In a brief way this covers the position of the ammonia industry to-day. The old gas retort is gradually losing ground while the output of the coke oven is increasing by leaps and bounds. Meanwhile, in the manufacture of synthetic ammonia and nitric acid, we seem standing on the threshold of a period of such chemical and electrochemical activity as the world has rarely seen. When we remember that it is only a few decades since ammonia made from camel's dung was still coming into Europe we realize the great strides which the industry has already taken, and the most interesting chapters in its history are apparently still to be written.

### ON THE PROPERTIES AND PREPARATION OF THE ELEMENT BORON.<sup>1</sup>

#### By E. WEINTRAUB.

## Received March 25, 1911

I will describe the properties of the element boron isolated in pure fused form in the West Lynn Research Laboratory of the General Electric Company, and also give you in brief the methods used for the preparation of the element and a survey of its possible applications.

It will be best perhaps to first make you acquainted with the properties of the element (author shows a large lump of fused boron and small broken-up pieces, to show the fracture, and also a bottle filled with crushed boron).

Both in appearance and in its curved, conchoidal fracture the lump and the broken-up pieces most nearly resemble black diamond. They are very hard and scratch with ease the known hard substances except diamond. The surface is a very shiny black and takes a beautiful polish.

To my knowledge this is the first artificial product (not an imitation of a natural product) which combines great hardness with an amorphous structure. Boron is, however, inferior to diamond of good quality in its strength. It rubs off rather readily on the diamond lap and even on the carborundum wheel. I do not consider it improbable that in further continuation of the work additional toughness may be imparted to boron and the product become a cheap substitute for black diamond.

I have not determined the melting point accurately, but estimate it to be between  $2000^{\circ}$  and  $2500^{\circ}$  C., nearer the second figure than the first.

Boron is a rather volatile element, its vapor tension being appreciable at 1200° C. It can, however, be fused readily not only under atmospheric pressure but also in vacuum.

The properties so far mentioned are in rather good accord with the position of the element in the periodic system. Boron has its place to the left of carbon and has, so to say, right to be hard; conchoidal in its fracture—both properties of fused carbon; and to have relatively high melting point and a vapor tension of such magnitude that it volatilizes to a considerable extent while melting in vacuum.

<sup>1</sup> Address presented before the Northeastern Section of the American Chemical Society, February 17, 1911.

In fact this similarity of properties might be used to determine in its turn properties of carbon. Thus the high vapor tension of boron would make it probable that the volatilization of carbon at high temperatures (as in incandescent lamps) is a thermal process and not due primarily to electric discharges or chemical processes. The search for a form of carbon having a low vapor tension comparable with that of metals such as tungsten would, in the light of this, be futile and I admit that the argument is weighty enough with me to have caused me to singularly reduce my efforts in that direction.

We come now to a property of boron which is entirely unexpected and places boron in a position all by itself. I refer to its electrical characteristics. When cold, boron is a very poor conductor, its specific resistance being about 1012 times that of copper. In this it still shows its similarity to amorphous carbon, which is a very poor conductor, and to diamond, which is an insulator. But where it differs is in the abnormal value of its temperature coefficient of resistance. The resistance of boron very rapidly drops as the temperature rises, so that between room temperature and dull red heat (400°) the resistance drops in the approximate ratio of  $2 \times 10^6$  to 1. Around room temperature the resistance falls to half its value for every 16° C. In other words, the resistance drops geometrically with arithmetic increase of temperature. The law is, however, only approximate. If extended over large temperature intervals, the interval corresponding to equal resistance ratios increases with the temperature. The relation between temperature and resistance was studied quantitatively up to red heat. When red heat is reached the resistance, however, still continues to drop rapidly.

This enormous influence of temperature on the resistance of boron, combined with the fact that it occurs at ordinary temperatures, makes the behavior of boron as an electrical conductor entirely different from that of ordinary conductors. Thus Ohm's law becomes useless almost to the same extent as in case of gaseous media. In fact the behavior of boron is more like that of a spark gap or arc than that of a solid conductor. There exists, for instance, a "break down" voltage in case of boron as in that of an air gap. Below the break-down voltage only very small current flows through a boron conductor, but once current is started (the air gap is "bridged" over) boron becomes a relatively good conductor.

The potential drop across a boron conductor falls first very rapidly as the current increases, but has a tendency to become constant and is usually approximately constant through quite a range of current. This potential-current curve is again very much like that of a discharge through gases.

The conception of a steadying resistance which has the function of preventing the conducting medium from running away is applicable as in the case of arcs.

Similarly to arcs it is impossible without special arrangements to run two or more boron conductors in parallel as one robs the others of current. Before an audience of chemists, these remarks on the electrical characteristics of boron will suffice. To the electrician there is almost an endless variety of surprising phenomena.

Speculation as to the cause of this abnormal behavior of boron might be of interest, but I would like to emphasize only the following point, namely, that the enormous drop in resistance here takes place in an elementary substance, the conductivity of which is wholly metallic. Whatever theory may be proposed for the explanation of the behavior of boron, this fact must be taken as fundamental.

In fact the abnormal value of the temperature coefficient (as well as the high specific resistance) are preculiarly properties of *pure boron*. When foreign elements are added to boron the conductivity increases (in analogy to ordinary solutions) and the temperature coefficient of resistance becomes reduced in value until with a sufficiently large percentage of the foreign element the characteristic properties are entirely obliterated.

Boron presents a very grateful case for exact measurements, as the drop in resistance occurs at ordinary temperatures, and it would be very desirable to determine the temperature resistance curve with great accuracy. The curve thus obtained would be of theoretical interest and could also be used as the basis of a very delicate method of temperature measurements.

It would also be interesting to determine the law connecting the resistance of boron and its negative coefficient of resistance with the amount of foreign elements, such as carbon, magnesium, etc., added. The effect of these additions is very large and I have determined it with only an accuracy sufficient for technical purposes, but it would be interesting to find out the exact relation between the concentration of the dissolved substances and the conductivity as well as the coefficient of resistance. I am inclined to believe from my experiments that the law is an exponential one.

And now that I am started in the direction of suggesting work for others, I am tempted to make a few more suggestions as to lines of work which I for the immediate present cannot take up.

It would be interesting to measure the heat conductivity of boron at different temperatures and compare it with the electrical conductivity. If the parallelism between these two which holds in the case of metals should hold approximately in the case of boron, then we should expect an enormous increase of the heat conductivity with the temperature.

It would also be interesting to study the specific heat of boron at different temperatures. Weber had at his disposal only impure boron powder and his results must, therefore, be unreliable.

No matter how interesting the investigations outlined would be, there are others of technical nature referring to applications of boron to electrical machinery, telegraphy, etc., which at present require all my attention and I am in the position of a man who is regretting that he cannot find more than 24 hours in a day.

I will now give a brief description of the methods used in the preparation of the element.

We are using two different methods. In the first we start with the reduction of boric anhydride by magnesium. This reaction was carried out by various chemists, beiginning with Berzelius, Wohler, etc., and recently by Moissan. I must refer for a description of the results obtained by myself to my article in the Transactions of the American Electrochemical Society, Vol. 16, 1909. It will suffice here to state that as a result of a thorough study of the reaction we made one step in advance of the previous workerswe found, that under certain conditions of temperature, proportion of reacting substances, etc., a perfectly homogeneous product is obtained which contains as chemical constituents only boron and oxygen, in proportions very nearly corresponding to the formula B<sub>6</sub>O. We called the substance "boron suboxide" without, however, desiring thereby to express a definite opinion as to its chemical nature. At the time this seemed to be an important improvement, as the elimination of magnesium from the final product seemed to be desirable. Further work has shown, however, that in the treatment to which the impure product has to be subjected in order to obtain pure boron it matters little whether the impurity is oxygen or magnesium or nitrogen, etc.<sup>1</sup> This treatment consists in heating the impure boron whether containing boron suboxide or magnesium boride or nitride to a temperature near the melting point of boron. At this temperature all these compounds dissociate, magnesium and nitrogen come off as such, oxygen as boric anhydride.

The main difficulty encountered in the development of this method was that of obtaining on a large scale high temperatures in the neighborhood of 2000° without the use of carbon in any form whatever, as boron has a great affinity for carbon and carbonaceous gases at that temperature.

The second method is based on the decomposition of boron chloride by hydrogen at good red heat. This reaction is carried out in two different ways: (I) in an arc discharge taking place between two boron or water-cooled copper electrodes in an atmosphere of boron chloride and hydrogen, and (2) by deposition on a hot graphite tube heated by current passing through it. The temperature and conditions can be so adjusted that practically no combination takes place between the boron and the graphite and very pure boron can be obtained. Boron chloride is best prepared by passing chlorine over boron carbide, which latter can be made in the electric furnace from boric anhydride and carbon.

I want to add a few words on the possible applications of boron in science and industry.

The first thing that suggests itself is its use for accurate measurement of temperatures. In view of the exceeding accuracy of electrical measurements

<sup>&</sup>lt;sup>1</sup> The preparation of boron suboxide free from other impurities proved, however, useful in connection with the solution of the problem of producing sound copper castings for the description of which the reader may be referred to the *Transactions of the American Electrochemical Society*, Vol. **18**, 1910.

and the rapid change of resistance of boron with the temperature an accuracy in temperature measurements could be obtained which would be greater than anything yet available, especially as the boron resister could be introduced in form of a very small filament, thus disturbing but very little the thermal conditions. Of course the boron thermometer would have to be calibrated and above red heat it would have to be enclosed in an envelope filled with inert gas.

Closely connected with this would be the use of boron as a temperature regulator in a way so obvious as to require no particular description.

Finally, in the same line of thought, boron could be used for measuring radiant energy. A rough surface of boron would probably behave very nearly like a black body, but if necessary a part or the whole of its surface could be covered with fine carbon. One way in which the measurement of radiant energy could be carried out would be by determining the radiant energy input as a difference between electrical energy inputs before and after the radiant energy falls on the boron piece. The temperature of the boron piece is recognized to be the same by the fact that its resistance is the same. This ought to be a very delicate zero method.

The industrial applications, however, are those which have first claim on my attention. Without going into details, I may say that these are based on the electrical characteristics of boron and on its mechanical properties.

The large drop of resistance with the temperature which transforms boron under certain conditions from a very poor conductor for normal voltages into a good conductor for abnormally high voltages is certain to make it valuable for protection of electrical circuits.

The potential current curve which shows a drop

in potential with increase in current makes possible the use of boron either alone or in connection with an ordinary resistance (so as to give a unit with a constant potential drop) for the purpose of regulating electrical machinery.

The influence of small amounts of other elements (carbon especially) on the specific resistance and temperature coefficient of boron, which was described above, gives a very delicate means for adjusting the boron resister to any prescribed requirements.

The valuable mechanical property of boron consists, of course, in the fact that it combines hardness with amorphous structure and in the course of our work we have already succeeded in producing meter jewels superior in quality to sapphire.

Will it be possible to approach the properties of diamond or perhaps by combining boron and carbon even exceed diamond in its hardness? I can only say that we are working on this problem.

In conclusion, I wish to attract your attention to the close interrelation of electrical and chemical methods in the work I have tried briefly to describe to you tonight. The investigation was started originally for the purpose of determining whether boron is a suitable element for incandescent lamp filaments. In the course of the investigation, in order to isolate the element, electrical methods had to be used to obtain the high temperatures needed. In fact, the isolation of the pure element is practically impossible without the use of electrical methods, and the failure of previous chemists can easily be explained by the fact that they did not possess the necessary electrical tools. Finally, after the chemical problem had been solved and the element isolated, its main applications have been found again in electrical machinery.

How many other interesting and useful applications may not yet be found in this vast field of electrochemistry in its broadest sense?

# ORIGINAL PAPERS.

## THE CHEMISTRY OF ANAESTHETICS, I: ETHYL ETHER.<sup>1</sup>

## By CHARLES BASKERVILLE AND W. A. HAMOR.

Experiences of expert anaesthetizers, not accounted for by idiosyncrasy, obtained in the use of ethyl ethers supplied by various manufacturers in numerous surgical cases,<sup>2</sup> furnished the motive for this investigation. The standards laid down by the various pharmacopoeias of the world are not uniform. In view of that fact alone, a thorough investigation seemed called for. We have not carried out any physiological experiments, however. Inquiries addressed to large consumers of the solvent in manufacturing processes adduced further need for satisfactory methods of determining the purity of ethyl ether and of detecting impurities introduced, or prov-

 $^1\,\mathrm{Read}$  before the New York Section of the American Chemical Society.

<sup>2</sup> Our attention was specifically directed to the question by Dr. J. T. Gwathmey, of New York City, a member of the Anaesthetic Committee of The American Medical Association.

ing their absence, if eliminated, in the modification of raw products used in its manufacture. The presence of small amounts of substances has oftentimes been the cause of a chemical reaction proceeding in a particular direction by virtue of a "catalytic action." So the presence of even traces of certain substances, as peroxidized compounds, aldehyde, etc., may have caused some reactions to be incorrectly explained, or to follow an unusual, or unaccountedfor, route.

For convenience, the investigation has been subdivided under the following heads:

I. (a) The Tests for Odor of Ethyl Ether; (b) A Study of its Physical Properties; (1) Density, and (2) Boiling Point.

2. Tests for the (a) Residue; (b) Acidity; (c) Sulphur and Sulphur Compounds of Ethyl Ether.

3. (a) Detection of Water and Ethyl Alcohol in Ethyl Ether; (b) Dehydrat on of Ethyl Ether; (c) Tests for