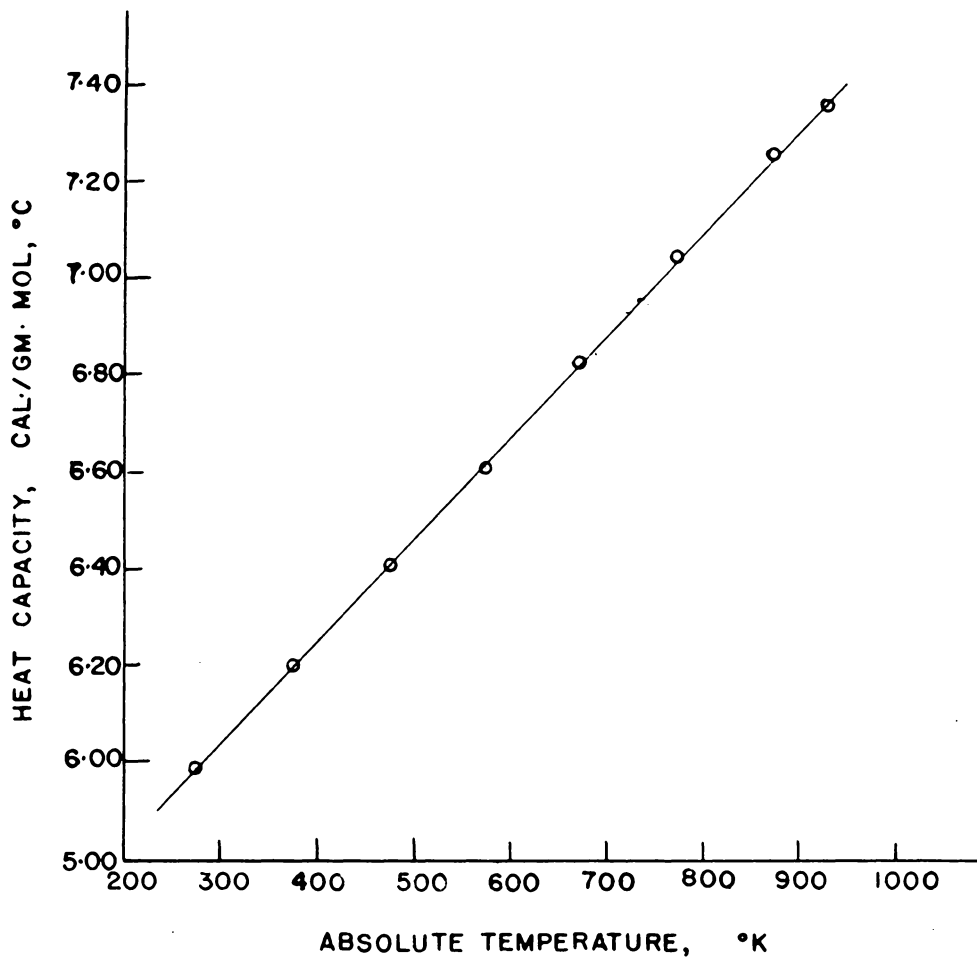


FIGURE 16. HEAT CAPACITY OF ALUMINUM

EDWARDS, J. D., F. C. FRARY AND Z. JEFFRIES: "THE ALUMINUM INDUSTRY, ALUMINUM PRODUCTS AND THEIR FABRICATION", P. 33, MCGRAW-HILL BOOK CO. INC., NEW YORK, N. Y., 1930, 1 ED.

TABLE XXVIII
Graphical Integration of
Entropy of Aluminum Oxide

Absolute Temperature, T,		Heat Capacity,
^o K	log T	cal/gm mol
291	2.463	18.2
323	2.509	20.2
473	2.571	21.7
673	2.674	23.6
873	2.828	26.0

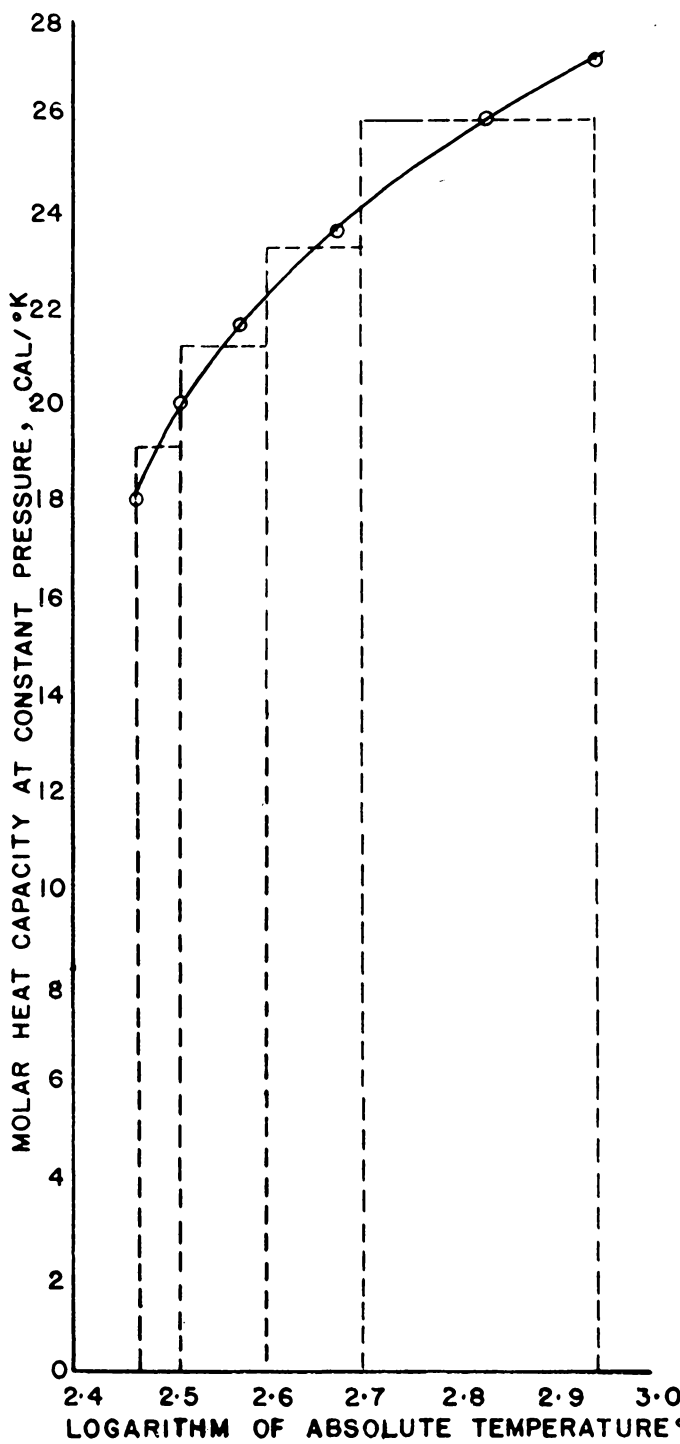


FIGURE 17. GRAPHICAL INTEGRATION OF THE ENTROPY FOR Al_2O_3

is:

$$\begin{aligned} S_{298} &= 3 \times 1.36 + 2 \times 12.5 - 3 \times 51.08 - 4 \times 6.75 \\ &= -151 \text{ calories per } ^\circ \text{C} \end{aligned}$$

$$\begin{aligned} S_{870} - S_{298} &= (S_{870} - S_{298})_{\text{products}} \\ &\quad - (S_{870} - S_{298})_{\text{reactants}} \\ &= -151 + 2 \times 25.8 + 3 \times 4.11 - 3 \times 11.16 - 4 \times 6.41 \\ &= -145.2 \text{ calories/}^\circ \text{C} \end{aligned}$$

The free energy change of the reaction was then calculated by the equation:

$$\Delta F_T = (\Delta H)_T - T \Delta S_T$$

$$\begin{aligned} \Delta F_{870} &= (\Delta H)_{870} - 870 \Delta S_{870} = -579,690 - 870(-151) \\ &= -452,700 \text{ calories} \end{aligned}$$

The free energy decrease of the reaction:

$3\text{CO}_2 + 4\text{Al} \longrightarrow 2\text{Al}_2\text{O}_3 + 3\text{C}$ at 870 °K is 452,700 calories, or 113,200 calories per mole of aluminum.

IV. DISCUSSION

The previous work of electrodeposition with aluminum and the results of the investigation on the borates, phosphates and borates-phosphate systems will be reviewed, analyzed and criticized under the general headings of discussion of previous work, discussion of results, recommendations and limitations.

Discussion of Previous Work

The previous work will be discussed under the topics of disadvantages arising from use of aluminum halides as electrolyte, systematic review of the use of aluminum salts as electrolytes, conductivity of electricity and molecular structures of aluminum complex compounds and the selection of systems for electrodeposition study.

Disadvantages of Using Aluminum Halides as Electrolytes. Aluminum halides, especially the chloride, have been the salt most frequently used to supply aluminum ions for the electrodeposition of aluminum. According to Pavelka and Zuchelli⁽¹⁵¹⁾, aluminum chloride is a strong peptizing agent for aluminum oxide and its hydrate. The decisive factor in the corrosion of aluminum is the behavior in the system of the aluminum and aluminum oxide which is always present as a surface film. Articles plated in a bath con-

taining aluminum chloride may have aluminum chloride occluded on the surfaces. Therefore, severe corrosion of aluminum coatings from a bath containing halides is expected. This is the reason why steel coated with aluminum by the Blue and Mather's method⁽²⁶⁾ is said by them to afford no better protection against rusting than a coating of an equivalent weight of zinc.

Furthermore, because of the moisture-absorbing property of aluminum halides, all processes involving them require special precautions to maintain the life of the electrolytic bath. Even the bath suggested recently by Couch and Brenner⁽⁴¹⁾ will have a longer life if protected from the moisture in the air.

Systematic Review of the Use of Aluminum Salts as Electrolytes. Since halides promote the corrosion of the aluminum coating, other aluminum salts seem to be more promising. In selecting possible aluminum salts, those which are insoluble in water will probably not peptize the film formed on the surface of the aluminum plate. The fused bath should possess low viscosity and a melting point below the melting point of aluminum. High conductivity of electricity is another criterion for the utility of a salt.

A systematic study of the inorganic salts shows that the available salts are very limited. Aluminum chloride,

aluminum bromide and aluminum iodide have the defects mentioned previously. Molten metal sulfates react with aluminum vigorously. Violent explosion may occur when sulfates and aluminum are melted together⁽⁷²⁾. Thus the possible use of a fused sulfate bath is excluded. Cyanides and cyanates of many metals are successfully used for the electroplating of certain metals. Unfortunately, there is no literature evidence that aluminum cyanide exists. Williams⁽²¹⁰⁾ states that aluminum cyanide does not appear to have a separate existence. Forbes and Anderson^(69,70) have prepared a number of inorganic cyanides and cyanates, but no reference was made to aluminum in the work of these authors. The American Cyanamide Company⁽¹¹⁾ has no evidence of the existence of aluminum cyanide or cyanate. An attempt was made to correlate the knowledge of existing cyanides and cyanates with their position in the periodic table to try to predict the possibility of existence of an aluminum salt. In the same group as aluminum, the only element that forms a cyanide is boron. Forbes and Anderson⁽⁶⁹⁾ prepared boron cyanide, but were unable to determine any of its properties or characteristics because of its instability and extreme deliquescence. In the same series as aluminum, the cyanide of the adjacent magnesium is unknown and silicon forms a stable cyanide, but is difficult to isolate. Therefore, it seems that existence of aluminum

cyanide is improbable. Even if it did exist, it probably would be extremely unstable and not easily isolated.

Another possible method of utilizing the cyanide system is to use an aluminum anode immersed in the fused cyanide to supply the aluminum ion for the electrodeposition of aluminum by dissolving anodically. However, because of the toxic nature of cyanides and the possibility of a violent explosion, such as occurred to Forbes and Anderson⁽⁷⁰⁾ in the investigation of chromyl cyanide, the possibility of electrodeposition of aluminum from fused cyanide electrolyte was not investigated.

Aluminum oxide has a very high melting point, 2050 °C. There is no known liquid which can dissolve it, forming a mixture melting below 660 °C.

Puschin and Baskov⁽¹⁷⁵⁾ reported that potassium fluoride and aluminum fluoride formed an eutectic mixture containing 40 mole per cent aluminum fluoride and 60 mole per cent potassium fluoride, which melts at 568 °C. Fedotieff and Timofeeff⁽⁶⁴⁾ gave the eutectic composition at 45 mole per cent aluminum fluoride with melting point at 575 °C. Though the data for composition differs, the melting point data may be said to agree. The eutectic temperature of this fluoride mixture is about 100 °C below the melting point of aluminum, but because of the very corrosive nature of the fused fluorides, their use as electrolyte for electrodeposition work does not seem promising.

Aluminum sulfide has been said to be successfully utilized as the electrolyte for the isolation of aluminum. Rontgen and Borchers⁽¹⁷⁸⁾ electrolyzed a mixture of 40 per cent sodium chloride and 60 per cent aluminum sulfide at 700 °C. Elementary aluminum was obtained. They claimed that the electrolysis of this aluminum sulfide-sodium chloride system had the advantages of one volt lower decomposition potential and 25 per cent higher current efficiency than Hall's process. A similar report was made by Khazanov and Belyaev⁽⁹⁹⁾ with aluminum sulfide dissolved in a fused mixture of 70 per cent of sodium chloride and 30 per cent sodium hexafluoroaluminate (Na_3AlF_6) at 800 °C. Rontgen and Borchers also tried to reduce the working temperature by utilizing the eutectic mixture of sodium chloride-potassium chloride or lithium chloride-potassium chloride to dissolve aluminum sulfide. No melt of the system sodium chloride-potassium chloride-aluminum chloride is sufficiently fluid below the melting point of aluminum. The melting point of the eutectic mixture of the potassium chloride-lithium chloride system is rather low at a composition of 40 mole per cent potassium chloride, at about 352 °C. But an addition of 2 per cent of aluminum sulfide raises the melting point to 500 °C. Electrolysis of such a mixture only produces finely divided, incoherent aluminum accompanied by an anode effect. Addition of more aluminum sulfide can eliminate the anode effect, but the

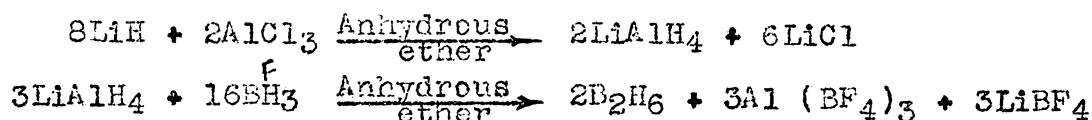
melting point of the electrolyte then rises above the melting point of aluminum.

It seems of interest to study the utilization of the eutectic of the sodium sulfide-sulfur system as solvent for aluminum sulfide. The melting point of this eutectic composition, as reported by Thomas and Rule⁽¹⁹²⁾, is 142 °C, with the empirical formula, $K_2S_{3.5}$, but this polysulfide is combustible in air, as the temperature is raised above its melting point. For this reason, even if this system were promising, it must be operated in an atmosphere of nitrogen, and therefore, it is considered as impractical. Scott⁽¹⁸⁶⁾ studied this system without obtaining aluminum by electrodeposition.

Aluminum thiocyanate is another aluminum compound of doubtful value. It is said to be unstable⁽³⁶⁾ and must be kept dry and out of contact with air.

Aluminum fluoborate, as prepared by reacting freshly precipitated aluminum hydroxide with fluoboric acid, according to Berzelius⁽²¹⁾, contains an unknown amount of water of crystallization. It decomposes on fusion at red heat, giving off water and hydrogen fluoride and leaving aluminum borate.

Kirk and Othmer⁽¹⁰⁰⁾ have shown a method of preparing an anhydrous, fluoborate mixture by the following reactions:



Because no details of this reaction are given, it is still difficult to say whether or not this compound can be used for electrodeposition of aluminum.

Smith⁽¹⁹⁰⁾ has shown that aluminum metal and potassium nitrate can be fused together without reaction, if the temperature is not high enough to decompose the niter. But aluminum nitrate crystal, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, can only be partially dehydrated to $\text{Al}(\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$. Because of the water content present in the crystal, a trial with this salt seems unnecessary.

A systematic survey of organic aluminum compounds suitable for use as electrolytes, is rather difficult. There is little information on organic aluminum compounds in the literature. The criterions useful for choosing promising organic aluminum compounds are: a melting point below its decomposition temperature, or solubility in other organic solvents or in fused salt at temperatures below those causing decomposition, and suitable conductivity of the fused organic aluminum compounds or its solutions. Generally, the melting points of organic aluminum compounds are below the melting point of aluminum. Many organic aluminum compounds have a melting point below their decomposition temperature, but they do not conduct electricity; for example, aluminum derivatives of alcohols.

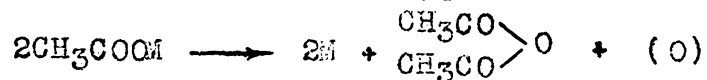
Aluminum derivatives of beta-diketones, beta-ketonic aldehydes and beta ketonic-esters are a class of compounds

which seem promising on study of their melting points. But for such a type of compound, only the derivatives of the alkali metals possess typical salt-like properties⁽¹²³⁾. Whenever the coordinate number of a metal atom is twice that of its oxidation state, the chelate compound formed is a nonelectrolyte, or it is an inner complex compound of the first order. Unfortunately, aluminum derivatives belong to this class. It is still possible that aluminum derivatives may form complex ions with sodium derivatives, but the complex ions formed are limited to the compounds with coordination number less than twice the value of that of the oxidation state. For this reason, it does not seem promising to experiment with this type of compound.

Aluminum derivatives of phenols may be considered. It is true that simple phenols are acids, nitrophenols are strong acids, and their sodium derivatives are true salts, but all phenols are subject to oxidation. The products of oxidation will coat the anode and hinder the passage of the current.

Aluminum derivatives of fatty acids are another series of compounds that might be studied. Bourgoin⁽³⁰⁾ explained the well known Kolbe's synthesis by assuming the salt itself was decomposed, during electrolysis, into the metal and the acid radical, and that subsequently two acid radicals condensed to form a molecule of the anhydride of the acid with

the liberation of an atom of oxygen.



As to the electrolysis of anhydrous fused salts, Brockman quoted Faraday⁽⁶³⁾ as saying: "Acetate of soda, fused and anhydrous, is directly decomposed, being, as I believe, a true electrolyte, and evolving soda and acetic acid at the cathode and anode. These, however, have no sensible duration, but are immediately resolved into other substances; charcoal, sodiuretted hydrogen, etc., being set free at the former,....". Berl⁽²⁰⁾ repeated the work of Faraday, using pure, fused, potassium acetate and also a fused mixture of sodium and potassium acetates. He suggested "The decomposition of the electrolyte is due to the action on the fused salt of metallic sodium liberated at the cathode." This mechanism was sustained by experimental evidence.

As a deduction from this mechanism, aluminum may be expected to be electrodeposited from either a bath of fused salt or from the nonaqueous solution of the aluminum salt.

The possibility of electrodeposition of aluminum from a bath of aluminum hydride in organic solvent has been suggested by Gibb⁽⁷¹⁾.

Selection of Systems for this Study. In this thesis, aluminum phosphate was utilized as the compound supplying aluminum ions to the fused electrolytes. Aluminum phosphate is insoluble in water. Although aluminum phosphate or metaphosphate has high melting point, greater than 1500 °C, it was shown by James A. Lee⁽¹¹⁵⁾ that "Fusibility and meltability can be greatly improved by small additions of various common oxides or fluoride fluxes". As shown by Kreidl and Weyl⁽¹¹⁰⁾, the mixture of aluminum phosphate with other oxides may have a softening point below 400 °C. The phosphate glasses possessing such low softening points are constituted from the following oxides: phosphorus oxide, aluminum oxide, boric oxide, potassium oxide, sodium oxide and zinc oxide. From the deposition potential study of Yntema and coworkers^(218,219), made in the presence of only alkali or alkaline-earth metal salts, the fused aluminum salt bath can deposit pure aluminum. If other heavy metallic ions are present in the bath, the heavy metal will deposit before the aluminum. Thus the use of zinc salt in the electrolyte was excluded. The successful use of potassium salt in the bath was doubtful, because Beketoff⁽¹⁹⁾ showed that aluminum reacted with potassium hydroxide at high temperatures. As to the sodium salt, there is no danger that it will attack the aluminum. Deville⁽⁴⁵⁾ showed that even fused sodium hydroxide did not attack aluminum. Klooster⁽¹⁰⁴⁾ said that the eutectic

mixture of lithium metaborate-sodium metaborate melted at 650 °C, while that of sodium metaborate-potassium metaborate melted at 850 °C. Therefore, it seems more promising to use a lithium salt instead of a potassium salt in the melt.

The literature also gives some information as to the possibility of deposition of aluminum from the fused borate mixture. Andrieux⁽¹³⁾ showed that metallic sodium might be obtained by electrolyzing fused borax. The product of electrolysis, which may be metallic sodium, boron or a mixture of two, depends on the temperature of the cathode and the introduction of slightly soluble oxides, such as alumina or calcined beryllia. Since aluminum is easier to deposit than sodium, there seems a possibility of obtaining aluminum by deposition from a borate mixture in presence of aluminum ion.

Another method of approach was to utilize the fused eutectic mixture of sodium metaphosphate and sodium pyrophosphate as the solvent to dissolve the aluminum phosphate.

Conductivity of Electricity and Molecular Structure of Aluminum Complex Compounds. A study was made of the relationship between the conductivity of electricity and the molecular structure of aluminum complex compounds so as to know how to select aluminum compounds for supplying aluminum ion in the electrolyte. Coordination compounds,

except those which are neutral, are good electrical conductors⁽¹⁹⁴⁾. There is still no known complex cyanide, ammine of aluminum which occurs very frequently for transition elements in the periodic table. A survey of the derivatives on aluminum halides indicates that, the structure of the cryolite-complex type of compounds: $3KF \cdot AlF_3$, $3NaF \cdot AlF_3$ and $3LiF \cdot AlF_3$ can be explained in the term of the coordination theory. The structure of all other complexes of aluminum halides cannot be explained by this theory. A list of complex compounds of chlorides and bromides is shown in Table XXIX.

Alum is representative of another type of important, complex compounds. The conductivity of a solution of potassium alum is equal to that of an uncombined mixture of potassium and aluminum sulfates⁽²²⁶⁾. This shows that alum is not a coordination compound, since it is decomposed in solution, into its components.

Groggins⁽²²³⁾ states that stable, stoichiometric addition products of alkyl halides and aluminum halide have not yet been isolated. But this does not preclude their existence in solution. Wohl and Wertyporoch^(228,229), by means of electrical conductivity measurements, have succeeded in indicating the formation of complexes of the metal halides. The conductivity was traced to the formation of solute-solvent complexes. According to Groggins⁽²²²⁾, "Meerwin has shown that many weak electrolytes are increased in

TABLE XXIX

Complex Compounds of
Aluminum Chloride and Aluminum Bromide*

Aluminum Chloride Complex Compounds:

$\text{AlCl}_3 \cdot \text{LiCl}$, $\text{AlCl}_3 \cdot \text{NaCl}$, $\text{AlCl}_3 \cdot \text{KCl}$, $\text{AlCl}_3 \cdot \text{NH}_4\text{Cl}$;
 $2\text{AlCl}_3 \cdot \text{NaCl}$, $2\text{AlCl}_3 \cdot \text{KCl}$

Aluminum Bromide Complex Compounds:

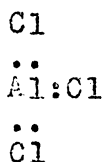
$\text{AlBr}_3 \cdot \text{LiBr}$, $\text{AlBr}_3 \cdot \text{NaBr}$, $\text{AlBr}_3 \cdot \text{KBr}$, $\text{AlBr}_3 \cdot \text{NH}_4\text{Br}$;
 $7\text{AlBr}_3 \cdot \text{LiBr}$, $7\text{AlBr}_3 \cdot \text{NaBr}$;
 $3\text{AlBr}_3 \cdot \text{NH}_4\text{Br}$;
 $2\text{AlBr}_3 \cdot \text{KBr}$, $2\text{AlBr}_3 \cdot \text{NH}_4\text{Br}$.

* Kendall, J., E. D. Crittenden and H. K. Miller:

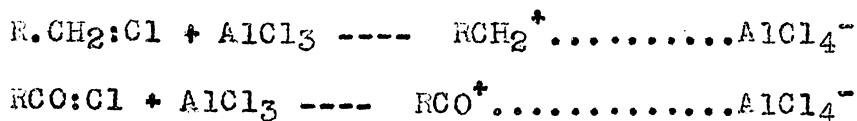
A Study of the Factors Influencing the
Compounds Formation and Solubility in
Fused Mixtures, J. Am. Soc. 45, 963-96 (1923)

strength by the formation of complex ions. Although simple solvation leads to ionization of molecules as a precursor of electrolytic dissociation, in complex formation there is also the formation of a chemical bond between one of the potential ions and part of its environment. This union results in the nascence of an ion of larger radius and the same charge which is, consequently, less firmly bound to its fellow."

In the organic field, the formation of binary, ionized addition compounds with aluminum chloride or bromide, is similar to solvent-solute complexes, which are characterized by conductivity. Because the aluminum and three chlorine atoms in the aluminum chloride molecule combine by a process of electron-sharing, the aluminum atom in the aluminum chloride molecule is an electron acceptor.



Hence, it causes atoms or groups coming within the orbits of influence to migrate with their bonding electrons so that there is a virtual conversion of a covalent to an electrovalent bond as shown by Fairbrother⁽⁶²⁾.



Such reactions are only known for aluminum chloride and bromide. Such complex formation is not a property of the aluminum atom alone, but may be ascribed to the covalent combination of the aluminum atom and chlorine atoms.

Chelate formation is a reaction which may prevent solutions of complex aluminum compounds from conducting the current. For example, aluminum derivatives of beta-diketones, beta-ketonic aldehydes and beta-ketonic esters, which form chelate structures, do not conduct the electric current. On the other hand, the alkali salts of these same compounds possess typical salt-like properties and conduct the current.

Discussion of Results

The results obtained in this investigation will be discussed and criticized under following topics:

The Limiting Composition of Borates Mixtures. Boric acid is a weak tribasic acid. Theoretically, one mole of boric acid can decompose one and one-half moles of alkali carbonates. Morey and Merwin⁽¹⁴⁰⁾ claim to have obtained a compound of $2\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$. They further showed that the liquids in the region between $\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ and $2\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$, contained about one per cent carbon dioxide. Therefore, for complete decomposition of sodium carbonate, the molar ratio of sodium carbonate to boric acid may be still smaller than 1 to 1. This ratio may be different for carbonates

of different alkali metals. In order to avoid the disturbing effect of evolution of carbon dioxide gas in electrodeposition, the limiting composition of the resulting mixture made from maximum ratio of carbonates to boric acid was determined.

From the data of the reaction of a single carbonate with boric acid, it was shown that lithium carbonate was completely decomposed by a stoichiometric ratio of boric acid, but sodium carbonate was not. Therefore, in the three components system, the undecomposed carbonate is wholly attributed to sodium carbonate. The calculation of undecomposed carbonates for the three components system was based on the assumption that equal amounts of both carbonates were left. The error caused by such an assumption is small. This method of calculation gives directly limiting composition for a given ratio of lithium carbonate to sodium carbonate used. Otherwise, the limiting composition for mixture of a certain ratio of lithium carbonate to sodium carbonate can only be obtained by extrapolation, which would probably result in greater error than the direct method just described. This calculation was justified by the results of the test for absence of carbon dioxide in new mixtures which were prepared with composition based on the above assumptions.

In the first stage of fusion of boric acid and carbonates mixture, there was a loss by spattering. In the second stage of heating the mixture to 900 °C, there might have been some volatilization loss. The total loss during fusion can be estimated from the experiment in which boric acid was fused with lithium carbonate alone. It was estimated that the maximum loss during fusion is about one gram per mole of boric acid used, which corresponds to an error of 1.4 mole per cent of B_2O_3 in the estimation of the limiting composition.

A check on this method of determining the limiting composition for the reaction of boric acid with alkali carbonates can be made from Morey and Merwin's data⁽¹⁴⁰⁾. The compound $2Na_2O \cdot B_2O_3$ which they claim to have formed contains 33.3 mole per cent boric oxide, but the molten mass, from which the compound $2Na_2O \cdot B_2O_3$ crystallizes, contains about one per cent of carbon dioxide. Therefore, the limiting composition of the $Na_2O-B_2O_3$ system should contain more boric oxide than 33.3 mole per cent. The composition determined by the proposed method is 34.0 mole per cent boric oxide..

"Fluid Range" of Fused Mixtures. Methods of determination of the melting point of a system may be divided into two general classes: the static and dynamic.

Heating and cooling curves are the usual dynamic methods used for the determination of the melting point. The experimental arrangement for this method consists of a crucible containing a substance in which a thermocouple either protected or unprotected is concentrically inserted. The crucible is placed in a uniformly heated portion of an electric furnace. When a melting or a freezing point is to be observed, the temperature of the furnace is gradually raised or lowered, and the temperature as indicated by the thermocouple is noted at frequent and preferably uniform intervals of time.

If all the conditions were ideal, the temperature of the charge would remain constant during melting or freezing. Thus the temperature-time curve would be characterized by a straight line exactly parallel to the time axis and by a discontinuous change of slope at either end of the line marking the beginning and ending of the period of melting or freezing. Actually, however, the change of state shown by the curve, even for pure metal is not sharp, but more or less gradual. Only a part of the freezing curve will be flat, and the melting curve usually possesses greater obliquity than the freezing curve. The reason for the obliquity and for its existence to a greater degree in melting curves have been discussed in detail by White⁽²⁰⁸⁾. The first part of the approximately flat

portion of the freezing curve corresponds to the true freezing point, and the latter part of the flatter portion of the melting curve corresponds to the true melting point.

Heating and cooling curve methods are suited to the study of systems which reach equilibrium rapidly and where the heat effect in transition is large.

The most useful static method is the "quenching method" since it permits the use of small samples. It is suited for a system where the change is sufficient sluggish to prevent transition during quenching. The melting point of silicates and other compounds of metallic oxides are usually comparatively high and their great viscosity when liquid, slow melting, slow crystallization and undercooling introduce many difficulties in determination of the melting point by a cooling curve method. Many crystalline silicates which have a definite melting point do not show a sharp freezing point on account of the high viscosity of the liquid, thus preventing the formation of crystal nuclei. The liquid subcools and the viscosity may so increase that a glass is formed. In another case, the melting of the substance requires a large time-interval, probably on account of the high viscosity of the liquid, so that the material will easily superheat as well as supercool. Both the melting and cooling curve will be so oblique that no halt in the curve is perceptible.

The procedure of the "quenching method" was developed by Geophysical Laboratory, Washington, D.C. Shephard, Rankin and Wright⁽¹⁸⁷⁾ and Ferguson and Merwin⁽⁶⁶⁾ used this method in the study of the silicate system. Morey and Ingerson⁽¹³⁹⁾ and Hill, Faust and Reynolds⁽⁸⁴⁾ applied it to determine the melting point of the phosphate system.

The procedure for the quenching method is very tedious. A small sample is enclosed in a small container, usually an envelope of platinum foil and heated in a specially designed quenching furnace held at a constant temperature within 1 °C for a sufficient time (20 minutes to three weeks) for equilibrium to be established. The sample is then rapidly quenched from that temperature by dropping it into a liquid at low temperature and the equilibrium conditions prevailing at high temperature are frozen. Phases are identified by petrographic microscopy and X-ray powder diffraction methods. If the sample is all glass, the temperature of treatment is above the liquidus; the presence of crystals indicates that the temperature is below the liquidus; and by successive approximations, the melting temperature can be located as closely as desired.

In some systems, such as sodium oxide-boric oxide, the heating-curve method cannot be used to determine the melting point, because of its glass-like properties.

The quenching method is also not good, because the hygroscopicity and the existence of more than one form, of some of the compounds may cause confusion as to the identity of the material. Furthermore, a study of the melting points shows that they do not help too much in the actual application of the fused salt to the electro-deposition work. For example, though the melting point of boric oxide is reported around 577 °C, the viscosity of the resulting mass is so high that even when the temperature is increased to 800 °C, the salt is still in a pasty state. Other substances like aluminum tristearate may be reported to have a sharp melting point, but is very viscous up to a temperature of decomposition. For this reason, the melting point was not determined, but a new term "fluid range" was introduced.

This "fluid range" is a temperature range, the upper value of which is that temperature at which a thick liquid starts to form, while the lower value is the temperature at which the first appearance of the solid mass occurs. The lower value sometimes can be observed from the freezing curve, but is generally obtained by direct observation and by using a freezing curve as reference. As to the upper value, it is always obtained by visual observation and by the resistance offered during stirring. For pure metals, both end values of the fluid range are the same and become

identical with the melting point. For glass, no lower value can be observed. In general, even the lower value of the fluid range is higher than the melting point. The fluid range defined and determined in this way is more or less arbitrary, but it is more significant for electro-deposition investigation than the melting point determination.

The ideas of using a special term in working with fused salts is not new. In other technical fields, many similar terms are used instead of the melting point; for example, no melting point is determined for lubricants. The general terms used in lubricant field are "cloud point" and "pour point". In the glass industry, "softening point" is generally used instead of the melting point of the glass. Recently, a further new term "flow point"⁽¹¹⁷⁾ has been introduced as describing the behavior of glass.

Fluid Range of Fused $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ System. The binary system of sodium oxide-boric oxide has been systematically studied by Ponomareff⁽¹⁷⁴⁾ and Morey and Merwin⁽¹⁴⁰⁾. Most of the information relating to the phase equilibrium was obtained by the quenching method. In the case of sodium metaborate, the crystallization takes place so rapidly that the phases cannot be determined by the quenching method, so it was studied by the heating-curve method. The investigation of this system is further complicated by the hygroscopicity of different borates of sodium and the existence

of more than one form of some of different borates. This has caused confusion in the identification of different borates. For this reason, Morey and Merwin did not comment on the discrepancy of the data, from different observers^(35, 39, 40, 43, 104, 140, 184) for the same compounds, as shown in Table XXX, page 207.

Except for these investigations on the compound $2\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ reported by Morey and Merwin, all investigations were on compounds in this system with a content of boric oxide greater than 50 mole per cent.

A survey of the data of previous investigators, shows that except in the region where the boric oxide is greater than 95 mole per cent, the melting point of all mixtures with a molal ratio of B_2O_3 to Na_2O greater than 1, is higher than the melting point of aluminum (660 °C). Therefore, no determination of the fluid range was made in the region where the content of B_2O_3 is greater than 50 mole per cent.

The binary system of lithium oxide-boric oxide has been systematically studied by Mazzetti and Carli⁽¹²⁹⁾. Here again, the data show that where the molar ratio of Li_2O to B_2O_3 is smaller than 1, the melting point of the mixture is generally higher than 660 °C. The eutectic mixture having a boric oxide content of about 81 mole per cent would be viscous at 660°C. Therefore, no determination of the fluid range was made in the region where the boric oxide content is greater than 50 mole per cent.

TABLE XXX

Melting Points of Compounds in Na₂O-B₂O₃
System Reported by Different Investigators

	Melting Point °C			
	Na ₂ O.B ₂ O ₃	Na ₂ O.2B ₂ O ₃	Na ₂ O.3B ₂ O ₃	Na ₂ O.4B ₂ O ₃
Burgess and Holt ^(a)	930	791	---	838
van Klooster ^(b)	966	---	---	---
Morey and Merwin ^(c)	966	738	766	816
Cole, Scholes and Amberg ^(d)	965	---	---	---
Cole, Taylor and Scholes ^(d)	---	735	720	810
Day and Allen ^(e)	---	742	---	---
Ponomareff ^(f)	---	732	694	783

- a) Burgess, C. H. and A. Holt: Proc. Roy. Soc. (London) 74, 285 (1904); Morey, G. W. and H. E. Merwin: Phase Equilibrium Relationship in the Binary System Sodium Oxide-Boric Oxide, J. Am. Chem. Soc. 58, 2250 (1936).
- b) Klooster, H. S. van: Behavior of Metaboric and Metaphosphoric Acids in Fusion of Their Alkali Salts, A. anorg. Chem. 69, 122-34 (1911).
- c) Morey, G. W. and H. E. Merwin: Phase Equilibrium Relationship in the Binary System Sodium Oxide-Boric Oxide, J. Am. Chem. Soc., 58, 2243-54 (1936).
- d) Cole, S. S., S. R. Scholes and C. R. Amberg: The System R₂O-B₂O₃. II. Properties of Anhydrous and Hydrated Metaborates of Sodium and Potassium, J. Am. Ceram. Soc. 18, 58-61 (1935).
- e) Day, A. L. and E. T. Allen: "The Isomorphism and Thermal Properties of the Feldspar", p. 29, Carnegie Institute of Washington, Publ. No. 31 (1905).
- f) Ponomareff, J. P.: Z. anorg. allgem Chem. 89, 383 (1924); Morey, G. W. and H. E. Merwin: Phase Equilibrium Relationship in the Binary System Sodium Oxide-Boric Oxide, J. Am. Chem. Soc. 58, 2248 (1936).

Klooster⁽¹⁰⁴⁾ studied a mixture of sodium metaborate and lithium metaborate in a wide range of compositions, and observed that a eutectic mixture is formed at a composition of 66.7 mole per cent of lithium metaborate and 33.3 mole per cent of sodium metaborate. This is the only literature reference to the three components system $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$.

The literature dealing with the system $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ concerns itself only with the melting point-composition relation for the system containing more than 50 mole per cent B_2O_3 . No information is given concerning the viscous behavior of the system at 660 °C. For example, although the melting point of boric oxide is reported to be about 577 °C, the viscosity of the resulting fluid is so high that even when the temperature is increased to 800 °C, it is still in a pasty state. This is the reason why Andrieux⁽¹³⁾ electrolyzed fused borax at 880 °C, while the melting point of borax was reported at 742.5 °C.

The accuracy of the fluid range as given in this study is 5 to 10 °C which is better than the difference of melting point for the same compounds as reported by different investigators and summarized in Table XXX. The smooth curve obtained by interpolation for the 600 and 660 °C upper fluid range further indicates the utility of the proposed method.

Effect on the Fluid Range of Adding Aluminum Phosphate to Fused Borates. In the first place, the fused mixture, $B_2O_3 \cdot 1.94Na_2O + 1.06Na_2CO_3$, has a sharp melting point. The fluid range of the mixture is lowered by the addition of aluminum phosphate. A plot of the weight percentage of aluminum phosphate in the above mixture, against the fluid range of the mixture gives a very sharp eutectic point as shown in Figure 7, page 130, but the melting point of the eutectic was above $660^\circ C$.

On the other hand, the fused salt, $5Na_2O \cdot 10Li_2O \cdot 6B_2O_3$, is more or less vitreous. Any change in the fluid range of the fused mixture on the addition of aluminum phosphate is rather obscure, as shown in Figure 8, page 132, since the fluid range is affected by both the lowering of the melting point and the increase in viscosity.

Corrosion by Fused $5Na_2O \cdot 10Li_2O \cdot 6B_2O_3$. The attack of $5Na_2O \cdot 10Li_2O \cdot 6B_2O_3$ on various materials was studied by using the materials as containers for the melt, and observing the deterioration of the container and the contamination of the fluid.

From the standpoint of contamination, crucibles made of porcelain, graphite and platinum were satisfactory, but from the standpoint of corrosion, only graphite and platinum crucibles could be used for containers.

The Decomposition Potential of the Fused Borates and Borates-Phosphate Mixture. The voltage-current curves for aluminum anode in both $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ and in the mixture of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ as shown in Figure 9, page 138, are straight lines. This shows that the anode is in equilibrium with the electrolyte and the electrolyte was not decomposed. The aluminum ions in the fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, probably came from solution of the aluminum anode in the fused electrolyte, since the presence of aluminum ion in the fused electrolyte has been identified by the chemical test. Since both of the straight lines did not start from the zero point of the coordinate axes, it is impossible to conclude whether or not there was electrodeposition of aluminum on the cathode. The sudden drop of the current at 2.6 volts in curve A in Figure 9 may be explained as resulting from concentration polymerization at the high current.

The accurate data for the above experiments were difficult to obtain, because the current under the working condition was rather unstable as shown in Figure 10 on page 141 and Figure 14 on page 153.

After electrolysis, the aluminum anode was yellow-brown in color, which shows that some displacement reaction has taken place. The yellow-brown color may be due to the formation of an alloy of the liberated substance with the aluminum.

In the fused mixture of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, if platinum electrodes were used, the electrolyte was decomposed as is shown by the curves C and D in Figure 9, page 138.

Electrodeposition from a Phosphates Mixture. The eutectic mixture of sodium metaphosphate and sodium pyrophosphate as determined by Morey and Ingerson⁽¹³⁹⁾ can be used as a solvent for aluminum phosphate. The resulting solution is a good electrical conductor, but has a strong oxidizing power. It oxidizes the surface of the aluminum anode to a non-conducting oxide film which is not dispersed by the fused mixture as shown by Table XVIII, page 154. The copper cathode is also oxidized by the electrolyte to copper oxide.

The formation of the non-conducting film of aluminum oxide on the anode surface can be prevented by using an aluminum-copper alloy made as is used in Hoop's process⁽⁸⁶⁾ for refining aluminum.

The purpose of using platinum as an anode in the second test is to show that the black copper oxide is formed on the copper cathode was not related to material transferred from the anode.

Electrodeposition from Borates and Borates-Phosphate Mixture. As shown in Table XX, page 159, no aluminum can be electrodeposited on the copper cathode from a fused

mixture of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ with aluminum anode and copper cathode, within the range of 1.5 to 5.5 volts and current densities from 1.0 to 10.4 amperes per square decimeter. The aluminum anode was always coated black which was also the result of the reaction between the aluminum and the fused electrolyte, without passage of current. The mechanism of such a reaction will be discussed later. The brown color on the copper surface might be phosphide of copper, formed by the reduction of phosphate at the bath temperature. But when the voltage applied was smaller than 1.5 volts, there was no change on the copper cathode. This is probably because the potential is too low to cathodically reduce the phosphate.

In Table XX, it was shown that a copper cathode was not always coated with a black deposit. The properties of this black deposit were the same as those of the black deposit obtained on aluminum reacting with the fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, and analyzed as shown on pages 158, 160, and 161. On this basis, it is assumed that the black deposit was obtained by electrodeposition of aluminum from the melt, which then reacts with carbonates absorbed by the electrolyte. As shown in Table XX, page 159, the amount of black deposit formed on a copper cathode from the molten electrolyte containing aluminum depends on time as well as on the current

density. The time must be sufficient for absorption of appreciable carbon dioxide from the atmosphere.

Accurate results in quantitative electrodeposition tests can not be expected from a borates-phosphate bath or mixed borates bath, Table XIX, page 157, because the anode was slightly eroded away during cleaning in boiling water. Also the black coat on both electrodes partially separated on boiling the electrodes with water. A further difficulty was that the surface of the aluminum anode was oxidized to aluminum oxide during immersion in the fused electrolyte.

In the first quantitative electrodeposition test with fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, aluminum anode and platinum cathode, in Table XIX, page 157, the low electrode efficiency may be ascribed to loss of black particles when the electrodes were heated in boiling water to remove the adhering salts. The electrode during electrolysis, turned red. The aluminum anode was covered with a brass-yellow coating spotted with red-brown. The reason for such a color change has been given already on page 210, in the discussion of the decomposition potential of the fused borates and borates-phosphate mixture. In the third test, cavities were observed on the surface of the aluminum anode. It was impossible to calculate the cathode efficiency for this test because part of the platinum cathode broke off.

In the first test of the quantitative electrodeposition from the fused electrolyte consisting of 9.4 per cent of

aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ with aluminum anode and platinum cathode, as shown in Table XIX, page 157, the cathode was surrounded by a porous lump of solids which was lost as an attempt was made to remove it from the electrodes. No cathode efficiency could be determined.

It seems that an aluminum anode will be really dissolved during the electrolysis, but the gain in weight of the cathode is doubtful. The anode loss is a better measuring stick for the efficiency than the cathode gain. In the fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ alone, so long as the applied voltage is greater than the decomposition voltage, the anode efficiency is greater than 100 per cent. It is therefore logical to say that the anode loss is a combined action of both chemical attack and anode reaction.

In the fused electrolyte of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, the anode loss is generally smaller than that under the same applied potential in the fused electrolyte $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$. No case is found with an anode efficiency greater than 100 per cent, even when the current density is so high that the cathode is surrounded by a big porous bulk of solids which caused difficulties in determination.

Determination of the Carbon Dioxide in $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$.

A quantitative determination of carbon dioxide in fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ was made by the method used for the determi-

nation of carbon dioxide in limestone. Because the fused salt contained boric acid, which is a very weak acid and may have buffering action, the quantity of acid used to decompose the carbonate in this process was increased. According to the method recommended by Kolthoff and Sandell⁽¹⁰⁸⁾, only 50 per cent excess acid is used to decompose the carbonate. In this experiment, for the total alkali, both combined and free, equal to 0.1248 gram equivalent, in presence of 0.150 gram equivalent of boric acid, the acid used to decompose the possible carbonate was varied from 0.712 to 3.560 gram equivalents.

Another modification used was that, in the case of limestone, since calcium chloride is water soluble and calcium sulfate is insoluble, hydrochloric acid rather than sulfuric acid is used to decompose the carbonate. In this investigation, both the sulfate and chloride of the alkali metals are very soluble. Hydrochloric acid, if too much in excess or too concentrated in the decomposition flask, is likely to pass along with the carbon dioxide.

Except in the second test, Table XXII, page 163, where too much concentrated hydrochloric acid was used, the results may be said to check within experimental error. Because of the limited accuracy of analysis as shown by Willard and Furman⁽²⁰⁹⁾, one cannot say that the electrolyte is absolutely free of carbon dioxide.

The Properties of the Black Powder Obtained from the Action of Fused Borates on Aluminum. X-ray analysis and spectrographic analysis, Table XXI, page 161, show certain inorganic constituents in the black powder, but these substances are not responsible for the black color. Chemical tests show that the black appearance of the powder may be attributed to carbon. The presence of carbon in the black powder was further proven by the combustion test. The carbon content in the black powder was 80.85 per cent. This value is very near that of loss on ignition, 83.6 per cent. These seem to be a good indication of the presence of carbon in the black powder.

Mechanism of Formation of Black Powder from the Action of Molten Borates on Aluminum. There was a possibility that the black deposit might be formed from the residual carbonate left in preparing the molten mixture. To test this possibility, a mixture, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 7.5\text{B}_2\text{O}_3$, which contained six mole per cent of B_2O_3 more than that on the limiting composition curve, but still had a fluid range below 600°C , was chosen for study. The reason for selecting such a mixture was to prove that the formation of carbon on the aluminum was not due to the presence of carbonate left in the preparation and resulting from an error in locating the limiting composition curve. The mixture selected for electrodeposition studies, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, had only one

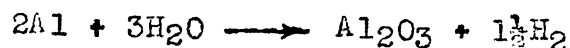
mole per cent more boric oxide than that on the limiting composition curve, and the experimental error in determining the limiting composition may be as large as 1.4 mole per cent of boric oxide.

As shown in Table XXIII, page 165, aluminum does not react with fused alkali carbonate mixtures. The normal carbonates do not attack aluminum. However, if an aluminum anode and a platinum cathode were first connected to the direct current source, then inserted in the molten alkali carbonates mixture, carbon formed on the surface of the aluminum anode. It may be conjectured that the reaction may take place between the aluminum and the bicarbonate ion at the anode. The bicarbonate ion may be formed from a minute quantity of free carbonic acid dissolved in the molten borate electrolyte, which is in equilibrium with the carbon dioxide and water in the air. Thus, at anode: $2Al + HCO_3^- \longrightarrow Al_2O_3 + C + \frac{1}{2}H_2 + e$

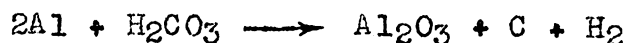


As soon as the quantity of boric acid added to the mixture exceeds 0.10 mole per 1.5 moles of the molten alkali carbonates, the direct attack on aluminum starts as evidenced by the evolution of gas bubbles and the formation of aluminum oxide on the surface of the aluminum. This action is explained by assuming that the presence of boric oxide in the molten alkali carbonates increases the absorptive power of the fused mixture for moisture, and the mixture is then

sufficiently active to react with aluminum according to the reaction:



As the addition of boric acid exceeds the quantity of 0.20 mole per 1.5 moles of molten carbonates, the effect of more borate in the mixture shows its influence further by formation of carbon on aluminum in the melt. More carbon dioxide and moisture are absorbed in the molten mixture to such a degree that the concentration of free carbonic acid is sufficient to react with aluminum as follows:



Though the liberation of hydrogen gas in all reactions has not been proved directly, the presence of hydrogen in the black powder has been determined by the quantitative combustion method.

The product formed from the reaction between the boric acid and aluminum is not well defined as reported by different analyses, but it is certainly known to contain aluminum oxide mixed with some boron or boron compounds. There is sufficient reason for the presence of the above mentioned materials in the product, for when boric acid is fused with aluminum, a part of aluminum is oxidized to aluminum oxide and meanwhile, a part of boric oxide is reduced to boron or boron compounds by aluminum⁽²²⁵⁾. It was also shown that the product from the reaction between the boric acid and aluminum, did not give the positive test for carbon by the combustion method.

A negative test for carbon, on the insoluble residue formed by fusing the product, from the reaction between the boric acid and aluminum, with alkali carbonates mixture, showed that the formation of carbon is not by the reaction of boric acid with aluminum first and then by the reaction of such products with fused carbonates.

The Source of Carbon in the Black Powder Obtained from Action of Fused Borates on Aluminum. Black powder was prepared by the action of the fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ on the metallic aluminum in a platinum dish. The mixture was in turn prepared by fusing together sodium carbonate, lithium carbonate and boric acid. Before this mixture was treated with aluminum, it was tested with 3-normal hydrochloric acid to show that no carbon dioxide bubbles were evolved. The maximum carbon dioxide content of such a sample, as determined by acid digestion, was 0.37 per cent by weight. However, the presence of carbon dioxide in the mixture is still doubtful, since this method only can be checked within 0.3 per cent of carbon dioxide in the sample.

Furthermore, one gram of black powder with a carbon content of 80.5 per cent has been prepared from 172.8 grams of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$. This would correspond to a carbon dioxide content in the molten electrolyte of 1.65 per cent, which is much greater than the carbon dioxide content obtained by analysis.

However, 1.65 per cent of carbon dioxide in the fused electrolyte, as calculated above, does not mean that no more carbon can be obtained from the fused salt. When pieces of aluminum foil were continuously added to the fused mixture, black deposits continue to form on the surfaces. Therefore, it seems that the formation of carbon is due to aluminum reacting with the carbon dioxide absorbed in molten mixture from the air. The view is supported by Mellor⁽²²⁴⁾ that potassium metaborate absorbs gas while being melted, and that the gas is rejected on cooling. This would also explain why the fused salt, after cooling gave a negative test for carbon dioxide, but would form a black deposit with aluminum when the salt was molten.

Such explanation is also supported by the observation that the molten mixture, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 7.5\text{B}_2\text{O}_3$, reacted with aluminum to form black deposits. This mixture should be free of carbon dioxide because of the high boric oxide content.

This theory might be more directly proved by electrolyzing the molten $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ in an atmosphere not containing carbon dioxide. But in order to perform this experiment, a large gas-tight cabinet with a height at least three times that of the heating furnace should be used to enclose the furnace and the rack of electrodes. The material used to build such a cabinet must be capable

of withstanding high temperatures, be gas-tight and permit observation of the experiment. The position of the electrodes should be adjustable from outside the cabinet. Because of the limited time available, this experiment was not performed.

Unsteady Electrolysis in Fused Borates and Borates-Phosphate Mixtures. For the fused electrolyte of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, when aluminum anode and copper cathode were used for electrolysis, the current readings were rather irregular under various constant voltages as shown in Table XI and Figure 10 on pages 140 and 141. If a platinum anode and cathode were used, the current was constant. With platinum electrodes, at 1.5 volts, the current reading was not changed by stirring, presence of moisture and by alternating immersion, as shown on pages 142 to 150. In a separate experiment, a test with aluminum anode and platinum cathode gave the same irregular current reading as in the case of using aluminum anode and copper cathode. Thus the irregular changes of the current reading at constant voltage seem to be attributable to the aluminum anode, and are not related to the material of the cathode.

With platinum electrodes, the steady electrolysis only took place at two constant voltages: 1.5 and 2.5 volts, as shown in Tables XII and XVI and Figures 11 and 13 on pages

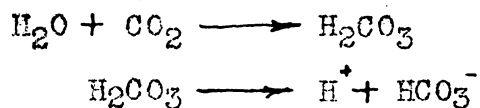
144 to 150. The reason for not working at higher voltages is that even at a voltage of 2.5 volts, the platinum cathode was destroyed while no harm was done to the platinum anode. The damage to the platinum cathode was assumed to be due to the formation of platinum phosphide by the cathode reduction of phosphate. Platinum phosphide is a rather brittle substance, as was the case with the products of the destroyed platinum cathode.

For a further study of the reason for irregular current readings at constant voltage during electrolysis, fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ alone without aluminum phosphate, was used as the electrolyte, as shown in Table XVII, page 152, and Figure 14, page 153. Except at the start, the maximum current in duplicate tests was nearly the same: 0.9 ampere in the first test and 0.7 ampere in the second test.

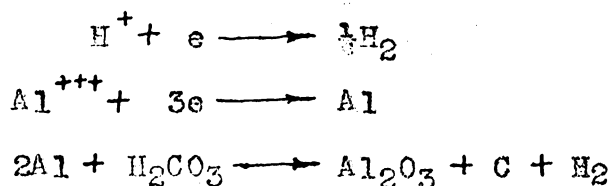
The general tendency of the current-time curve is toward a decrease of current with time. At the start of the electrolysis, the current was high, around 1.7 amperes at 1.5 volts. The current was rapidly decreased as the deposit on the electrodes was continuously built up. When the current became very small, the building-up of the deposit on the electrodes ceased. Then the deposit already built up dispersed into the fused mixture and the current increased again. The process was repeated in this way periodically.

As was shown for the mechanism of formation of the black powder, page 217, the chemical reactions during the electrolysis probably are:

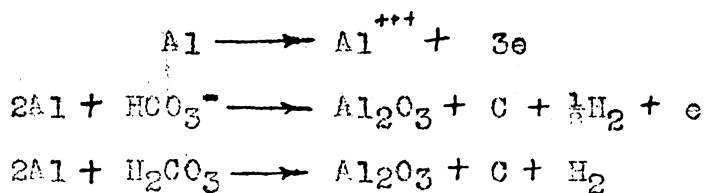
At surface of electrolyte:



At cathode:



At anode:



In the period when the current dropped below 0.05 ampere at 1.5 volts in the same electrolyte, the evolution of the gas bubbles around platinum cathode stopped. There was still slight evolution of gas bubbles around the aluminum anode. This may be explained by assuming there is some water present in the fused salts, and the hydroxyl ions are neutralized, setting free oxygen. Further evidence of the presence of water is the observation of hydrogen in the black powders as reported on page 160.

Recommendations

On the basis of experiments done on the borates, and borates-phosphate systems, it is recommended that further work be done on these systems as follows:

Proposed Work to Check the Conclusion. To check the conclusion of this work, that the carbon dioxide in the electrolyte came from the atmosphere over the cell, the following experiment is suggested. A large gas-tight cabinet, with a height at least three times that of the heating furnace, should be used to enclose the furnace and the rack of the electrodes. The material used to build such a cabinet must be capable of withstanding high temperatures, be gas-tight and permit observation of the experiment. The position of the electrodes should be adjustable from outside the cabinet. It is recommended that an electrolysis be carried out in the hood in an atmosphere from which carbon dioxide is removed by absorption in soda lime.

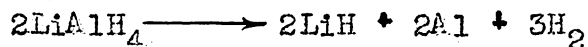
For further work on the study of the possibility of electrodepositing aluminum, the following recommendations are made:

From Anhydrous Aluminum Fluoborate. From the systematic review of the use of aluminum salts as electrolyte, anhydrous aluminum fluoborate seems to be a promising inorganic alu-

minum salts worthy of trial. It may be prepared from lithium aluminum hydride and boron hydride as a mixture with lithium fluoborate and diborane. The presence of lithium fluoborate should offer no difficulty in electrodeposition of aluminum, because aluminum should deposit before the lithium on electrolysis. (218, 219)

From Aluminum Hydride and Lithium Aluminohydride. The possibility of electrodeposition of aluminum from a bath of aluminum hydride in organic solvent has been suggested by Gibb⁽⁷¹⁾. It seems that lithium aluminohydride will also be a possibility for it is similar in properties to aluminum hydride.

Lithium aluminohydride is a white crystalline material, moderately stable in dry air at room temperature, but decomposing rapidly in moist air. It reacts violently with water and with alcohols. It melts with decomposition at 150 °C on rapid heating. At 120 °C, it loses hydrogen slowly and irreversibly in accordance with the equation:



It is quite soluble in a number of organic solvents, particularly the lower ethers, for example, diethyl ether dissolves 30 parts per 100 parts of ether. Aluminum hydride shows many of the reactions of lithium aluminohydride, although its tendency to polymerize to an insoluble mass is a disadvantage.

From Aluminum Derivatives of Fatty Acids. In the field of possible organic electrolytes, aluminum derivatives of fatty acids should be first prepared and the melting point of the products determined. The general tendency of the properties of the aluminum salts of fatty acids is that when the molecular weight is low, the salt decomposes without melting; when the salts are those of high molecular weight fatty acids, they possess low melting points, but the molten liquid has a high viscosity up to the decomposition temperature. An α -carbon branch of a straight chain fatty acids has the effect of stabilizing the aluminum salt on heating. Suitable aluminum salts may be obtained by varying both the number of carbons in the chain and the different branches on the α -carbon atom.

If the organic solution system of aluminum salt of fatty acid is investigated, the method of approach may be to find suitable conductive solvents for different aluminum salts of various fatty acids.

The method of finding a solution to the problem of electrodeposition of aluminum is to make a study of aluminum chemistry and synthesis of new aluminum compounds. Aluminum is a metallic element, but the chloride possesses the properties of a compound of nonmetallic salts. Thus the property of its compound is difficult to predict from other metallic salts. If more aluminum compounds are investigated, the electrodeposition problem may be more rapidly solved.

Limitations

The limitations of this investigation into the possibility of depositing aluminum from the system containing sodium and lithium borate were as follows:

1) The limiting composition curve was determined with an accuracy of ± 1.4 mole per cent of boric oxide. The accuracy of the fluid range determination was ± 10 °C.

2) Corrosion studies in the fused mixture, $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, were limited to seven kinds of materials: porcelain, nickel, ampco metal, armco iron, plumbago, graphite and platinum at 650 to 700 °C.

3) The determination of the current-volt relationship was limited to the use of an aluminum anode with a platinum cathode, and a platinum anode with a platinum cathode.

4) The quantitative electrodeposition test for this fused borates was limited to current densities from 2.67 to 26.7 amperes per square decimeter.

The limitations of this investigation into the possibility of depositing aluminum from 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ were as follows:

1) The determination of the current-voltage relationship was limited to the use of an aluminum anode with a copper cathode, aluminum anode with a platinum cathode, and a platinum anode with a platinum cathode.

2) The qualitative electrodeposition test with an aluminum anode and copper cathode was limited to an applied voltage from 1.5 to 5.5 volts and a current density from 0.733 to 10.4 amperes per square decimeter.

3) The quantitative electrodeposition test was limited to current densities from 6.67 to 13.3 amperes per square decimeter.

The limitations of this investigation into the possibility of depositing aluminum from 10 per cent of aluminum phosphate in the fused eutectic mixture of sodium metaphosphate and sodium pyrophosphate were as follows:

1) The anode used in the electrolytic experiment was of pure aluminum, of an alloy of three parts by weight of aluminum to one part by weight of copper, and of platinum with copper as the cathode in all cases.

V. CONCLUSIONS

A. An exploratory investigation of the possibility of using fused aluminum phosphate-eutectic mixture of sodium pyrophosphate and sodium metaphosphate as the electrolyte for the electrodeposition of aluminum at the temperature below the melting point of aluminum, 660 °C, led to the following conclusions:

1. The molten eutectic mixture of sodium pyrophosphate and sodium metaphosphate has strong oxidizing power.
2. Copper cathode and aluminum anode were oxidized by the electrolyte immediately after the electrodes were immersed and a layer of the oxide formed on the surfaces.
3. No aluminum could be electrodeposited from this bath.

B. An exploratory investigation of the possibility of using the fused system $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ as the electrolyte for the electrodeposition of aluminum at the temperature below the melting point 660 °C, led to the following conclusions:

1. The limiting composition or the maximum number of moles of alkali carbonates which are completely decomposed by one mole of boric acid, in the system $\text{Na}_2\text{O-Li}_2\text{O-B}_2\text{O}_3$ was found to be between 25 and 34 mole per cent boric oxide

for mixtures of sodium borate and lithium borate respectively. The accuracy of such determination was within 1.4 mole per cent of boric oxide.

2. Isothermal fluid range curves at 600 and 660 °C of various mixtures in $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system were made. The reliability of this curve is ± 10 °C.

3. The mixture in the $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ system having a melting point about 550 °C, and which contains no residual carbon dioxide will have a composition approximately $5\text{Na}_2\text{O}.10\text{Li}_2\text{O}.6\text{B}_2\text{O}_3$.

4. The corrosive activity of the selected mixture $5\text{Na}_2\text{O}.10\text{Li}_2\text{O}.6\text{B}_2\text{O}_3$ was rather high. Crucibles made from porcelain, nickel, ampc metal, armco iron and plumbago were all attacked. Only crucibles made from platinum and graphite were suitable for use as containers.

5. The fused electrolyte, $5\text{Na}_2\text{O}.10\text{Li}_2\text{O}.6\text{B}_2\text{O}_3$, does not show a decomposition potential when electrolyzed with an aluminum anode and a platinum cathode.

6. The current was unstable in the fused, $5\text{Na}_2\text{O}.10\text{Li}_2\text{O}.6\text{B}_2\text{O}_3$ with aluminum anode and platinum cathode at 1.5 volts and 560 ± 10 °C, varying from 0.05 to 2.0 amperes.

7. A black deposit, formed during electrolysis of $5\text{Na}_2\text{O}.10\text{Li}_2\text{O}.6\text{B}_2\text{O}_3$, with aluminum anode and platinum cathode, at 600 ± 10 °C, 2.7 to 27 amperes per square

decimeter, was proved to be carbon.

8. The source of the carbon to be from the carbon dioxide absorbed from the air by the fused mixture.

9. Aluminum was not electrodeposited from the fused $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ electrolyte.

10. The aluminum anode loss, which was greater than 100 per cent based on current efficiency, was a combination of direct chemical and electrolytic action.

C. An exploratory investigation of the possibility of using the fused mixture of aluminum phosphate and $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ at a temperature below 660°C , led to the following conclusions:

1. The addition of 20 per cent by weight of aluminum phosphate to $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, did not change the fluid range more than 20°C .

2. Aluminum can not be electrodeposited from a mixture of 9.4 per cent by weight of aluminum phosphate in 90.6 per cent by weight of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, at $560 \pm 10^\circ\text{C}$, using an aluminum anode, and platinum or copper cathodes.

3. If a platinum anode and a platinum cathode were used, the current was stable at 1.5 and 2.5 volts. At 1.5 volts, the amount of current was not changed by stirring, moisture and alternating immersion. If an aluminum anode and copper cathode were used, the current was stable at

1.5 and 2.5 volts also, but at a potential of more than 2.5 volts up to 5.5 volts, the current for the cell was erratic.

4. In the cell containing 9.4 per cent aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$, at 600 ± 10 °C, at 13.3 and 6.7 amperes per square decimeter, the anode efficiency was 49 to 56 per cent of theoretical respectively.

VI. SUMMARY

This investigation was conducted to attempt to find an electrolyte that would be suitable for the electrodeposition of aluminum from a fused salt bath at a temperature below its melting point.

Aluminum coated metals combine the desirable mechanical properties of the base metal and the good chemical resistance of aluminum. Electroplating, gives an even and controlled thickness of coating and possesses very high corrosion resistance.

Methods for the deposition of aluminum previously investigated have not been used commercially, to any extent. Most attempts at the electrodeposition of aluminum were from nonaqueous organic solutions and from fused mixtures. Aluminum halides, especially aluminum chloride, are the solutes most frequently used. It is known that aluminum oxide is peptized by aluminum chloride. Severe corrosion is expected on articles electroplated in the presence of aluminum chloride.

In the present investigation, the use of aluminum halides was avoided. Aluminum phosphate was employed in the system $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ as well as in the eutectic mixture of sodium metaphosphate and sodium pyrophosphate. In none of the investigations was electrodeposition of aluminum obtained.

In investigation of the borate-phosphate system, a fluid range-composition diagram of sodium oxide-lithium oxide-boric oxide was first determined and plotted on a triangular diagram. The fluid range here denotes the temperature at which the cooling liquid starts to become appreciably viscous. This diagram consists essentially of a limiting composition curve and two isothermal, fluid range-composition curves at 600 °C and 660 °C. The limiting composition is expressed as the minimum content of boric oxide which will eliminate all carbon dioxide from the sodium oxide-lithium oxide-boric oxide mixture. The area encircled between the 660 °C and the limiting composition curve is the possible working region. In this region, a mixture of the composition $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ was taken as the solvent for the aluminum phosphate and the fluid range-composition curve of this mixture was determined. It was found that the addition of aluminum phosphate to the $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ has little effect on the fluid range up to 18.68 per cent by weight of aluminum phosphate.

Because of the highly corrosive property of the fused electrolyte, its action on different containers was studied; these included porcelain, nickel, ampco metal, armco metal, plumbago, graphite and platinum. Except for the graphite crucible and the platinum dish, no material was suitable for use as a container.

Electrochemical properties of the system

$5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ as well as its solution with aluminum phosphate was studied. Both the molten $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ and the mixture of 9.4 per cent of aluminum phosphate and 90.6 per cent of $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ showed no decomposition potential on electrolyzing with aluminum anode and platinum cathode. The current was unstable when both electrolytes were electrolyzed with aluminum anode and platinum cathode. If platinum electrodes were used for the borates-phosphate system, the current was constant when stirred, when moisture was added, and when the electrodes were immersed periodically. The decomposition potential determined for the borates-phosphate system with platinum electrodes was about 1.40 volts, at 600 ± 10 °C. Qualitative electrodeposition tests showed that no aluminum could be deposited from either electrolyte. Quantitative electrodeposition test on the molten $5\text{Na}_2\text{O} \cdot 10\text{Li}_2\text{O} \cdot 6\text{B}_2\text{O}_3$ showed that the weight loss of the aluminum anode consisted of both electrolytic loss and direct chemical attack.

The electrodeposition product was studied by chemical methods, spectrographical analysis and X-ray analysis. Final results showed that only carbon was deposited.

A study of the source of carbon formed in the electrodeposition indicated that it came from the carbon dioxide in air absorbed in the fused electrolyte. A mechanism for the reactions was proposed.

Also, a eutectic mixture of sodium metaphosphate and sodium pyrophosphate was used as the solvent to dissolve aluminum phosphate for electrolysis. The molten mixture had strong oxidizing power and a strong anode effect if an aluminum anode was used. Black coatings were formed on the copper cathode with either an aluminum anode or an anode of an alloy of 75 per cent of aluminum and 25 per cent of copper, or a platinum anode. The black coating on the copper cathode was found to be copper compound by chemical analysis.

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