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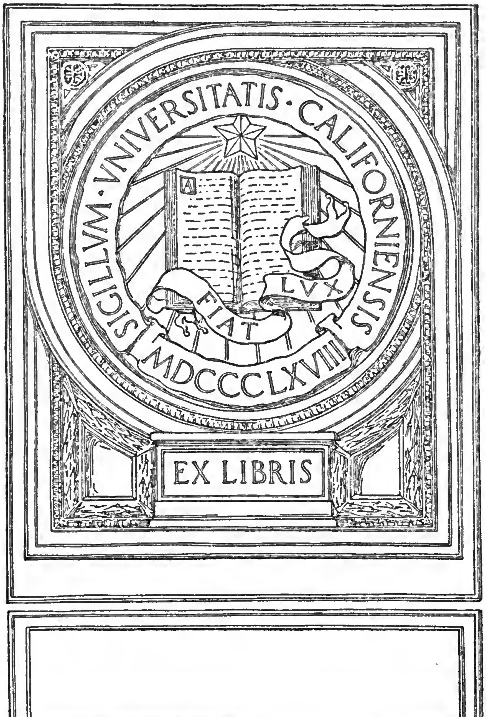
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The Electric Furnace

The Electric Furnace

by

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PREFACE TO THE ENGLISH EDITION

To understand fully the importance of this work, it is necessary to go back to the time of our first experiments with the electric furnace, that is, to the latter part of 1892. At that time, acetylene was still an uncommon gas, which could only be obtained pure with great difficulty. Crystallized calcium carbide was unknown, as were the richer alloys of chromium, manganese, vanadium, and titanium with iron. Finally, a large number of refractory metals, and more especially chromium and manganese, were real museum curiosities, and their properties in the pure state were unknown.

This was not due to the lack of experiments along these lines. Following the important discovery and application of the electric arc by Sir Humphry Davy, came the work of Despretz, the interesting furnace of Siemens and Huntington, in which, however, they were unable to melt any considerable amount of tungsten, and the commercial methods of Cowles, who used the electric arc to prepare alloys of aluminium and copper.

Since we began our work on this subject, the group of metallic carbides, then almost unknown, has received many additions, as have also the groups of the silicides and borides. Further, among the refractory metals, for which we have described an easy method of preparation, we may mention uranium, whose interesting properties have attracted the attention of many physicists.

The most important result of our work with the electric furnace has been to obtain temperatures of 3,500–4,000° C., and to show that under these conditions all the known elements and compounds may be vaporized. Those bodies which remain undecomposed by heat are all liquefied and volatilized. Further, at these high temperatures, chemistry assumes a special aspect, and series of new compounds are formed, some of which we have studied.

It is interesting to note that while we were extending the province of chemistry at high temperatures, the study of low temperatures was being carried to its furthest limits by Cailletet, Olzweski, and Dewar. So that the chemist has at his disposal to-day a scale of temperature ranging from $-257°$ to $+4,000°$ C. But Sir James Dewar, who has been able to liquefy and solidify hydrogen in considerable quantities, has been more fortunate than ourselves in one respect; he has determined accurately the temperatures in the neighbourhood of the absolute zero by gas and electrical resistance thermometers.

These new discoveries enable chemists to undertake researches which were formerly impossible; old methods have been modified, and inorganic chemistry, whose field has been thus extended, enters on a new era of development in which phenomena may be studied under all conditions of temperature.

Many chemists and manufacturers have repeated our experiments. Some of these have found it difficult to obtain our results, and the opinion has been expressed that success in this work requires a special 'modus faciendi.' In reality, the 'modus faciendi' consists in repeating the same experiment many times over till success is assured.

We may remark, however, that, since it is impossible to measure these very high temperatures, it is of vital importance to follow exactly the working conditions we have laid down as to the size of the furnace cavity, the diameter of the electrodes, the strength of the current, and the duration of the experiment. If these precautions be taken, the experiment may be carried out successfully, although the exact temperature may not be known. Finally, the investigation of a reaction-product requires a large number of delicate tests and analyses ; the classes of compounds formed at these temperatures—oxides, double oxides, carbides, and silicides—must be studied beforehand, and it must not be forgotten that, in all new work, technical skill is only attained after much practice.

I have in conclusion a pleasant duty to discharge : to thank Dr. de Mouilpied, who has kindly undertaken the translation of this volume, and Mr. Arnold, who has brought it out with so much care. Their united efforts will, I hope, cause this edition to be as successful as its French and German predecessors have been.

HENRI MOISSAN.

PARIS,
July, 1904.

TRANSLATOR'S NOTE

The brilliant researches of Professor Henri Moissan are familiar to all chemists. It was thought that many would be glad to have at hand for reference an English version of *Le Four Électrique*, and this belief has led to the appearance of this edition. It incorporates the new matter which was added to the German translation, and Professor Moissan has been kind enough to add a new chapter embodying the most recent work he and his pupils have carried out. I desire to express to him here my best thanks for his kindness in this matter.

My thanks are also due to my friend, Mr. R. S. Hutton, for his invaluable help and suggestions, and to my colleague, Mr. B. C. Burt, who assisted me during part of the work of translation.

A. T. de Mouilpied.

The University of Liverpool,
July, 1904.

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Researches on the Different Varieties of Carbon

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CHAPTER V

ABBREVIATIONS

Ann. de Ch. et de Ph. = *Annales de Chimie et de Physique.*
Ber.=*Berichte der deutschen chemischen Gesellschaft.*
C. R. = *Comptes rendus de l'Académie des Sciences de Paris.*
Proc. R. S.=*Proceedings of the Royal Society.*
Proc. R. S. E.=*Proceedings of the Royal Society of Edinburgh.*

INTRODUCTION

This book is divided into five chapters. In the first are described the different types of electric furnaces used in these researches, and their application to the study of the fusion and the volatilization of a number of refractory bodies.

The second chapter contains a study of the three varieties of carbon: amorphous carbon, graphite, and the diamond.

Chapter III deals with the preparation of some elements in the electric furnace. The elements investigated were Chromium, Manganese, Molybdenum, Tungsten, Uranium, Vanadium, Zirconium, Titanium, Silicon, and Aluminium.

Chapter IV contains an account of the researches carried out on some new series of binary compounds—the carbides, the silicides, and the borides. The preparation, properties, and analyses of hitherto unknown compounds are given. More especially, the preparation of calcium carbide has been subjected to fresh investigation, and this is dealt with in some detail.

The last chapter contains an account of recent work.

THE ELECTRIC FURNACE

CHAPTER I

DESCRIPTION OF DIFFERENT TYPES OF ELECTRIC FURNACE

The highest temperatures reached in fuel furnaces for technical purposes lie between 1,700° and 1,800° C. In laboratory furnaces, even with the use of retort carbon, the temperatures attained do not usually exceed 1,500° to 1,600° C.

Already, under these conditions, research becomes difficult, and scientific experiments reach their limit at the melting-point of fire-clay and porcelain.

The oxyhydrogen blowpipe, discovered by H. Sainte-Claire Deville and Debray, has been of great service to chemistry. It has not only rendered it possible to melt and to refine platinum with ease and to form new alloys, but certain questions of mineral chemistry have been extended and generalized.

A temperature of 2,000° C. may be reached by means of this apparatus when fed with coal gas and oxygen. According to Violle, platinum melts at 1,775° C. Quicklime was the only material found by Deville and Debray capable of withstanding these high temperatures. In my researches on the different forms of carbon, I desired to submit metals to a temperature above 2,000° C., and I then thought of making use of the temperature of the electric arc.

Theoretically, the problem to be solved was very simple. It consisted in placing a very powerful arc in a cavity of minimum size and at a certain distance above the substance to be heated. Difficulties arose when the attempt was made to meet these conditions in a type of furnace easy to handle and not too costly.

The forms described in this chapter are the first in which the heating action of the current has been clearly separated from the electrolytic action.

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Earlier attempts had been made to utilize the great heat of the electric arc.

More especially should be mentioned the work of Despretz, bearing the title of 'The fusion and volatilization of some refractory bodies. Note on some experiments carried out with the triple aid of the voltaic pile, the sun, and the blowpipe [1].'

In later work Despretz made special use of the heat produced by the arc from a powerful pile [2]. We shall have occasion to mention his results in succeeding chapters.

In the investigations of Despretz and in other similar researches, the reacting bodies were placed within the arc itself. Under these conditions the vapour of carbon and the impurities of the electrodes, which are usually far from negligible, take part in the reaction and greatly complicate the conditions of the experiment [3]. The same objection may be raised to the numerous forms of technical electric furnaces, among others those devised by Siemens and Huntington, Cowles, Grabau, and Acheson.

In the first of these models, the crucible formed one of the electrodes, and the current passed through the mass to be fused in such a way that it was difficult to differentiate between the part due to the electrolytic action of the current and that played by the temperature of the arc.

Further, Siemens and Huntington used a crucible made of carbon. The latter being a good conductor much heat was lost by radiation. For this reason Siemens had much difficulty in melting tungsten, and even then succeeded with but small quantities [4]. It is true that he mentions, in one of his English patents, the possibility of using a covering of lime, but he does not seem to have made many experiments on the point, or else he would have been struck by the difference in the results.

Nevertheless, it must not be forgotten that we owe to Siemens and Huntington the first practical electric furnace.

Cowles's furnace answers very well for the chemical work for

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[1] *C. R.*, xxviii. 755 (1849).

[2] *C. R.*, xxix. 48, 545, 709 (1849).

[3] The action of the electrode impurities is all the more important because the amount of substance used is small and the period of reaction very short.

[4] *Brit. Assoc. Reports*, Southampton, 1882, 496; *Ann. de Ch. et de Ph.*, sér. 5, xxx. 465 (1883).

which it was designed, but the objections raised against the model of Siemens and Huntington apply here also.

In the furnace designed by Acheson a carbon core, placed in the middle of the reaction mixture, acts as a conductor and divides the current by forming at the outset a large number of smaller arcs of variable intensity. A simple arc is replaced by a resistance whose heating power does not reach a constant point till some five hours after the beginning of the experiment.

The different forms used for technical purposes were bulky, and not readily adaptable to the many laboratory requirements. For the most part they could not be used with currents of different intensities.

I wished, on the contrary, to find a form of furnace which could lend itself to general and methodical researches.

In the forms to be described, the arc is very regular during the whole of the experiment and it may be easily handled.

My electric furnace is not designed for industrial purposes, it is an apparatus for research. A profit and loss account should therefore not be based on the results to which it may lead. The manufacturer always desires to generate his power at a low price, and to obtain a large yield.

I had not to take these considerations into account. I aimed at enclosing in a minimum cavity the most powerful arc possible, in order to obtain a maximum temperature. The following comparison may help to make my meaning clear. In order to fill a leaking tank the supply of water must be largely in excess of the amount lost by leakage. Further, that the leakage may be reduced to a minimum, the material of the furnace must be as bad a conductor as possible. Quicklime fulfils this condition. In proof of this I may quote the following experiment:—The dome of the furnace consists of a slab of quicklime some 3 cm. thick, under which the arc plays for ten minutes. The covering, whose external temperature has not changed, may then be removed by hand, although the internal surface consists of molten lime over an area of several square decimeters. The latter substance yields a light whose intensity is such that the eye cannot bear it. This tremendous heat is thus completely kept in by a layer of lime 3 cm. thick.

The form of furnace used in the earlier experiments on the preparation of the diamond underwent various modifications as the work grew. In this chapter are described various simple and practical forms which are subdivided as follows:—

1. Electric furnace made of quicklime.
2. Electric furnace of limestone for crucibles.
3. Electric furnace for tubes.
4. Continuous electric furnace.
5. Multi-arc electric furnace.

Our first experiments, relative to the method of heating with the electric arc, were carried out by means of a 4 H.P. gas engine. The small dynamo used at the time was of the Gramme type, and yielded a current of 35 to 40 amperes at 55 volts.

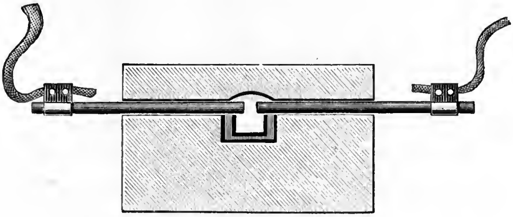

FIG. 1.—Diagram of electric furnace.

When a more powerful current was required we made use of the facilities afforded at the Conservatoire des Arts et Métiers, kindly placed at our disposal by Colonel Laussedat.

Here we were able to use for several years a 45 H.P. steam engine which worked an Edison dynamo capable of yielding a current of 440 amperes at 80 volts.

When we required still more powerful currents, we had recourse to technical plant, and M. Fontaine of the 'Société Gramme' was kind enough to lend us one of his dynamos worked by a 100 H.P. engine. Later, the Eastern Railway Company placed a current produced by 60 to 100 H.P. at our disposal. Finally, as we desired to prosecute our work still further, M. Meyer, director of the 'Société Edison,' graciously offered us the use of the central generating station of the Avenue Trudaine, where a force of 2,000 H.P. is nightly at work.

In many experiments we have used 150 and even 300 H.P., but having regard to our scientific aim it seemed unnecessary to go beyond this.

It is a pleasant duty for me to offer my sincere thanks to those who have helped me in this way, and who have thus become my fellow workers.

Quicklime electric furnace.

Our first model, shown to the Académie des Sciences in December, 1892, was made of quicklime[1]. It consisted of two slabs of lime carefully cut and superposed.

The lower slab has a long groove in which rest the electrodes, and in the middle is a small cavity which acts as a crucible (Fig. 1). The depth of the latter may vary and contains a layer some centimeters thick of the substance to be heated.

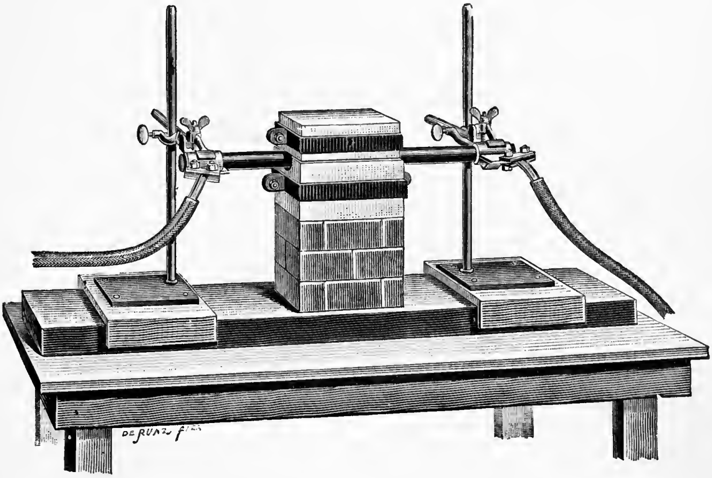

Fig. 2.—Electric furnace for currents of 70 volts and 400 amperes.

Or, one may place in the cavity a small carbon crucible holding the substance to be investigated.

The upper slab is slightly scooped out just above the arc. The intense heat of the current soon melts the lime and gives it a polished appearance, so that a small dome is obtained which reflects all the heat on to the cavity or on to the crucible. The electrodes are easily rendered movable by means of two adjustable supports, or, better, by using two

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[1] *C. R.*, cxv. 1031 (1892).

sliders which rest on a bed-plate (Fig. 2). The difference between this and earlier models is that the substance to be heated does not come into direct contact with the electric arc, that is, with the vapour of carbon.

This form is a reverberatory electric furnace with movable electrodes. The last feature is important, for the freedom of motion enables one to set the arc going with ease, and to lengthen or shorten it at will; in short, it simplifies greatly the carrying out of the experiments.

Arrangement of the furnace.—In our first experiments, as already observed, we used a small Gramme dynamo worked by a 4 H.P. gas engine. The current usually obtained was one of 35 to 40 amperes at 55 volts. Under these conditions the lower lime slab was 16 to 18 cm. long by 15 cm. broad and 8 cm. thick. The upper slab, which served as a covering, had the same area, and a thickness of 5 to 6 cm. This size may also be used for currents of 100 to 125 amperes at 50 to 60 volts.

For more powerful currents it is advisable to increase the three dimensions by 2 to 3 cm. With a length of 22 to 25 cm. one may use currents up to 450 amperes at 75 volts.

The lime used was slightly hydraulic, and belonged to the 'green stratum' of the Paris basin. It may be cut and shaped with ease. Deville and Debray highly recommended this variety for their small fusions of platinum.

Electrodes.—The electrodes were made of cylinders of carbon, as free from mineral matter as possible; we had at first some difficulty in obtaining them commercially in a state of sufficient purity. These electrodes must be made of retort carbon taken from the dome of the retort.

The powder is treated with acids to free it from the contained iron; it is then washed, calcined, and finally rendered coherent by means of pitch. The cylinders are formed by means of pressure, which must be very high and regular; finally they are carefully dried and calcined at a high temperature[1].

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[1] At the outset of this work I used electrodes of retort carbon turned on a lathe. Under the action of the current the extremities of these electrodes assume a fan-like shape at the moment of the conversion of the carbon into graphite. Despretz had already made this observation. *C. R.*, xxix. 716 (1849).

The presence of boric acid and silicates must be tested for, as these are sometimes used to facilitate the preparation of the carbon. We refused any carbon which contained these substances, or any which yielded more than one per cent. of ash. The electrodes used for the smaller lime furnaces were 20 cm. long and 12 mm. in diameter.

For currents of 120 amperes at 50 volts we used rods 40 cm. long and 16 to 18 mm. thick. With a 40 to 45 H.P. machine the electrodes were 40 cm. long and 27 mm. thick. The ends of the electrodes between which the arc plays were given a sharply-pointed conical form. This is important, especially for weak currents. Otherwise it is sometimes very difficult to restart the arc should it have gone out at the beginning of the experiment.

With currents of 350 amperes at 68 volts, one only of the electrodes was pointed, the other ending in a flat surface. In any case, difficulties cease as soon as the furnace is warm and filled with conducting vapours, for then the arc can be started with the greatest ease. The cables which conduct the current are connected to the electrodes by copper sheaths which are bolted down. This device has long been used technically for powerful currents.

Crucibles.—In the first part of our work we used crucibles of retort carbon made in one piece and lathe-turned. They are cylindrical, and are grooved in two places at the ends of the same diameter in such a manner that the electrodes pass through with ease.

With a power of 4 to 6 H.P. we used crucibles of 3 cm. external diameter and 2 cm. internal diameter. They were 4 cm. high and the groove was 1·5 cm. deep.

These crucibles of retort carbon have the drawback of increasing considerably in volume as they undergo transformation into graphite under the heating influence of the arc. At our request, several manufacturers have made crucibles for us of one piece, by compression in a mould, and these preserve their shape at the highest temperatures. At the end of the experiment they are found to consist of a felting of graphite lamellae possessing a sufficient rigidity.

It is a good thing to have an empty space around the crucible so that the heat reflected from the dome may surround it completely. One must also bear in mind that lime is easily reduced by carbon at these high temperatures to form a carbide of calcium[1]. So that when a crucible is to be heated in this lime furnace, a layer of magnesia must be spread in the cavity of the furnace. For magnesia is the only oxide we have met which is not reduced by carbon. When the experiment is prolonged, magnesia may melt and combine with the lime which is already molten in the furnace; it may even be volatilized, but no carbide is formed.

Description of an experiment.—Let us take as an example the experiment which demonstrates the volatilization of quicklime.

No crucible is required in this case, as we are operating on the substance of the furnace itself. A small cavity from 2 to 3 cm. deep is first cut out of the lower block. The electrodes are then placed in the channels and clamped to the sliding stands (see Fig. 2), and then brought to within 2 or 3 cm. of each other, so that one of them is exactly above the middle of the cavity. The dynamo is then switched on to the circuit, and by slowly bringing up the second electrode to the first, contact is established and the arc is started. One notices at once a very penetrating smell of hydrocyanic acid. The small amount of water contained in the electrodes reacts with the carbon to form acetylene. This gas, in presence of the nitrogen contained in the furnace at the outset and under the powerful agency of the arc, brings about the elegant synthesis of hydrocyanic acid first carried out by Berthelot.

The light emitted by the furnace, coloured by the flame of cyanogen, has at first a fine purple tint which soon disappears. At the outset one must be careful not to separate the electrodes too far apart, for while the furnace is still cold the arc easily goes out. A little later this is no longer the case; the length of the arc may then be increased. At first the arc, even with powerful currents, is not 1 cm. long; but at the end of the experiment it is usually from 2 to 2·5 cm. long. If the furnace be filled with a good conducting metallic vapour (e. g. aluminium) the electrodes may be 5 to 6 cm. apart. The length of the arc will thus be regulated according to the readings of the voltmeter and the ammeter, so that one may always have an approximately constant resistance, together with a normal working of the dynamo. With a current of 360

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[1] Moissan, 'Preparation of a crystalline carbide of calcium,' *C. R.*, cxviii. 501 (1894).

amperes at 70 volts, after three or four minutes, the electrodes soon begin to glow; then bright flames from 40 to 50 cm. long shoot out from the openings through which the electrodes pass, on either side of the furnace (Fig. 3). Above the flames rise clouds of white vapour; this is produced by the volatilization of the lime, and it may be partially condensed with ease on a cold surface. This vapour permeates the atmosphere and may remain in suspension for hours.

With a current of 400 amperes at 80 volts, the experiment is over in five to six minutes; under the action of a current of 800 amperes at 110 volts, over 100 grms. of lime may be volatilized in five minutes.

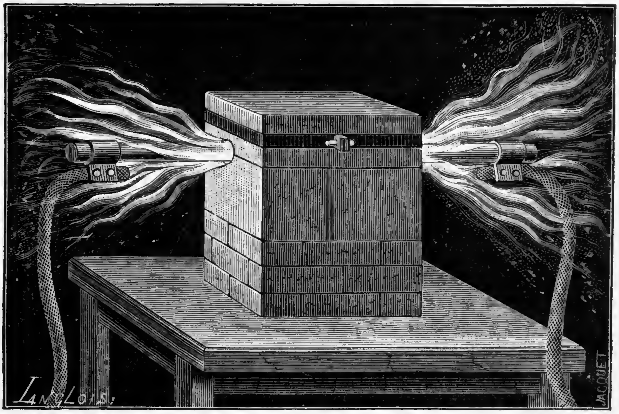

Fig. 3.—Electric furnace at work.

At the beginning of the heating the arc fluctuates to some extent and there is a roaring noise, but in a short time the metallic vapours increase the conductivity, and the current passes regularly and noiselessly. The heat and light inside the furnace then become very intense. When the experiment is finished the upper lime block is removed, and one observes at once that the part exposed to the heating action of the arc is completely fused. With a power of 50 to 100 H.P. there are formed on the lid regular stalactites of molten lime, which have slowly run down from the dome and have solidified at the end of the experiment; when cold, they have the appearance of wax.

The conductivity of quicklime is so small that, as we have already remarked, this upturned lime block may be held in the hand while the lower surface has been brought to such a high temperature that it has been melted, and that it still gives off by radiation an enormous amount of heat and light. The low conductivity of lime has been entirely favourable to our experiments; it prevents the loss of the heat which we attempt to store in the least possible space. When we made use of a furnace consisting entirely of magnesia, the latter being a far better conductor of heat than lime, the results were less satisfactory. A similarly shaped furnace built of carbon led to an enormous loss of heat, although the electrodes were insulated in tubes made of magnesia.

After the experiment the positive carbon was but little worn, but the negative carbon was more or less eroded. The ends of the electrodes for some 8 to 10 cm. are entirely converted into graphite.

With high-tension currents it is advisable to take certain precautions, and to insulate the conductors carefully; moreover in all cases care should be taken to securely fix the cables and clamp the electrodes, so as to avoid any heating due to bad contacts.

'Since the tensions employed are relatively low, any shocks experienced when the hands come in contact with the supports need not be feared.'

In any case, even when working with currents of 30 amperes at 50 volts, such as we used at the outset of this work, the face should not be exposed to the prolonged action of the electric light, and the eyes must always be protected by means of dark-coloured spectacles. Cases of 'arc blindness' were frequent at first, and the irritation of the eyes produced by the arc may lead to very painful congestions. The latter effect is produced more especially in the experiments with a small power, for, the heat being less, one strives to see what is happening while the furnace is at work.

In all our experiments we have made use of continuous currents exclusively.

Finally, there is one point which cannot be emphasized too strongly for the sake of workers or manufacturers who may repeat these experiments. When a limestone furnace is used a large amount of carbon dioxide is formed. This compound in contact with red-hot electrodes and vaporized carbon produces a constant stream of carbon monoxide. The carbon electrodes also produce a small amount. This gas undergoes but an incomplete combustion, and if the greatest precautions for ventilating the working room be not taken, those operating soon show symptoms of carbon monoxide poisoning. Racking headaches, nausea, and a general weariness are first experienced. Under these conditions, it is absolutely necessary to cease experimenting for some weeks, for the poisonous effects of carbon monoxide are cumulative and its evolution is never completely prevented.

This first model of the electric furnace enabled us to study the crystallization of metallic oxides, to prepare intumescent graphite, to demonstrate the easy volatilization of platinum and the solubility of carbon in silicon, in platinum, and in a great number of metals.

The difficulty of finding, especially in winter, blocks of lime of some size, without fissures and homogeneous, led us fairly soon to substitute limestone or building stone for quicklime. However, I still use the earlier model when I wish to avoid a large evolution of carbon dioxide. In refining certain metals, chromium for example, we still use this furnace.

Limestone electric furnace for crucibles.

Quicklime may be replaced by a block of any calcareous stone containing but little silicon, as was shown by Deville and Debray in their work on the fusion of platinum.

This limestone, which should be fine grained, has two advantages; first, it is harder and, secondly, it may be obtained easily in as large blocks as one may desire.

Arrangement of the furnace.—The stone is given the form of a regular parallelepiped, whose size varies with the intensity of the current.

With a power of 4 H.P. the furnace consists of two blocks, the lower of which is 10 cm. high, 18 cm. long, and 15 cm. wide. The upper has the same area and a thickness of 8 to 10 cm.

For 45 H.P., the measurements are as follows:—height of lower block 15 cm., width 20 cm., length 30 cm.; upper block, height 11 cm.

With 100 H.P., height of lower block 20 cm., length 35 cm., width 30 cm.; upper block, height 15 cm. A furnace of this type, if well looked after, may serve easily for seven or eight consecutive experiments.

If a greater power be used, the shape of the furnace may be adapted to the particular experiment, and as under these conditions the lime becomes volatile, it is advisable to construct the interior of the furnace of alternate slabs of magnesia and carbon. This model we shall describe later.

It is very important to dry the blocks of stone which form the furnace. This is done by keeping them for twelve to twenty-four hours on top of a steam boiler or under the hearth of an engine fire or of a stove.

If the block of stone be quite dry, it but rarely happens that it cracks under the action of the heat of the electric arc. To prevent this accident we generally fix a metallic band around the furnace and the lid, taking care to place it sufficiently far from the electrodes to render short circuiting impossible. The lower parallelepiped may also be placed in a box of sheet iron of chosen dimensions. Previous to the drying, a cylindrical cavity is cut out of the middle of the block, of somewhat greater dimensions than the crucible it is to hold. Two channels allow the electrodes to be moved, their size depending on the diameter of the latter.

The crucible should always be placed on a bed of magnesia, in order to avoid the formation of calcium carbide, which would soon render it useless. It is also advisable to have a space of 1 to 2 cm. between the crucible and the cylindrical wall of the furnace, so that the heat may have free access all round.

When it is desired to condense the vapours of substances which are only volatilized with difficulty at high temperatures, one may use a metal tube cooled interiorly by a current of water. This device enabled Deville to obtain some interesting results in his splendid researches on dissociation.

In these experiments, we made use of a copper U tube some 15 mm. in diameter, through which passed a stream of water under one atmosphere pressure. The bent part of the U tube was introduced into the furnace and placed 2 cm. below the arc and above the crucible containing the substance to be volatilized; further, a sheet of asbestos placed over the opening which allowed the cold tube to pass, allowed of the condensation of the metallic vapours arising in large quantities from the furnace. The temperature of the water passing through the copper tube does not rise more than 2 or 3 degrees.

Electrodes.—The diameter of the electrodes varies with the intensity of the current, as already noticed in connexion with the quicklime furnace. When more than 100 H.P. are used, the carbon cylinders are 50 cm. long and 4 cm. in diameter. For a power of 200 to 300 H.P. we have used electrodes 5 cm. in diameter.

In the latter cases, the connecting up of the flexible cables, which lead the current to the electrodes, presents some slight difficulty. Any but a perfect contact is to be carefully avoided, or an arc is formed of sufficient intensity to melt the clamp and the ends of the cable. To avoid these accidents we have made use of copper clamps as seen in Fig. 4. Contact is made perfect by means of copper gauze wound tightly round the end of the electrode, passing around it several times and held firmly by the clamp.

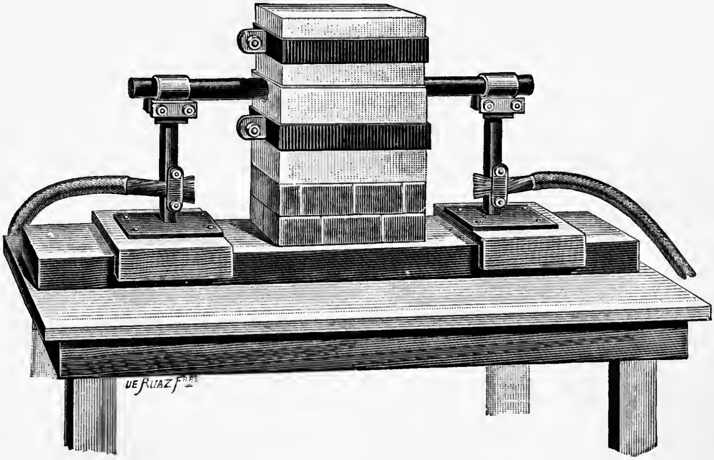

Fig. 4.—Electric furnace, with supports, for currents of 110 volts and 1,000 amperes.

Crucibles.—We have already indicated the precautions to be taken in the manufacture of crucibles.

For a power of 45 H.P. the crucibles are 6 cm. in diameter and have a 3 cm. groove.

With power up to 800 amperes at 110 volts, the crucibles have an inside diameter of 7·5 cm., an outside diameter of 9 cm., and an exterior height of 10 cm. without groove. In these crucibles one may prepare in five or six minutes from 300 to 400 grms. of molten uranium or tungsten.

We have also made use of magnesia crucibles of the same dimensions; this magnesia was prepared in a special manner, as we shall describe below.

Arrangement of alternate layers of carbon and magnesia.—With currents of 1,200 to 2,000 amperes at 100 volts, the lime furnaces, if the cavity be small, are soon useless. By placing the intense arc obtained from such a current in a limestone cavity of 10 cm. diameter we obtained the following results: fusion of the lime, which flows like water; volatilization of the lime, which in a few moments causes clouds of smoke; a violent projection of the vapours through the electrode openings; continual decrepitation produced by the fall of small fragments of limestone into the mass and consequent immediate dissociation; spitting out of molten lime, and finally a lifting up of the lid under the action of the gases and the superheated vapours. Under these conditions, the experiment is not easy to control. If the cavity of the furnace be increased the arc may then yield better results.

When these high powers are to be used, it is advisable to hollow out a rectangular cavity of sufficient size in the middle of the block, and to place in it alternate plates, 1 cm. thick, of magnesia and carbon. These plates, which are four in number, are so arranged that the magnesia is always in contact with the quicklime, and the carbon plate on the inside of the furnace. Magnesia, not being reduced by carbon, could only disappear by volatilization, whereas at these high temperatures, lime in contact with carbon would melt and readily form a liquid calcium carbide. The cover of the cavity of the furnace may also be made from plates of magnesia and carbon; but a limestone cover provided with an ellipsoidal cavity 3 to 4 cms. deep was generally found sufficient.

A furnace arranged in this manner may work with ease for several hours and renders possible the carrying out of lengthy experiments.

Preparation of magnesia.—The magnesia used in these experiments was prepared in the manner described by Schlœsing[1]. It is necessary, as a matter of fact, to remove the small quantity of impurities which may be in the oxide, as these lower its melting-point greatly. To this end, hydrated

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[1] *C. R.*, ci. 131 (1885).

magnesium carbonate is calcined for several hours in a Perrot furnace. The magnesia so obtained is finely powdered and digested with a dilute solution of ammonium carbonate, then washed freely with water and calcined at the highest temperature obtainable in a good blast furnace. By the addition of water, a thick paste is obtained which is formed into small plates by compression in wooden moulds. These plates are allowed to dry slowly and are finally baked in a muffle[1].

Schlœsing demonstrated that this magnesia undergoes no shrinkage in a blast furnace and that it is unattacked by atmospheric agencies. It need scarcely be said that it does shrink at the temperature of the electrical furnace. But under these new conditions, although remaining quite light, it becomes crystalline and its hardness increases.

It has already been shown by Ditte[2] that magnesia easily undergoes polymerization under the influence of heat and that its density may rise from 3·193 to 3·569. The magnesia plates of the electrical furnace acquire a density of 3·589, and after melting this rises to 3·654. We have shown previously that quicklime melted or crystallized in the electrical furnace has the same density as when prepared at 800° C. The fact that magnesia cannot be reduced is perhaps connected with its power of polymerization.

The form of electrical furnace built in calcareous stone has enabled us to perform our experiments far more quickly. It is thanks to this apparatus that I have been able to prepare the black diamond, the transparent and crystallized diamond, and to carry out the preparation, kilograms at a time, and the refining of chromium, uranium, tungsten, molybdenum, zirconium, and vanadium.

By its means I have been able to bring about the distillation and gasification of silica and zirconia, to demonstrate the volatilization, at the temperature of the arc, of copper, aluminium, gold, iron, uranium, silicon, and carbon. Further, in this form of furnace I have prepared with ease carbon silicide, carbon boride, silicon boride, the carbides of calcium, barium, and strontium in a crystalline state, aluminium carbide, the different crystalline borides and silicides, &c.

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[1] This magnesia, to which a little water has been added, yields, by compression in a hydraulic press, a very hard substance which scratches marble.

[2] *C. R.*, lxxiii. 111, 191, 270 (1871).

Electric furnace for tubes.

The arrangement of the furnace for crucibles, which we have just described, allows one to bring fairly large quantities of material to a high temperature, but with this type of furnace one cannot eliminate the action of the gases which fill the apparatus. During the whole of the experiment, the carbon dioxide resulting from the decomposition of the limestone is converted largely into carbon monoxide. The water, which is always present in the stone, however carefully it may be dried, yields a continual supply of a mixture of hydrogen and carbon monoxide.

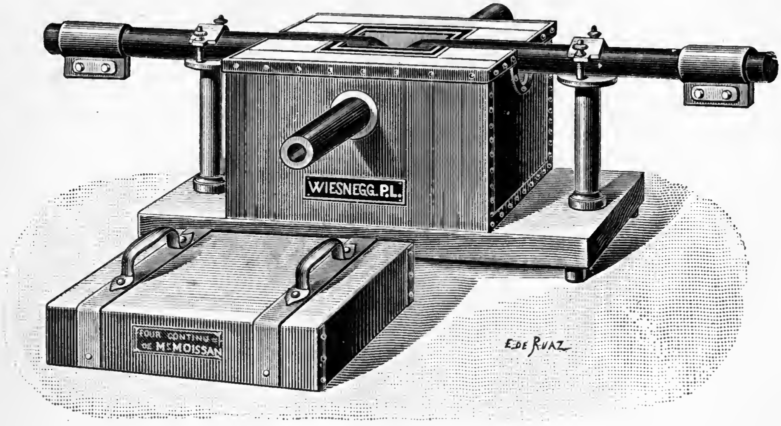

Fig. 5.—Furnace with horizontal tube.

In order to avoid the action of these gases in certain reactions, we have modified our electric furnace as follows: A block of fine-grained stone (as free as possible from silica) is cut into the form of a parallelepiped 15 cm. high, 30 cm. long, and 25 cm. wide. The walls of the internal cavity are lined with alternate plates of magnesia and carbon, as already described, and the cover consists of a block of the same stone. Finally, a carbon tube passes through the furnace and the side plates and lies at right angles to the electrodes. The internal diameter of the tube may vary from 5 to 40 mm., and it is made to rest 1 cm. below the arc and 1 cm. above the floor of the cavity.

So arranged (Fig. 5), the apparatus may be heated for several hours by means of currents which have varied from 300 amperes at 70 volts to 1,000 amperes at 60 volts. The part of the carbon tube which is exposed to this high temperature is entirely converted into graphite. But if the tube consists of pure carbon, and is not in contact with the limestone[1], and if it has been prepared with care and under strong pressure, the graphite forms a regular felting, and the diameter of the tube is not changed perceptibly.

In other experiments we have placed the tube above the arc, but a lower temperature is reached under these conditions.

If it be desired to avoid the direct action of carbon on the substances used, an internal or external lining of magnesia may be given to the tube. It is true that the vaporization of this oxide limits the experiment, but before this temperature is reached there are of course a great number of interesting points to be worked out.

No substance other than carbon can be used for the horizontal tube. All other substances, whether found native or prepared in the laboratory, melt and are volatilized before carbon.

These carbon tubes have the serious drawback of being rather porous; we have attempted to overcome this as far as possible by using double tubes or tubes lined with magnesia. All attempts to melt on to their surface carbon silicide, or boride, or other carbides, failed; nevertheless, we are continuing this work, for it would be highly useful to be able to prepare perfectly non-porous tubes for the delicate researches which still have to be carried out at high temperatures.

These carbon tubes were closed by stoppers of moulded magnesia or of cut pumice-stone. These stoppers were perforated along their axes to allow the passage of glass tubes. These different pieces fitted easily into one another with a minimum of friction, and the whole was luted by means of a cement of magnesia and alkaline silicate. Carbon tubes 4 cm. in diameter and 50 cm. long were used when the substances to be heated had to be placed in a boat.

Under these conditions we have been able to melt and to volatilize with ease various compounds in a stream of nitrogen or of hydrogen. The gaseous currents used in these experiments had, however, to be very rapid, and the gases dried with the greatest care.

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[1] The electrodes and the tube are separated from the limestone by a thin layer of magnesia.

This type of furnace has enabled us also to approach the study of certain gaseous reactions at the high temperature of the electric arc. We hope to publish later the results of the delicate experiments we are carrying out in this field.

By means of this electric furnace for tubes we have prepared crystalline carbon silicide, pure and colourless, by the direct union of the vapours of carbon and silicon. We have used this apparatus in our work on the crystalline borides of iron, cobalt, and nickel; for the preparation of zirconium, of pure aluminium carbide, of titanium carbide, of the carbides of the cerite metals, and for the study of different nitrides. It may be used with ease whenever it is desired to prepare a compound in a given gaseous atmosphere.

Continuous electric furnace.

The apparatus just described has a horizontal carbon tube; if the latter be inclined at 30 degrees, the furnace is changed into an apparatus for the continuous preparation of refractory metals, into the middle of which one may introduce the mixture of oxide to be reduced and of carbon, while the molten metal easily flows down the slope.

In this continuous furnace, as also in the tube furnace, the electrolytic phenomena are completely separated from the heat phenomena.

With a current of 600 amperes at 60 volts one may easily obtain in an hour a molten mass of chromium weighing some 2 kilos. The metal collects in a cavity in the calcareous stone, lined internally with chromium sesquioxide. The metal remains liquid for some time, gives up all dissolved gases, and is thus partially refined. In this way one obtains after solidification a mass of very hard, white metal, fine-grained and susceptible of a high polish.

Furnace with several arcs.

Two clearly defined cases may present themselves in researches undertaken with the electric furnace:

1. If a very high temperature be desired, a powerful arc is placed in the smallest cavity possible. This is done in the limestone and crucible models we have described. Under these conditions the heat acts quickly on the walls of the furnace; the lime or the magnesia melts and is rapidly volatilized.

With currents of 1,200 amperes at 110 volts the apparatus is rendered useless in ten to fifteen minutes.

2. On the other hand, should it be required to prepare a considerable amount of a metal obtained at a high temperature, the cavity must be enlarged and the heat of the furnace used up as produced by giving it some continuous work to do. In this case one must use the inclined tube furnace or the furnace provided with a hearth.

In most cases it is possible to make a hearth of material sufficiently refractory to bear the desired metal in the liquid state, and in this case, to give a uniform heating over a larger surface, the current is divided between several arcs.

By using a slightly inclined hearth one may place the mixture of oxide and carbon at the top. Under the action of one or two arcs the metal is obtained and gathers in the lower part, where another arc keeps it in the liquid state while the refining is going on. The molten metal may be removed through an orifice which is opened at the end of the operation. In one small-scale experiment we were able to remove at one time 10 kilos. of molten chromium. In another experiment we melted 12 kilos. of molybdenum.

The intense heat produced by an electric arc may thus be utilized in a continuous furnace, and enable one in this way to obtain a regular supply of a metal whose melting-point may be much above 2,000° C.

In bringing to a close the description of the various types of electric furnaces used in our researches, we may notice that one important point remains for investigation.

We do not know the temperature of these pieces of apparatus; it depends on the temperature reached by the electric arc, which may be, according to Violle, 3,500°.[1] The opinion of physicists on this point is varied. After some hundreds of experiments carried out under very varied conditions, it seems to us that, in a closed furnace with a small cavity, the temperature rises with the intensity of the current. It is likely that the vaporization of the carbon may limit to a certain extent the temperature of the arc, when the power used is not very high; the same is true of the depolymerization phenomena of carbon, which complicate the thermal conditions of the experiment. But in the numerous researches on this point, carried out with very different currents, it has always seemed

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[1] *C.R.*, cxv. 1273 (1892).

to us that the more powerful the machines used the higher was the temperature obtained.

With 400 amperes at 70 volts we could not effect the reduction of vanadium oxide by means of carbon, the crucible being 1 cm. from the arc. With a current of 1,000 amperes at 70 volts, the reduction takes place at several centimetres from the arc, and some 100 grms. of the metal may be obtained in a few minutes.

That the rise of temperature is a function of the intensity of the current was further borne out by the reduction of titanic acid by carbon. With an arc of 50 amperes at 50 volts, the blue suboxide of titanium is the sole product, whatever be the length of the experiment; an arc of 350 amperes at 50 volts yields the nitride and nothing else; finally, with 1,000 amperes at 70 volts, the nitride is dissociated completely, and one obtains liquid titanium containing more or less carbide.

Conclusions.—Many workers have already used the electric arc to obtain high temperatures; but those who have preceded me have not separated the electrolytic from the heating action of the current. This I have attempted to do by making use of the powerful heating phenomena of the arc alone, leaving aside the purely electrolytic action.

The furnaces I have described are simple and practical, and enable one to extend greatly the chemistry of high temperatures. They may be of the greatest help both in the laboratory and in works. These types of furnaces enable us to reach with ease temperatures of at least 3,500° C.; there are thus a whole mass of researches to be prosecuted, and the results already obtained show the importance and the extent of the work which may be carried out along this new line.

CRYSTALLIZATION OF METALLIC OXIDES

At the outset we applied our electric furnace to the study of the crystallization of metallic oxides, and then to the volatilization of some elements.

The quicklime furnace already described was the one used to study the action of a high temperature on metallic oxides. The latter were prepared pure and anhydrous. The powdered oxides were then heaped up in the cavity beneath the electrodes and the arc produced. For the first part of these researches, when only a 4 H.P. machine was used, the carbon electrodes had been subjected to the action of chlorine at a high temperature, and then allowed to cool in an atmosphere of nitrogen. For experiments in which a motive power of 30 to 45 H.P. was used, the electrodes consisted of carbon of the highest purity possible and prepared with minute care. Moreover, with an intense current, the reactions may be carried out with amounts of substance sufficiently large to minimize the influence of the small quantity of impurities contained in the electrodes.

Calcium oxide.—Lime subjected to the arc produced by a dynamo yielding 50 volts and 25 amperes is soon covered with white and shining crystals, which consist of pure calcium oxide.

Small amounts of these crystals may also be obtained by means of the oxyhydrogen blowpipe in the hottest part of the flame, that is, near the jet of the blowpipe [1].

If instead of pure lime a slightly hydraulic lime be used, as for instance that of which the furnace is built, a fine crystallization is still possible. These crystals have a density of 3·29; they are easily soluble in water, and on analysis are found to consist of:

Lime	97·30	per cent.
Alumina	1·60	„
Silica	0·45	„
Iron	Traces.	

Although the lime used was rich in alumina coloured yellow by iron, the crystals obtained were colourless; they are analogous to those obtained by St. Meunier and Levallois in a continuous lime furnace heated by combustible gases [2].

If a more powerful arc be used, taking 50 volts and 100 amperes, the crystallization becomes more abundant and rapid; but an arc of 350 amperes at 70 volts is required to bring about a complete fusion, and the subsequent indistinct crystallization of the molten mass. Under these conditions the inner cavity becomes deeper and deeper, the two quicklime bricks adhere to one another, and the experiment is limited by the melting of the substance of the furnace. Pure lime, quite free from silica, alumina, or magnesia, melts quite as well and as quickly.

After fifteen to twenty minutes, with an ordinary size of

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[1] *Ann. de Ch. et de Ph.*, sér. 7, xxvi. 280 (1902).

[2] *C. R.*, xc. 1566 (1880).

furnace, the inner walls attain a bright redness, and the experiment must be ended.

Working with 1,200 amperes at 110 volts, the melting and then the volatilization of the lime are brought about in a few minutes with great intensity. Several hundred grams of quicklime may be volatilized in five minutes. If the experiment be stopped, the upper part of the furnace is covered with a layer of molten quicklime 2 to 3 cm. thick, and possessing a crystalline fracture. The melted part assumes a somewhat milky transparency, and has a density of 3·12 at 18° C.

Identical results are obtained with a limestone furnace. The arc soon hollows out an egg-shaped cavity of melted lime, surrounded by a white layer of quicklime some 2 cm. thick.

On the addition of a considerable amount of alumina, the melting-point of the lime is notably lowered and its limpidity increased.

The hydration of melted lime is unexpectedly difficult. In three test glasses containing distilled water we placed:

1. Lime obtained from marble.
2. A compact lime of good quality.
3. Some pieces of melted lime.

The lime from marble dissolves at once, and the liquid gives an immediate white precipitate with ammonium oxalate.

The rich lime soon swells up and dissolves rapidly. The solution is complete in twelve hours. On the other hand, the melted lime is unaltered in appearance after being in contact with water for twenty-four hours, and the liquid contains no trace of dissolved lime. After another twenty-four hours an increase of volume may be observed, and some calcium hydrate is produced. After seventy-two hours this melted lime is completely dissolved. Boiling water acts in exactly the same way.

From these experiments we may conclude that calcium oxide, as long as it is not hydrated, is insoluble in water, and that melted lime resists the action of water for a much longer time than ordinary quicklime.

Air saturated with aqueous vapour at the temperature of the laboratory gave us the following results: The lime from marble broke up completely in twenty-four hours, the compact lime in forty-eight hours, and the melted lime only began to lose its wax-like aspect some forty-eight hours later; after three days it still contained some non-hydrated fragments. These experiments were carried out under a bell-jar standing over a large crystallizing dish full of water, and the small fragments of lime were placed in glass dishes which floated on the liquid. The same gradation was maintained when these different samples were attacked by dilute acids.

Strontium oxide.—Strontia crystallizes like lime under the action of an arc of 75 amperes at 50 volts. With currents ot 350 amperes at 70 volts pure strontia melts to a transparent liquid, which on cooling passes into a mass of indistinct crystals. Strontia is more easily melted than lime.

Barium oxide.—Baryta is known to melt at a lower temperature than lime. With an arc of 25 amperes at 50 volts it becomes perfectly liquid; under the action of a more powerful arc it is easily volatilized. On cooling, liquid baryta yields a mass of intertwined crystals possessing a brilliant crystalline fracture.

Magnesium oxide.—Magnesia crystallizes at a higher temperature than lime; it yields brilliant crystals which are sometimes several millimeters long.

The experiment is quite successful if an arc of 120 amperes at 50 volts be maintained above a mass of pure magnesia placed in the middle of the furnace. With a current of 360 amperes at 70 volts magnesia yields a molten mass, milky in appearance and translucent.

Ditte showed in 1871 that magnesia underwent polymerization, as the result of successive rises of temperature, and that the whole of its chemical and thermal properties underwent a continuous change in consequence. More especially the density of this oxide increases rapidly with the temperature. Ditte gave the following figures:

Heated.	Density at 0° C.
At 350° C.	3·1932
At dull redness	3·2482
At a white heat	3·5699

In our experiments in the electric furnace we have always noticed that magnesia purified by Schlœsing's method was not reduced by carbon. The knowledge of this fact was of great importance to us, as it enabled us to build the interior of our furnaces of alternate plates of magnesia and carbon, and to use this magnesia in the making of our crucibles. In view of the easy reduction by carbon, at the temperature of the electric arc, of the oxides of the alkaline earth metals, of alumina, and of uranium oxide, the stability of magnesia seemed of sufficient interest to lead us to determine the density of this oxide after melting in the electric furnace. The determinations were carried out in benzene and in absolute alcohol, following the directions well laid down by Ditte in his paper [1]. Each of the values given below represents the mean of four experiments.

The first sample had been heated for ten hours in a wind furnace fed with retort carbon.

The second sample was derived from magnesia plates, partially crystalline, which had been exposed to the action of the electric arc for two hours. The third was obtained from a lump of magnesia weighing 50 grms., which had been melted into a single piece in an electric furnace crucible.

The following were the values obtained :

	Density at 20° C.
1. MgO (blast furnace)	3·577
2. MgO (furnace plates)	3·589
3. MgO (fused mass)	3·654

This increase of density shows that the polymerization of magnesia goes on up to its fusion point. The density may thus vary from 3·19 to 3·65.

Aluminium oxide.—To study the action of the arc on pure alumina, the latter is placed in a carbon crucible in the middle of a lime furnace. It is in fact not possible to work with a small quantity of alumina placed in the cavity of a lime furnace, for, under these conditions, a very liquid aluminate of lime would soon be formed. With an arc of 50 volts and 25 to 30 amperes alumina fuses, and crystallizes quickly on cooling. If a small amount of chromium sesquioxide be added, small red crystals of ruby are seen to separate themselves from the mass. These rubies are much less fine than those prepared by Frémy and Verneuil ; but the rapidity of the experiment, which lasts but ten to fifteen minutes, may enable one to produce easily the crystallized ruby. Moreover, the ease with which alumina is volatilized would, in all probability, render it possible to obtain well-defined crystals by this method. We have not carried this work any further.

With a more powerful arc, reaching to 75 amperes at 250 volts, operating for twenty minutes, the alumina is not only

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[1] *C. R.*, lxxiii. 111, 191 (1871).

melted but volatilized, and nothing remains in the crucible. Under these conditions one may repeat in a few minutes Ebelman's classical synthesis of corundum by the volatilization of boric acid in a porcelain oven. If the experiment be very short, from three to five minutes, the crystallization is not well defined, and the crystals lose some of their clearness. In a few minutes the fused boric acid is completely volatilized with an arc of 300 amperes and 60 volts.

Oxides of the Iron group.—Chromium sesquioxide, heated by an arc of 30 amperes at 55 volts, fused to a black and glistening mass, mammillated, and bristling in parts with small dark-coloured crystals, which gave the following figures after fusion with potassium nitrate and precipitation by mercuric nitrate:

	1	2	3	Theory.	
Chromium . . .	51·82	51·60	52·32	52·22	per cent.
Oxygen . . .	—	—	—	47·78	,,

These crystals are very hard, and leave a green streak on porcelain.

Sesquioxide of chromium in a state of fusion combines rapidly with calcium oxide. Hundreds of grams of this double oxide, well crystallized, are often to be obtained in the lime furnaces used for the refining of molten chromium. The same brilliant crystals in lamellae are sometimes found on the lid of the furnace.

We have prepared several of these double oxides by heating varying mixtures of quicklime and sesquioxide of chromium in a limestone furnace with a current of 50 volts and 1,000 amperes. The fused mass, on removal from the furnace, frequently contained geodes full of small crystalline lamellae, transparent and yellow in colour, which are slowly decomposed by water or moisture. This compound consisted solely of lime and sesquioxide of chromium.

On analysis it gave the following results:

	1	2	3	Theory for Cr_2O_3, 4 CaO.	
Chromium . . .	26·9	26·8	27·6	27·2	per cent.
Calcium . . .	41·4	42·5	—	41·1	,,

These figures thus agree with the formula

$$Cr_2O_3, 4\,CaO.$$

By the side of these yellow lamellae we have often found dark green needles, several millimeters long, which have not been studied further.

Manganese dioxide liquefies quickly under the action of the arc; it boils, giving off oxygen and yielding the monoxide in a liquid state, this being absorbed by the lime, leaving behind a brown crystalline mass which seems to consist of a mixture of the two oxides.

Ferric oxide melts rapidly, losing some of its oxygen. It yields the magnetic oxide Fe_3O_4, partly liquid and partly crystallized. This oxide, like the sesquioxide of chromium, gives well crystallized combinations with lime. Indeed these are formed so easily that we found it impossible to melt iron in small quicklime crucibles, heated from below by means of the oxygen blowpipe. The magnetic oxide produced under these conditions unites at once with the lime; the latter becomes brown, pasty, softens, and allows the metal it contains to escape. After the experiment the lower part of the crucible is converted into a mass of the double oxide of calcium and iron.

Nickel suboxide yields a fused mass covered with small green transparent crystals.

Cobalt suboxide, which also melts very quickly, yields rose-coloured crystals.

Titanium oxide.—Titanic acid, under the influence of a current of 25 amperes at 50 volts, yields beautiful prismatic crystals of a dark colour, corresponding in appearance and properties to the suboxide of titanium.

With a current of 100 amperes at 45 volts, this oxide first melts, then after three minutes is partially dissociated, and after eight minutes is completely volatilized.

All the experiments just described were carried out on oxides which were not in contact with carbon, and the mass to be heated was placed at several centimeters from the arc, so as to avoid the reducing action of carbon vapour.

Copper oxide.—This oxide is completely dissociated in the electric furnace, yielding small masses of metallic copper and a crystalline double compound of calcium and copper oxides.

Zinc oxide.—Amorphous zinc oxide is volatilized in a few moments, yielding long transparent needles several centimeters long, which are deposited on the openings of the furnace and on the electrodes.

Conclusions.—At a temperature somewhat above 2,000° C., quicklime has a sufficient vapour tension to produce an abundant crystallization. When the heat from the electric arc is more intense, quicklime melts and the liquid crystallizes on cooling. At a still higher temperature, quicklime boils and distils easily.

Strontia and baryta crystallize and melt at lower temperatures.

Magnesia also gives off vapours before melting which condense to brilliant crystals. On heating more strongly it melts, but not so readily as quicklime, and is finally vaporized.

Alumina is far more volatile than quicklime or magnesia. One can readily understand the volatilization of alumina and the formation of corundum in ordinary blast furnaces. After fusion one obtains a crystalline mass to which a trace of chromium imparts the tint of the ruby.

Boric acid, titanium protoxide, and zinc oxide are quickly volatilized in the electric furnace. Copper oxide is at once dissociated into oxygen and copper, which then distils.

The oxides of the iron group are stable at high temperatures and yield molten masses studded with small crystals.

We thus see that in all our experiments a rise of temperature has been sufficient to determine the crystallization of metallic oxides.

Since our earlier work on this subject, Dufau, pursuing this line of research, has obtained a chromite of calcium, $Cr_2O_3.CaO$, atetrachromite of barium, $4Cr_2O_3.BaO$, a cobaltite of magnesium, $CoO_3.Mg$, and a nickelite of barium, $2\,NiO_2.BaO$.

Finally, applying the same method to the crystallization of sulphides, Mourlot has prepared alabandite or manganese sulphide, already obtained in the wet way by Baubigny, and in the dry way by Gautier and Hallopeau. He has also prepared the sulphides of chromium, zinc, cadmium, and aluminium.

FUSION AND VOLATILIZATION OF SOME REFRACTORY SUBSTANCES

We shall deal more particularly, in this chapter, with the experiments which demonstrate the volatilization of certain metals and metalloids and with the easy distillation of silica and zirconia.

To effect the condensation of the vapours of these refractory substances volatile at very high temperatures, we used the metal tube, cooled interiorly by a stream of water, already described when dealing with the limestone furnace for crucibles. As examples of the use of this tube, we may take the action of heat on two stable compounds of mineral chemistry: magnesium pyrophosphate and magnesium silicate.

Magnesium pyrophosphate was heated for five minutes in the furnace under the action of a current of 300 amperes at 65 volts. In a few moments copious vapours were formed. The cold tube, placed in the apparatus at the outset, was traversed at first by a current of water at 15·4° C. At the end of the experiment, when the furnace was fully at work, the temperature of the escaping water was only 17·5° C. Under these conditions the vapours produced in the middle of the furnace are condensed very easily on the cold tube. On removing the tube from the furnace, we observed that it was covered in part with ordinary phosphorus, igniting when rubbed or oxidizing slowly in the air, yielding a syrupy substance which reduced silver nitrate freely. In addition to phosphorus, we were able to prove the presence of magnesia on the tube[1].

In another experiment we heated asbestos (magnesium silicate containing a little iron) in a carbon crucible for six minutes. The current was of 300 amperes at 75 volts. After the experiment there remained in the crucible but a very small quantity of fused silicate and a ferruginous globule

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[1] There remained in the crucible a grey mass, fused and porous, which on analysis gave figures for magnesia and phosphoric acid very different from that of the pyrophosphate used.

	Pyrophosphate.	Fused mass.
Phosphoric acid	63·96	43·84 per cent.
Magnesia	36·04	55·58 ,,

possessing a bright fracture and containing 1·6 per cent. of magnesium and 0·7 per cent. of silicon.

The cold tube was covered with a grey powder containing a large excess of silica, of magnesia, and small amounts of carbon and silicon. We found in it transparent spherules of silica which scratched glass, and giving clearly the reaction of silica in the microcosmic bead.

These two preliminary experiments, taken from many others, show that the most stable salts are dissociated at the temperature of the electric arc, and that it is possible to collect with ease and to study the products of their decomposition.

A. Volatilization of metals.

Copper.—A piece of copper weighing 103 grms. was placed in a carbon crucible in the furnace and heated for five minutes by means of a current of 350 amperes at 70 volts. After a minute or two, dazzling flames 0·4 to 0·5 meter long burst out violently through the electrode openings on either side of the furnace. These flames were crowned with clouds of yellow smoke resulting from the formation of copper oxide due to the combustion of the metallic vapour.

After five minutes the current was cut off. The regulus left behind weighed but 77 grms., 26 grms. of copper having been vaporized under these conditions.

All around the crucible, in the horizontal part between the cover and the furnace, was found a crown of globules of fused copper, resulting from the distillation of the metal. The yellow sublimate gives up copper oxide by treatment with cold dilute hydrochloric acid, leaving, as a residue, small spheres of metallic copper, black on the surface and soluble in nitric acid.

Large amounts of metallic copper were found on the cold tube.

Silver.—It has long been known that silver is volatile at high temperatures. It may be made to boil vigorously in the electric furnace, when it distils more easily than silica or zirconia. There result large quantities of fused globules, an amorphous grey powder, and tree-like fragments.

Platinum.—Heated in the electric furnace, platinum melts and before long begins to volatilize. Small shining globules of metallic platinum are found, and platinum dust on the cooler parts of the electrodes or on the surface of the lower block some few centimeters from the crucible.

Aluminium.—Heated for six minutes with a current of 250 amperes at 70 volts. On the cold tube is found a grey powder, slightly compact, yielding, on shaking with water, small spherules of aluminium, which sink to the bottom of the glass. These spherules have a metallic appearance and are attacked by hydrochloric and sulphuric acids with evolution of hydrogen. Small spheres covered with aluminium are also deposited on an asbestos thread placed in the vapours escaping from the furnace.

Tin.—The experiment lasted eight minutes with a current of 380 amperes at 80 volts. When the furnace is at work, fairly dense white fumes are evolved near the electrodes. A small amount of stannous oxide, soluble in dilute hydrochloric acid, is found on the tube, together with small shining globules and a grey, fibrous-looking substance, the whole closely interwoven. The fibrous substance and the metallic globules evolve hydrogen unmistakably with hydrochloric acid; they consist of metallic tin. Small globules of tin mixed with oxide may be easily condensed on the exterior part of the furnace.

Gold.—Duration of experiment, six minutes. Current, 360 amperes at 70 volts. Of 107 grms. of gold placed in the crucible, only 59 grms. remained after the experiment. Copious fumes of a greenish yellow colour were evolved. The cold tube was covered with a dark powder of purplish hue. Under a low-power microscope one could see clearly small regular spheres of fused gold, possessing a fine yellow colour. These dissolve easily in aqua regia and behave in every way like gold.

On the hottest part of the asbestos thread on which some of the vapours were condensed, we found numerous minute globules of metallic gold. Around this part, which had a decided yellow colour, was a red ring, and somewhat further off a beautiful dark purple tint.

Manganese.—This metal, about whose volatilization Jordan has recently given new details, yielded us very interesting results. We shall recall but one thoroughly characteristic experiment. Period of heating, ten minutes, with a current of 380 amperes at 80 volts. 400 grms. of metallic manganese were placed in the crucible. Copious fumes were evolved, and at the end of the experiment we found a regulus of metallic carbide weighing but a few grams.

In any case, whenever, in the preparation of manganese in the electric furnace, heating is continued too long, no metal is left in the crucible.

Iron.—Experiment lasted seven minutes, with a current of 350 amperes at 70 volts. On the cold tube is found a grey powder presenting some shining surfaces, very thin and granular and sufficiently malleable to bend under the pressure of a knife blade; with this is mixed a grey dust having the colour of iron reduced by hydrogen. This dust is susceptible of polish by friction, and the whole sample dissolves in dilute hydrochloric acid with evolution of hydrogen. On the asbestos board, on which the metallic vapours play, are found small spheres of magnetic oxide and globules of the same, black in colour and rough on the surface.

Uranium.—A current of 350 amperes at 75 volts passed for nine minutes. Numerous solid metallic globules collect on the cold tube, mixed with a grey powder easily soluble in acids with evolution of hydrogen. These solutions have all the properties of uranium salts. On the asbestos board are found numerous yellow spheres which lose a crust of oxide by pounding in an agate mortar, becoming grey and of metallic appearance.

These globules of distilled uranium contain no carbon and are not attracted by a magnet.

B. **Volatilization of metalloids.**

Silicon.—Silicon may be volatilized with a current of 300 amperes at 80 volts. On the cold tube are found small spheres of fused silicon, which are attacked by a mixture of nitric and hydrofluoric acids. They are mixed with a grey powder and a small quantity of silica. If the vapours be cooled on an asbestos board, one sees that much of the silicon has been converted into silica.

This vaporization of silicon may be rendered visible by means of the arrangement described on p. 108[1].

Crystallized silicon, prepared either by the method of Deville or of Vigouroux, is placed between two vertical electrodes. As soon as the arc plays, one can see in the projected image the silicon melting and then starting to boil. At the top of

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[1] See also Moissan, *Ann. de Ch. et de Ph.*, sér. 7, viii. 466 (1896).

the cooled electrodes one finds, amid the graphite formed, light green crystals of carbon silicide.

Boron.—It is not possible to carry out the volatilization of boron in a crucible as, under these conditions, it is transformed into carbon boride. If pure amorphous boron prepared by means of magnesium[1] be placed in the arc, then, on projecting the image, the boron is seen to become red-hot and a green aureole is developed around it; finally it disappears without any sign of fusion.

After the experiment the end of the electrode bears small black particles, presenting a fused appearance and some crystalline points, and consisting of a definite boride of carbon.

It is highly important that, in this experiment, the carbon of the electrodes should be as pure as possible. Nor must it be forgotten that, if the quantity of boron used be fairly large, simultaneously with the union of boron and carbon, boric acid may be formed, which melts quickly and boils, but may be easily removed subsequently by means of boiling water.

From this experiment we may conclude that boron passes from the solid to the gaseous state without liquefaction.

Carbon.—Carbon was heated for fifteen to twenty minutes by means of a current of 370 amperes at 80 volts. On heating a crucible full of lumps of carbon in the neighbourhood of the arc, the carbon is before long changed into graphite, and after the experiment one finds on the cold tube thin translucid plates, which are very light and are brown by transmitted light. Berthelot, in his numerous experiments on the progressive condensation of carbon, has already indicated the existence of a light carbon having a brown colour. This substance is separated from the lime, which has volatilized at the same time, by means of dilute hydrochloric acid. The residue thus obtained burns easily in oxygen with the production of carbon dioxide. We shall study later in greater detail the properties of this carbon vapour.

C. **Oxides.**

The researches on the crystallization of oxides already described proved absolutely the volatility of these compounds. This will be emphasized by considering such oxides as quicklime, magnesia, and zirconia.

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[1] 'Preparation of amorphous boron,' *C. R.*, cxiv. 392 (1892); *Ann. de Ch. et de Ph.*, sér. 7, vi. 296 (1895).

Quicklime.—Lime may be volatilized in eight to ten minutes by means of a current of 350 amperes at 70 volts. Under these conditions one finds on the cold tube quicklime as an amorphous powder containing no spherules. Copious vapours of calcium oxide will escape from the surface. With a current of 400 amperes at 80 volts the experiment lasts but five minutes.

Finally, with a current of 1,000 amperes at 80 volts, over a hundred grams of calcium oxide may be volatilized in five minutes.

Magnesia.—Magnesia is more difficult to vapourize than quicklime; further, its boiling-point is not far removed from its melting-point. As soon as magnesia is melted it gives off vapours which may be condensed on the cold tube. This experiment requires a current of 360 amperes at 80 volts. The distillation becomes very striking and very rapid with currents of 1,000 amperes at 80 volts.

Zirconia.—This oxide is soon melted at the high temperature of the electric furnace. After ten minutes, with a current of 360 amperes at 70 volts, copious white vapours are formed. This smoke consists of the vapour of zirconia, for, at the high temperature, zirconia boils vigorously. By condensing the vapours on a cold body one obtains a white dust, which is treated with very dilute hydrochloric acid to remove the lime it contains. After washing with boiling distilled water and drying there remains a white powder, seen, under the microscope, to consist of white rounded masses containing no transparent particles. This powder has all the properties of zirconia. It scratches glass easily and has a density of 5·10. After cooling one finds in the crucible a mass of fused zirconia, possessing a crystalline fracture. Finally, in the cooler interior parts of the furnace one finds occasionally characteristic crystals of zirconia; they have a dendritic appearance and are transparent, possessing a glassy lustre; they scratch glass and are not attacked by sulphuric acid. A crystalline combination of zirconia and lime has also been noticed.

Silica.—Fragments of quartz, placed in a carbon crucible, were submitted to the action of an electric arc resulting from a current of 350 amperes at 70 volts. The silica is melted in a few moments and begins to boil after seven or eight minutes. A bluish smoke, lighter than that produced by zirconia, is then seen to issue from the furnace through the electrode openings.

This is given off copiously as long as the experiment continues. These vapours may be condensed by placing an inverted crystallizing dish at some distance from the openings. The interior of the dish becomes coated with a light substance, not very transparent and of a slightly bluish white colour. On treating the contents of the dish with water and examining the residue with a lens or under the microscope with a low power, it is seen to consist mostly of opalescent spheres, which are readily soluble in hydrofluoric acid. These little spheres of silica (Fig. 6), visible to the naked eye, are solid; they are occasionally depressed at one point, tending to show that the molten silica undergoes a diminution of volume in passing from the liquid to the solid state.

In addition to these spheres many particles of amorphous silica are to be seen.

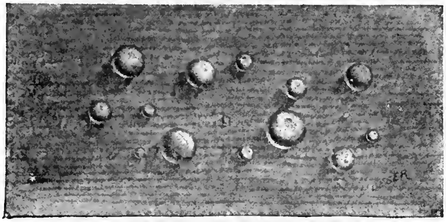

Fig. 6.—Spheres of silica.

Should it be desired to collect a large amount of this product, it is advisable to use a furnace whose lid is provided with a vertical opening above the crucible, allowing the vapour of silica to pass. A glass jar or a metallic receiver is placed above the opening (Fig. 7), and in this way one may obtain, in ten to fifteen minutes, some twenty grams of a very light white power, from which any admixture of lime is removed by washing with dilute hydrochloric acid.

The form assumed by the condensed silica depends of course on the rate at which the vapour is cooled. The cooling must not be too rapid if one wishes to obtain a large number of silica spherules. This silica is readily soluble in hydrofluoric acid, dissolving in the cold with a slight hissing. It is easily attacked by fused potash and by alkaline carbonates.

It has a density of 2·4, this being a little less than that of quartz; finally, these small spheres scratch iron with ease.

On examining the deposit found in the glass globes used for electric arc lighting, we found small silica spheres identical with those just described. The opalescence which these globes acquire after a time is thus chiefly due to the volatilization of silica. This silica is contained as an impurity in the carbon poles.

We may add that, at this temperature, silica is easily reduced by carbon, yielding a carbide ot silicon and even pure silicon.

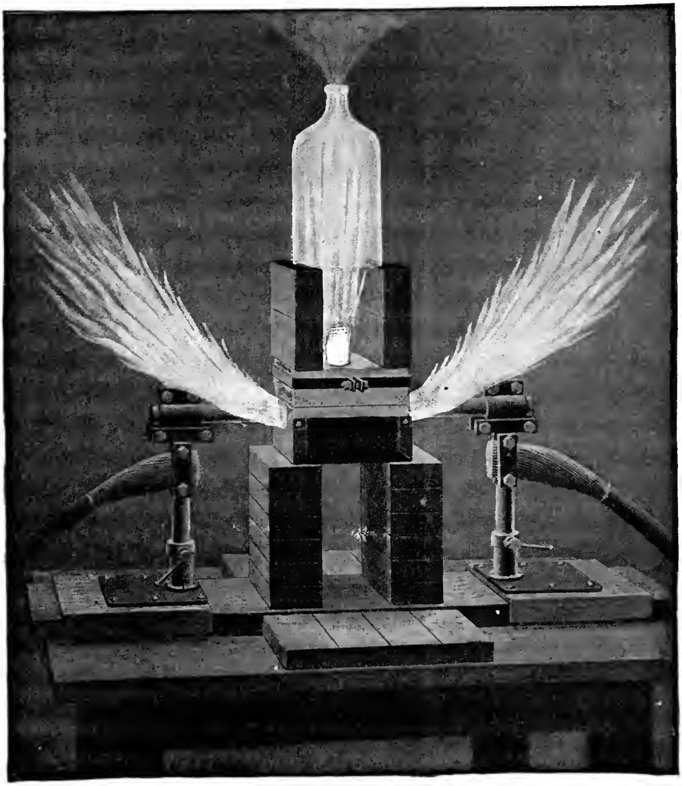

Fig. 7.—Electric furnace arranged for the volatilization of silica.

We thus see that zirconia and silica melt quickly in the electric furnace, and that after seven or eight minutes they begin to boil and to pass into the gaseous state.

Conclusions.—At the high temperature reached in our experiments by means of the electric arc the metalloids and the metals, which had hitherto been looked upon as refractory, are volatilized. The most stable compounds known to mineral chemistry disappear in the electric furnace, owing either to dissociation or to volatilization. There remains but one series of compounds capable of resisting these high temperatures; this series consists of new compounds, crystallizing perfectly and of exceptional stability, whose properties we shall describe shortly. It comprises the borides, the silicides, and, more especially, the metallic carbides.

CHAPTER II

RESEARCHES ON THE DIFFERENT VARIETIES OF CARBON

PART I

AMORPHOUS CARBON

Carbon is the element which presents the most interesting allotropic varieties. It has long attracted the notice of workers by its contradictory properties and by the differences existing between the specific heats of the diamond, of graphite, and of lamp-black. After having separated and identified most of the constituents of the animal and of the vegetable kingdoms, the chemistry of carbon has led to the production of a vast number of new bodies. Its development has been such that one may apply to it with special appositeness the saying of M. Berthelot:—'La chimie crée l'objet de ses études.'

But in this imposing collection of researches, chemists have striven rather to produce curious derivatives or new syntheses, some of which have profoundly altered technical processes, than to extend our knowledge of the properties of the element which serves as starting-point. Theses have often been written on the hypothetical shape of the carbon atom, but there are relatively few experiments on the physical and chemical properties of this same carbon. Consequently, the subject deserved new researches.

In order to reproduce the diamond, we were led to take up again a general study of the different varieties of carbon.

We give here a study of the whole subject and propose to deal in order with amorphous carbon, with graphite, and with the diamond.

In the first part we shall deal solely with the amorphous kinds of carbon. The properties of these are known to vary within fairly wide limits. The resistance they offer to oxidation, for example, has already been studied by Ditte[1]. He showed by a number of comparative experiments that the different varieties, when heated in sealed tubes with a concentrated solution of iodic acid, are attacked at different temperatures.

After some attempts with iodic acid, potassium permanganate, chromic acid, and nitric acid, we used by preference a mixture of sulphuric acid and potassium bichromate as oxidizing agent.

Several chemists have busied themselves with the preparation of amorphous carbon. From among the researches on this subject we may mention more especially those of Gore[2], who showed that carbon is insoluble in carbonic acid, in cyanogen, and in hydrochloric acid when in the liquid state. He studied the action of carbon bisulphide on silver, lead, and mercury at ordinary temperatures.

The action of voltaic couples, consisting of thin plates of platinum and aluminium, on hydrocarbons or organic compounds was also investigated. In most cases decomposition was not brought about. As is known, amorphous carbon may be formed in a number of decompositions, as for example in that of carbon dioxide brought about by sodium or magnesium. Winkler[3] studied more particularly the action of magnesium on the carbonates of the alkalies and of the alkaline earths; he demonstrated the production of amorphous carbon under these conditions without investigating its properties.

On similar lines is the research of Dragendorff on the liberation of carbon by the action of phosphorus on the fused alkaline carbonates[4], as also the work of Gore on the reaction between phosphorus and molten potassium cyanide.

It is manifest that much heat is evolved in these various reactions. We shall not deal with the forms of carbon obtained under these conditions; on the contrary, all our work has been directed to the study of the liberation of carbon at temperatures as low as possible and in very slow reactions.

The splendid researches of Berthelot on the different states of carbon, on the theory of pyrogenetic carbides, on the synthesis of acetylene by means of carbon vapour, on the humic

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[1] *Researches on iodic acid.* Thesis presented to the Faculté des Sciences, Paris, 1870; *Ann. de Ch. et de Ph.*, sér. 4, xxi. 5 (1870).

[2] *Chem. News*, l. 125 (1884).

[3] *Ber.*, xxiii. 2642 (1890).

[4] *Chem. Centralblatt.* (1861), 865.

acids, constitute the most important series as yet undertaken on this subject.

Commercial lamp-black. The lamp-black we studied was produced by the pyrogenetic decomposition of petroleum oil. The temperature at which it is formed, although irregular, is in the main but little above a dull red heat. We used this product as a standard of comparison in the study of amorphous carbon.

The lamp-black was purified by successive washings with benzene, alcohol, and ether. This is absolutely necessary, and the quantity of hydrocarbons so removed was considerable. After the ether washing, the air-dried powder is placed in an oven and the temperature slowly raised to 150° C.[1]

This lamp-black floats on allyl iodide of 1·87 density and sinks in propyl iodide of 1·78 density.

Lamp-black so prepared is far from being pure. It holds tenaciously small quantities of hydrocarbons and water from which it cannot be freed. It contains also a little nitrogen.

To analyse this variety of carbon, it is first heated in vacuo, at the softening point of glass, in order to cause it to polymerize and to be handled more easily. Some water and traces of hydrocarbons are set free. The black powder then gives the following figures[2]:

	1	2	
Ash	0·22	0·34	per cent.
Carbon	93·21	92·86	„
Hydrogen	1·04	1·20	„

If the hydrogen be expressed as water, it is seen at once that the figures add up to more than 100, which shows that a small amount of hydrogen, less than 1 per cent., is still there in the form of hydrocarbon; the remainder comes from the water whose complete removal from lamp-black is not possible.

The amount of water contained is much larger if the drying in vacuo at a dull red heat be neglected.

The unpurified lamp-black gave the following figures:

Carbon	87·49	per cent.
Hydrogen	2·76	„

If the hydrogen be expressed as water, one gets

$$C\ 87{\cdot}49 + H_2O\ 24{\cdot}88 = 112{\cdot}37.$$

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[1] The treatments with alcohol and ether must be repeated often to remove the last traces of benzene, which are easily retained by lamp-black.

[2] These were two different samples.

This total of 2·76 per cent. of hydrogen includes the hydrogen of water and combined hydrogen. The latter belongs to some organic substance, probably in the form of a hydrocarbon.

The invariable presence of hydrocarbons, of hydrogen, or other elements in amorphous carbon has long been known. Of this we shall have many examples.

From these important facts Berthelot has drawn the following conclusions:

'In truth, carbon is not comparable to a real elementary substance; on the contrary, it may be likened to an extremely condensed carbide, very poor in hydrogen and possessing a very high equivalent. Pure carbon is, as it were, a limiting state scarcely to be realized under the influence of the highest temperature known to us. As we know it in the free state, it represents the extreme limit of molecular condensations, that is, of a state as far removed as possible from that of the element carbon, brought into the state of a perfect gas and comparable to hydrogen. This explains why carbon is never liberated in a natural state in low temperature reactions, differing in this respect from hydrogen and most of the chemical elements[1].'

After the composition of this lamp-black had been determined, the following experiments were carried out on a washed but non-calcined specimen[2]:

On treatment with a mixture of 100 grms. H_2SO_4 and 16 grms. $K_2Cr_2O_7$, a reaction begins at 60° C. A slight boiling takes place at this temperature and carbon dioxide is evolved.

In this experiment about 0·01 grm. of lamp-black is placed in a glass tube 1 cm. in diameter, containing at the bottom 2 c.c. of the oxidizing mixture. The top part of the tube is drawn out, bent into an inverted U shape, and the end is allowed to dip into a test tube containing clear baryta water. As soon as gas is evolved, the baryta solution becomes milky. This small apparatus is suspended in a glycerine bath, by the side of a thermometer.

The temperature of combustion in oxygen was determined by means of the thermo-electrical couple of Le Châtelier and was found to be 371° C.[3]

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[1] *Ann. de Ch. et de Ph.*, sér. 4, ix. 475 (1866).

[2] Berthelot has shown that lamp-black contains a trace of graphite due to the double influence of heat and oxidation. *Ann. de Ch. et de Ph.*, sér. 4, xix. 392 (1870).

[3] Moissan has recently carried out experiments on the temperature of inflammation of the different varieties of carbon. *C.R.*, cxxxv. 921 (1902).—[Tr.]

Lamp-black, purified in this manner, has enabled us to establish clearly the influence of temperature on the polymerization of this elementary substance. On this point we carried out the following experiments:

1. This lamp-black was calcined for five minutes at 910° C. in a small porcelain crucible, by means of an air blowpipe.

After calcination the reaction with the bichromate mixture only began at 90° C., and the temperature of combustion in oxygen rose to 440° C.

2. Calcination at the same temperature was carried on for three hours. This new sample was attacked at 95° C. and the combustion temperature rose to 476° C. At this stage the density was 1·87.

3. After six hours of calcination lamp-black is attacked by the oxidizing mixture at 99° C., and it burns in oxygen at 506° C.

The polymerization of carbon under the action of heat at a constant temperature is thus shown to be not instantaneous, but to increase with the time.

Amorphous carbon from the incomplete combustion of acetylene.—The easy preparation of acetylene from fused and crystallized calcium carbide, whose preparation in the electric furnace has been described, has enabled us to use this hydrocarbon of known composition and in a pure state for the production of amorphous carbon.

Acetylene is burnt at the end of glass tubes some 6 mm. in diameter. Above each flame is placed a copper cylinder 3 cm. in diameter, through which passes a stream of cold water. Lamp-black is deposited on the metal in a bulky mushroom-like deposit.

Under the microscope this carbon does not present a uniform tint; some particles are more or less brown; if heated, it gives up some volatile products, and if extracted with benzene it yields a small quantity of carburetted compounds. It also contains a little nitrogen but no cyanides. This carbon is purer than commercial lamp-black.

This sample was purified by successive extractions with benzene, alcohol, and ether.

In the main the properties of this amorphous carbon are like those of lamp-black; it is attacked by the bichromate mixture at 92° C. The temperature of combustion in oxygen is 375° C. and the density is 1·76.

Heated at a dull red heat in vacuo it yielded no volatile hydrocarbons; some water was given up and on subsequent analysis it gave:

Ash	0·12	0·80 per cent.
Carbon	92·71	92·53 ,,
Hydrogen	0·96	1·00 ,,

so that carbon obtained by the incomplete combustion of acetylene is purer than lamp-black; its analysis further shows that some water is retained which is not volatile at a dull red heat.

Amorphous carbon resulting from the explosion of acetylene.—Berthelot has shown that one may easily bring about a sudden decomposition of acetylene into carbon and hydrogen by means of a small cartridge of fulminate of mercury[1].

Thanks to the kindness of M. Vieille, we have been able to use considerable quantities of this amorphous carbon.

This variety of carbon retains but traces of hydrogen, but contains a certain amount of lead, derived from the washers of the explosion apparatus.

Under the microscope this carbon has a fine black colour. On analysis it gave:

	1	2	3[2]
Ash	7·21	7·51	8·03 per cent.
Carbon	92·30	92·61	92·52 ,,
Hydrogen	0·41	0·40	0·40 ,,

Leaving the lead out of account, this carbon is one of the purest we have studied. It contains but little hydrogen, and we were careful not to submit it to the action of any liquid reagent.

It gives up no carbon compounds under the action of acids, alkalies, or carbides, and it contains no trace of nitrogen.

It was attacked by different oxidizing agents at the following temperatures:

Permanganate of potassium (6 grms., 5 per cent. H_2O)	98° C.
Commercial fuming nitric acid	80° C.
Pure ,, ,,	106° C.
Bichromate mixture (as above)	98° C.

Combustion in oxygen took place at 385° C.

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[1] Berthelot, *De la force des matières explosives*, i. 109.

[2] These analyses, as also the preceding ones, show that this amorphous carbon is not absolutely homogeneous.

The influence of temperatures and perhaps of pressure on this amorphous carbon is apparent. It is attacked by the bichromate mixture, and burns in oxygen at higher temperatures than the lamp-black obtained by the combustion of acetylene in air.

Action of sulphuric acid on starch.—When fuming sulphuric acid acts on starch at 200° C. for forty-eight hours, there results a black substance which was purified by successive washings with cold water, alcohol, and ether.

The black powder thus obtained, which is fairly homogeneous when viewed under the microscope, is not pure carbon; it is an organic substance. It is richer in carbon than the humic acids obtained by Berthelot and André[1], and by its partial solubility in alkalies it is proved to be a transformation product, a step towards the elementary state.

This black substance, dried at 400° C., gave on analysis:

Ash	2·64 per cent.
Carbon	79·69 ,,
Hydrogen	2·29 ,,

If this black product, resulting from the decomposition of the sugar by fuming sulphuric acid, be heated, the larger part of the organic compounds is destroyed, yielding a purer carbon[2]. Its analysis gave:

Ash	4·26 per cent.
Carbon	88·21 ,,
Hydrogen	0·75 ,,

But this impure carbon is already polymerized by the action of heat; it has no further interest for us.

Action of ferric chloride on anthracene.—When lamellar crystals of pure anthracene are heated at 180° C. in a reflux apparatus in presence of a saturated solution of ferric chloride, there results a fairly vigorous decomposition. After twenty-four hours of heating, there remains in the apparatus a dark brown substance which becomes black on drying.

After being washed several times with hydrochloric acid,

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[1] Berthelot and André have recently studied the black substance produced by the action of sugar on a solution of boiling concentrated hydrochloric acid. They obtained a humic acid which contains but 63 to 64 per cent. of carbon. *Ann. de Ch. et de Ph.*, sér. 6, xxv. 364 (1892).

[2] This carbon always contains a certain amount of sulphur, forming part of the molecule.

then with boiling water, the substance is extracted with benzene, alcohol, and finally ether; these last operations must be lengthy and often repeated if the last traces of carbides, which are held tenaciously, are to be removed.

Thus prepared, the product is a mixture of ferruginous organic substances which gives up some volatile products on heating.

It gave on analysis:

Ash	21·29	per cent.
Carbon	62·17	„
Hydrogen	0·91	„

We have here again a transition carbon compound. The substance is not homogeneous under the microscope; more especially, fine needles were met with, which were easily characterized and identified as hexachlor-benzene.

The ash is very rich in ferric oxide, and this metal forms part of the compound.

This preparation does not yield pure carbon.

Action of heat on the tetra-iodide of carbon.—Carbon tetra-iodide was obtained pure and crystallized by the method we have already described—the action of boron iodide on carbon chloride [1].

Carbon iodide, heated up to 200° C. in vacuo, is decomposed into proto-iodide, iodine, and a black substance which is perfectly amorphous under the microscope.

At first sight this black amorphous powder might have been thought to be a variety of carbon. This is not the case; it is a compound of iodine and carbon, showing once again how difficult it is to separate carbon at low temperatures from the substances to which it is bound.

On analysis, we got but 45·44 per cent. of carbon, free from hydrogen.

We may mention also that lamp-black results from the pyrogenetic decomposition, at a dull red heat, of the fluorides of carbon [2].

Decomposition of carbon tetra-iodide by light.—We showed, in some earlier researches, that, under the action of light, carbon tetra-iodide lost iodine yielding a new iodide C_2I_4, which we have called proto-iodide of carbon. If the experiment be done in vacuo with dry tetra-iodide, this decomposition

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[1] Moissan, *C. R.*, cxiii. 19 (1891).

[2] Ibid. cx. 276, 951 (1890).

takes place in three to four weeks. It is complete and no carbon is liberated. Should the tube contain a little moisture the decomposition may become more complicated, and there result black amorphous substances which do not consist of pure carbon; they contain traces of hydrogen and considerable quantities of iodine.

Action of the Smithson pile on the proto-iodide of carbon.—This experiment was done as follows: A Smithson pile, consisting of a piece of tin around which a gold leaf was wound, was placed in a carbon bisulphide solution of tetra-iodide. The tube containing the liquid was pulled out, filled with carbon dioxide, evacuated, and then sealed.

The experiment, begun in August, 1892, and ended on May 6, 1896, lasted four years. Fine crystals of tin iodide were found on the surface of the tin, and a slight deposit of black powder on the gold. Examined under the microscope this deposit was seen to be perfectly amorphous. It has a brown colour and is easily attacked by nitric acid. It was deposited uniformly on the metal, and would seem to have limited the electrochemical action owing to its low conductivity. The amount obtained was too small to allow of an analysis, or to determine the temperature of combustion. It is not likely that the substance thus obtained is pure carbon.

It is, however, insoluble in acids, with the exception of concentrated nitric acid, and in hydrocarbons, and gives no coloration when treated with a 25 per cent. solution of potash.

In this experiment, carried out at ordinary temperatures, and under the slow action of a weak electrolytic agency, the black residue obtained was amorphous; that is the point we wished more particularly to investigate.

Berthelot had already called attention to the formation of amorphous carbon, as the result of the slow decomposition of copper acetylide at ordinary temperature.

Decomposition of carbon tetra-iodide by zinc dust.—In a glass tube, prepared as already described, were placed zinc dust and a solution of carbon tetra-iodide in carbon bisulphide. The experiment, begun in August, 1892, ended in May, 1896.

When the tube was opened the liquid was coloured yellow, indicating the transformation of tetra-iodide into proto-iodide. The metallic dust was covered with a dark brown layer. After being washed with carbon bisulphide the metal was treated with very dilute hydrochloric acid ; a gas having the smell of sulphine compounds was evolved, leaving behind a brownish black powder.

The residue was suspended in water, then collected and extracted with alcohol, pure benzene, and finally washed with alcohol at 95° C.

This substance, dried at 100° C., is a black powder, amorphous and very light, yielding up nothing to hot benzene, and insoluble in a boiling solution of potash and in hydrochloric acid. Judged from its appearance and its properties, this powder is very much like that obtained by means of Smithson's pile.

It burns easily on platinum foil, leaving a slight residue of zinc oxide.

Action of some metals on carbon tetra-iodide.—At the time of the above experiment we prepared a number of tubes under the same conditions. They contained a solution of carbon tetra-iodide in carbon bisulphide in presence of sodium, silver, lead, and magnesium. These experiments also lasted four years.

Sodium, silver, and lead reduced the tetra-iodide to the proto-iodide without liberation of carbon. Magnesium alone gave a different result. The wire used in this experiment was covered with a slight brown deposit ; by treatment with cold and very dilute nitric acid, we were able to isolate as a fine powder this brown covering, which, on liberation, floated to the surface of the liquid.

Viewed under the microscope, this substance is amorphous, of a dark brown colour, yields carbon dioxide by its combustion in oxygen, and contains but traces of iodine and magnesium. It had completely covered the metallic wire, forming a layer which seemed to prevent further decomposition. I believe that this liberation of carbon is due to an electrochemical action similar to that of Smithson's pile, and to the magnesium wire not being homogeneous. Whether it be so or not, this carbon, slowly deposited on the magnesium wire, has all the properties of the most readily attacked variety. It is very light and soft and perfectly amorphous.

Carbon obtained by the reduction of carbon dioxide by boron.—Pure boron is placed in a tube of Bohemian glass through which passes a stream of dry carbon dioxide. On being heated to dull redness the boron burns with incandescence. There remains a black porous cylinder which yields amorphous carbon on treatment with water. This powder is treated with chlorine, at a dull red heat, to remove the last traces of boron, and finally washed with water and dried.

This carbon results from a reaction at high temperature, in which hydrogen does not enter; it is pure, but already polymerized and not easily attacked. With the oxidizing mixture it gives carbon dioxide at 85° C. and burns in oxygen at 490° C. It thus resembles calcined lamp-black. On analysis this carbon gave:

Ash	0·96 per cent.
Carbon	86·16 ,,
Hydrogen	1·41 ,,

giving a total of 99·82.

Conclusions.—We have studied a well-known form of amorphous carbon, such as lamp-black. This was purified, and we have shown that its polymerization under the action of heat was not instantaneous, but a function of the time. This polymerization raises the temperature of combustion in oxygen and increases the stability towards a standard mixture of sulphuric and chromic acids.

Then we have examined the amorphous carbon derived from the incomplete combustion of a definite hydrocarbon, such as acetylene, as well as from the explosion of the same hydrocarbon under slight pressure. The latter form was already more stable.

These varieties of carbon being formed by reactions in which a good deal of heat is developed, we tried to prepare carbon at a low temperature.

Organic products alone were obtained by the action of sulphuric acid on starch and of ferric chloride on anthracene. Decomposition takes place, yielding finally black compounds, richer in carbon than the humic acids prepared by Berthelot and André.

The pyrogenetic decomposition of carbon tetra-iodide at 180° C. yielded a black powder, still containing iodine, to be considered as an intermediate stage between the original compound and carbon itself. This experiment bears out the theory of Berthelot on the pyrogenetic decomposition of organic substances. The slow action of Smithson's pile on the protoiodide of carbon dissolved in carbon bisulphide yielded a very small amount of a dark brown powder, insoluble in potash and easily attacked by concentrated nitric acid. Zinc dust acting on carbon tetra-iodide led to similar results.

Finally, we have studied another variety of carbon, produced by the decomposition at a dull red heat of carbon dioxide by means of boron.

The density of the purest non-calcined lamp-black is 1·76. These experiments show how difficult it is to obtain amorphous carbon in a pure state.

When carbon is deposited at ordinary temperatures and pressures, it assumes the form of a brown impalpable dust. It is very light, soft, and is easily oxidized by nitric or chromic acid.

This carbon always contains a certain amount of the elements—hydrogen, iodine, lead, zinc, &c.—with which it is in contact during the reaction. To remove these impurities the carbon must be heated, and it then polymerizes.

All the varieties of amorphous carbon hold water very tenaciously.

Finally, whatever be the method of preparation, slow or rapid, in the cold or at a dull red heat, resulting in a pure or impure carbon, the product is soft, its density is below 2, and it is always amorphous.

PART II

STUDY OF GRAPHITE

General.—Graphite was not characterized as a definite substance prior to the researches of Berthelot. Formerly, all the varieties of carbon leaving a grey mark on paper were grouped under the vague term—graphite. At that time molybdenum could be confounded with graphite.

By applying Brodie's[1] curious reaction to a mixture of the different varieties of carbon, Berthelot was able to define graphite as any variety of carbon yielding graphitic oxide on oxidation[2].

This behaviour classified the various carbons in a definite manner, and the three groups—diamond, graphite, and amorphous carbon—thus comprised all the forms of that element to be met with in nature or capable of artificial preparation.

Graphitic oxide is usually obtained by Brodie's method,

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[1] *Phil. Trans.*, cxlix. 249 (1859).

[2] 'On the different forms of carbon,' *Ann. de Ch. et de Ph.*, sér. 4, xix. 392 (1870).

oxidizing graphite by means of a hot mixture of potassium chlorate and nitric acid. A compound is formed, usually in a crystalline state, which, on heating, deflagrates and increases largely in volume, leaving a black residue of pyrographitic oxide[1].

Berthelot has carefully described the conditions of this oxidation and has applied it to the graphites then known. I have extended this work to some native graphites, and to the numerous samples obtained in my work at high temperatures.

The mixture of fuming nitric acid and potassium chlorate, used in the manner described by Berthelot, leads to a graphitic oxide varying in colour from green or dark brown to yellow, and the complete oxidation requires six to eight successive treatments. This is no longer the case, when nitric acid prepared from recently fused nitre and a large excess of boiling sulphuric acid is used.

Under these conditions, on adding the dry graphite to the concentrated nitric acid, and then small amounts of dry chlorate, the oxidation is far more rapid and, in the case of natural graphites, the result is apparent at the end of the first treatment. Far more chlorate than graphite must be used, weight for weight. The oxidation must last some twelve hours and finish at 60° C.

One must be careful at the outset not to bring the mixture of chlorate, nitric acid and carbon up to 60° C., or rather violent explosions may take place. The admixture of the smallest amount of organic matter must also be avoided.

At the end of these oxidations, the graphitic oxide, obtained in more or less well-defined crystals, has always the same greasy appearance and the same light yellow colour.

In some cases the graphitic oxide obtained was almost colourless. We have also observed that if perfectly dry chlorate be introduced into very concentrated nitric acid, solution is instantaneous with the production of an orange red colour and under these conditions, at 60° C., every variety of graphite is completely transformed into graphitic oxide after ten hours. The smallest trace of moisture prevents the formation of this red coloration and diminishes greatly the

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[1] This reaction takes place even at ordinary temperatures, but takes a very long time. Ceylon graphite, with potassium chlorate and strong nitric acid, sealed up in a tube for a year, was partially converted into graphitic oxide.

rate of transformation. To this first research was added the measurement of the temperatures of combustion of graphite in oxygen and the determination of the density of the chief varieties. The latter determination presents considerable difficulty. Certain samples could not be freed from the gases which they seem to retain mechanically; so that the densities did not increase in as regular a manner as the rate of oxidation.

Certain natural graphites, heated in presence of sulphuric acid or of a mixture of this acid and potassium chlorate, acquire the property of increasing largely in volume when subsequently heated on a platinum foil (Schafhäutl, Marchand and Brodie). Luzi[1] has recently shown that it is sufficient to moisten these natural graphites with a very small amount of nitric acid to cause them to swell when heated, with the production of worm-like or dendritic projections. From these properties Luzi has divided the graphites into two large classes—those which swell after the action of nitric acid and to which he restricts the name *graphite*, and those which do not swell under these conditions, termed by him *graphitites*. The graphite of cast iron and that of the electric arc do not show this behaviour after treatment with nitric acid.

We have resumed the study of some natural graphites, obtained from our planet or from meteorites.

We then obtained graphites by a simple rise of temperature, and we have examined the properties of these varieties. Numerous samples of graphites were then prepared by dissolving carbon in various metals, and finally we have been able to prepare at will intumescent graphites, whose preparation was hitherto unknown.

These researches have enabled us to determine the conditions under which all the varieties of carbon, diamond or amorphous carbon may be converted into graphite.

A. Native graphites.

Ceylon graphite.—This variety has been studied by numerous workers. Luzi showed that it was intumescent; it is so, however, to a much smaller extent than the graphite obtained when platinum is melted in the electric furnace, in presence of an excess of carbon. On treatment with non-dehydrated

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[1] *Ber.*, xxiv. 4085 (1891); xxv. 214 (1892).

potassium chlorate and commercial nitric acid, this graphite yielded, at the seventh handling, a dark green graphitic oxide, and at the ninth, a pale yellow oxide whose particles become irregular in shape. The same graphite, treated with dry chlorate and concentrated acid, yields some graphitic oxide at the first handling. The details of the latter experiment are as follows:

First treatment. The graphite becomes dark green with reddish tints. Numerous points of graphitic oxide are seen under the microscope.

Second treatment. Apparently homogeneous green mass. No graphite is left.

Third treatment. Yellow mass still containing green particles.

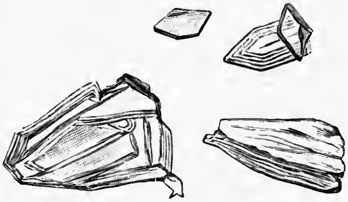

FIG. 8. × 10.

Fourth treatment. The oxide is pale yellow and has a bright appearance. Under the microscope it is plainly crystalline (Fig. 8).

Temperature of combustion of Ceylon graphite in oxygen, 665° C.; ash, 0·093; density, 2·23.

This graphite, when first purified by fused potash and by hydrofluoric acid, may be completely converted into graphitic oxide and leaves no residue containing the other varieties of carbon. This experiment was repeated with other samples and always with the same result.

Graphite from Borrowdale (Cumberland).—This form exists in compact fragments, possessing a non-lamellar, amorphous structure; treated with fuming nitric acid and heated on platinum, it does not swell; at the seventh handling with the oxidizing mixture it yields a pale yellow oxide, which is not crystalline[1].

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[1] Native graphites were attacked with commercial concentrated nitric acid and undried potassium chlorate.

When calcined this graphite deflagrates and breaks up into small pieces. We thought it might contain gases and we heated 1 grm. in vacuo at a dull red heat. 4·1 cc. were evolved, of which 0·7 was air. The remainder, 3·4 cc., proved on analysis in a eudiometer to be a mixture of hydrocarbons and hydrogen. This occlusion explains the explosive behaviour of Borrowdale graphite when heated. It is impure and contains 3 per cent. of ash. The latter retains the shape and the volume of the graphite, and contains iron, aluminium, manganese, lime and silica, iron and manganese being the most abundant.

Graphite from Ticonderoga.—This graphite has been studied in detail by Luzi. It occurs in brilliant lamellae marked with numerous rectilinear striae. It swells under the action of nitric acid, yielding a foliated mass of crystalline appearance, which returns to its original volume under pressure. Under the action of the oxidizing mixture, it is wholly converted into a light green oxide at the seventh treatment. The crystals retain the form of the graphite, and at the ninth treatment the oxide becomes pale yellow. Examined under the microscope the residue is seen to have lost all crystalline appearance.

Graphite from Greenville.—This graphite occurs in small crystals mixed with a calcareous gangue. Under the microscope the latter does not show impressions of the striae or of the equilateral triangles of graphite. It is a swelling graphite as Luzi has shown, and requires eight treatments to be converted into yellow graphitic oxide.

Graphite from Omenask (Greenland).—This is an amorphous and very impure variety; at a dull red heat it lost 0·09 per cent. and gave 21·04 per cent. of ash. The latter is nearly white, containing but little silica and much alumina; it also contains lime and magnesia.

Under the microscope very small crystals may be seen. It is a non-swelling variety (Luzi).

Graphite from Mugrau (Bohemia).—No regular crystals are seen with a lens. Very small crystals are to be seen with a high power. Its appearance recalls that of graphites obtained by the action of a high temperature on amorphous carbon; it has certainly not been produced in a liquid metallic bath nor from fused matter.

Loss at a red heat, 9·21 per cent.; ash, 37·32 per cent. The ash is yellow and contains a considerable amount of silica, alumina, iron and traces of manganese.

This variety does not swell, and its graphitic oxide, which is easily obtained, appears to be quite amorphous.

Graphite from Scharzbach (Bohemia).—This graphite is somewhat soft and has the appearance of the Mugrau specimen. Loss on heating, 6·82 per cent.; ash, 44·27 per cent., containing silica, iron, alumina, lime and manganese. Non-swelling, yielding a yellow, amorphous graphitic oxide. Temperature of combustion in oxygen, 620° C.

Graphite from South Australia.—Very impure variety, not crystalline as seen with a lens. Non-swelling, yielding a yellow, amorphous oxide.

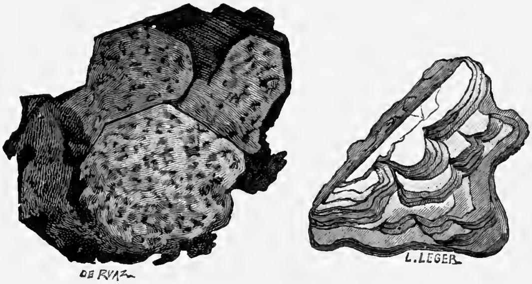

FIG. 9. × 40.

Graphite from Karsok (Greenland), brought by Nordenskiöld.—Compact fragments, with lamellar structure, but not clearly crystalline. Ash, 17·9 per cent. Non-swelling, yielding a green, amorphous oxide.

Graphites from the Cape 'blue ground.'—In this earth we found two very different graphites. The first (*a*) in regular crystals, and the second (*b*) in rounded masses with superposed layers (Fig. 9).

The latter sample seems to have been formed under pressure. These varieties are intumescent; they are clearly transformed into graphitic oxide by the oxidizing mixture, opening up as the pages of a book and keeping their shape.

Graphite from a pegmatite.—The sample studied came from an American pegmatite (locality unknown) which I owe to M. Damour.

This pegmatite is very interesting. For it is an igneous rock which has reached the surface after being subjected to a high temperature.

In this sample the graphite exists in fine lamellar crystals, often more than 1 cm. in diameter, spread throughout the substance. These crystals may be easily separated by treating the mineral, on the water-bath, with successive amounts of a large excess of 50 per cent. hydrofluoric acid. All the felspar and silica soon disappear. The residue is washed with boiling water and dried.

The sample studied contained 12·77 per cent. of graphite. The fine lamellae thus obtained are flexible and shiny, and the surface is marked with striae and equilateral triangular impressions, which are characteristic. This graphite burns in oxygen at 690° C., and gave 5·01 per cent. of ash, consisting chiefly of silica, alumina and lime, and containing but traces of iron.

The latter was detected by means of potassium ferrocyanide and sulphocyanide; the ash is white and retains the shape of the crystals. The temperature of combustion is higher than that of Scharzbach or Ceylon graphite. Moistened with nitric acid and then heated at a dull red heat, this graphite swells greatly.

The action of the oxidizing mixture of potassium chlorate and nitric acid brings about a curious phenomenon.

Six grms. of graphite were placed in a 500 cc. flask together with 3 grms. of $KClO_3$ and about 20 cc. of nitric acid. The graphite assumes at once a fine greenish tint resulting from superficial action, and after a few hours it so increases in volume that it half fills the flask. Attacked with a new portion, it swells further, and the volume attained is such that the flask must be changed. This is the only graphite which increased in volume in this manner at a temperature of 60° C., in presence of a liquid like nitric acid.

After the deflagration and destruction of the graphitic oxide, the residue contained no trace of either black or transparent diamond.

At the seventh handling with the oxidizing mixture the conversion into a green oxide is complete, and, with a further treatment, the oxide becomes colourless.

On examining, with a low-power microscope, the fragments of quartz or felspar on which the graphite crystals had rested, I was surprised to find on them impressions reproducing exactly the surface of these crystals. The same striae and triangles are found and cannot be removed by vigorous friction.

This led us to suppose that the graphite existed before the rocks whose crystallization gave rise to the pegmatite.

The characteristic properties of this graphite resemble closely, as we shall see later, the samples obtained from fused metals in the electric furnace. It must have been formed under similar conditions. At the moment of formation of the pegmatite, the graphite was moulded by the crystals of quartz and felspar, leaving on the latter the impress of its surface markings.

Study of some meteorites.—The discovery of graphite in the Diablo Cañon meteorite led me to take up the study of some metallic meteorites or holosiderites (Daubrée), in order to find out whether they all contained carbon, and if so, in what form.

Meteorites consisting entirely of iron alloys occur much less frequently than any others found on the earth. Their number is, however, sufficiently large to justify a methodical study of these metallic holosiderites in the hope of getting interesting results as to the carbon they contain[1]. As it is impossible for us to seek at great depths the metals which are there, and which in all probability are the cause of the high density of the globe as compared with the surface rocks, we must be satisfied with the fragments resulting from the breaking-up of other planets. The number of samples we have been able to study is unfortunately rather small. We owe nearly all of them to the kindness of M. Stanislas Meunier, who is still diligently pursuing his important researches on this subject.

No. 1. Iron from Kendall county (Texas).—Small sawn fragment weighing 59·950 grms., of polished surface marked with rectilinear figures. It encloses some geodes which, when examined with a lens, seemed lined with a black substance. The sample was attacked with hydrochloric acid diluted with its own volume of water. Its substance is rapidly disintegrated, and there remains a crystalline, metallic powder which soon dissolves in aqua regia. After this treatment with aqua regia, the residue consists of a black amorphous substance and

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[1] According to Stanislas Meunier the number of meteoric irons known in 1880 was about 110, of which more than half had been gathered in the United States. [Frémy, *Encyclopédie chimique*, p. 439.]

of numerous small and irregular crystals which are transparent. After repeated treatment with boiling sulphuric acid and then hydrofluoric acid, the transparent part disappears entirely. The black residue burns in oxygen giving carbon dioxide. It consists of an amorphous carbon, not easily attacked by the ordinary mixture of nitric acid and potassium chlorate. No trace of graphitic oxide is formed during the oxidation. The transparent part consists of sapphires and of small bottle-green grains, corroded at the edges by acids, and not well defined. They are completely destroyed when the residue is successively treated with the double fluoride of potassium and hydrogen and with boiling sulphuric acid. In recapitulation, the iron mass from Kendall county contains amorphous carbon, but neither graphite nor diamond.

No. 2. Iron from Newstead (Roxburghshire) found in 1827. Sample in the British Museum.

Sample weighed 8·10 grms., had a polished surface, and was black in parts.

After treatment with dilute hydrochloric acid there remains a bulky black residue, very rich in carbon. No fibrous brown carbon is to be seen under the microscope, but graphite is easily distinguished.

After treating three times with the oxidizing mixture, one obtains a yellow graphitic oxide of rounded appearance, but of no definite crystalline structure. On heating this compound deflagrates forming pyrographitic oxide.

After destroying this graphitic oxide by boiling sulphuric acid and treating with the double potassium hydrogen fluoride, and then again with sulphuric acid, there remains a small residue consisting of a few transparent grains with corroded surface. On renewing the treatment with the double fluoride, and with boiling sulphuric acid, nothing is to be seen under the microscope.

The Newstead iron contains carbon and graphite but no diamond.

No. 3. Déesite found in 1866 in the Sierra de Déesa, in Chili.—This non-homogeneous meteorite yielded, after treatment with hydrofluoric acid, a bulky residue consisting of (1) irregular transparent grains; (2) rounded masses rich in silica; (3) a black substance of low density containing amorphous fragments having the glance of graphite. We did not find any black fibrous carbon.

The black substance consists entirely of graphitic carbon. After the first treatment with the oxidizing mixture, one obtains a green graphitic oxide and, after the third treatment, there remain transparent fragments of elongated or rounded form which deflagrate on heating yielding pyrographitic oxide. In submitting the residue to the usual handling with sulphuric acid, and finally boiling sulphuric acid, there remained but three small fragments, two of which were distinctly corroded, while the third was perfectly clear. The latter was placed in a small platinum boat and heated up to 1,000° C. in a stream of oxygen. On examining the boat under a low-power microscope, it was seen that this fragment had lost its brilliancy, but had not burnt in the oxygen. This meteorite from Déesa contains no diamond, but a small quantity of graphite, and the form of graphitic oxide obtained showed that it had been submitted to some pressure.

No. 4. Caillite, iron from Toluca-Iliquipilso, Mexico (fall of 1874).—The specimen attacked had a well-polished surface and weighed 69·05 grms. The residue obtained was very slight; on examining it under the microscope some transparent grains, were found, a few greenish particles and some black grains, but no amorphous carbon and no graphite. After treatment with acids all the small transparent particles disappeared, and nothing remained after treatment with the double fluoride of hydrogen and potassium.

Iron from Ovifack.—Following the publication of our work on the blue earth from the Cape and on the meteorite from the Diablo Cañon, M. Daubrée kindly placed at our disposal samples of iron from Ovifack, discovered in Greenland by Nordenskiöld, in order to find what variety of carbon they contained. Nordenskiöld himself studied the question, as was evidenced by the publication of a note in the *Comptes Rendus*.

According to Daubrée[1], these iron blocks belong to at least three types. The first has a metallic lustre and is almost black; the second has a light grey metallic appearance and, in the third, the metallic substance is no longer continuous but appears in small globules or in grains in a stony matrix of silicates possessing a very dark green colour.

These three samples were treated separately, according to the method employed for isolating microscopical diamonds from the Cape 'blue ground'[2].

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[1] *C. R.*, lxxiv. 1541; lxxv. 240 (1872).

[2] Moissan, *C. R.*, cxvi. 292 (1893).

Sample No. 3.—Large fragments, weighing 34 grms., after complete extraction with hydrochloric acid, left behind a bulky residue. After treatment with boiling hydrofluoric acid, then with sulphuric acid, there remained a much smaller residue which, examined under the microscope, was seen to contain :

1. Dark green globules of perfect spherical shape.
2. A few transparent and elongated prismatic crystals.
3. Fragments of sapphire coloured blue, which were taken out with pliers and clearly identified.
4. A few particles of amorphous carbon, irregular in shape, and of a density below 2.

On repeating the alternate treatment with hydrofluoric and sulphuric acids, the bulk of the powder was further reduced. Attacked by means of potassium chlorate and nitric acid the carbon quickly disappeared. Finally, a last treatment with fused potassium bisulphate, followed by a washing with hydrofluoric acid, left no residue.

Sample No. 2.—18 grms. of this sample, treated with hydrochloric acid, yielded a small quantity of a powdery substance and of light carbon. Under the microscope one can distinguish with ease a few particles of schreibersite, a white opaque substance in irregular masses, and a large number of refracting grains of various shapes. A first treatment with hydrofluoric acid reduces the volume of this residue. After being attacked with boiling sulphuric acid, the quantity of amorphous carbon increases, showing the presence of an intumescent graphite. The treatment with hydrofluoric and sulphuric acids is repeated. The residue was attacked eleven times by the mixture of potassium chlorate and of nitric acid (formation of graphitic oxide), then taken up with potassium bisulphate, and finally with hydrofluoric acid. There then remain but a few microscopic black grains superficially corroded which disappear on fusion with potassium bisulphate.

Berthelot, in his research on a sample of Ovifack iron, had already indicated the existence of an analogous substance which is not diamond.

Sample No. 1.—Weight 11 grms. After treatment with hydrochloric acid, there remained a small quantity of very light amorphous carbon. This was diminished by a first treatment with hydrofluoric acid; but, under the action of boiling sulphuric acid, the quantity of amorphous carbon increased. This sample also contains intumescent graphite. It contained some non-swelling graphite, well crystallized under the microscope, and yielding graphitic oxide on treatment with chlorate. After fusion with bisulphate, nothing remained.

In these samples of Ovifack iron, kindly given to us by M. Daubrée, we have thus been able to characterize sapphire in one, and amorphous carbon in all three; in two of them intumescent graphite, in one only ordinary graphite, and we found neither black nor transparent diamonds in any of them.

B. **Artificial graphites.**

Graphites produced by simple rise of temperature.—We shall discuss in this section some of the graphites which may be prepared in the laboratory.

Diamond.—Jacquelin was the first to show that diamond heated in the electric arc became graphite; to this important observation we may add the following facts: the graphite obtained crystallizes in an irregular manner. The interwoven crystals are short and thick, of a brilliant black, showing occasional level faces. If the experiment be carried out with a current of 350 amperes at 70 volts, the graphite is fairly quickly attacked by means of ordinary monohydrated nitric acid and potassium chlorate. After three attacks the transformation is complete, and one obtains a yellow graphitic oxide. On combustion this graphite gave: carbon, 99·88; ash, 0·016.

Sugar carbon.—Sugar carbon, purified by chlorine and placed in a closed crucible, was heated for ten minutes by means of a current of 350 amperes at 70 volts. The appearance of the carbon is much the same after as before; its colour has however become greyer. No particle has a crystalline appearance, however high the magnification may be. It leaves a grey mark on paper and, when crushed, has decidedly the character of graphite. At the third attack with the oxidizing mixture it is changed into a pale yellow graphitic oxide. This graphite burns in oxygen at 660° C. and has a density of 2·19. On analysis it gives: carbon, 99·87; hydrogen, 0·032; ash, 0·110.

Charcoal.—Charcoal, purified beforehand, was heated in a covered crucible for ten minutes, with a steady current of

2,200 amperes at 60 volts for half the time. The experiment was brought to a close on account of the spurting of molten lime all around the furnace. This charcoal kept its original appearance, but on the slightest friction it becomes grey and shiny. Under the microscope the wood fibres, although slightly altered, are seen to have nearly kept their form. This graphite is not easily attacked by the oxidizing mixture, and it yields a very pale yellow graphitic oxide, generally consisting of a mass of small elongated rectangles, or of aggregates possessing a fibrous texture (Fig. 10).

Sublimed carbon.—Sublimed carbon collected on the positive electrode of the arc was only transformed at the fourth attack, using ordinary fuming nitric acid and potassium chlorate. The graphitic oxide, green at first, finally became yellow. The perfectly transparent particles had the appearance of twisted leaves; on analysis we obtained: carbon, 99·90; hydrogen, 0·031; ash, 0·017.

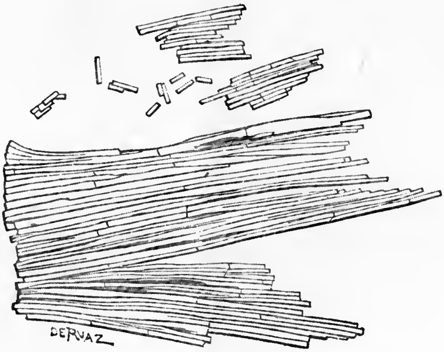

FIG. 10. ×20.

Carbon from the ends of the electrodes[1].—The ends of the electrodes are transformed into a compact soft graphite, without a trace of crystallization, becoming grey at the slightest rubbing and yielding a yellow graphitic oxide with concentrated acid.

Graphites resulting from the solution of carbon in various metals.—These graphites may be obtained by two different methods, either by displacing the carbon combined with the

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[1] Fizeau and Foucault, Despretz, and then Berthelot, have demonstrated the formation of graphite under the action of the electric arc.

molten metal by means of some other element, or by making use of the different solubility of carbon in the liquid metal at very high and lower temperatures.

Generally, in order to obtain graphites from refractory metals, the carbides were first prepared; in a subsequent operation these were saturated with carbon in the electric furnace. The regulus thus obtained was, in each case, attacked by acids or heated to redness in a stream of pure and dry chlorine. The residue, consisting of a mixture of amorphous carbon and graphite, was digested with fuming nitric acid at 40° C., to destroy the first variety of carbon. The graphite left behind was treated with boiling hydrofluoric acid, then with tepid sulphuric acid, and finally washed and dried.

Aluminium.—Aluminium heated for five to six minutes in the electric furnace (350 amperes at 70 volts) in presence of sugar carbon or merely in a carbon crucible, is converted into the carbide, and on cooling one obtains a regulus possessing a yellow crystalline fracture and containing aluminium carbide C_3Al_4. If heated for ten to twelve minutes, the carbide is partially volatilized, leaving behind a grey substance, brittle, porous, and bristling with crystals of graphite. The latter is isolated by means of hydrochloric acid, and purified by sulphuric and hydrofluoric acids. Finally, it occurs in aggregates of small and brilliant crystals, mixed at times with some black filaments. It has a density of 2·11. On first treating with the oxidizing mixture the graphite swells, and, at the second treatment, the smallest particles are entirely converted into graphitic oxide. Concentrated acid yields, on a first treatment, a light green oxide becoming yellow at the second handling.

Silver.—This metal dissolves but little carbon, even at its boiling-point. The ingots of silver, slowly cooled in the electric furnace, are generally covered with a thin film of graphite. After dissolving away the metal with nitric acid, one finds shining lamellae of graphite irregularly crystallized. This graphite is not intumescent. When first attacked with the oxidizing mixture it yields graphitic oxide, and is completely transformed at the sixth handling.

Manganese.—Manganese, when prepared in a wind furnace, has been shown by Berthelot to contain only amorphous carbon; but if this carbide be heated, in presence of excess of carbon, for four to five minutes (350 amperes at 50 volts), the metallic regulus remaining contains crystals of graphite and is covered with them[1]. This graphite is in rather large shining plates, of regular hexagonal form. With the oxidizing mixture it is completely converted at the third attack into a well-crystallized, yellow graphitic oxide.

Nickel.—Nickel, heated in the electric furnace, yields a graphite which by its appearance and form resembles grey cast iron, but its crystals are much better defined. At the second attack they are easily transformed into graphitic oxide.

Chromium.—The chromium carbides, to be described later, dissolve carbon easily. On cooling they yield a metallic regulus, and the latter, on treatment with acids, gives up graphite crystals much smaller than those obtained from manganese. They are irregular, less brilliant, and are not so easily attacked as the iron and manganese graphites, this being due to the higher melting-point of chromium. The oxidizing mixture begins to react distinctly only at the third treatment.

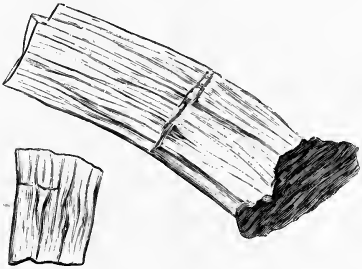

FIG. 11. ×40.

There results a bulky pale yellow graphitic oxide in irregular masses (Fig. 11).

Tungsten.—The melting-point of tungsten is higher than that of chromium; the graphite it gives occurs in small black crystals of regular shape. It scarcely begins to be converted into graphitic oxide at the third handling.

Molybdenum.—The molybdenum graphite consists of a mass of small brilliant crystals, black in colour. These crystals

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[1] This experiment seems to contradict the statement already given of the ready volatilization of manganese in the electric furnace. This is because the pure metal is far more volatile than the metal containing carbon. The latter, however, disappears under the prolonged heating action of the arc.

sometimes form a regular network or occur in rounded masses. They are less easily attacked by the oxidizing mixture than the preceding varieties.

Uranium.—A mass of small black shiny crystals not easily attacked by the oxidizing mixture. The uranium graphite is converted into a yellow oxide of irregular shape.

Zirconium.—The graphite from this metal occurs as a network of small distorted masses, with perforated surface, generally surrounded by threads of varying length (Fig. 12), slowly attacked, yielding a yellow graphitic oxide (Fig. 13).

Vanadium.—Vanadium is one of the most infusible metals prepared in the electric furnace. Its graphite is rarely crystalline ; it occurs generally in very thin, irregular fragments, perforated or slightly cut into, which sometimes have rounded extremities.

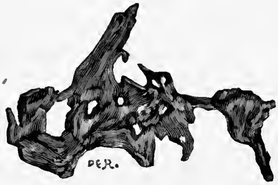

Fig. 12. ×40.

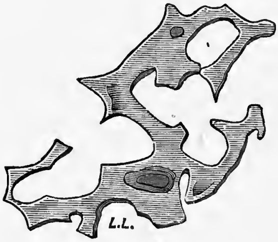

Fig. 13. ×40.

Titanium.—Titanium carbide, whose preparation we have described, dissolves carbon easily, giving it up on cooling in the form of graphite.

The latter is slightly intumescent and occurs crystallized or in forms similar to those of the vanadium graphite. The oxide it yields is brown at first and rapidly becomes yellow.

Silicon.—Heated in a wind furnace molten silicon dissolves carbon, giving it up subsequently as graphite, in the form of crystalline particles of a brilliant black hue yielding a yellow graphitic oxide.

At the temperature of the electric furnace silicon no longer yields graphite, but forms crystalline carbon silicide. At the fourth treatment with the oxidizing mixture the conversion of graphite into oxide is scarcely to be observed. On further treatment one obtains a yellow graphitic oxide in the form of the original fragments.

To recapitulate, artificial graphites may be amorphous or crystalline. Their density varies from 2·10 to 2·25. They burn in oxygen at about 660° C.

There are several varieties of graphite, as there are of amorphous carbon.

The stability of graphite increases with the temperature to which it has been subjected. This reveals itself in the greater or lesser resistance offered to the conversion into graphitic oxide. Further, as the melting-point of the metal in which the graphite has been formed rises, the resistance offered to oxidation plainly increases.

The influence of temperature on the stability of graphite may be shown by a simple experiment. Native graphite from Ceylon is transformed at the first attack by the anhydrous oxidizing mixture. If this graphite be heated for ten minutes in the electric furnace (1,200 amperes at 70 volts), a few yellow dots of graphitic oxide are barely to be observed at the third attack.

A simple rise of temperature thus causes graphite to be less easily attacked.

Displacement of carbon in molten cast iron by boron and silicon.—The study of the solubility of carbon in different metals, at increasingly high temperatures, led us to investigate the possible action of boron and silicon on iron carbide kept in the liquid state.

The action of boron on iron has not yet been studied [1], or at least, in the few attempts made, boron could not be clearly detected after the experiment in the metal subjected to its action.

As far as silicon is concerned no research has been systematically prosecuted. It has long been known in the working of iron that the richer cast iron is in silicon the poorer it is in carbon; but the action of silicon on cast iron has not been clearly determined.

We shall show that the reactions taking place in cast iron are sometimes as plain as those taking place in aqueous solutions in the laboratory at ordinary temperatures.

The complex nature of certain samples, which may contain a large number of compounds as impurities, is alone capable of obscuring the reactions.

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[1] More especially because the preparation of pure boron was hitherto unknown. We gave a method of preparation in 1892. *C. R.*, cxiv. 392. *Ann. de Ch. et de Ph.*, sér. 7, vi. 296 (1895).

Action of boron on grey cast iron.—We first studied a grey cast iron from Saint-Chamond, containing a total of 3·18 per cent. of carbon and 0·5 per cent. of ash[1].

10 grms. of this sample were placed in a porcelain boat brasqued with carbon, together with 2 grms. of boron, and the whole was strongly heated in a reverberatory furnace in a porcelain tube full of dry hydrogen. After the experiment a well-fused regulus was found in the boat, covered with a black network of graphite. The metal had a yellowish tint and bore on the surface a few long well-crystallized prisms. It contained on analysis 8 to 9 per cent. of boron. It is an iron containing boron mixed with partially crystallized iron boride. This specimen contained now but 0·27 per cent. of carbon, and yielded no ash on combustion in oxygen.

Thus boron easily forms compounds with the impurities of cast iron taking them into the slag. It plays towards the oxide of iron in solution in the metal an analogous rôle to that assigned by Troost and Hautefeuille[2] to manganese.

We may conclude from this experiment that boron has displaced carbon in the proportion of 1 to 10, and has eliminated at the same time the ash constituents. This experiment was repeated four times with another sample of grey Saint-Chamond cast iron, containing 3·24 per cent. carbon and 0·418 ash. The following figures were obtained after the reaction with boron :

	1	2	3	4	
Carbon . .	0·36	0·28	0·17	0·14	per cent.
Ash . . .	0·02	0·00	0·03	0·01	,,

We then experimented with a white refined cast iron from the St. Louis furnace in Marseilles, containing 3·85 per cent. carbon and 0·36 per cent. ash. After the reaction with boron it contained 0·24 per cent. carbon and 0·06 ash.

We wished to vary the conditions of the experiment and to avoid the use of a large excess of boron. To that end 500 grms. of grey Saint-Chamond cast iron were melted in the furnace, and, when it was quite fluid, 50 grms. of cast iron containing 10 per cent. of boron were added. The whole was shaken, the crucible closed, and the heating stopped. Upon adding

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[1] In the analysis of iron samples, the mixture of the different varieties of carbon is separated by chlorine or by mercuric chloride. The unattacked portion is burnt in oxygen and the residue termed ash.

[2] *Ann. de Ch. et de Ph.*, sér. 5, ix. 68 (1876).

the alloy of boron and iron to the molten metal, it remained for some time on the surface and only dissolved on shaking.

After cooling, the regulus obtained had a lamellar structure, was very hard, not being marked by a steel point and had the appearance of white cast iron. The action of boron caused the percentage of carbon to sink from 3·75 to 2·83. Boron had thus displaced some of the carbon, part of which was found as graphite between the regulus and the crucible.

Displacement of carbon by silicon.—A similar experiment was carried out by heating fragments of grey cast iron in a boat with powdered crystalline silicon. Under these conditions silicon also displaces carbon, and the latter is found as graphite above the metal.

But, as already observed, white or grey cast iron as prepared in the furnace is a somewhat complex mixture and hence the experiments were continued under simpler conditions. An iron rich in carbon was first prepared in the electric furnace from soft iron and sugar carbon. Then a few grams of fused silicon were scattered over this fluid bath. After cooling, the regulus, which is polished on its upper surface, had the appearance of a silicized iron, and possessed a white and brilliant fracture. This sample contained but very little combined carbon and no graphite. But in the middle of the regulus was found a deep cavity which nearly divided it in two. This cavity contained a considerable amount of bright, very well crystallized graphite.

In short, boron and silicon undoubtedly displace carbon in cast iron or in a molten iron carbide[1]. These substances, when kept at a sufficiently high temperature, behave exactly like the aqueous solutions of certain compounds, in which we precipitate or displace this or that dissolved or combined substance.

The fact that this replacement of carbon is not complete is due to the equilibrium established between the silicide and carbide of iron, depending on the temperature of the bath and on the impurities contained in it. This is the usual behaviour of white and grey cast iron.

We are thus led to the study of iron graphites.

Graphites from iron.—We have already dealt with the

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[1] The temperature at which all these experiments were carried out was not so high as to allow of the formation of silicide or boride of carbon in any quantity.

graphites obtained, either by the action of a simple rise of temperature on any variety of carbon, or by dissolving carbon in various refractory metals.

It seemed advisable to complete these first researches by a further study of the different varieties of graphite obtained from one and the same metal, under varying conditions of temperature and pressure. With this end in view we studied the case of iron as being technically the most important metal.

The melting-point of grey cast iron being in the neighbourhood of 1,150° C., the graphite we obtained from a Saint-Chamond sample must have been formed at or near this temperature. The mixture of graphite and amorphous carbon obtained from this iron, after having been attacked by chlorine at a dull red heat, was treated several times with fuming nitric acid and then with hydrofluoric acid. The graphite remaining after washing and drying has the following properties: density, 2·17; temperature of combustion in oxygen, 670° C.; it occurs in aggregates of very small crystals, possessing well-defined hexagonal points, and some irregular masses whose fracture is very brilliant (Fig. 14). It has a greyish colour. Treated with the oxidizing mixture of nitric acid and potassium chlorate it gives some oxide already at the second attack, and is completely transformed into a green, fairly well crystallized oxide at the third attack. If concentrated nitric acid be used, as previously indicated, and moisture carefully excluded, a light green oxide is formed at the first treatment, becoming yellow at the second.

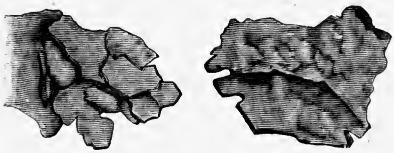

FIG. 14. ×20.

In another series of experiments we isolated the carbon from the same cast iron by treating it with hydrochloric acid, to which had been added a small quantity of nitric acid. The latter was added to convert the iron into ferric chloride, which is very soluble in dilute acids. The larger part of the amorphous carbon is destroyed by this treatment. The residue, washed and dried, is treated several times with fuming nitric acid. To free the graphite from the mineral matter it still contains, it is treated with hydrofluoric acid, and finally with boiling sulphuric acid. Under these conditions one obtains a substance having the appearance of graphite but containing only 80 to 85 per cent. of carbon, 1·3 per cent. of ash, and 0·15 per cent. of hydrogen. The percentage of hydrogen varied from 0·15 to 0·80[1]. As this graphite was kept at a dull red heat during the analysis, everything seems to point to the formation, during the treatment with the acids, of a complex body containing carbon, hydrogen, oxygen, and even nitrogen, this body being sufficiently stable to withstand a temperature of 400° C.

The formation of these compounds in connexion with metallic graphites is of importance, when these graphites are not prepared at very high temperatures. These compounds seem to be formed by the hydrogenization and subsequent oxidation of the iron carbide. They are similar to those obtained by Eggertz by the action of aqueous iodine on cast iron, and by Schützenberger and Bourgeois on treating white cast iron with aqueous copper sulphate[2].

Iron graphite strongly heated.—Soft iron of very good quality was placed in a crucible of sugar carbon. The whole was heated in the electric furnace (2,000 amperes at 60 volts) for ten minutes. Under these conditions the iron dissolves considerable quantities of carbon, loses its fluidity and becomes pasty. We found to our surprise that, at this high temperature, the crucible might be inverted without losing any of its contents. On cooling away from the air one finds, at the bottom of the crucible, a brittle mass covered with very fine crystals of graphite, some of which are several millimeters in diameter. At the surface are found some fragments which contain but very little iron and which consist of a mass of graphite crystals. At this high temperature some of the metal has even been volatilized. The metallic regulus is then attacked at a red heat by chlorine and the residue is treated with warm fuming nitric acid to destroy any existing amorphous carbon.

This graphite is generally obtained in bulky crystals of a

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[1] This graphite contained nitrogen which was transformed into ammonia by heating with soda lime, and was indicated by the appearance of ruddy vapours during the combustion in oxygen.

[2] *C. R.*, lxxx. 911 (1875).

brilliant black colour and, not seldom, of regular shape. Agglomerations of very small crystals are sometimes met with, closely interwoven and resulting apparently from the condensation of carbon vapour. This graphite has a density of 2·18 and burns in oxygen at about 650° C.; it contains 99·15 per cent. of carbon and only 0·17 per cent. of ash, and 0·28 per cent. of hydrogen. It is therefore very much purer than the graphite from ordinary iron, and contains but a very small amount of those complex hydrogen compounds so often met with in the graphites obtained from ordinary cast iron after treatment with dilute acids.

As one would expect, this graphite, which has been so strongly heated, possesses a great stability towards the oxidizing mixture. The first two treatments have no effect; only at the third is the formation of a slightly tinted oxide to be observed, possessing the appearance of smoked glass. The graphitic oxide occurs in regular hexagons (Fig. 15).

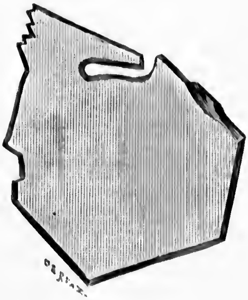

Fig. 15. × 20.

With concentrated acid, a complete transformation into yellow graphitic oxide is only achieved at the fourth treatment.

These two experiments demonstrate clearly that the resistance offered by iron graphite to oxidizing agents is a function of the temperature to which it has been heated.

Iron graphite cooled in water.—To bring in pressure as a factor in the preparation of graphite, we made use of the device which enabled us to compress strongly carbon dissolved in liquid iron; the fused iron regulus was suddenly cooled in cold water. After treatment with chlorine, as already described, a shining graphite remained, black in colour, whose form was very different from that of the other graphites. It occurs in short thick crystals whose angles are often blunted, and in irregular masses whose rounded form seems to indicate an incipient fusion (Fig. 16).

In appearance it resembles the sample of graphite *b* met with in the Cape blue earth. Its density is 2·16 and it burns in oxygen at 660° C.; on analysis it gives

Ash	1·29 per cent.
Hydrogen	0·64 ,,

On treatment with the ordinary oxidizing mixture, it begins to be converted into graphitic oxide only at the third attack.

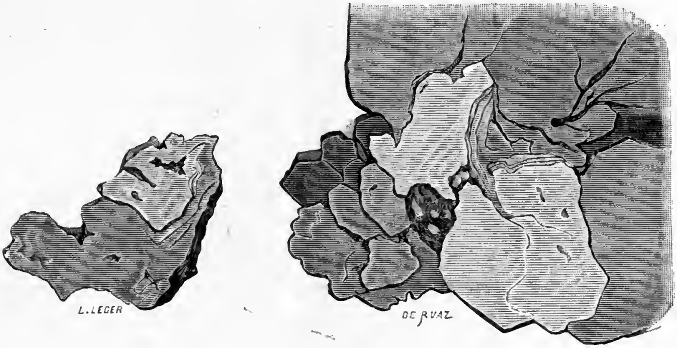

Fig. 16. × 20.

Four treatments with concentrated nitric acid are required to convert it into the crystalline oxide.

Graphite produced by the action of silicon on cast iron.—In the preceding experiments the graphite was obtained by making use solely of the solubility of carbon in iron. I wished to examine graphite produced by a chemical reaction, and to that end I replaced the combined carbon in a specimen of cast iron by silicon, making use of the reaction already described.

The details have been given and need not be repeated here. The graphite so obtained has a fine black colour and occurs in crystals which are often of regular shape (Fig. 17).

It has a density of 2·20 and gave on analysis 98·82 per cent. of carbon, 0·85 per cent. of ash and 0·20 per cent. of hydrogen. It is easily destroyed by the oxidizing mixture and at the first attack with ordinary nitric acid and potassium chlorate, the graphite opens, yielding on the edges fragments of graphitic oxide (Fig. 18).

The transformation is almost complete at the third attack; the greenish yellow oxide has a fine lustre and its crystals preserve in a remarkable manner the original form of the graphite.

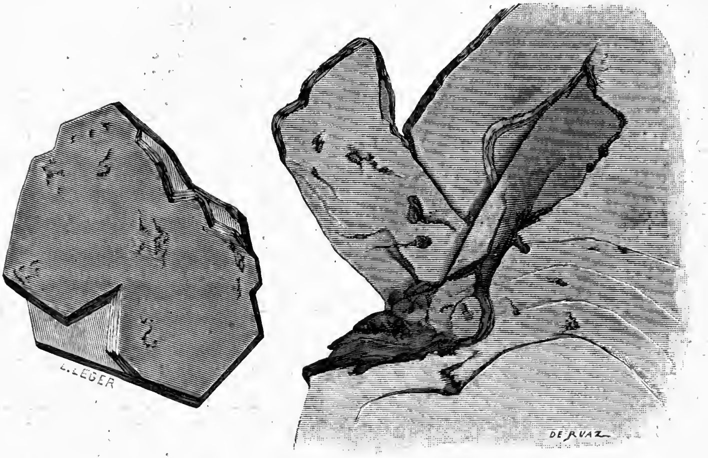

FIG. 17. × 20.

With concentrated nitric acid the change into yellow crystalline oxide is complete at the third treatment.

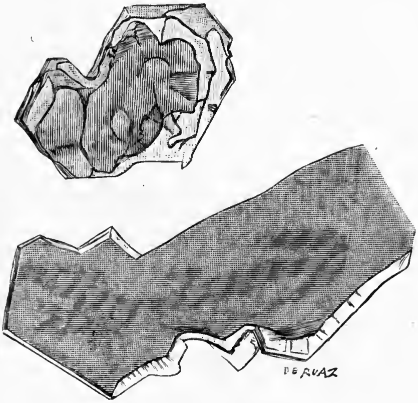

FIG. 18. × 20.

Presence of hydrogen in the various graphites.—All the graphites examined up to now contained hydrogen. This hydrogen results either from a physical phenomenon, e. g. condensation of gaseous hydrogen in graphite[1], or from chemical action, e.g. hydrogenization of iron carbide or of certain varieties of amorphous carbon in the iron.

We performed the following experiment to show clearly that the hydrogen does not exist in the graphite in a state of combination. A regulus of iron saturated with carbon under the action of an arc of 2,200 amperes at 60 volts is left in the closed electric furnace. On cooling the metallic regulus becomes covered with a considerable quantity of graphite. The latter is collected and without either removing any particles of iron it may contain or subjecting it to any treatment, a small quantity placed in a boat is heated for ten hours in vacuo at 500° C.

When the temperature is still at 200° C. dry air is admitted, the whole is weighed in a polished tube and the boat, still hot, is finally placed in a combustion apparatus previously heated. Under these conditions the combustion of 0·076 grm. of graphite in oxygen yielded but 0·001 grm. of water corresponding to 0·014 per cent. of hydrogen, an amount which seems to us to be within the limit of experimental error.

Thus, if the conditions of formation of graphite be studied in one metal, iron for example, at varying temperatures and pressures, the following results are obtained:

1. At ordinary pressures, the graphite is the purer the higher the temperature of formation.
2. The higher the temperature of formation, the greater is the stability towards nitric acid and potassium chlorate.
3. Under the influence of pressure, the crystals and the mass of graphite have the appearance of a fused substance.
4. The small quantity of hydrogen, always found in graphites, diminishes clearly as their purity increases.

A graphite which has not been treated in any way, and which is first heated in vacuo, no longer yields water by its combustion in oxygen.

5. Compounds containing hydrogen and oxygen are formed by the action of acids on cast iron; these compounds are

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[1] Cailletet showed long ago, by some delicate experiments, that molten iron dissolves a considerable quantity of hydrogen. *C. R.*, lxi. 850 (1865).

undecomposed at a dull red heat but, like graphite, are destroyed on combustion.

C. Intumescent graphites.

We have found a variety of swelling graphite in the Cape blue earth, thus increasing the large number of similar graphites discovered by Luzi, in Ticonderoga (New York), Ceylon, Quebec, Spain, Norway, &c.

Our study of the different varieties of carbon has enabled us to reproduce at will this particular form of graphite, so largely distributed in nature, but not hitherto prepared in the laboratory.

To obtain swelling graphite, it is sufficient to cool molten cast iron suddenly in water. At the surface of the regulus one finds ordinary graphite and, at a slight depth, a considerable quantity of graphite which swells quickly on treatment with nitric acid. In this way one obtains a mixture of two graphites or, in the nomenclature of Luzi, a mixture of graphitite and graphite.

When swelling graphite alone is required, it is better to use some other metal than iron as the carbon solvent. Platinum has yielded us the best results.

Platinum intumescent graphite.—About 400 grms. of platinum, placed in a carbon crucible, are melted in the electric furnace (450 amperes at 60 volts). The platinum melts quickly and, after a few minutes, distils and condenses in small molten globules on the cooler parts of the electrodes. The fused platinum is allowed to take up carbon for a few moments at this high temperature, and the experiment is finished after six to eight minutes. The metal cools slowly in the carbon crucible. Under these conditions carbon dissolves in the platinum and the excess of carbon crystallizes out in the metal as graphite. The regulus is then treated several times with aqua regia; finally, the residue is washed with boiling water and dried. The yield was 1·45 per cent.

Properties.—This graphite is of a slate grey colour, less dark than that from iron. It occurs in detached hexagons which are generally superposed. Under the microscope the hexagonal plates, which are highly reflecting, are seen to have some parallel striations and occasionally triangular impressions, which do not stand out like those found in the diamond. A few bright surfaces possess also parallel lines of varying shape. The density of this graphite varies from 2·06 to 2·18, and it burns in oxygen already at 575° C. It has been subjected to the action of nitric acid in the treatment with aqua regia, and it swells greatly on being heated to dull redness. At 400° C. it swells in the manner of mercury sulphocyanide. The light mass thus obtained consists of graphite, for, on treatment with the mixture of nitric acid and potassium chlorate, there results at the first attack a beautiful green oxide, becoming light yellow at the second.

Fused potassium nitrate has no action on this variety of carbon. If the temperature be raised a little, the graphite swells and is then destroyed fairly rapidly, but seldom with incandescence. Fused chromic acid has but very little action. However, at the point of decomposition of this agent, owing to the rise of temperature, a small amount of carbon dioxide is evolved. Iodic acid, slightly heated, attacks it on the other hand with ease, dense vapours of iodine and carbon dioxide being produced. In hot sulphuric acid the graphite is unaltered and no sulphur dioxide is evolved, even at the boiling-point. Finally, fused sodium carbonate destroys it rapidly. This swelling graphite was analysed by burning it in pure oxygen and weighing the carbon dioxide formed. Results obtained:

	1	2
Carbon	99·02	98·84 per cent.
Ash	1·10	1·02 ,,

The increase in weight of the water absorption tube was but 0·0015 grm., and we may conclude that this graphite contains no hydrogen, or at any rate only a very insignificant amount.

The ash, examined under the microscope, had the appearance of spongy platinum and, on treatment with aqua regia, this metal was easily detected.

Cause of swelling.—The cause of the swelling of this variety of carbon had still to be investigated.

The following experiment has a bearing on the question. About 1 c.c. of this graphite was heated in a glass tube through which passed a current of air free from carbon dioxide. At a heat approaching dull redness the mass swelled rapidly, and, at the same time, were evolved nitrous fumes, and a small amount of carbon dioxide which was absorbed by baryta. After the evolution of this gaseous mixture, and in presence of a fresh portion of nitric acid, only traces of carbon dioxide were produced. A last treatment with nitric acid caused no milkiness in the baryta water.

It seems to us, therefore, that this swelling may be attributed to the sudden evolution of gas resulting perhaps from the destruction at a dull red heat of a small amount of amorphous carbon, compressed between the hexagonal plates of graphite, or to the pyrogenetic decomposition of a very small quantity of graphitic oxide, produced by the action of the nitric acid on a trace of amorphous graphite, mixed with the crystallized mass and more readily attacked. In either case it is the sudden evolution of a small volume of gas expanded by the heat which seems to cause this particular swelling.

Intumescent graphites obtained from various metals.—In prosecuting this work we found that many metals might replace platinum in the preparation just described.

From the whole of our researches on the different varieties of graphite, we have obtained the rather curious result that all the graphites obtained solely by the help of a very high temperature on any variety of carbon (diamond, lamp-black), or by condensation of carbon vapour, showed no tendency to swell under the action of concentrated nitric acid. On the contrary, all graphites prepared at a high temperature by dissolving carbon in a given metal swelled readily.

Zirconium, vanadium, molybdenum, tungsten, uranium, chromium yield swelling graphites. The same is true of aluminium, which takes up carbon only at a high temperature. The phenomenon of swelling under the action of nitric acid is the result, not only of the action of the metal on the carbon, but more especially of the temperature at which the graphite is formed.

Thus, a grey cast iron from Saint-Chamond yielded, after treatment with chlorine and destruction of the amorphous carbon by nitric acid, a graphite which did not swell, in presence of nitric acid, on being slightly heated. The same iron, strongly heated in the electric furnace (2,000 amperes at 50 volts), yielding on cooling a graphite which swelled abundantly[1].

It may be recalled that this swelling takes place under the action of monohydrated nitric acid. The graphite saturated

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[1] In our study of the diamond earth from the Cape we showed that the breccia contained, in larger amounts than the diamond, an intumescent crystalline graphite whose ash was very rich in iron.

with acid may even be dried for a whole day at 120° C., nevertheless, as soon as the temperature rises, the mass swells abundantly.

The temperature at which swelling occurs is not high for any of the graphites produced under the action of intense heat. It varies between 165 and 175° C. It is thus unnecessary to heat them to dull redness.

We enclosed in a glass tube a small quantity of this swelling graphite treated with nitric acid and then dried in an air bath. The tube was evacuated and then sealed. Swelling takes place in vacuo at the temperature already mentioned, and a gaseous mixture is evolved containing carbon dioxide, nitrogen and red fumes, while a few drops of nitric acid are condensed on the sides of the tube.

Hence, as already remarked, this swelling may be due to the sudden evolution of a certain volume of gas expanded by heat.

These experiments show that swelling graphites prepared in the laboratory may be as numerous as those found native; they may enable us to explain the formation of the latter, some of which yield, as is well known, ash generally rich in iron oxide. These graphites would seem to have been formed at a rather high temperature without any great pressure, at the heart of iron masses which may have subsequently disappeared under the action of gaseous substances, such as hydrochloric acid[1].

Graphite is a substance which remains unattacked by most chemical reagents. Water vapour and air have no action on it at a dull red heat. It has thus become separated from metallic admixture, forming more or less extensive deposits, or being disseminated through the rocks.

Conclusions.—Accepting the definition of Berthelot, we shall give the name of *graphite* to that variety of carbon, generally crystallized, whose density is about 2·2, and which yields easily recognized graphitic oxide on treatment with potassium chlorate and nitric acid.

These graphites are found in surface rocks and in some meteorites. They may be divided, as suggested by Luzi, into swelling and non-swelling graphites when slightly heated in presence of a trace of nitric acid. We came across a graphite,

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[1] This formation of a ready volatile chloride of iron might account for the dissemination of iron during the first geological ages.

in an American pegmatite, whose increase of volume was extraordinary. The iron from Ovifack and from the Cape blue earth also yielded intumescent varieties.

Some graphites, as those from Borrowdale, are filled with gas which they hold tenaciously.

Graphites obtained in the electric furnace by a mere rise of temperature do not swell. On the contrary, all those obtained from a liquid metal at a high temperature, whether by difference of solubility or by a chemical reaction, have the property of swelling readily. This variety is easily prepared in the electric furnace by keeping platinum at its boiling-point in a carbon crucible. The swelling of this variety of graphite is to be attributed to a sudden evolution of gas.

Artificial graphites may be amorphous or crystalline. Their density varies between 2 and 2·25. They burn in oxygen at about 660° C. When they are pure they contain no hydrogen.

Graphite formed in the electric furnace and not treated with any reagent yields no water by its combustion in oxygen, if it be first heated in vacuo. On the contrary, ordinary cast iron, treated with dilute acids, yields compounds containing hydrogen and oxygen which are not destroyed at a dull red heat.

When a graphite is prepared in the electric furnace, its resistance to oxidation is proportional to the temperature to which it has been subjected. A readily attacked graphite, such as that from Ceylon, becomes difficult to attack if strongly heated. This fact establishes the existence of several varieties of graphite, analogous to the different varieties of amorphous carbon.

PART III

ARTIFICIAL PRODUCTION OF THE DIAMOND

General.—Attempts to produce the diamond artificially soon followed on Lavoisier's memorable demonstration of the fact that it consisted of crystallized carbon. The investigations begun in this direction are fairly numerous, but few have been carried out with method and perseverance. With the exception of a few important papers, we shall see when dealing with the matter historically, how much that is contradictory or doubtful has been published on the subject. Further, numerous though the investigations have been, there have been fewer papers published than one might have supposed. This is owing probably to the fact that many workers have busied themselves with the reproduction of the diamond rather than with the study of the allotropic forms of carbon. This aspect of the question is incomplete. Bearing this in mind, we set out to study in as general a manner as possible the three varieties of carbon: amorphous carbon, graphite, and the diamond. In the preceding chapters have been given the results obtained in relation to the amorphous varieties and to graphite. In the present chapter are summarized the results relative to the diamond.

At the outset we felt that, granted the possibility of reproducing the diamond, the first crystals obtained would be microscopic. Bearing in mind the relative size of natural quartz crystals to those obtained artificially by M. Daubrée's successful method, one could scarcely expect to produce at first diamonds of several carats. Were a further example necessary, one might recall how many researches and repeated attempts were required to carry out the synthesis of rubies of any size, possessing the colour and purity met with in some rare specimens of this beautiful stone.

In prosecuting this work we have therefore studied with great care, and always under the microscope, the residues, sometimes very slight, obtained after the various chemical manipulations to be described later. We owe our success in this work to the microscope.

Finally, we had to separate finely divided crystallized carbon, not only from a large excess of amorphous carbon and of graphite, but also from silica, silicates, crystallized or molten alumina, in a word, from all the substances the mineral world might furnish. Under this head M. Berthelot's[1] important work has been our guide and our model.

The diamond may be defined as follows: An elementary substance of maximum hardness, possessing a density of 3·5, burning in oxygen above 700° C., 1 grm. yielding in this way 3·666 grms. of carbon dioxide.

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[1] 'On the different forms of carbon,' *Ann. de Ch. et de Ph.*, sér. 4, xix. 392 (1870).

Thus the three important features are: the hardness, the density, and the combustion in oxygen.

Up to the present the ordinary clear diamond cut all other substances and was not cut by any. We have shown that this great hardness, imagined to be the peculiar property of the diamond, was also met with in some of the new substances we have prepared in the electric furnace.

The boride of carbon cuts slowly into the diamond and the carbo-silicide of titanium is almost as hard as the transparent diamond. On the other hand, a certain variety of boart of undefined crystallization, well known to jewellers, and the black diamond still deserve the title of ἀδάμας, and their hardness is superior to that of the substances just mentioned.

The electric furnace has enabled us to increase notably the number of hard substances capable of scratching the ruby with ease. We may mention carbon silicide, and many metallic carbides, borides, nitrides, silicides, and carbo-silicides.

From this brief summary we see that a number of substances can scratch the hardest corundum without being diamonds. The power of scratching the ruby is therefore a criterion of small value.

The high density of crystallized carbon (3·5) is of itself equally insufficient to characterize the diamond. Certain compounds of titanium, various complex metallic carbo-silicides and carbo-borides may have densities equal to or greater than that of crystallized carbon.

Finally, the combustion in oxygen at a bright red heat with formation of carbon dioxide is not sufficiently characteristic. Carbon boride or certain metallic carbo-borides, which are very hard and dense, may burn partially to carbon dioxide at a red heat. Only when the weighed amount of carbon dioxide produced corresponds to the atomic weight of carbon does the combustion in oxygen acquire a definite value.

That a body may be looked upon as a diamond it must possess these three properties: hardness, density, and produce 3·666 grms. of carbon dioxide for every gram of substance burnt. Any test based on one of these properties alone is incomplete, and may lead to a false interpretation.

Before describing my researches on the reproduction of the diamond, I wish to thank my assistant, P. Lebeau, who throughout this work has helped me in the most devoted and painstaking manner possible.

Historical.—It is not possible for us to give in this chapter a complete survey of the attempts made to reproduce the diamond; this would take us too far. We shall briefly summarize the more important work on this subject.

In 1828 J. N. Gannal presented to the Académie des Sciences a paper entitled: 'Observations on the action of phosphorus in contact with pure sulphur carbide.' Gannal declared that crystallized carbon was easily formed from a solution of phosphorus in carbon disulphide, kept for three months under water, and that certain fragments so obtained were as large as a millet-grain.

These experiments we have repeated, at first in the manner described by Gannal, and we have never obtained anything but small pieces of glass or small grains of silica completely soluble in hydrofluoric acid. We then increased the time of the experiment. We obtained nothing after six months, a year, and even five years. Finally, we replaced the phosphorus by antimony, and under identical conditions the result has always been a negative one. We never obtained crystals visible to the naked eye, and the microscopic particles obtained after washing with carbon disulphide and then with distilled water were always soluble in boiling hydrofluoric acid.

This work had already been repeated fruitlessly by Gore.

We need but name the researches of Cagniard-Latour.

Following up his work on the volatilization of refractory bodies in the electric arc[1], Despretz tried to reproduce the diamond. His experiments have been much discussed. He caused an electric arc to play between a carbon electrode and a bunch of platinum wires and obtained a crystalline dust which scratched the ruby, and this one test led him to look on this substance as crystallized carbon.

Several chemists have viewed the experimental result with distrust. It is nevertheless highly probable. The small glistening particles obtained by Despretz must have consisted of crystals of carbon silicide and perhaps boride, whose hardness is sufficiently great to cut the ruby with ease and even to scratch a soft diamond.

The action of the electric arc on carbon has never yielded any crystallized carbon. In the paper already quoted, Berthe-

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[1] 'Fusion and volatilization of some refractory bodies under the triple influence of the voltaic pile, the sun, and the blowpipe,' *C. R.*, xxviii. 755; xxix. 48, 545, 709 (1849).

lot has resumed the study of the extremities of the electrodes of arc lamps which had been working for some time, and, after removing the graphite, he never found a trace of diamond.

We may add that the small carbon crucibles and the electrodes used by Despretz, which had remained at the Sorbonne, were examined by Berthelot in 1870. These crucibles and the electrode ends were entirely converted into graphite, as Despretz had indicated, and into nothing but graphite. M. Berthelot proved this by the transformation of this variety of carbon into graphitic oxide.

Following up a geological theory propounded by M. de Chancourtois, M. Lionnet presented in 1866 a note to the Académie des Sciences—'On the natural and artificial production of carbon.' He showed that carbon bisulphide is decomposed by a couple consisting of a leaf of tin wound round a gold leaf. This experiment we have repeated, and we have found that if the carbon bisulphide be quite pure no deposit is formed even after five years.

Should moist carbon bisulphide be used in the experiment, small glistening particles are deposited on the glass as soon as the temperature is lowered; these are small drops of water which might be mistaken at first sight for small crystals.

We then studied the conditions to be observed for the electrolytic precipitation of carbon, and we have already shown that the carbon so obtained is always amorphous.

On February 19, 1880, J. B. Hannay published a preliminary note on the diamond, entitled—'On the artificial production of the diamond[1]' and soon after a paper—'On the artificial preparation of the diamond[2].'

In this work, Hannay took up the study of the carbon obtained from hydrocarbons by the action of the alkali metals. It has long been known that, at a high temperature, this reaction yields a glistening carbon of considerable hardness. Hannay first used distilled paraffin, but, after a number of experiments, the somewhat variable decompositions of this substance yielded no result. He then worked with a more complex substance, Dippel's oil. To this was added 10 per cent. of distilled paraffin. Lithium was the alkali metal used. The mixture is heated for fourteen hours in an iron tube

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[1] *Proc. R. S.*, xxx. 188 (1880).

[2] ibid., xxx. 450.

which is closed by softening in a forge fire and then hammering, and, should it not explode, one may find at times small black or transparent crystals having the properties of the diamond and yielding when burnt in oxygen a weight of carbon dioxide proportional to the atomic weight of carbon. Hannay found that the carbon dioxide thus produced contained 3 per cent. of nitrogen which leads him to say: 'From the fact that the diamond has only been obtained in presence of nitrogenous matter and that the product (only a part of the 14 mgrms. being transparent) contains nitrogen, I am led to conclude that the diamond is produced in this reaction by the decomposition of some nitrogen compounds and not by that of a hydrocarbon.'

Hannay's experiments are rather complicated and somewhat contradictory. The method by which the diamond is separated from the carbonaceous layer which lines the iron tube is by no means clear. In one experiment he found at the bottom of the tube a smooth covering on the walls. Never having obtained this result, he cut off the extremity of the tube. The product was black and was removed with a chisel; it consisted apparently of iron and lithium. He powdered it in a mortar and came across some very hard particles, which however did not resist the blows. On examination they were found to be transparent and were supposed to be diamonds.

It seems to us that this product, removed with a chisel, yielded up with surprising ease the diamonds which it contained. Further, Hannay constantly mentions the presence of silica which ought not to be met with in his experiments. If Hannay really obtained some diamond, it was formed under pressure, as we shall see later, owing to the solubility of carbon in a fairly fusible alloy of lithium and iron, and not from the nitrogen compounds contained in Dippel's oil.

Be that as it may, I determined to repeat the work of Hannay.

Tubes of soft iron of the following dimensions were made: height, 60 cm.; thickness, 14 mm.; internal diameter, 6 mm. They were filled with the mixture of lithium (which I owe to the kindness of M. Guntz), of Dippel's oil and distilled paraffin. However, when I wished to seal the tube by melting up the open end, as advised by Hannay, I noticed that the liquid contents distilled away before the seal was completed.

Even when the tube was surrounded by a lead coil through which cold water was circulating, the temperature acquired by the extremity of the tube before it could be closed rendered it impossible to keep the mixture inside.

After several unsuccessful attempts I had to give up the repetition of these experiments.

Marsden has published some very interesting work on the same point, and this we will summarize.

In a preliminary note, 'On the preparation of adamant carbon [1],' Marsden states that he heated silver, or an alloy of silver and platinum, in a brasque made of sugar carbon, up to the melting-point of steel. At this high temperature the silver dissolves a small quantity of carbon, which is given up on cooling. The metal is dissolved in nitric acid, and in the residue are found amorphous carbon, graphite, and some small black or transparent crystals. The quantity so obtained was much too small to allow of a combustion in oxygen in order to weigh the carbon dioxide formed. According to Marsden the properties of these small crystals approximate to those of the diamond. At the end of the paper he announces his intention of prosecuting the work, but his researches have not been continued.

The work of Marsden is of the highest interest, because he observed quite correctly the great number of different crystallized products which may be formed at the solidifying point of silver giving up oxygen, alumina, silica, &c. For example, in a research on the same lines, to study the solubility of silica in silver [2], he speaks of hexagonal lamellae of a pale yellow colour, which he at first mistook for graphite and which he did not examine further. These beautiful hexagons consisted of crystallized silicide of carbon, which is formed with great ease in silver at a high temperature, and which is now prepared commercially under the name of carborundum.

To return to the researches of Marsden which I have often repeated, I believe that one may obtain by chance some more or less well crystallized black diamond by using the method he describes. This may happen more especially when the crucible is heated in a wind furnace by means of retort carbon. As is well known, this material leaves but little ash; in consequence the fire goes out suddenly, and, owing to the powerful draught of the chimney, a rapid current of air passes through

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[1] R. Sydney Marsden, *Proc. R. S.*, xi. 20 (1880–1).

[2] ibid., xi. 37.

the furnace. The crucible cools quickly; the silver contained in a Doulton graphite crucible cools superficially. A hard metallic crust is thus formed, and when the still molten silver in the interior passes from the liquid to the solid state, an increase of volume takes place and pressure is exerted on the small amount of carbon still in solution which is tending to separate out. Under this pressure some black diamond is formed. Up to this time the excess of carbon had always been deposited as graphite.

We shall see later that this preparation of black diamond in silver yields results which are satisfactory and constant when a small mass of silver saturated with carbon is suddenly cooled.

This method has never yielded us transparent diamonds. In reality the black residue obtained by treating the silver mass with nitric acid, then with sulphuric acid, and finally with hydrofluoric acid, yields a mixture of graphite, of black diamonds, and of transparent crystals, which might at first sight be taken for diamonds. By the action of potassium chlorate and nitric acid the graphite is converted into graphitic oxide and finally destroyed; but the transparent crystals disappear when the residue is fused with acid potassium sulphate. The black crystals, however, remain and show all the properties of black diamond or carbonado.

On the whole it is probable that Marsden obtained some black diamond, but by chance and without realizing the important part played by pressure.

In conclusion, I wish to emphasize again the interesting nature of Marsden's results, and the fact that I have been able to confirm some of them in my work. More especially, I have obtained with ease the crystals of silica which he mentions in the paper already quoted.

A. **Preliminary researches.**

Our earlier researches on fluorine and its compounds led us to undertake some experiments on the crystallization of carbon. For fluorine is known to be an intensely reactive element, yielding well-crystallized products in the majority of the reactions in which it takes part. We have therefore studied first of all the hitherto unknown combinations of fluorine and carbon.

We have prepared different fluorides of carbon and have decomposed them under various conditions, hoping that a reversed reaction might enable us to obtain crystallized carbon[1].

In all the decompositions of the fluorides of carbon we carried out, we never obtained anything but lamp-black at a dull red heat and graphite at a high temperature. We were thus led to generalize our work and, as already mentioned, to undertake as complete a study as possible of the three varieties of carbon.

As far as the diamond is concerned, it seemed advisable to us to make at the outset a number of preliminary investigations before taking up the question of the reproduction of crystallized carbon. The course of research is ever the same, and analysis must precede the first gropings of synthesis. In this particular case it was highly important to study completely not only the properties of the diamond but further the geological conditions under which it may have been formed. Hence the preliminary researches here briefly summarized.

Some new properties of the diamond.—The chemists who have studied the properties of the diamond have investigated more especially the action of oxygen upon it at a high temperature. The reaction taking place has long been known, but there were no exact data as to temperature of combustion of the diamond. Dumas and Stas[2], in some important researches which helped to determine the atomic weight of carbon, carried out the combustion in a porcelain tube heated in a fireclay furnace. Most chemists who since then have had to carry out the combustion of the diamond used a porcelain vessel heated in a good organic analysis furnace[3].

At the outset we noticed great differences between the temperatures of combustion of various samples, whether from Brazil or from the Cape.

To determine these temperatures we made use of the thermo-electrical couple of H. Le Chatelier, placed inside a porcelain tube glazed outside and inside. The junction was borne on a small support made of platinum on which the diamond to be burnt was also placed. The apparatus was closed at each end by pieces of glass cemented on to the porcelain tube, and this rendered it possible to watch the combustion taking place in

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[1] Moissan, *C. R.*, cx. 276, 951 (1890).

[2] *Ann. de Ch. et de Ph.*, sér. 3, i. 5 (1841).

[3] Friedel, 'Combustion of the diamond,' *Bull. Soc. Chim.*, xli. 100 (1884).

a current of oxygen[1]. Two small washing-tubes containing baryta solution were included, one after the oxygen, to make certain of its purity, and one after the porcelain tube, to indicate the beginning of the combustion. If the temperature be raised under these conditions the combustion of the diamond, revealed by the action of carbon dioxide on the baryta, proceeds slowly at first without production of light. But if this point be exceeded by 40 to 50° C., a vivid combustion takes place and the fragment is surrounded by a distinct flame.

Another rather interesting occurrence has been observed in these experiments. At the instant of combustion of the diamond small opaque spots have always been observed on its surface, indicating that the transformation of transparent into black carbon is simultaneous with the combustion.

The results of our experiments were as follows:

No. 1. Carbonado of yellow colour: burns with production of flame at 690° C.

No. 2. Black, very hard carbonado, with grained surface: burns with flame production between 710 and 720° C.

No. 3. Transparent diamond from Brazil: begins to burn without flame between 760 and 770° C.

No. 4. Transparent, well-crystallized diamond from Brazil: burns slowly between 760 and 770° C. This diamond, which weighed about 1 carat, had first been heated in a brasque at the usual temperature of the oxygen blowpipe, and it was covered with a thin layer unattacked by aqua regia. This superficial layer disappears a little below the temperature of combustion of the diamond.

No. 5. Cut diamond from the Cape: begins to burn without flame between 780 and 790° C.

No. 6. Boart[2] from Brazil: begins to burn slowly at 790°, breaking into flame at 840° C.

No. 7. Boart from the Cape: burns dully at 790° and with flame at 840° C., like No. 6.

No. 8. A fragment of very hard boart, which could not be cut and which marked the steel grinding wheels; it was not cut into by diamond dust. It only begins to burn slowly at 800° and with flame at 875° C.

We then studied the action of different gaseous substances on the diamond. These experiments were carried out with

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[1] The oxygen was prepared from a mixture of potassium chlorate and manganese dioxide, the latter being strongly heated beforehand. The oxygen was analysed with alkaline pyrogallate before each combustion. It was not used if found to contain more than 3 per cent. of foreign gases.

[2] See footnote 2, p. 89.

most carefully prepared gases, above all free from oxygen. The diamond to be experimented upon was placed in a platinum tube in a small boat of the same metal. The diamonds used were cut and transparent, so that the slightest chemical action might be observed.

Heated in hydrogen up to 1,200° C., Cape diamonds do not change in weight. Moren[1] had already observed that the diamond might be heated to a white heat in hydrogen without alteration. When slightly yellow cut stones are used, they generally undergo some slight change of tint; they become clearer and assume a lighter yellow colour. Sometimes, however, they lose some of their limpidity and become milky.

The diamond heated to redness in fluorine does not change in weight, whereas graphite is attacked at dull redness and lamp-black at ordinary temperatures[2].

Dry chlorine has no action on the diamond between 1,100° and 1,200° C.; it has no action on cut Cape diamonds, which alter neither in weight nor in colour. The same is the case with gaseous hydrofluoric acid under similar conditions.

Sulphur vapours attack the diamond with difficulty. The temperature required for the reaction is 1,000° C., as measured by the thermo-electric couple. But carbon bisulphide is easily formed at 900° C. in the case of black diamonds.

Sodium vapour has no action on the diamond at 600° C. Liquid iron combines energetically with the diamond, yielding a mass which deposits graphite on cooling. Molten platinum also combines rapidly at a very high temperature.

Fused potassium bisulphate and alkaline sulphates do not attack the diamond. The same is true of calcium sulphate, which is not reduced at 1,000° C.

The action of oxidizing agents has already been carefully studied.

We may recall the separation of the different varieties of carbon carried out by Berthelot by means of potassium chlorate and nitric acid. In an important research Ditte[3] showed that anhydrous iodic acid attacks all the varieties of carbon except the diamond at 260° C. Potassium chlorate, as also the fused nitrate, have no action on the diamond, whereas carbonado is attacked under these conditions, as was shown by Damour.

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[1] *C. R.*, lxx. 990 (1870).

[2] Moissan, *C. R.*, cx. 276 (1890).

[3] A. Ditte, 'Research on iodic acid and its chief metallic compounds.' Thesis presented to the Faculté des Sciences, Paris, 1870.

The alkaline carbonates offer a curious reaction. If a diamond be kept in fused carbonate of potassium or of sodium between 1,000° and 1,200° C., it disappears rapidly yielding carbon monoxide. This reaction led us to investigate whether the diamond does not contain a small quantity of hydrogen which, in this case, would be evolved as a gas and easily identified.

The experiment was arranged as follows: a platinum boat containing perfectly dry alkaline carbonate and the diamond was placed in a porcelain tube glazed inside and outside, which was evacuated after having been first filled with carbon dioxide. The tube was then heated to 1,100° or 1,200° C., and the evolved gases were collected for analysis.

Carbon dioxide was absorbed by potash and carbon monoxide by cuprous chloride solution; the small residue underwent no change of volume when sparked in presence of oxygen. We may conclude from this experiment that the sample examined contained neither hydrogen nor gaseous hydrocarbon. We believe, however, that it would be worth while repeating this work with a larger weight of diamond, and more especially with that variety which assumes such a beautiful blue fluorescence when illuminated by blue light. These fluorescent diamonds may contain traces of hydrocarbons.

We may conclude from these first experiments that the temperature of combustion of the diamond varies with the different samples; it varies from 760° to 875° C. Generally speaking, the purer the diamond, the higher is its temperature of combustion. This variation of temperature establishes clearly the existence of several varieties of diamond. Though the diamond resists at 1,200° C. the action of chlorine, of hydrochloric acid, and of various salts, it is, on the other hand, easily attacked at this temperature by the alkaline carbonates, and the resulting gaseous decomposition has enabled us to demonstrate that the sample examined contained neither hydrogen nor hydrocarbon.

Analysis of diamond ash.—After these first researches, it seemed to us essential to identify the mineral matter forming the ash of the diamond. Dumas had already pointed out how useful the traces of impurities contained in the crystals might be in tracing the medium of crystallization of the carbon.

The amount of ash obtained from clear crystals is extremely small, so that we studied samples of boart, which is less valuable and contains more foreign matter than the colourless stones.

The method of analysis varied with the substance to be estimated. Microchemical examination more especially has enabled us to establish some very clear reactions. We used also the spectroscope, but the presence of iron, which gives such a large number of lines, complicated the work greatly. This last method made it possible to verify the presence of traces of some elements, whose existence was indicated by microchemical reactions.

Iron was identified by potassium sulphocyanide. The ash was dissolved either in hydrochloric, or in sulphuric acid, or an acid solution was obtained after fusion with a trace of absolutely pure sodium carbonate.

Silica was detected by means of the microcosmic bead. With a lens one could see a trace of insoluble silica in the middle of the bead. This is the most delicate reaction we know for this substance.

Titanium was sought for by means of L. Lévy's reaction: action of titanic oxide on a sulphuric acid solution of morphine[1]. The test was carried out with the ash directly or after its treatment with bisulphate.

Calcium was detected microscopically by the formation of calcium oxalate. Similarly, magnesium was characterized by the formation of the ammonium magnesium phosphate.

All the fragments of diamond before being burnt in oxygen were treated with hydrofluoric acid, then with boiling aqua regia, finally washed with water and dried in an oven. The weight of ash is not given when it was below 0·0005 mgrm.

D = density. W = weight taken in grms.

No. 1. Boart[2] from the Cape: greasy appearance, violet tint, irregular crystallization. D = 3·49, W = 0·387, Ash = 0·0005, that is, 0·13 per cent. The ash was white with the exception of a yellow point; very light, having retained the general outline of the crystal, although having the appearance of slightly parted leaves.

Iron . . .	Abundant, identified at once with ease in the hydrochloric acid solution of the ash.
Silica . . .	Clear reaction with microcosmic bead.
Calcium . .	Traces by oxalate method, verified by spectroscope.

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[1] *C. R.*, ciii. 1074 (1886).

[2] Boart, a semi-crystalline translucent variety of the diamond, generally dark in colour, with a curved drusy surface. Also applied to inferior crystals. Boart has an irregular crystallization and does not cleave easily.

Magnesium	Very clear though very weak reaction with ammonium phosphate.

No. 2. Two fragments of Cape boart: greasy appearance, crystalline edges, iron grey colour. D = 3·49, W = 0·146. Ash extremely small (below 0·0005 mgrm.), yellow in colour, preserving the original shape of the crystal. Abundant iron. Good silica in bead. No titanium. Traces of calcium and magnesium.

No. 3. Boart from the Cape: iron grey colour. D=3·48, W=0·093. Very faint grey ash. Iron and silica—characteristic reactions.

No. 4. Boart from the Cape: cubical shape, curved surfaces. D=3·48. W=0·100. Iron and titanium—clear reactions.

No. 5. Boart from Kimberley (Cape): greasy aspect, brilliant. W = 0·212. White ash, slightly yellow at edges. Iron clearly; no titanium.

No. 6. Boart from Jagersfontein (Cape): reddish colour, greasy aspect. W = 0·272. Fair amount of yellow ash. Silica; abundant iron; clear reaction for titanium.

No. 7. Carbonado from Brazil; very hard, greasy aspect. D = 3·50, W = 0·0397. Ash below 0·0005 grm., but relatively more abundant than No. 3. Brick-red ash, very hard and granular.

Iron	Very clearly, forming greater part of ash; may be detected by ferrocyanide and even by the borax bead.
Calcium	Very small amount. Verified by spectroscope.
Magnesium	Doubtful.
Titanium	Absent.

No. 8. Carbonado from Brazil: black, with grained surface seen to possess, under the microscope, alternate black and white striae. W=0·354, Ash=0·017 or 4·8 per cent. This could be analysed quantitatively.

	Per 100 parts of ash.	Per 100 parts of carbon.
Iron sesquioxide	53·3	2·2
Silica	33·1	1·4
Lime	13·1	0·6
Magnesia	Trace	—

No. 9. Boart from Brazil: red fragments. Crystalline surface traversed by transparent yellow veins. D = 3·49, W = 0·130. Very slight ash, in white and yellow leaflets. This ash, less easily attacked than that of the carbonado, was treated with potassium carbonate.

Iron	Definite reaction with sulphocyanide and ferrocyanide.
Silica	Abundant, as shown by bead reaction.
Magnesium	Doubtful.
Calcium	Very faint.
Titanium	Absent.

No. 10. Boart from Brazil: green fragments, highly refracting, with a few sharp crystal faces. D=3·47, W=0·093. Very slight ash, faint yellow. Transparent diamonds alone yielded less ash.

Iron . .	Absent.
Silica . .	Clear bead reaction.

No. 11. Cut Cape diamond: very slightly yellow, beautifully limpid, fluorescent. D=3·51, W=0·126. Ash scarcely visible; iron was very clearly identified.

To recapitulate, all the samples of boart and of diamond from the Cape which we studied contained iron. This metal, moreover, made up most of the ash. It was found in the ash of carbonado and of diamonds from Brazil, except in the case of a green variety of boart which contained none at all. Finally, we have demonstrated in all these samples the presence of silica, and in most that of calcium. The existence of this alkaline-earth metal has been demonstrated by Daubrée in certain meteorites, such as those of Ovifack.

Study of the 'blue ground' from the Cape.—As is known, diamonds are found in Cape Colony in enormous wells filled with a serpentinous breccia containing more than eighty varieties of minerals and only 0·1 to 0·5 grm. of crystallized carbon per cubic meter. Only diamonds of a certain size, which could be extracted by hand, were at first sought for in this 'blue earth,' as it is termed at the Cape. When the method of working was changed and machines replaced manual labour, it became possible to separate much smaller diamonds by means of fine sieves; but the presence of microscopic diamonds in this breccia had not been suspected up to now. These diamonds, commercially unimportant, interested me from the point of view of the reproduction of this variety of carbon.

I was able to take up this study, thanks to the kindness of M. de Monmort, to whom I wish to tender here my best thanks, and who procured the necessary samples for me at the time of the Paris Exhibition of 1889. The samples came from the Old mine belonging to de Beers. To bring to light the microscopic diamonds contained in this earth, it was necessary to destroy all other mineral matter accompanying them.

Two kilograms of the blue ground, divided into lots of 250 grms., were treated with an excess of boiling sulphuric acid for twelve hours. After cooling the mass was washed with water and attacked by aqua regia. A large amount of soluble matter was removed by washing, and the residue was placed in a platinum dish and treated with a large excess of boiling hydrofluoric acid. The residue weighed about 100 grms.; some unattacked fragments and the larger rubies were removed with forceps. The further treatment consists of boiling up with sulphuric acid, washing with water, drying and treating again with hydrofluoric acid; this is repeated ten to fourteen times with the main object of removing the crystallized alumina which is very difficult to attack.

There then remained but 0·094 of substance, and this residue was treated fifteen times with a mixture of potassium chlorate and strong nitric acid to destroy the graphite. This last residue, after being washed with hydrofluoric acid and then with boiling sulphuric acid, is divided into fractions of different density by means of bromoform (D = 2·9) and methylene iodide (D = 3·4).

We may state here that the residue was examined microscopically during the whole of the preparation.

Previous to the treatment with potassium chlorate, we recognized clearly the presence of graphite in fine brilliant crystals, lamellar or hexagonal in shape, sometimes in the form of small domes. We also came across bulkier fragments of a certain thickness, marked with triangular depressions. This graphite yielded a greenish graphite oxide, which became yellow and which was destroyed by sulphuric acid to prevent its transformation into pyrographitic oxide by deflagration. Berthelot has shown that iron graphite also yields a greenish oxide. At the same time we were able to isolate a graphite having the property of being destroyed by sulphuric acid at 200° C., swelling up considerably in the process[1].

The residue which remains at the bottom of the methylene iodide, and which therefore has a density greater than 3·4, was found after all these treatments to contain several substances:

1. An amber-yellow substance in irregular masses.
2. Carbonado or black diamond.
3. Microscopic diamonds.
4. Small transparent crystals occurring in the form of elongated prisms, which do not burn in oxygen, show no fluorescence in a violet light, and act on polarized light.

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[1] We have shown, in the section on graphite, how this new variety might be prepared.

The fragments of yellow substance which have withstood this energetic treatment possess a certain degree of transparency; some possess square cavities which must have held crystals. Heated up to 1,000° C. this substance leaves a grey residue, slightly magnetic and containing a large amount of iron. We have found the same substance in the depressions of large natural diamonds and in some of the iron ingots we used in the reproduction of the diamond.

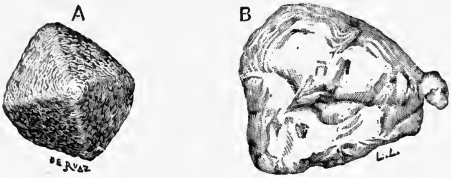

FIG. 19.—Microscopic diamonds from the Cape. × 100.

The pieces of black diamond seen under the microscope were rounded and sometimes grained; some have rectilinear angles while others have curved edges, and resemble octahedral solid angles (Fig. 19, A); a few have a distinct greasy polish.

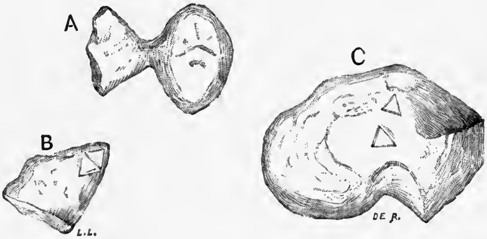

FIG. 20.—Microscopic transparent diamonds from the Cape. × 100.

Some pieces are irregular and pitted. Their density varies from 3 to 3·5; they mark the ruby and burn in oxygen at 1,000° C.

The size of the transparent diamonds varies extremely; some are scarcely visible when magnified 500 times. The more numerous are rounded (Fig. 19, B); the others have a very distinct crystalline appearance (Fig. 20, B), and some have the appearance of transparent drops (Fig. 20, A and C), marked with striae and triangular impressions; they burn in oxygen yielding carbon dioxide, and they scratch the ruby with the greatest ease. Together with these diamonds are found a few fragments of boart and smoked diamond.

Some of the transparent crystals occurring in the form of elongated prisms contain silica; they may be destroyed, together with the amber-yellow substance already mentioned, by two careful treatments with fused potassium bisulphate, followed by a treatment with hydrofluoric acid and finally with sulphuric acid.

In short, our study of the Cape blue earth revealed the existence of numerous microscopic diamonds, of boart, of carbonado or black diamond in various forms and of variable density, and finally of graphite.

The quantity of graphite contained in the blue earth is certainly larger than that of diamond, and the graphite crystals are separated from one another.

I wish to mention that the discovery of carbonado or black diamond in the blue earth was made by Couttolenc, who found it in de Beer's Old mine[1]. Although my analytical work had been finished for two years, I had published nothing on the subject and the priority belongs to Couttolenc.

Study of diamondiferous sands from Brazil.—Thanks to M. Lacroix, professor at the 'Muséum d'Histoire naturelle,' we have been able to investigate whether the diamondiferous sands of Brazil also contained microscopic diamonds.

4,500 kilos. of sand were passed through a sieve, yielding 1,350 grms. of dust consisting almost entirely of silica. The destructive treatment is a very lengthy one, and a residue of 2 grms. was obtained only after a dozen alternate treatments with hydrofluoric acid and boiling sulphuric acid.

The substance is treated with the fused double fluoride of hydrogen and potassium and then with potassium bisulphate.

This residue contained partially corroded particles, small transparent grains, a few specks of native gold and platinum, and small, black, shining crystals, having the appearance of graphite. A few of these were picked out and transformed

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[1] 'Examination of the diamondiferous earth from de Beer's Old mine.' Couttolenc (*Société d'Histoire naturelle d'Autun.* Dec. 1892). That this worker did not observe the presence of microscopical diamonds is due to the fact that, in his treatment of the blue earth, he made use of a fusion with caustic soda, which always contains more or less carbonate; I have shown that the diamond is easily destroyed by fused alkaline carbonates.

into graphitic oxide, which yielded pyrographitic oxide on deflagration.

After having identified the graphite the whole residue was treated with methylene iodide. The part denser than the iodide was separated off and again treated with potassium hydrogen fluoride and then with bisulphate. The precious metals were dissolved in aqua regia.

We were then able to separate out black particles and transparent fragments having no action on polarized light, which burnt completely in oxygen yielding a white precipitate with baryta.

The residue also contained some bright incombustible grains, acting on polarized light, possessing an elongated form and a corroded surface, which finally disappeared after repeated attacks.

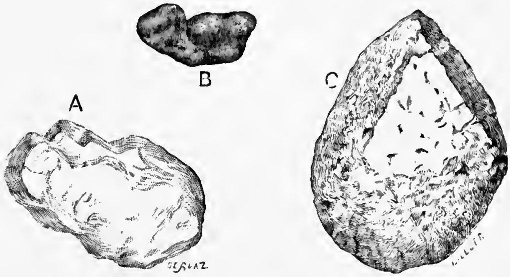

Fig. 21.—Microscopic diamonds from Brazil. × 100.

This Brazil sand therefore contains some black diamond with grained surface (Fig. 21, B), transparent diamonds (A and C) of irregular shape, and finally, graphite as already demonstrated.

There are thus, whether at the Cape or in Brazil, native microscopic diamonds both black and transparent, and in both cases these particles of carbon of high density are accompanied by graphite.

Study of a meteorite from the Diablo Cañon.—Following the interesting presentation to the Académie des Sciences by M. Mallard[1] of a meteorite from Arizona, we were able to obtain some samples of it and to study the variety of carbon therein contained. Our results were not published at once, and we must here recall the interesting paper communicated by Friedel[2] on the subject. He was the first to demonstrate the existence of carbonado in the Diablo Cañon meteorite.

[1] *C. R.*, cxiv. 812 (1892).

[2] *C. R.*, cxv. 1037 (1892).

Among the samples analysed there was one of great importance, although it weighed but 4·216 grms.; it had a very distinct point, distinguished by great hardness, on which a steel grinding wheel had no action. On careful examination the fragment which marked steel was found to be surrounded by a black sheath consisting of carbon and iron carbide (Fig. 22).

This sample was treated with boiling hydrochloric acid till no trace of iron remained; there is thus obtained a mixture containing:

1. Some very light carbon as an impalpable dust, taking twelve hours to sink in water and resulting possibly from the decomposition of the iron carbide.

2. Carbon in very thin, ribbon-like fragments, of a brown colour under the microscope, apparently eaten into and seeming to have been strongly compressed.

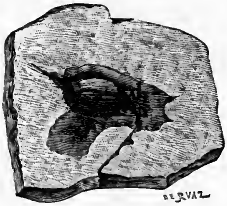

Fig. 22.—Diablo Cañon meteorite. × 3.

3. A dense carbon in rounded fragments mixed with small pieces of iron and nickel phosphides possessing a reddish brown tint[1].

This mixture was treated alternately with boiling sulphuric acid and hydrofluoric acid: its density then was such that part sinks in methylene iodide.

This last residue was treated eight times with potassium chlorate and nitric acid. The dark-coloured fragments gradually disappear, a small amount of iron passing into solution at the same time. Finally, there remained but two identical yellow fragments, possessing a greasy appearance and having no triangular impressions; their surface was rough and irregular and recalled the irregular crystallization of boart.

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[1] According to Friedel, this phosphide of iron and nickel has all the characteristics of schreibersite.

These two fragments sink in methylene iodide; they mark the rubies distinctly, and one of them, burnt in oxygen, gave a yellow ash which retained the shape of the fragment and in which iron could be detected. The larger diamond (Fig. 23) measured 0·7 mm. by 0·3 mm.; it had a yellow tint, a rough surface, and was transparent to light.

In another sample we found, together with the dense carbon just mentioned, and mixed with sulphides and phosphides of iron and nickel, a dendritic grey crystalline substance, duller than platinum, which did not disappear on treatment with hydrofluoric acid and aqua regia. We found in addition some fragments of black diamond whose surface was either grained or brilliant, possessing a density of about 3 and burning in oxygen at 1,000° C.

FIG. 23.—Transparent diamond from the Diablo Cañon.

One must not mistake for carbon a few particles of magnetic iron oxide, which of course does not burn in oxygen and which is quite unattacked by sulphuric acid, this being the result of production at a high temperature.

It is further of interest to observe the non-homogeneous nature of this Diablo Cañon meteorite. For example, we took two samples from the same fragment, 1 cm. apart; on analysis they gave the following figures:

	1	2
Iron	91·12 per cent.	95·06 per cent.
Nickel. . . .	3·07 „	5·07 „
Silica	0·050 „	—
Insoluble . . .	1·47 „	0·06 „
Magnesia . . .	Trace.	—
Calcium . . .	Absent.	—
Phosphorus . .	0·20 „	—
Sulphur . . .	Absent.	—

These two samples, containing varying amounts of carbon, contained no sulphur.

Another meteorite from the same source, in which we could detect no trace of carbon, gave on analysing fragments taken a few centimeters apart:

	1	2
Iron	91·09 per cent.	92·08 per cent.
Nickel. . . .	1·08 ,,	7·05 ,,
Silica	0·05 ,,	—
Insoluble . . .	Absent.	—
Magnesia . . .	,,	—
Calcium . . .	,,	—
Phosphorus . .	Not estimated.	—
Sulphur . . .	0·45 ,,	—

A third sample weighing 20·200 grms. yielded but three particles of black diamond and no transparent diamond.

To recapitulate, the fragment of Diablo Cañon meteorite studied contained transparent diamond, black diamond, and a brown carbon of low density. It may be added that graphite was detected in some samples in the form of small masses possessing a greasy appearance. This graphite was converted into a graphitic oxide easily recognized under the microscope, which deflagrated on raising the temperature.

The transparent diamond may thus exist in planets other than the earth, if the Diablo Cañon be a meteorite; in this sample it is found at the centre of the metallic mass.

Iron from Novy-Urej, Krasnoslobodsk, Russia.—Fell on August 23, 1886.

Small dark coloured fragment, seen under the microscope to possess some bronze coloured points; weight, 0·410 grm. This meteorite is carbonaceous and not ferruginous.

It is the first meteorite in which Yerofeïeff and Latchinof detected the presence of black diamond.

It is slowly attacked by dilute hydrochloric acid, and on examining the residue under the microscope it is seen to be rich in siliceous matter. At the first treatment with boiling sulphuric acid, the body is disintegrated, and finally all siliceous matter disappears in fused potassium hydrogen fluoride. Small dark coloured masses of irregular shape are to be seen under the microscope.

No trace of graphitic oxide could be detected under the microscope after treatment with potassium chlorate and nitric acid and subsequent deflagration. It must not, however, be forgotten that the sample examined did not weigh half a gram.

On treating again with potassium hydrogen fluoride and then with boiling sulphuric acid, a dark coloured residue was seen under the microscope, having the appearance of black diamond and made up of agglomerations of small granular masses. All the black grains burn in oxygen at 1,000° C., and a small transparent grain, which had resisted all these attacks, was found unaltered after the combustion. The small particles of black diamond sink in methylene iodide.

These experiments only confirm those of Yerofeïeff and Latchinof. The meteorite from Novy-Urej contains some black diamond.

Technique of these researches.

The problem of the separation of a mixture of the different varieties of carbon and of all the substances which the mineral kingdom may furnish may well seem, at first sight, almost unsolvable.

It is nevertheless fairly easy to separate some few tenths of a milligram of diamond from a kilogram of foreign matter. An example of this was given in the research on the Cape blue earth.

As a matter of fact, the diamond and graphite resist most reagents sufficiently to enable one to remove most mineral substances by repeated treatments with concentrated hydrofluoric acid, and then with boiling sulphuric acid. All the silicates disappear easily. Fused or crystallized alumina and crystallized aluminium fluoride are at length corroded, eaten into, and dissolved. When substances such as titanic acid have to be dealt with, it may be advisable to treat with nitric acid and then with ammonia. Separation from the solid residue is always effected by decantation. When substances other than the diamond or graphite are destroyed or still exist merely as traces, the graphite is converted into graphitic oxide, and by this method of separation, which we owe to Berthelot, the diamond is left as a last residue. Berthelot's method was to make a thick paste of the different carbon varieties with potassium chlorate and nitric acid, the whole being kept at a temperature of 60° C. for five to six hours. This treatment, repeated six to eight times, brought about the complete conversion of graphite into graphitic oxide. The latter compound deflagrated on heating to dull redness. The pyrographitic oxide thus obtained was in its turn destroyed by potassium chlorate and nitric acid.

As we did not propose to study and to compare the various graphitic oxides, we modified Berthelot's method as follows:—All amorphous carbon is first destroyed by means of nitric acid or aqua regia; the residue is then washed by decantation, as before; it is dried and the mixture is brushed, without being powdered, into a small glass flask.

About 2 grms. of potassium chlorate are then added, if the quantity of graphite be small. The whole is mixed up and 8 to 10 cc. of commercial strong nitric acid are added. The flask is kept between 60° and 80° C. in a water bath for a day. The mass is then washed with boiling water, dried in an oven, and the same proportions of chlorate and acid are again placed in the flask. This second treatment goes on through the night, the temperature being maintained at 60° C. These operations are continued till all the graphite is converted into graphitic oxide.

By carefully destroying all the amorphous carbon beforehand, we never had any explosion during the oxidation. When there is but little graphite, it is advantageous to use a large excess of nitric acid which dissolves it or keeps it in suspension in a gelatinous form. In this case the graphite thus disappears by simple decantation.

If, on the other hand, the graphite be abundant, it is converted into graphitic oxide, which may be destroyed either by deflagration or by a prolonged treatment with boiling sulphuric acid.

The rate of oxidation of a given graphite varies with the concentration of the nitric acid. In our earlier experiments we made use of ordinary monohydrated nitric acid, and the treatment was repeated several times. Later we made use of concentrated nitric acid obtained by the decomposition of dry potassium nitrate by means of a large excess of monohydrated sulphuric acid. Under these conditions, as we have already shown, the attack is far more rapid.

In these rather lengthy operations, vessels are changed as seldom as possible. When the graphite has been destroyed in the small flask mentioned above, the traces of diamond contained are removed by filling the flask with water, closing the mouth with the thumb and inverting it in a dish containing water. Owing to their density, the heavy powders collect rapidly at the bottom of the dish.

To examine these powders under the microscope, a glass pipette closed at the top with the finger is introduced among the particles in the dish. On removing the finger the atmospheric pressure causes liquid mixed with solid to enter the pipette, and these may then be deposited on a glass slip and examined.

From the rate at which they fall through the liquid, one may form some idea of their density. After the microscopical examination the glass slide and the cover-glass are washed with distilled water above the dish.

This examination shows first that, in spite of all precautions, these residues always contain a small quantity of glass fragments, derived either from the vessels or the liquids used. When glass-blowing is carried out in the laboratory, glass dust is permanently in the air and may be found at the bottom of test-glasses and dishes.

One also finds small grains of silica, possessing a bright fracture or a rounded surface; to avoid these one must be careful to recrystallize in closed flasks the potassium chlorate used for the destruction of graphite. On the same ground, bottles containing acids must never be shaken nor should the bottom liquid be used.

The invariable presence of glass and silica in the residue necessitates a final treatment with boiling hydrofluoric acid. With this object, the small residue remaining in the dish is washed into a platinum dish. The excess of liquid is decanted off and 50 per cent. hydrofluoric acid is poured on to the still wet particles. This acid was obtained in a pure state by decomposing potassium hydrogen fluoride in a platinum retort. The acid liquid is kept near its boiling-point for two to three hours. After cooling the residue is washed by decantation with distilled water. Sometimes it has increased in bulk, and under the microscope may be seen regular crystals consisting of fluorides insoluble in an excess of acid.

The treatment with boiling sulphuric acid must then be repeated, and these compounds are destroyed after a few hours. After cooling, water is added and the hydrofluoric acid treatment repeated. After washing with water, the volume of the residue has considerably diminished.

Throughout these various operations one must be careful never to dry the light residue completely. Only at the very end is the platinum dish heated in an oven. The residue is then treated with methylene iodide, of 3·4 density, in which the diamond sinks with ease. The particles must be left for several hours in contact with methylene iodide, shaking from time to time. This is done in a small corked test-tube. We also made use of bromoform (2·9) to separate the different samples of carbon.

When the fragments of carbon and diamond have been treated with chlorate, it often happens that they are no longer wetted by water and other liquids. As soon as the surface of the particles is perfectly clean, owing to a well-known capillarity phenomenon, they float on water and are only with difficulty precipitated to the bottom of a test-glass. Under these conditions it is useful to sprinkle a small quantity of concentrated alcohol over the surface of the liquid. We have often lost small diamonds through these capillarity phenomena.

B. Solubility of carbon in some elements at ordinary pressure.

We have shown in an earlier chapter that carbon prepared at a low temperature, that is between +20° and +200° C. is always obtained in the amorphous condition.

Following up this earlier work, we tried to separate carbon from a solvent by a simple change of temperature. The best solvent for carbon is molten iron, and this metal we first studied. Many other metals, however, possess the same property. That little has been known up to now on the subject is due to the fact that researches have been carried out within too narrow limits of temperature. The use of the electric furnace has enabled us to extend the number of our observations.

Finally, we have varied the nature of the solvent, hoping thereby to observe some differences in the properties of the carbon thus obtained.

Silver.—Our first experiments were carried out with silver at 1,000° C. Pure silver, fused in a crucible of sugar carbon, does not dissolve carbon appreciably. The regulus treated with nitric acid yielded a very small residue which was carefully examined under the microscope. When a Doulton crucible had been used, or when the carbon crucible contained silicates, we often found the piled-up crystals of silica described by Marsden, of which we spoke at the outset of this work. When the carbon crucible has been treated with chlorine, or when the silver has been melted under a layer of sodium chloride, there are seen, under the microscope, some minute crystals which are very bright, heavy, refracting, insoluble in nitric acid and in water, capable of remaining for several hours in dilute ammonia without appreciable solution, having no action on polarized light and belonging to the cubical system. They are small crystals of silver chloride, soluble in ammonia after long standing and decomposed at once by boiling sulphuric acid. If silver be heated in presence of sugar carbon at a wind furnace temperature, a small amount of carbon is dissolved and after treatment with nitric acid the residue, examined under the microscope, is seen to contain amorphous carbon and graphite. Should the crucible or the brasque contain silica, one obtains, even at this temperature, small rather thick crystals of carbon silicide which are yellow or transparent. This compound marks the ruby, resists all acids, even hydrofluoric acid, and has sometimes been mistaken for the diamond; its appearance, its action on polarized light, its incomplete combustion in oxygen at 700° C., and the fact that it is attacked by alkalies, all serve to identify it with ease.

To reach a high temperature we devised our first lime electric furnace, which has been so helpful to us along other lines[1]. By means of this apparatus we could heat a metal up to nearly 3,500° C. We noticed at once that silver, at its boiling-point, dissolved a small amount of carbon, and that, on cooling, the latter separated out as graphite[2]. After dissolving the metal in nitric acid and treating the residue as already described, we never obtained any residue visible under the microscope.

After conversion into graphitic oxide all the graphite was

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[1] *C. R.*, cxv. 1031 (1892); *Ann. de Ch. et de Ph.*, sér. 7, iv. 365 (1895).

[2] At a high temperature carbon silicide is easily formed in this metal. Moissan, *C. R.*, cxvii. 425 (1893).

destroyed, and none of the dust which remained sank in methylene iodide. This experiment was repeated many times, but always with the same result.

Iron.—When iron is saturated with carbon at temperatures between 1,100° and 3,500° C., various results are obtained on cooling, according to the temperature to which the body has been heated and to the speed of cooling. If the temperature attained be only 1,100° to 1,200° there remains, after treatment with acids, a mixture of amorphous carbon and graphite in small crystals. At 3,500° C. graphite in very fine crystals is chiefly obtained. When graphite is prepared at a high temperature, it is so bright that it reflects as much light as the mirror of the microscope and, at first sight, appears transparent. Between 1,100° and 3,000° C. the molten iron behaves as a solvent, dissolving more and more carbon as the temperature rises. This explains the formation of graphite on cast iron which has been strongly heated in the furnace, and which in passing from 1,700° to 1,100° C. the point of solidification, gives up a large quantity of crystallized graphite.

In the numerous experiments carried out on molten iron, whether at a furnace or oxyhydrogen blowpipe temperature, or in the electric furnace, we never obtained anything but graphites, whose properties have already been given.

Aluminium.—The solubility of carbon in aluminium is easily demonstrated at the temperature of the electric furnace, and some carbon dissolves at the ordinary furnace temperature.

One may prepare in this way a transparent aluminium carbide in yellow crystals having the formula Al_4C_3, which is slowly decomposed by water with evolution of pure methane. As the carbide forms, the excess of aluminium or the fused carbide gives up fine crystals of graphite and nothing but graphite.

Beryllium.—Beryllium carbide, prepared by P. Lebeau in the electric furnace, easily dissolves carbon at a very high temperature. Upon treatment with dilute hydrochloric acid it yields graphite.

Chromium.—We have had occasion to prepare some 20 kilograms of this metal in the electric furnace under various conditions. Chromium combines readily with carbon at a high temperature yielding two definite crystalline carbides Cr_4C and Cr_3C_2. On further raising the temperature, these compounds dissolve large amounts of carbon which they subsequently give up in the form of a well-crystallized graphite in small, very bright lamellae.

Manganese.—Manganese dissolves carbon rapidly at the temperature of the electric furnace. As this metal is very volatile, the excess of manganese may be removed as vapour, leaving behind well-crystallized graphite. After treatment with acids and with the oxidizing mixture, this graphite leaves no residue.

Nickel.—In the electric furnace this metal behaves like iron with regard to carbon. It seems, however, to dissolve a smaller quantity.

Cobalt.—Cobalt dissolves carbon which it gives up as graphite.

Tungsten.—Tungsten, prepared in the electric furnace from a mixture of oxide and carbon in which the latter is not in excess, may contain no carbon and be polished with ease. The metal is thus first obtained without carbide. This experiment may be carried out in a carbon crucible, for tungsten is sufficiently difficult to fuse to allow of the spongy metallic mass, weighing about one kilo., only touching the crucible at a few points. This tungsten is very pure, as even when examined spectroscopically, very little impurity can be detected.

If this spongy mass be further heated by means of a powerful current, it melts and then combines with the carbon of the crucible to form a carbide, W_2C, which dissolves sufficient carbon to give it up on cooling as graphite.

Molybdenum.—This metal dissolves more carbon in the electric furnace than tungsten. It is also somewhat more fusible and gives a definite carbide Mo_2C. On cooling, the dissolved carbon separates out as graphite.

Uranium.—Uranium, more fusible than the two preceding metals, approaches iron in regard to the solubility of carbon. On cooling, it produces a considerable quantity of graphite. It must not be forgotten that uranium is fairly volatile and that if the heating be too prolonged, much of the metal is lost. Uranium gives a definite crystalline carbide U_2C_3.

Zirconium.—Zirconium also dissolves carbon which is given up as graphite and remains in the metal. This is due to its high melting-point. As soon as the arc is stopped, the surface of the metal solidifies and the graphite cannot make its way out. On attacking the carbide ZrC with acids, the excess of carbon held is seen to consist solely of graphite.

Vanadium.—This metal behaves like zirconium. It is difficult to fuse and the dissolved carbon crystallizes out in lamellae of graphite between the crystals of the carbide VC.

Thorium.—Thorium carbide, ThC_2, of a golden yellow colour and well crystallized, dissolves sufficient carbon to give it up on cooling as crystals of graphite. It yielded no other variety of carbon.

Metals of the alkaline earths.—The carbides of these metals, CaC_2, BaC_2, SrC_2, when liquefied, dissolve carbon which they give up as graphite.

The same is true of cerium carbide CeC_2, of lanthanum carbide LaC_2, and of yttrium carbide YtC_2.

Titanium.—Molten titanium containing carbon has a pasty consistency and easily creeps over the edges of the crucible. It has not the fluidity of molten molybdenum, tungsten, or iron. This element yields a definite carbide TiC. At an increased temperature, the latter may dissolve carbon, which it gives up as graphite either on the exterior or in the interior of the metal.

Platinum.—At the moment when it begins to boil, platinum dissolves carbon which it gives up, before solidifying, as graphite. Distinct and well-formed crystals may be obtained in this way. This graphite is of the swelling variety, as already shown.

Iridium, palladium, and rhodium behave similarly.

Silicon.—We prepared some crystalline silicon, by Deville's method, as pure as possible, and we melted it into globules of the size of a hazel-nut at the temperature of an ordinary furnace. That this experiment may fully succeed, one must prevent the access of nitrogen by surrounding the crucible with a brasque of titanium oxide and carbon. One may also add a small piece of sodium to the silicon to lower its melting-point, and to render more easy the formation of large fused globules.

The crystals of silicon to be melted were heaped up at the bottom of a small crucible of retort carbon and covered with powdered sugar carbon. This first fusion once accomplished, the mass was again heated in the middle of a brasque of sugar carbon, either in a wind or other laboratory furnace.

After cooling, these globules are broken, and one finds inside graphite and small geodes lined with brilliant crystals.

These may be separated by dissolving the silicon in a mixture of monohydrated nitric acid and hydrofluoric acid. They may be several millimeters long; they mark the ruby with ease and have a density of 3·12. They consist of carbon silicide SiC, first prepared in the amorphous state by Schützenberger.

On repeating this experiment in the electric furnace, the yield of silicide is much increased, but it contains no other variety of carbon.

In all the experiments described, the element which dissolved the carbon was attacked by an acid or by a mixture of suitable acids, and the residue treated by the method described in the chapter on the technique of these experiments. The graphite was converted into graphitic oxide, then destroyed, and the treatment was continued long enough to dissolve all the corundum which is often found in these ingots.

After this complete treatment, absolutely nothing remained to be seen under the microscope. We never obtained either black or yellow unattacked fragments, sinking in methylene iodide, which might be thought to be diamond. The following conclusion is to be drawn from these experiments:—At ordinary pressure and at a sufficiently high temperature, many elements and carbides may dissolve carbon, giving it up subsequently on slightly lowering the temperature. The carbon is always liberated in the form of graphite.

C. Action of a high temperature on the diamond and on different varieties of carbon.

After observing this invariable formation of graphite in difficultly fusible metals, it seemed useful, before going further, to investigate the action of a very high temperature on the different varieties of carbon.

Diamond.—In a memoir published in the Annales de Chimie et de Physique (sér. 3, vol. xx) in 1847, Jacquelin showed that the diamond was converted into graphite when heated in the electric arc. This may be easily demonstrated to a large audience by modifying the experiment as follows: by means of a fairly strong beam of electric light, one may project on to a screen the image of two vertical cylindrical carbons between which a less intense arc may be produced.

One of the carbons is slightly hollowed to support a rough or cut diamond weighing 100 to 200 mgrms., whose image is clearly seen under these conditions.

The two carbons are then slowly brought nearer to one another so that the arc may be produced sideways, and that the diamond may be slowly heated to prevent its bursting. As soon as the temperature is sufficiently high, the diamond is brought to a state of incandescence, and it is soon seen to swell without melting and to become covered with black masses consisting entirely of graphite. On examination after the experiment, this graphite is seen to consist of hexagonal lamellae, separated from one another, and easily converted into graphitic oxide by the oxidizing mixture.

This experiment may be arranged differently by placing the diamond, enclosed in a small crucible of retort carbon, in the middle of the electric furnace already described. We made use of a current of 70 volts and 300 amperes; the crystal first breaks up into small fragments, following the planes of cleavage. Finally, if the temperature be raised, each particle swells considerably and the conversion into graphite is complete. The irregular or hexagonal lamellae break up easily and yield a fine yellow graphitic oxide on oxidation. Thus, at the temperatures of the arc, even when the latter is not very powerful, graphite is found to be the stable form of carbon[1].

In numerous experiments, rough or cut diamonds, surrounded by a brasque of carbon, had to be heated up to about 2,000° C. by means of the oxygen blowpipe. Under these conditions the diamond occasionally became covered with an adhesive black layer which disappeared slowly in the oxidizing mixture, but we never obtained any graphite.

It may be mentioned here that in burning Cape diamonds in order to obtain ash for purposes of analysis, it was always observed that, at the moment of combustion, the diamond became covered with a black layer, a fact noticed by Lavoisier and since confirmed by Berthelot.

Sugar carbon.—Sugar carbon placed in a closed crucible, and heated in the electric furnace, is completely converted into graphite, yielding no other variety of carbon. The

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[1] We converted with ease a diamond into graphite, in a small carbon crucible forming the extremity of the positive electrode of an arc of 30 volts and 40 amperes. The arc was produced by a dynamo worked by a 4 H. P. gas engine.

outward appearance of the carbon was unchanged and we could observe no crystallization under the microscope.

Wood charcoal.—Heated under the same conditions, wood charcoal is also transformed into graphite without trace of crystallization. Under the microscope, the wood fibres are seen to have preserved their form. Details of these experiments are given in the section on graphite.

Retort carbon.—The transformation into graphite of the carbon of the electrodes used in the electric arc was first observed by Fizeau and Foucault—'Recherches sur l'intensité de la lumière émise par le charbon dans l'expérience de Davy[1]'.

In his experiments on the reproduction of the diamond, experiments which we noticed at the outset of this work, Despretz observed that his electrodes and small crucibles marked paper and had acquired the appearance of graphite. Berthelot has shown that these crucibles, which had remained at the Sorbonne, were in fact converted into graphite as was proved by their oxidation with potassium chlorate and nitric acid.

We have had many opportunities of confirming this behaviour in our experiments in the electric furnace.

Lamp-black.—Lamp-black, carefully dried and placed in a small carbon crucible, was heated for ten minutes in the electric furnace with a current of 1,000 amperes at 70 volts. After the experiment the density of this carbon rose to 2·12. It is not attacked by nitric acid and yields graphitic oxide with the oxidizing mixture of chlorate and nitric acid.

After the deflagration of the graphitic oxide and treatment with the oxidizing mixture, and finally with hydrofluoric acid, there was no residue.

So that, whatever be the variety of carbon examined, it is always converted into graphite by a sufficient rise of temperature. This graphite, as already shown, may be more or less stable, amorphous or crystalline, but it can always be converted into graphitic oxide by the oxidizing mixture.

These experiments were carried out at the temperature of the electric arc, that is, at a very high temperature. Certain compounds, notably iodo-compounds, may bring about this transformation into graphite at a lower temperature, as has been shown by Berthelot. These reactions are comparable to those of iodine on ordinary phosphorus, and allow

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[1] *Ann. de Ch. et de Ph.*, sér. 3, xi. 371 (1844).

polymerization to take place somewhat sooner without altering the general character of the phenomenon.

From all these experiments we may conclude that graphite is the variety of carbon which is stable at high temperatures under ordinary pressure.

Study of the vapour of carbon.—Before going further it seemed to us essential to study the vapour of strongly heated graphite.

Up to now the formation of carbon vapour has only been observed in the electric arc, either by means of the spectroscope or in Berthelot's classical synthesis of acetylene.

The existence of this vapour may be demonstrated without the use of the arc in the following manner. A carbon tube, some 2 cm. in diameter, is placed in the middle of a quicklime electric furnace, heated by means of a powerful arc of 2,000 amperes at 80 volts. The interior of the tube is seen to become filled with a very light deposit produced by the condensation of carbon vapour.

This carbon vapour may also be rendered visible by placing some crystallized silicon in a boat inside the carbon tube and heating strongly. The silicon is seen to melt, to begin to boil and, as its vapour rises, it meets the vapour of carbon descending from the top part of the tube under the heating action of the arc. A network of fine needles of carbon silicide is produced between the boat and the tube. This compound, crystalline and transparent, is formed by the direct union of the two vapours. At a very high temperature, such as that attained in the electric furnace, one may therefore vaporize carbon outside the arc.

It seemed to us that a study of the formation of this vapour would be of interest. Generally, a body passes from the solid to the liquid state, and from this, on raising the temperature sufficiently, to the gaseous state. Does carbon behave in this way or is it an exception to the general rule? The question is answered by the following experiments.

We placed inside the electric furnace, heated by a current of 1,200 amperes at 80 volts, a small crucible of pure carbon, whose heavy lid fitted deeply and smoothly into it. This crucible rested on a disk of carbon placed on a bed of compressed magnesia. The heating lasted ten minutes, and the heat produced was sufficiently intense to volatilize several hundred grams of lime and magnesia.

After cooling, the lid, which had kept its place, did not stick in the least to the crucible; the whole mass was converted into graphite, but the two surfaces had not fused together. If a carbon boat be heated in a tube of the same substance, either superficially or from below, by means of a powerful arc or of several arcs, the boat is never found to stick to the tube.

By using an arc of 1,000 amperes at 80 to 90 volts in our tube furnace, it often happens that the upper part of the tube, which is most exposed to the heating action of the arc, develops holes whose edges, after cooling, show no trace of fusion[1].

We have heated sugar carbon in a closed crucible by means of an arc of 1,000 amperes at 70 volts. The sugar carbon kept its form and still retained the small cavities through which the hydrocarbons escaped during its preparation. The conversion into graphite is complete, but the powdery mass, examined under the microscope, shows no trace of fusion.

Graphite, wood charcoal or retort carbon purified by chlorine, heated under the same conditions yield nothing but graphite, but each variety keeps its form, and no trace of fusion or welding is to be detected.

On examining the electrodes used in these experiments, consisting of the purest carbon, the points are seen to be rounded and completely transformed into graphite, but show no trace of fused matter. With a current of 2,200 amperes at 70 volts, electrodes 5 cm. in diameter are transformed for a length of 15 cm.

Graphite, taken from the extremity of the electrode, gave on analysis:

Carbon	99·63	per cent.
Hydrogen	0·03	„
Ash	0·39	„

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[1] Thanks to the kindness of M. Meyer, director of the Société Edison, we were able to pursue further these experiments on the volatilization of carbon during the vacation of 1894, by means of a 300 H.P. machine. Under these conditions, we had in our furnace an arc of about 2,200 amperes at 70 to 80 volts. The power expended in the furnace was thus about 200 H.P. An intensely hot region is obtained and the parts of the cavity of the furnace furthest from the arc are just at the temperature of volatilization of quicklime. The cavity in fact gradually increases in size as the experiment goes on.

Before the experiment, the amount of ash in this carbon was about 1 per cent. All mineral substances being more volatile than carbon, the electrode becomes gradually purer by their volatilization.

The extremity of the positive electrode may be made to consist of a cylinder of carbon fitting on smoothly, and after the experiment this cylinder, which has been exposed to the hottest part of the arc, is deformed but is not welded to the electrode.

This ceases to be the case if the carbon used contains impurities such as metallic oxides, silica or boric acid. We have already mentioned that, under these conditions, boric acid yields a crystalline boride of carbon of definite composition B_6C. This crystalline boride may unite with an excess of carbon to form bodies of molten appearance and of more or less rounded form together with drops which are sometimes very hard, but which do not consist of pure carbon. A very small amount of metallic impurity may also yield fused or crystalline carbides; several of these have been described. It is thus essential in these experiments to use only the purest carbon obtainable. From these experiments we conclude that carbon passes from the solid to the gaseous state without intermediate liquefaction. We still have to study the variety of carbon produced by the condensation of this vapour.

Carbon vapour was collected in three different ways:

1. **By distillation.**—Carbon vapour condensed in a carbon tube, as already described, gave a black deposit consisting entirely of graphite.

2. **By condensation on a cold surface.**—When a copper tube, traversed by a current of cold water[1], was placed in the electric furnace, we obtained on its surface a black deposit which was treated with very dilute cold hydrochloric acid to remove quicklime and calcium carbide. This deposit contains small spheres of silica and other impurities, but it consists mainly of an impalpable dust, floating on water, of a greyish colour under the microscope, and possessing all the characteristics of amorphous graphite[2].

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[1] Moissan, 'Study of some new fusion and volatilization phenomena,' *C. R.*, cxvi. 1429 (1893).

[2] If one gathered the deposit condensed on the lower part of the copper tube, that is, the part directed towards the arc, small crystals of graphite were met with, resulting from the liquid drops of calcium carbide which are projected in all directions during experiments of long duration.

3. By condensation on a hot surface.—When the electric arc is made to play in a quicklime furnace to avoid the presence of carbon dioxide, which absorbs the vapour of carbon to form the monoxide, one obtains, especially on the negative pole, mushroom-like masses of carbon, resulting from the vaporization of this element in the arc itself.

After fifteen to twenty minutes one may often obtain such masses of carbon on both poles. In a few experiments, where a cold current of an inert gas passed through the furnace, we found filaments of carbon uniting the poles, and this soon became manifest in the rapid diminution of voltage.

This carbon, whose surface is more or less rounded, does not show any sign of fusion when seen under the microscope. It has a density of 2·10. On analysis it gave 99·61 to 99·90 per cent. of carbon and contained a mere trace of ash. The following figures were obtained:

Carbon .	99·61	99·84	99·90	per cent.
Hydrogen .	0·018	0·03	0·031	„
Ash . .	0·023	0·018	0·017	„

It is thus pure carbon produced by distillation. It has all the properties of graphite and burns in oxygen only at a fairly high temperature. The combustion can only be carried out in a porcelain tube.

Deslandres has studied the spectrum given by this carbon, and he finds it to contain fewer lines than the similar spectra published by Liveing and Dewar, Hartley and Adeney, Eder and Valenta [1].

In conclusion, these condensations of carbon vapour always yielded graphite.

When these various experiments were finished, we proposed to verify them by means of a small and very simple piece of apparatus, the incandescent lamp [2]. The construction of this apparatus is now known to all. A filament of carbon is joined to the ends of two platinum wires; these are sealed through the glass and enclose the filament in a glass globe, which is rendered vacuous by means of a mercury pump. After being in use for a time, varying from 500 to 900 hours, a slight veil forms over the glass. The deposit increases, and in time renders the lamp useless. At other

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[1] Deslandres, *C. R.*, cxx. 1259 (1895).

[2] Cf. Berthelot, *C. R.*, cxxxvii. 589 (1903).

times, under the action of too intense a current, the thread burns at one point, giving suddenly at the same moment the same deposit which is spread uniformly over the inside of the globe.

A trace of silica or of a calcium salt, accidentally deposited on the carbon filament, may yield a silicide of carbon or a carbide of calcium, which may be fusible or volatile, thus lessening the diameter of the filament. The resistance at this point is increased and the current produces a higher temperature; then the carbon begins to volatilize, and soon the filament breaks. If the black deposit found inside the globe be collected in water and examined under the microscope, one observes very small crystals of characteristic shape of carbon silicide, piled-up crystals, recalling the silica obtained by Marsden in fused silver, and more especially small black masses, sticking more or less together. The latter, seen under a high power, showed no trace of crystallization. We may mention at the same time that a thin film of a brownish hue floats on the liquid. The deposit in one of these globes was treated with the mixture of potassium chlorate and nitric acid, and the black matter was not destroyed at once. The mixture was kept for twelve hours at 60° C., and after washing and decanting, the slight deposit obtained, examined with the microscope, was seen to contain very distinct crystals of graphitic oxide, together with particles of the same. The cover-glass was then removed, the liquid evaporated off, and the residue brought to a dull red heat on the same piece of glass. A fresh microscopical examination showed that all the crystals and the yellow or green particles had deflagrated and were replaced by a flocculent black deposit of far greater bulk. This disappeared, in its turn, by combustion in air at a dull red heat. From this experiment we may conclude that the deposit formed inside incandescent lamps consists chiefly of graphite[1].

On examining with the microscope the ends of a filament which has been broken in an incandescent lamp, one sees that the points of the filament show no fused parts, and that the ends bristle with small graphite crystals[2].

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[1] The small film floating on the liquid consisted also of graphite which yielded an easily combustible pyrographitic oxide after deflagration.

[2] The graphite forming the filament is less easily transformed into graphitic oxide than the deposit gathered inside the lamp.

From all these experiments we may conclude that in vacuo, as at ordinary pressure, carbon passes from the solid to the gaseous state without liquefaction. From this standpoint it may be compared to arsenic.

When gaseous carbon returns to the solid state it always appears as graphite.

D. **Experiments under pressure.**

The foregoing experiments on the vaporization of carbon, the researches on the action of high temperatures on the different varieties of carbon, as also the invariable formation of graphite in fused metals, have led us to prosecute our work in a new direction.

The numerous geological researches on the different kinds of formations in which crystallized carbon is found seem to establish in an indisputable manner that the diamond is not a vein mineral[1]. No crystal has ever been found adhering to a rock which clearly acted as a support for it. Diamonds are sometimes found in alluvial sands, at other times in soft conglomerates or in serpentinous breccias. More important still, in the Cape pits the two pieces of the same broken fragment have never been found side by side. The material contained in the pit has been thrust up in channels lying side by side. The diamond existed already in this Cape serpentinous breccia, for, if that be incorrect, one would be bound to admit that the eighty varieties of minerals found in this broken-up rock had been formed under the same conditions. Is it possible that calcite, zeolites, the topaz, the garnet, the zircon, and titaniferous iron have been formed in the same substance and under the same conditions?

The diamond must therefore come from the deeper layers of the earth, it must have been formed there, and thus pressure must have played a part at the moment of its formation.

In any case there seem to us to be numerous proofs to establish the importance of pressure in the production of the diamond. The depth of the shafts, which is to-day more than 500 meters, is a fact which supports this theory.

Moule has shown that granite is met with in the vertical shafts at the Cape. All geologists are agreed that granite

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[1] Many works deal with this subject; I specially wish to recall the important work of Boutan, 'Le diamant,' published in Frémy's *Encyclopédie chimique*.

must have been formed under pressure. It must therefore have come from greater depths. Certain diamonds are striated, and, according to Daubrée, they owe their appearance to nothing else than the friction of diamonds against one another during the upward movement from lower to superficial layers.

It happens sometimes that diamonds obtained from the Cape blue ground split or burst after varying intervals. May not this phenomenon be looked upon as an indication of an unstable state, resulting from very high pressures which may have acted at the moment of the formation of the diamond?

In no case has a diamond, among the many which have been found, shown unmistakably a point of attachment to a rock. Some crystals have a perfectly regular form. It would thus seem that the diamond was formed in the midst of a liquid or pasty mass, and the question arises at once as to what solvent can have been employed.

From the known properties of carbon and from the experiments described in this work, we know that the metals more especially dissolve carbon with ease. In this respect iron is one of the best. If it be now remembered that the Cape blue ground, as we have shown, contains perfectly crystallized graphite, and that well-crystallized graphite is formed most easily in a fused metal and not by volatilization, one is led to look for the crystallization of carbon in molten iron under pressure.

We may add that the study of the diamond ash, which always contains iron, has led us to the same conclusion.

The objection may be raised that this metal is disseminated throughout nature; but the amounts found in certain boarts and in some black diamonds seem to us too great to be ascribed to a dissemination comparable to that of manganese or of boric acid.

From this point of view it is interesting to notice that of all the minerals found in a cubic meter of blue earth by far the most abundant is titaniferous iron, as has been shown by Stanislas Meunier.

Finally, should a last proof be required, it is provided by the Diablo Cañon iron, which in the middle of a metallic mass revealed two small transparent diamonds, of rough and grained surface, surrounded by amorphous carbon in distinctly compressed strips.

In this case nature seems to have been caught in the act.

This carbon must have crystallized out under strong pressure; the iron was liquid and, thanks to a sudden cooling due to some cause or other, the mass contracted violently and the carbon passed from a density of 2 to one of 3·5; it yielded a diamond.

Such are the ideas, correct or erroneous, which led me to change the direction of my researches and to bring in the factor of pressure. I do not know whether this theory will survive the work of my successors, but to it I owe the experiments to be described, which have led me to the reproduction of the diamond in microscopic crystals.

Experimental details.—To carry out these experiments I make use of the pressure resulting from the increase of volume undergone by a mass of molten iron as it passes from the liquid to the solid state. As one knows, solid iron has a lower density than the molten metal. It is a fact known technically that pigs of iron float in a bath of the same iron in the liquid state. Molten iron, like water, increases in volume at the moment of solidification.

Therefore we began these researches by heating in the oxygen blowpipe a small amount of iron in a carbon crucible, and then the whole was plunged into cold water.

These first attempts yielding but a doubtful result, it seemed to us essential to saturate the iron with carbon at a higher temperature. To this end we used the electric furnace. At the high temperature produced by this apparatus, iron dissolves a large amount of carbon, which is subsequently given up as graphite when the iron solidifies.

The experiment was carried out as follows: 200 grms. of soft Swedish iron, cut up into cylinders 1 to 2 cm. long and about 1 cm. in diameter, were placed in a carbon crucible and covered with sugar carbon. We need not describe here the arrangement of the furnace, as that was given at the outset of this work. The whole is heated for three to six minutes with a current of 60 volts and 350 amperes. The lid of the furnace is removed and, having wrapped one's hand in a cloth, the edge of the crucible is grasped with iron tongs and the whole suddenly plunged in a vessel full of cold water. The crucible and the contained metal remain red-hot for several minutes, producing bubbles of gas which burst at the surface of the liquid without burning. The temperature sinks rapidly, the crucible becomes cold and every gleam of light disappears; the experiment is then finished (Fig. 24). Not without a certain apprehension did we carry out this experiment for the first time; I wondered whether an explosion might not take place at the moment of placing in water a crucible full of molten iron at a temperature of 3,000° C. As a matter of fact, the experiment is quite safe, thanks to the calefaction. We have prepared from 250 to 300 ingots of iron, suddenly cooled in this way, without accident. This has not always been the case with other metals, especially with bismuth.

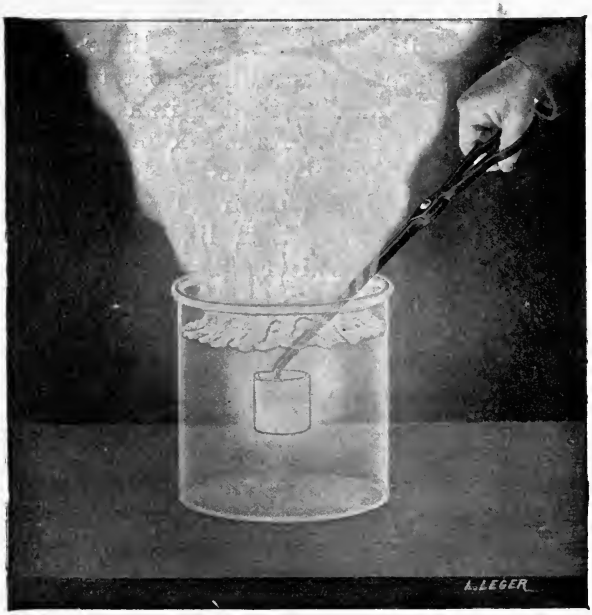

Fig. 24.

The regulus is then attacked with boiling hydrochloric acid till the acid no longer gives the reaction of iron salts. There then remain three kinds of carbon: a small quantity of graphite, when the cooling has been sudden; a brown carbon in thin convoluted strips, seeming to have been acted on by a strong pressure (we came across the same variety in various samples of the Diablo Cañon iron); finally, a very small amount of a somewhat dense carbon which had to be separated. The mass is treated several times with aqua regia, then alternately with boiling sulphuric acid and with hydrofluoric acid. The residue is then heated in sulphuric acid up to 200° C., and small quantities of powdered potassium nitrate are gradually added. All the amorphous carbon is destroyed. The denser part, examined under the microscope, contains but very little graphite and consists of different varieties of carbon. It is attacked six or eight times with potassium chlorate and fuming nitric acid which we prepared as free as possible from water. After a last treatment with boiling hydrofluoric acid, and after decantation with boiling sulphuric acid to destroy the fluorides formed, the residue is washed and dried and the high density particles are separated by bromoform.

After this first separation, the small residue found at the bottom of the bromoform is washed with ether and placed in a small tube containing methylene iodide. A few transparent particles sink, while some black fragments float on the liquid. Both parts are collected and placed in separate test-glasses of regular shape, in presence of a large excess of distilled water.

FIG. 25.—Black synthetical diamonds. × 100.

It is then easy to seize them with a pipette (see 'Technique of these researches') and to deposit them on a slip of glass. They are protected with a cover-glass and examined under the microscope.

The opaque fragments have a grained surface, and a greyish black tint. Their density varies from 3 to 3·5, since some of them sink in methylene iodide and some in bromoform. Others are blacker in colour and have a smoother surface and curved edges. Some have well-defined angles which, at first sight, might be mistaken for those of a cube (Fig. 25).

To see whether these fragments scratch corundum, a ruby presenting a very smooth face is cemented on to a thick piece of glass. The small black fragments are taken up with the moist end of a hard wood splinter, and they are rubbed strongly over the surface of the ruby which has first been examined in a good light under the microscope. The wood point is moved in a direction at right angles to the striae resulting from the polishing. The surface is again examined and if the particles dragged along by the wood splinter are sufficiently hard, one observes more or less deep lines produced on the surface of the ruby. This surface must be repolished after each test. This method has enabled us to observe the hardness of very fine powders. By causing the surface of the ruby to shine slightly, one may recognize the smallest striae.

The black powder described above scratched the ruby with ease.

The combustion in oxygen had still to be carried out.

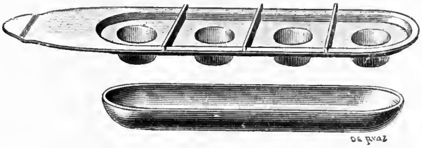

FIG. 26.—Platinum boat.

We devised a small platinum boat covered with a hollowed-out lid, out of which had been stamped four small cavities possessing a brilliant and well-polished surface (Fig. 26).

The small black fragments were taken from the water in the test-glass which contained them, by means of a pipette consisting of a drawn-out tube. Then, by placing the point of the pipette in one of these cavities and then holding it vertically, the fragments fell in owing to their density, together with a few drops of water. The boat was then dried in an oven. The small cavity containing the fragments was then placed in the field of the microscope and a drawing made of their shape.

FIG. 27.

The boat was finally placed in a small platinum apparatus (Fig. 27) consisting of a tube closed by a smooth-fitting cap and traversed by a stream of oxygen. The middle part of the tube, where the boat rested, was then heated by means of a gas blowpipe up to about 1,200° C. The heating lasted twenty to thirty minutes, the whole was cooled and the boat placed under the microscope in the same position as before and examined. A drawing was then made of the contents of the cavity by reflected light, which was easy because the bright bottom acted as a mirror, and on comparing the two drawings one could see what fragments had disappeared and whether any ash remained in their place. The platinum tube described could be replaced by a tube of Berlin porcelain, 30 cm. long, closed with caps which were cemented on. The apparatus was connected with a small washing-tube containing baryta water, which became milky as soon as any carbon dioxide was produced. A similar washing-tube was placed in front of the combustion-tube and was separated from the latter by a tube containing fused potash, so as to ensure that the oxygen used contained no trace of carbon dioxide. A trace of carbon may be easily identified in this way, as was proved by some preliminary experiments. The black diamonds of density 3 to 3·5, obtained from the iron regulus, burnt in oxygen with evolution of carbon dioxide, leaving behind a very slight yellowish ash in the place they occupied in the cavity. The transparent fragments have a greasy look; they flash and possess a number of parallel striae and sometimes triangular impressions. These latter fragments are generally surrounded

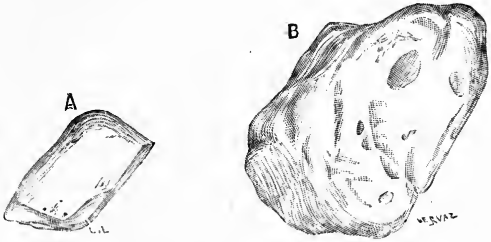

FIG. 28. × 100.

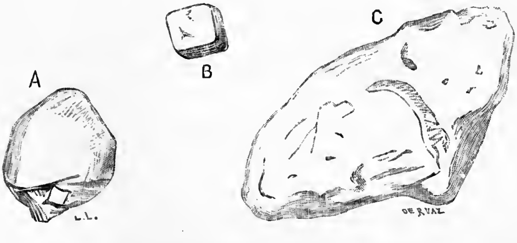

FIG. 29.—Synthetical transparent diamonds. × 100.

by a coating of black carbon; they are only recognized after treatment with potassium chlorate, a treatment occasionally repeated ten times.

Some of these diamonds have a rounded surface (Fig. 28, B), others seem to be broken up into small pieces (Fig. 28, A). One of these fragments A had a light yellow colour, as had the cube B in Fig. 29. Some have a cubical appearance (Fig. 29, B) or an irregular shape (Fig. 29, A and C). Their density is near 3·5, since they all sink in methylene iodide; they cut deeply into the ruby and they burn in oxygen leaving no ash or a mere trace slightly yellow with production of carbon dioxide.

As to the yield of these earlier experiments, it was so small that we were unable to gather the few milligrammes of transparent crystals necessary to be able to weigh the carbon dioxide produced by combustion. Moreover, a certain number of the ingots yielded nothing, due to the fact that the pressure was not sufficiently great. It happens sometimes that the metallic crust formed during the sudden cooling breaks, and that the still liquid metal at the interior comes to the surface. Further, the gases evolved form geodes in the mass and prevent the pressure from being regular. In these cases, which were only too common, absolutely nothing remains in the field of the microscope after treatment with potassium chlorate and hydrofluoric acid.

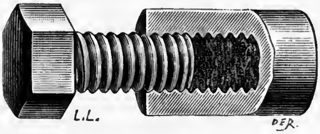

FIG. 30.

To render the preparation more successful, we tried to surround the metallic regulus with a coat of soft iron. This experiment is carried out as follows: some sugar carbon is compressed strongly in a cylinder of soft iron closed by a screw stopper of the same metal (Fig. 30). This cylinder is 4 cm. high, 1 cm. in diameter, and the walls are 8 to 10 mm. thick. 50 to 200 grms. of soft iron are then melted in the electric furnace in a few minutes, and the cylinder containing the carbon is then rapidly introduced into this liquid bath.

The crucible is at once removed from the furnace and plunged into a bucket of water. In this way a surrounding layer of solid iron is quickly formed, and when this crust is at a dull red heat the whole is removed from the water and allowed to cool in air.

When a regulus so obtained is broken, a layer of fused metal is found on the exterior, then metal containing less carbon, and at the centre a part rich in carbon in which are found small diamonds. The amount of black diamond formed is apparently larger than by the first method, although still very small. A certain number of ingots are useless because of the breaking of the outer crust or of the production of geodes. The specimens are attacked by the methods described above. We obtained in this way black diamonds (Fig. 31) and some transparent ones.

Fig. 31.—Black diamonds prepared in cylinder. × 80.

One of the latter (Fig. 32) measured 0·38 mm. along its greatest length. It had a characteristic appearance, sank in methylene iodide, and disappeared in oxygen at about 900° C. with production of carbon dioxide. By carefully withdrawing the boat from the combustion-tube, a trace of yellowish grey ash, scarcely visible under the microscope, was found in the place of the fragment, having retained its shape. Another preparation yielded a limpid and well-crystallized diamond

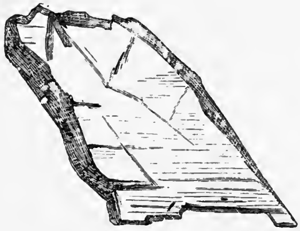

Fig. 32.—Transparent diamond prepared in cylinder.

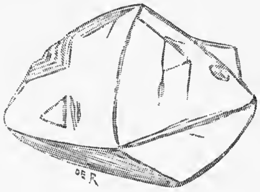

Fig. 33. × 100.

(Fig. 33), which also burnt in oxygen without leaving any residue.

In general, when the iron used in these experiments is free from silicon, and when the crucible contains no alumina, the black or transparent fragments yield no ash after their combustion in oxygen.

Cooling in iron filings.—It seemed to us that the rapidity of cooling exerted a vital influence on the formation of crystallized carbon. When the crucible is cooled in water, calefaction prevents all contact between the red-hot iron and the liquid body.

Cooling is thus, at the outset, the result of radiation. To increase the rate of cooling, we tried to cool the molten iron by conduction. To this end, 200 grms. of molten metal saturated with carbon in the electric furnace, are poured into a cavity made in the middle of a mass of iron filings, and the whole covered up at once with an excess of the same filings. The fused mass is surrounded with molten iron and the whole is cooled quickly thanks to the conductivity of the filings.

After treatment with acids, then with chlorate and nitric acid, and finally with hydrofluoric acid and boiling sulphuric acid, there remain small diamonds of rounded form possessing but rarely a crystalline appearance and nearly always containing internally small black points[1].

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[1] One finds in nature, both at the Cape and in Brazil, transparent diamonds containing inclusions of varying shape. These inclusions may vary in nature, but most of them are black, and when they are numerous they yield that variety of crystallized carbon of greasy appearance known as black diamond. We can show that these black inclusions are due to a variety of carbon differing from diamond, in the following way: a black diamond weighing 2·2365 grms., showing a few transparent areas, was wrapped up in a cloth and broken by a hammer on an anvil. It cleaved at the first blow, yielding a very distinct octahedral point. The whole was finely powdered in a mortar and this greyish black powder, examined under the microscope, consists of fragments containing numerous small black masses. About 10 mgrms. of this powder are then heated in a tube of Bohemian glass, in a current of oxygen and at a temperature 200° C. lower than the combustion temperature of diamond. The experiment lasts half an hour. A slight evolution of carbon dioxide is distinctly observed by means of baryta water and the evolution ceases after a time. After cooling, the diamond has lost its grey tint; it has become white and no black spots are to be seen under the microscope. The black matter contained thus burns in oxygen yielding carbon dioxide, and the diamond resumes its natural transparency. The experiment is only successful with very finely powdered

These diamonds have a density of 3·5, scratch the ruby, and burn with ease in oxygen yielding carbon dioxide. In this new experiment the pressure does not seem to have been so great, and the transformation of the carbon into diamond is less complete ; further, the yield is still very small. The cooling by means of iron filings was repeated some forty times altogether. Whenever the ingot was formed regularly and contained no cavity, the result was always the same. The form of the spots was variable, consisting at times of small black dots spread irregularly, at other times uniting into small areas (Fig. 34).

We look on this formation of diamonds with black spots as of the greatest importance, because it yields results comparable to those met with in nature. Further, owing to their characteristic habit, these fragments are at once recognized as diamonds. Small transparent grains are sometimes met with whose density is greater than that of methylene iodide, and which are not attacked by acids or potassium chlorate, but which nevertheless are not carbon. These particles never show definite angles, or striae, or triangular impressions; they are rounded and do not burn in oxygen. They are found in the platinum boat after combustion ; their shape is unaltered, but their surface is sometimes dulled.

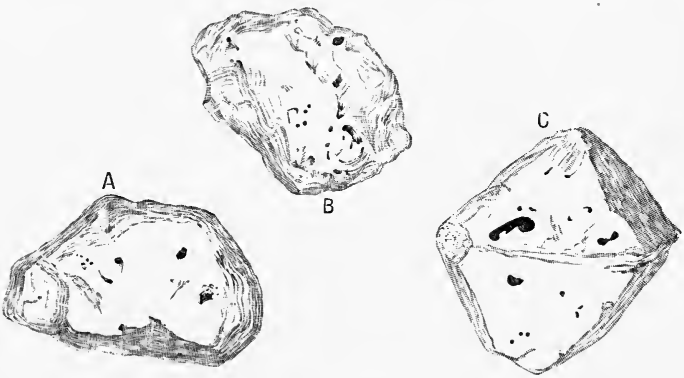

Fig. 34.—Diamonds with black spots. × 80.

This substance was formed more especially with iron rich

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black diamond. A chip of black diamond heated under the same conditions does not lose its colour. The experiment might succeed by carefully heating in oxygen under pressure.

in silicon, or when the electrodes contained a considerable amount of silica and alumina; we shall return to the subject when dealing with the quantitative analysis of synthetical diamond.

Rapid cooling in molten lead.—The formation of spotted diamonds led us to seek a more rapid cooling by conduction. We sought to cool the iron saturated with carbon by plunging it into a bath of molten tin. This did not yield good results because strongly heated iron unites easily with tin; long filaments of an alloy of tin and iron formed in the middle of the liquid and there was no solid mass.

Further, when the crucible containing molten metal at 3,000° C. was plunged into the liquid tin at about its melting-point, heat was evolved by the combination of iron and tin, and the whole mass was raised to too high a temperature for a successful experiment.

As tin yielded such unsatisfactory results, it was replaced by molten lead, kept as near as possible to its melting-point, 325° C. The crucible containing the fused metal was quickly introduced into a bath of lead some 10 cm. deep. The iron being lighter than the molten lead, masses separated themselves from the crucible tending to assume a spherical form and rose more or less quickly through the molten lead.

Iron saturated with carbon in the electric furnace becomes so pasty that the crucible may be inverted without loss.

As soon as the temperature sinks, the metal becomes liquid again, giving up graphite at the same time. The smaller spheres, which were only 1 to 2 cm. in diameter, were solid and sufficiently cooled on arriving at the surface of the bath. Those reaching the surface while still liquid caused the combustion of the lead in air giving off abundant fumes of litharge, and causing splutterings of the oxide or of the incandescent metal. A few minutes later all the metallic globules floating on the molten lead were removed, the covering of lead removed by nitric acid, and the remaining metal was treated in the manner already described.

Under these conditions the yield is somewhat better though still very small. But we were struck at the outset by the limpidity of the transparent diamonds thus obtained; there were no spotted diamonds, and the surface in some cases was distinctly crystalline. Numerous parallel striae were observed and small impressions of cubes, such as are sometimes met with in natural diamonds. One of these transparent diamonds (Fig. 35), whose diameter was 0·57 mm., had the form of a triangle with rounded angles.

It was perfectly clear; at one point on the right it had a small cavity, and its surface was covered with impressions having the appearance of small cubes. Three months after its formation, this diamond, which was wedged between two pieces of glass, split in two places. The widening of the small cracks could be observed for some time, and after three weeks the diamond was found to be broken up into several fragments on its support.

The same thing happened to another specimen, which was found reduced to small bits between two glass slips. This production of diamonds which burst several months after their preparation seems to us of importance. Certain diamonds from the Cape mines show identical phenomena. We believe that this behaviour of the microscopic fragments we obtained and of the Cape diamonds is due to the great pressure to which both were subjected at the moment of their formation.

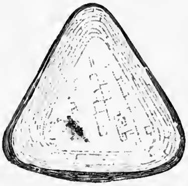

Fig. 35.—Diamond by cooling in lead.

The specimens obtained by this method of cooling in molten lead were very interesting when examined as to their form. The surface of these diamonds is generally polished and bright, sometimes it is grained, offering a peculiar pitted appearance often seen in natural diamonds.

They stand out conspicuously and always possess the greasy lustre characteristic of the diamond. Finally, when traversed by a beam of light, they shone and became as it were saturated with light. Some occurred in cubes or in octahedra with rounded faces. M. Bouchardat, Professor of Mineralogy at the 'École supérieure de Pharmacie,' was kind enough to examine these crystals as to their form, and he found one amongst others which had clearly the form of a trapezoid with twelve faces, that is, one of the hemihedral forms of the regular system.

Examined with convergent polarized light, these crystals (Figs. 35 and 36) show no colour phenomena as a rule, or only low tints (Fig. 37).

We have had more than once the opportunity of examining crystals of native diamonds showing far more intense colour phenomena. It seems to us that these well-recognized colorations may easily be explained by the pressure necessary for the production of these crystals.

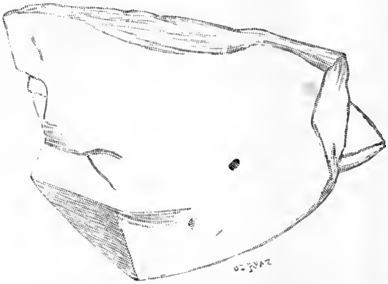

FIG. 36.—Diamond, by cooling in lead. × 100.

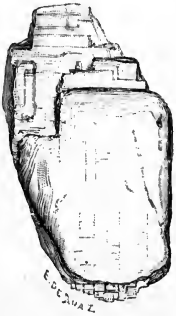

FIG. 37.—Diamond, crystallized as a cube. × 100.

We may describe some of them. The specimen figured (Fig. 37), which has a maximum length of 0·4 mm., is practically transparent, and by looking through it the smallest details of its lowest surface may be seen. It consists of superposed layers irregularly crystallized. Numerous parallel striae are to be seen on the sides.

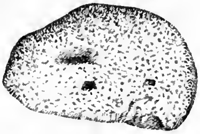

FIG. 38.—Drop-like diamond. × 80.

The specimen of Fig. 38 has the appearance of a suddenly solidified drop. Its surface is grained and its appearance is identical with that of certain Brazil diamonds. I may add that this appearance is thoroughly characteristic.

Experiments made with the granulated metal.—In a new series of experiments we sought to diminish the volume of the molten iron and to cool it with far greater rapidity.

The ideal experiment would consist in giving a spherical form to the molten metal and then to submit it to an enormous pressure. This result may be achieved on a small amount of substance by allowing the molten metal saturated with carbon in the electric furnace, to fall from a certain height and to cool it suddenly in a bath of mercury.

We arranged a limestone electric furnace similar to that used always, the bottom of which, however, had a cylindrical opening some 6 cm. in diameter. The electrodes were 5 cm. in diameter; the positive electrode was hollow and bore along its axis a cylindrical channel 18 mm. in diameter, in which an iron rod moved easily allowing of its backward or forward motion at will.

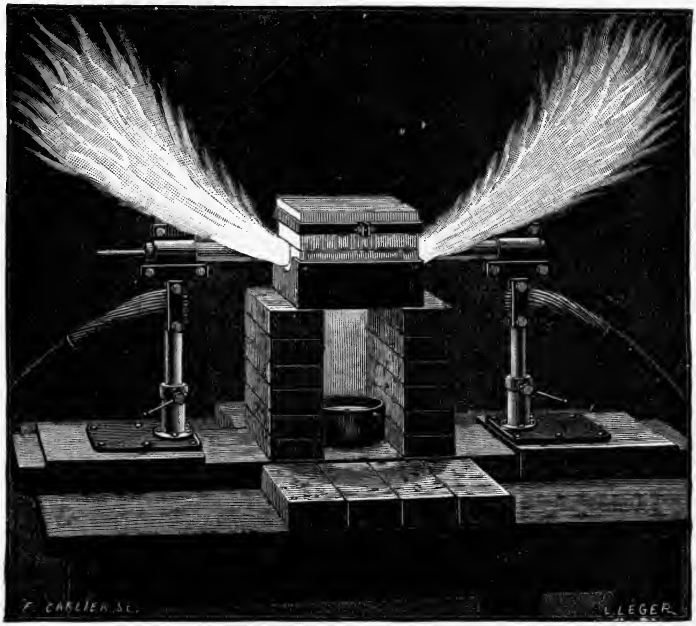

FIG. 39.—Granulating furnace.

This furnace (Fig. 39) rested on two supports, and underneath was an iron pan containing mercury to a depth of 10 cm., and above this a layer of water of twice the depth.

The arc was started with a current of 1,000 amperes at

60 volts. When it was working smoothly and the lime began to distil, which happens in two to three minutes at the most, the iron rod was slowly pushed forward; as the metal neared the arc it melted, took up carbon rapidly, and the molten metal then fell in very regular spheres. These incandescent spheres went through the water and, by virtue of their acquired velocity, fell to the bottom of the mercury, where they were cooled by conduction.

Once started the experiment is easily regulated, and several kilos. of iron could be granulated in a few moments.

When this granulated mass was removed from the mercury on which it floated, one came across a considerable number of spheres or of oblate spheroids of regular form and perfectly homogeneous. They were at the most 1 cm. in diameter, sometimes only 4 to 5 mm. They were placed on one side to be treated in the manner already described.

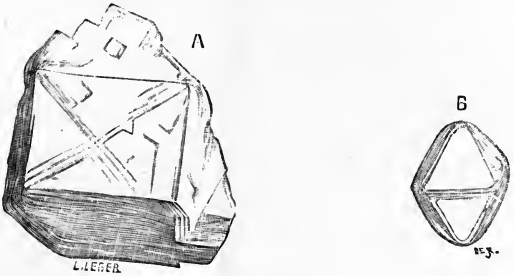

FIG. 40.—Diamonds from granulated iron. × 100.

The other grains which were irregular in shape, having touched the bottom or containing more or less big geodes which rendered them easy to crush under the hammer, were not treated with acids. We had ascertained at the outset that they contained no carbon of high density, and that, treated in the usual way, they left no residue under the microscope.

The whole mass was sufficiently saturated with carbon, for it contained graphite which could be seen in the geodes of the poor quality grains.

The spherules of regular shape yielded black and transparent diamond. The latter occurred in very small crystals, which is not surprising; but some of these crystals were remarkably regular; we may mention an octahedron (Fig. 40, A and B), measuring 0·016 mm. along its greatest length, which sank in methylene iodide and which burnt in the platinum boat without leaving any residue. These small crystals mark the ruby and have the lustre and the appearance of the diamond.

Thanks to the kindness of M. Guichard, of the 'Société Edison,' we have been able to repeat the experiment in another form. The electric furnace just described was placed over a well 32 meters deep, at the bottom of which hung an iron bucket containing the water and the mercury. As soon as the furnace had reached its normal temperature the iron bar was pushed forward, taking care to fuse sufficient metal to produce grains of a somewhat greater diameter. Spheres of fused iron 2 to 3 cm. in diameter were obtained, which fell vertically giving off a spark now and again, and which disappeared noiselessly into the water at the bottom of the well.

This preparation was a very bad one from the point of view of the production of the diamond, as the depth of mercury was inadequate to the velocity of the fall and the molten metal was scattered into fragments of various shape.

But two things are to be noticed in this experiment.

If one of these spheres happened to touch the edge of the tub in which stood the iron bucket, or if it fell on the ground, a flame was produced, and it broke up into sparkling globules with a report similar to that of a gun. This metallic sphere seemed to be saturated with gas and exploded like a bolide.

Secondly, we were struck by the following: At the instant when the metallic sphere leaves the furnace it has a dazzling appearance, but it has scarcely passed through 50 cm. in its rapid fall before this brilliant light has much diminished. From a recess made at the bottom of the well we could clearly observe the spheres as they came in contact with the water, and we could see from their colour that their temperature had already fallen greatly.

Rapid cooling in metallic blocks.—This last work led us to replace mercury by a metallic block. A cylinder of iron 18 cm. long and 14 cm. wide was turned on a lathe. A cylindrical opening of 3 cm. diameter and 12 cm. deep was then bored along its axis, and into this fitted smoothly a cylinder of the same metal. The whole was placed in a tub full of water. 400 grms. of iron were then melted in the electric furnace and saturated with carbon. This liquid was poured into the metallic block and the opening closed at once by means of the iron cylinder.

The cooling is very sudden under these conditions. The whole of the metal forming the block is removed on the lathe, and the mass of iron found in the interior is treated in the usual way.

This experiment gave better results; the yield, although not very high, was higher than from the granulated metal. The diamond occurred, together with graphite, in short thick crystals, having a density of 2·35. Some fragments of diamond were well crystallized and quite transparent, while others contained black spots.

To increase further the rate of cooling the experiment was carried out with a block of copper of the same size. The yield is not greater, but the diamonds are perfectly transparent, and the number of spotted diamonds is reduced. They are not accompanied by dense, transparent and non-combustible fragments.

The sheath of fire.—The phenomenon of the fire-sheath was discovered by Fizeau and Foucault[1]; it was studied later by Planté and then by Violle and Chassagny[2], and finally Hoho and Lagrange[3] have tried to apply it to technical purposes.

This phenomenon, which takes place when too intense a current is passed through a conducting liquid, enables one to bring the metal of an electrode to the point of fusion.

We carried out the experiment with a tube of iron enclosing a carbon cylinder, and we gathered drops of molten metal in the middle of the solution of sodium carbonate which served as electrolyte. The granules so obtained were always irregular in shape, and were not saturated with carbon; they contained no diamond.

Attempt to dissolve carbon in bismuth.—Bismuth is known to possess in a remarkable manner the property of increasing in volume in its passage from the liquid to the solid state. We desired to study the solubility of carbon in this metal.

Bismuth was first heated in a carbon crucible in a tube of the same material by means of a current of 350 amperes at 60 volts. The experiment was very short because of the

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[1] *Ann. de Ch. et de Ph.*, sér. 3, xi. 383 (1844).

[2] *Société de Physique*, 1889; *C. R.*, cviii. 284 (1899).

[3] *C. R.*, cxvi. 575 (1893).

volatility of the metal. After cooling, the non-volatilized mass contained neither graphite nor amorphous carbon.

Bismuth was then heated in contact with sugar carbon in a carbon crucible by means of a current of 350 amperes at 60 volts. When the mass was red-hot it was immersed in water, when a violent explosion took place, together with the projection of the water and of all the metal which was reduced to very small fragments.

The same results were obtained on repeating the experiment.

Sudden cooling of silver.—Silver saturated with carbon possesses also the interesting property of increasing in volume when passing from the liquid to the solid state[1].

At its melting-point, silver dissolves but traces of carbon, but if it be heated in the electric furnace in contact with a brasque of sugar carbon so as to cause it to boil, it then dissolves a certain amount.

By cooling it suddenly, as by immersing the crucible containing it in cold water, a regulus is formed enclosing a part of the molten silver, and the latter on solidifying is submitted to great pressure. The carbon deposited at the centre of the regulus has a density considerably higher than that of graphite. After the experiment the metal is attacked with boiling nitric acid, and there remains a powder which is examined under the microscope. This is a very complex mixture. If the electrodes or the crucible contain silicates it contains piled-up crystals of silica, as described by Marsden. Corundum and carbon silicide are also found.

This residue is treated as already described: alternate action of boiling sulphuric acid and hydrofluoric acid, treatment with the oxidizing mixture, hydrofluoric acid, and finally with sulphuric acid.

After these treatments and in all the experiments, which

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[1] When an ingot of silver containing no carbon is suddenly cooled in water it contracts on cooling; the ends of the cylinder become concave. On the contrary, if the experiment be done with silver saturated with carbon, the ends are convex. In the latter case, the cylindrical part reproduces very exactly the smallest details of the cylinder. It would seem that silver carbide alone increases in volume by passing from the liquid to the solid stage. These results agree with those of W. Chandler Roberts and T. Wrightson (*Proc. Phys. Soc.*, iv. 195 (1881).), who have shown that the density of liquid silver near its melting-point is 9·51, while that of solid silver is 10·57. We obtained an identical result for liquid iron and aluminium when saturated with carbon.

were often repeated, we never obtained anything but black diamond. There often remained, together with this carbonado, a few transparent crystals, some of which had an octahedral appearance[1], but they disappear slowly if repeatedly and energetically attacked with concentrated sulphuric acid. They may also be destroyed without affecting the black diamond, by fusion with potassium bisulphate at a low temperature. The residue is then treated with methylene iodide.

It is of great importance in this work to multiply the number of attacks with potassium chlorate and nitric acid, if all the silver which contaminates the black diamond is to be removed.

Under these conditions, the yield of black diamond is larger than in the case of iron. This black diamond or carbonado has either a grained appearance or occurs in dotted plates[2] or in masses possessing a conchoidal fracture, lustreless and greasy, and varying in density from 2·5 to 3·5.

This experiment, which does not yield transparent diamonds, is nevertheless interesting as demonstrating the existence of a series of carbons whose density increases from that of graphite to 3 and above. On treating the mixture with bromoform, we obtained some carbonado which scratched the ruby and burnt in oxygen at 1,000° C. This black diamond is always formed at the middle of the regulus; this may be demonstrated in the following manner: take one of the suddenly cooled silver masses, of regular shape and without any lumps, and saw it into two equal parts at right angles to the base; attack the section thus produced by means of nitric acid, when the bulk of the black diamond formed is obtained in a few minutes. On the other hand, if an unsawn ingot be taken and attacked superficially with acid, the black deposit obtained consists mainly of graphite and contains no carbonado.

We may add that the ingots of refined silver which we used at the outset, occasionally contained, unknown to us, a very small amount of gold; we came across a few fragments of black diamond impregnated with this metal which dissolved

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[1] Crystals of carbon silicide when broken and looked at edgeways might be mistaken for octahedral points.

[2] Some samples of carbon given by Marignac to M. Des Cloizeaux have the same appearance.

rapidly in aqua regia[1]. It is rather interesting to compare this observation with the discovery by Des Cloizeaux of carbonado containing small particles of gold.

E. **Combustion of synthetical diamonds.**

We have seen that the crystals obtained by means of iron and silver cooled in water, possess the density and hardness of black and transparent diamonds; further they burnt in oxygen at 700° C., yielding carbon dioxide.

To prove conclusively that this substance is diamond, there only remains a quantitative combustion to be carried out. This was the most delicate part of our work. The yield of these experiments is very small and the separation of the microscopic diamonds is tedious and difficult.

The small yield is due to several causes. When molten iron is cooled very suddenly, the dissolved carbon is not set free. Now the cooling must be rapid in order to form a solid and non-yielding crust on the surface of the regulus; this explains why the yield of diamonds is so small with 200 grms. ingots. The central part, which may still be liquid, has not got the time to give up much carbon before solidification. Theoretically one ought to act with a known pressure on a mass of iron saturated with carbon at a high temperature, which should then be cooled slowly. Further, at the moment of solidification, gases are evolved which prevent the pressure from being uniform. Finally, when the liquids are decanted off after these numerous treatments, and the small diamonds are quite clean, several of the fragments float on the water, and we thus lost some fine samples on several occasions.

By working up some thirty silver ingots by the methods described, we were able to separate 0·006 grm. of black diamond, sinking in methylene iodide and cutting deeply into the ruby.

To carry out the combustion of this substance, we arranged our apparatus as follows (Fig. 41).

A tube of Berlin porcelain, 60 cm. long and glazed outside and inside, was placed in a good combustion furnace whose maximum temperature as measured by a thermo-electrical couple was 1,050° C. Each end was fitted with a glass continuation which was cemented on. One of the ends

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[1] The gold gathers into the still liquid central part. This seems to indicate that there is no definite alloy of gold and silver.

was connected by a lead tube with a copper gas-holder quite full of oxygen prepared from potassium chlorate and manganese dioxide and free from carbon dioxide.

The oxygen was passed through two wash-bottles containing baryta, which remained perfectly clear. It was then dried by passage through towers containing potash fused in a silver dish. The other end of the tube was connected with a tube containing pumice moistened with sulphuric acid, then with absorption bulbs containing aqueous caustic potash, and finally

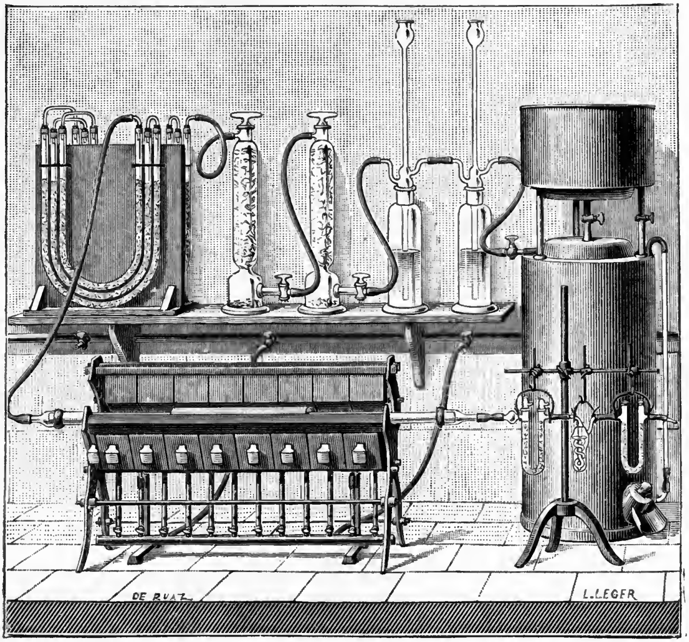

Fig. 41.—Apparatus for combustion.

with a small U tube full of fragments of fused potash. To prevent the absorption of moisture from the surrounding air, the latter was connected with a tube containing pumice and sulphuric acid.

Blank experiments were first carried out, to determine the limit of error of the apparatus. A platinum boat was weighed to ·1 mgrm., then introduced into the middle of the tube by means of a platinum wire. The latter was of such a length that it remained within 1 cm. of the end of the tube, and could be easily seized with tweezers. The glass continuation is then cemented on to the tube. The absorption tubes are weighed to ·1 of a milligram, and the current of oxygen slowly passed. The furnace is then heated and the experiment lasts two hours. When finished, the absorption tubes are reweighed and one should find again the original number. The error in a blank experiment may vary from 0·001 to 0·0015 grm. We never obtained a higher figure in any of the six comparative experiments carried out at different times.

Combustion of the black synthetical diamonds.—For this experiment we prepared 6 mgrms. of black diamonds by means of silver ingots rapidly cooled in water; the carbonado was placed in the platinum boat and heated for two hours in a stream of oxygen.

Results:

Tare of the boat before combustion	3·3035	grms.
,, ,, after ,,	3·3095	,,
,, ,, empty	3·3095	,,

Before the Experiment.

Tare of sulphuric acid tube	6·2675	,,
,, potash bulbs ,, tube with solid potash	1·0863	,,

After the Experiment.

Tare of sulphuric acid tube	6·2670	,,
,, potash bulbs ,, tube with solid potash	1·0633	,,

From these figures:

Substance burnt	0·006	grm.
Carbon dioxide formed	0·023	,,

The 6 mgrms. of black diamond burnt left but a trace of ash whose amount was much too small for determination. They gave 0·023 grm. of carbon dioxide, theory requiring 0·022 grm.

This substance possesses clearly the fundamental property of carbon, that of yielding 3·666 grms. CO_2 per gram.

Combustion of transparent diamonds.—We then prepared transparent diamonds from molten iron suddenly cooled by water and iron filings. Eighty ingots were required to obtain, after the numerous treatments already described, the minute quantity of 0·0155 grm. of small fragments denser than methylene iodide. About one-tenth of this consisted of black diamonds which could not be separated because of their small size. The remainder consisted of transparent diamonds among which were a fairly large number with black inclusions, resulting from the sudden cooling in iron filings. As already observed, all these diamonds sink in methylene iodide, cut deeply into the ruby, and some are very well crystallized.

The combustion was carried out with all the care required for a substance obtained with such difficulty, and the boat and tubes were weighed after a first blank experiment:

Tare of boat before combustion . . .	3·2928 grms.
„ after „ . . .	3·3058 „
„ empty	3·3083 „

	Before.	*After.*
Tare of sulphuric acid tube .	6·2402	6·2398 „
„ potash bulbs . . . „ tube with solid potash .	2·8307	2·7811 „

From these figures:

Substance burnt	0·0130 grm.
Carbon dioxide formed	0·0496 „

The weight of substance burnt in oxygen was thus 0·013 grm. and the weight of CO_2 formed 0·0496. Taking 12 as the atomic weight of carbon and 16 as that of oxygen, the theoretical amount is 0·0476.

The residue of 0·0025 mgrm. remaining in the boat was particularly interesting to study. Under the microscope, one could see at once that it consisted of bright rounded grains, which had withstood the action of oxygen at 1,000° C. These small grains were gathered and treated again with boiling sulphuric acid and then with the fused double fluoride of potassium and hydrogen. Under these conditions, they disappeared almost entirely after repeated treatments. Another portion of the same substance was easily attacked by fused potassium bisulphate.

This non-crystalline transparent substance which has a density above 3·5 and which marks the ruby is therefore not carbon. It may be a special variety of silicon or silicate resulting from an iron rich in silicon used in some of our experiments. The small amount of substance at my disposal did not allow me to clear up this point, but the same particles were always met with when electrodes rich in silicon or silicised irons were used[1].

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[1] In a few experiments on this particular point, carried out with iron melted in presence of alumina, we came across some transparent dusts, non-combustible, amorphous, with corroded surfaces, giving under the microscope with cœsium alum, the reaction of alumina. These fragments

After treating the combustion residue with the double fluoride of potassium and hydrogen, there remained two or three particles of carbon silicide easily identified by its appearance and crystalline form.

Finally, together with this residue, we saw under the microscope traces of light ash, whitish or slightly ferruginous which had the appearance of diamond ash. They were removed by blowing gently and the weight of the boat was unaltered.

We found among the incombustible particles no sample of transparent fragments with black dots, from spotted diamonds. The latter were all burnt.

This experiment shows that the 0·013 grm. of combustible matter yielded the amount of carbon dioxide corresponding to the atomic weight of carbon.

As these diamonds had yielded a small amount of non-combustible fragments, we wished to repeat the experiment.

New diamonds were prepared, partly by means of cylinders filled with sugar carbon (p. 122), and partly by means of blocks of iron and copper[1] (p. 131). They sank in methylene iodide, marked the ruby with ease, and contained no black diamonds.

The combustion yielded the following results:

Tare of boat before combustion . . .	2·1268 grms.
,, after ,, . . .	2·1325 ,,
,, empty	2·1325 ,,

	Before.	*After.*	
Tare of sulphuric acid tube . .	4·8670	4·8665	,,
,, potash bulbs . . .	3·8310	3·8105	,,
,, tube with solid potash .			

From these figures:

Substance burnt	0·0057 grm.
Carbon dioxide formed	0·0205 ,,

0·0057 grm. of transparent diamonds yielded 0·0205 grm. of carbon dioxide. Theoretical amount, 0·0209.

The ash in this experiment had no appreciable weight. These three experiments thus demonstrate that the black and transparent fragments of density 3·5 obtained in our experiments consist of pure carbon.

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always disappeared after repeated treatments, while the diamond is unaffected.

[1] These two methods yield the purest diamonds.

Conclusions.—Under the different conditions of our experiments, we have been able to obtain a variety of dense carbon, either black or transparent. Certain specimens had a very distinct crystalline appearance; they had a density of 3·5 and marked the ruby; they withstood twelve attacks with the oxidizing mixture of dry potassium chlorate and fuming nitric acid, with hydrofluoric acid and boiling sulphuric acid; finally, they burnt in oxygen at about 900° C. yielding 3·666 grms. of carbon dioxide per gram of substance. These properties are possessed by the natural diamond alone.

We have already shown, experimentally, that carbon may be compared to arsenic; that, in vacuo as at ordinary pressure, it passes from the solid to the gaseous state without liquefaction. When gaseous carbon resumes the solid state, it always takes the form of graphite. At ordinary pressure, any given variety of amorphous carbon polymerizes under the action of an increased temperature, passing into a stable crystalline state in which its properties become definite. This is graphite. At the same temperature, without passing through the liquid state, the diamond is also converted into graphite.

We believe nevertheless that carbon may be liquefied, but this will only take place under the action of very great pressure. The density of carbon increases under great pressure yielding diamond, as the preceding experiments have shown. From iron ingots cooled in lead, I have been able to prepare small diamonds having the form of a lengthened drop, such as are sometimes met with in nature. As is well known, diamonds are found at the Cape, as in Brazil, without the slightest appearance of crystallization, and having a rounded form such as may be assumed by a liquid in the middle of a pasty mass.

Were a fresh example required, we might recall the form of the microscopical diamonds we found in the Cape blue earth (Fig. 20, A and C).

Carbon may thus be liquefied under pressure; it becomes transparent, its density increases and it may then solidify either in a crystalline or in a rounded and amorphous form. An impurity, a trace of a body belonging to the regular system, may bring about a regular crystallization or a network of irregular crystals. If the pressure be somewhat less, the diamond is contaminated with particles of carbon which retain their black colour; thus arises the spotted diamond. Finally, if the pressure be lower still, there results black diamond or carbonado alone, more or less irregularly crystallized, whose density may be lower than that of the diamond.

All these different varieties of the diamond: regular octahedra, cubes, irregularly crystallized fragments, crystals splitting after a time, drops, carbonado, have been reproduced in our researches; they support the theoretical views we have expressed on the liquefaction of carbon.

CHAPTER III

PREPARATION OF VARIOUS ELEMENTS IN THE ELECTRIC FURNACE

General.—The high temperature of the electric furnace has enabled me to extend certain reactions which had hitherto been looked upon as limited, owing to the limited range of temperature available. One is familiar, for example, with the laws of complete or incomplete decomposition of calcium carbonate by heat, investigated in a masterly manner by Henri Debray. That barium carbonate should have been considered undecomposable by heat alone is due to the fact that the temperature of our furnaces was too low to bring about even its dissociation. Barium carbonate heated in the electric furnace decomposes in a similar manner to calcium carbonate; it loses carbon dioxide leaving behind barium oxide.

Certain oxides were known to be unreduced by carbon. Such were, for example, silica, the oxides of the alkaline earths, the oxides of uranium, of vanadium, and of zirconium. We shall show how these various compounds have been reduced in the electric furnace yielding the metals or carbides which are usually crystalline.

Powerful currents had been used previously in metallurgy to bring about electrolysis. The manufacture of aluminium is an example of this. But we believed that the heat of the electric arc might also be specially applied to the reduction, by carbon, of oxides hitherto considered irreducible.

Thus, the use of the electric furnace allows of the rapid preparation, in the molten state, of the refractory metals which were formerly very difficult to obtain or which had never been obtained. Most of these elements have, up to now, been studied as dark coloured powers of varying composition, whose physical state offered no guarantee of purity.

To obtain these refractory bodies in the fused state, it is sufficient to place in the cavity of a quicklime or limestone furnace, a certain amount of magnesia which is stable at the highest temperatures of the arc[1], and to place above this a carbon crucible containing the mixture of carbon and of oxide to be reduced.

If the metal be volatile, one uses the tube furnace in a stream of hydrogen and the metallic vapours are condensed in a cooled receiver. Calcium, barium, and strontium are prepared in this way. However, these metals are obtained in the form of fine powder which cannot be fused into a regulus[2].

If the metal be not appreciably volatile, it remains at the bottom of the crucible in the liquid state, solidifying as soon as the arc is stopped. Chromium, molybdenum, tungsten, titanium, uranium, and some other elements behave in this way.

Some of these preparations require a special arrangement to be described later.

The substances prepared in this manner generally contain a varying amount of carbon; they must be refined in a second operation, by means of molten quicklime or some oxide of the metal concerned[3].

We shall describe under each metal the special precautions to be taken, and give the analyses of the different samples.

A. **Chromium.**

Chromium, whose important discovery we owe to Vauquelin[4], has already been made use of in many ways. Its oxides and other compounds soon found their way into technical processes. That metallic chromium should have been but little used arises from its difficult preparation.

It has never been obtained in quantity, and when its remarkable properties were applied to the manufacture of

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[1] In all our experiments, solid, liquid, or gaseous magnesia remained as oxide in contact with carbon.

[2] Very finely divided mercury shows the same behaviour.

[3] A fairly large number of metals have never been obtained perfectly pure. Some contain carbon, silicon, or alkali metals; it is now known that a very small amount of impurity may alter the physical and even the chemical properties of these elements. It seems to us therefore of importance to determine the state of purity of the metals obtained in the electric furnace.

[4] On a new metallic substance contained in red lead from Siberia. *Ann. de Ch. et de Ph.*, sér. 1, xxv. 12 (1798).

chromium steel, it was necessary to prepare in the furnace an alloy of iron and chromium very rich in iron, the so-called ferro-chromium.

The presence of iron and carbon in this compound prevented further study, and the alloys which chromium may form with other metals were unknown.

The researches we have carried out will enable us to fill up this gap.

Preparation of crude chromium.—We showed, in 1893, that the high temperature of the electric furnace rendered it possible to reduce chromium sesquioxide with ease by means of carbon, either in the intermittent[1] or the continuous[2] furnace. With the latter we used a slightly inclined carbon tube, the mixture of sesquioxide and carbon being introduced at the upper end while the liquid metal flowed out at the lower. This tube was heated in the reverberatory type of furnace provided with movable electrodes, which we have already described.

It was by means of this apparatus that we prepared readily the 20 kilograms of metallic chromium used in our work. From first experiments, we obtained a carbide more or less rich in carbon according as to whether there was more oxide or more carbon.

The different specimens prepared in this way gave the following figures:

	I	2	3	4	
Chromium .	87·37	86·25	90·30	91·70	per cent.
Carbon . .	11·92	12·85	9·47	8·60	„

The metal thus contained fairly large amounts of carbon. We have studied the different conditions under which this metal is formed, and we have prepared two definite and crystalline compounds of chromium and carbon.

Carbide of formula Cr_3C_2.—When metallic chromium is heated in the electric furnace (350 amperes at 70 volts) in presence of a large excess of carbon, one obtains a brittle regulus full of crystals of chromium carbide corresponding to the formula Cr_3C_2. This carbide occurs in very bright, greasy looking lamellae, which are not attacked by concentrated hydrochloric acid nor by fuming or ordinary nitric acid and aqua regia, but are slowly attacked by dilute hydrochloric acid.

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[1] Moissan, *C. R.*, cxvi. 349 (1893).

[2] Ibid., cxvii. 679 (1893).

Fused potash has but little action, whereas fused nitre destroys it with ease. It has a density of 6·47. The carbide decomposes water neither at ordinary temperatures nor at 100° C. It is a carbide stable at high temperatures. It gave on analysis:

	1	2	Theory	
Chromium . . .	86·50	86·72	86·66	per cent.
Carbon . . .	13·10	13·21	13·34	,,

Carbide of formula Cr_4C.—In some of our numerous preparations of chromium, we observed that the surface of the metallic ingots became covered with reddish-brown needles, often 1 to 2 cm. long. These crystals correspond to the formula Cr_4C. They are also found in the geodes which form in the middle of the fused mass. They have a density of 6·75.

On analysis, the crystals gave:

	1	2	3	4	
Chromium .	94·22	94·02	—	94·55	per cent.
Carbon . .	5·40	6·11	5·24	5·45	,,

Chromium in the crystalline state.—We sought to refine the crude metal by heating it in presence of an excess of the oxide. The metallic carbide broken up into lumps is placed in a carbon crucible carefully lined with chromium oxide and is covered with a layer of the same oxide. The mixture is heated in the electric furnace; the surface oxide melts, then the metal, which gradually gives up all the carbon it contains. The chromium thus obtained, when heated in a stream of chlorine, is entirely converted into a volatile chloride leaving no trace of carbon. The carbon is thus all removed, but the metal is saturated with oxygen; it is what is known in metallurgy as a burnt metal. The refining was then carried out in presence of molten lime and, using from 500 to 1,000 grms. of metal at a time, we were able to remove most of the carbon. For one knows how easily carbon and lime combine to form calcium carbide [1].

This is the reaction we used, and it yielded generally a fine-grained metal containing from 1·5 to 1·9 per cent. of carbon. Thus purified, though still containing a little carbon, chromium crystallizes with ease. We have often obtained fine masses of crystallized chromium in which the crystals were as long as 3 to 4 mm. These crystals have, at first sight, the appearance of cubes and octahedra. Their grouping recalls that of the crystalline masses of bismuth. Fremy had already shown that crystalline chromium might be obtained by the action of sodium on chromium chloride.

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[1] Moissan, *C. R.*, cxviii. 501 (1894).

Chromium free from carbon.—The refining by means of fused lime just described does not, however, yield an absolutely carbon-free metal. We have in fact observed that, if chromium be sufficiently pure, an inverse reaction takes place in presence of liquid lime and of the furnace gases. All the metal was converted into a well-crystallized double oxide of calcium and chromium.

We then took this double oxide which forms so easily in the electric furnace and made a brasque of it in a quicklime furnace and fused some crude metal in it. Under these new conditions the metal is refined and there results a bright product which may be filed and polished with ease. This is pure chromium which gives no trace of carbon on analysis.

Physical properties.—The density of pure chromium was found to be 6·92 at 20° C. (mean of three experiments). It is thus somewhat different from that hitherto given. With the oxygen blowpipe, chromium, in contact with the tip of the blue flame, yields brilliant sparks, burns in part, but apparently only melts superficially owing to the heat of this combustion. Fusion is never complete; it is but superficial, and the fused part is still rich in carbon. Using the closed lime furnace in which Deville and Debray melted platinum, we were unable to fuse chromium containing 2 per cent. of carbon with the oxyhydrogen blowpipe after heating for forty-five minutes. The fragment of metal on which the blue flame impinged alone melted, owing to the oxidation phenomenon just mentioned.

When chromium is quite free from carbon, it burns quickly and its combustion under the blowpipe is even more brilliant than that of iron. Oxidation is rapidly completed and, after the experiment, there remains a rounded fragment of fused sesquioxide.

Pure chromium is more infusible than the unrefined metal; its melting-point is considerably higher than that of platinum, and cannot be attained by means of the oxygen blowpipe. On the other hand, chromium fused in the electric furnace has the appearance of a very fluid and bright liquid having in the crucible the appearance and mobility of mercury. It may even be removed from the furnace and poured into a mould. Using a current of 1,000 amperes at 70 volts, we were able to prepare at one time, in a sufficiently large furnace, 10 kilograms of refined chromium and to cast it with ease.

This cast metal had the following composition:

Chromium	97·14 per cent.
Carbon	1·69 ,,
Iron	0·60 ,,
Silicon	0·39 ,,
Calcium	traces.

Pure chromium quite free from iron exerted no magnetic influence.

Chromium carbide of the formula Cr_3C_2 marks quartz with ease and even the topaz, but it has no action on corundum. The carbide Cr_4C cuts deeply into glass but with difficulty into quartz. Pure chromium has no action on quartz and marks glass with great difficulty. Some fragments of very pure metal ceased to mark glass at all.

Fine-grained cast metal, whose percentage of carbon varies between 1·5 and 3, can only be worked and polished with the diamond wheel. On the other hand, refined chromium free from carbon may be filed with ease and takes a brilliant polish like that of iron though somewhat whiter.

Chemical properties.—The crude metal is not attacked by the carbon dioxide or the moisture of the air. Pure, well-polished chromium is slightly tarnished after a few days in moist air, but this slight oxidation is only superficial and does not go further.

Chromium may be looked upon as unalterable in air. Heated to 2,000° C. in oxygen it burns with the production of numerous sparks more brilliant than those of iron. Chromium filings become incandescent if heated up to 700° C. in sulphur vapour, producing the sulphide.

Pure chromium heated strongly in a carbon crucible at the forge fire yields, without melting, the carbide Cr_4C crystallizing in needles. Chromium may thus undergo the process of cementation like iron. In the electric furnace it yields the crystalline carbide Cr_3C_2.

Silicon and chromium combine easily. By heating a mixture of the two in the electric furnace one obtains a well-crystallized silicide, extremely hard, scratching the ruby, unattacked by acids, by aqua regia, and by fused potash or fused potassium nitrate.

Boron combines with chromium under the same conditions yielding a well-crystallized boride, which is also very hard and not easily attacked by acids.

Gaseous hydrochloric acid acts on chromium at a dull red heat yielding chromous chloride in large quantities. The aqueous acid attacks the metal slowly in the cold and more rapidly on heating. Dilute acid has no action at ordinary temperatures, but on boiling the attack becomes fairly vigorous. Under the action of the electric current, chromium forming the positive electrode, solution takes place in dilute acid.

Boiling concentrated sulphuric acid evolves sulphur dioxide with chromium and the liquid darkens in colour. The dilute acid has a slow action on heating, and when this takes place out of contact with the air one obtains crystallized chromous sulphate, blue in colour, which we described some years ago[1]. Fuming nitric acid and aqua regia, whether cold or hot, have no action of chromium. It is very slowly attacked by dilute nitric acid. Powdered chromium is equally slowly attacked by mercuric chloride.

Chromium kept at 1,200° C. in a stream of sulphuretted hydrogen is completely transformed into a fused sulphide having a crystalline appearance. At the same temperature carbon dioxide attacks chromium superficially, and the metal becomes covered with a crust of green oxide mixed with carbon. The carbon dioxide is thus reduced at this temperature, and the chromium takes up some carbon. This reaction shows how difficult it is to refine the metal ; it explains the impossibility of obtaining chromium free from carbon in an ordinary metallurgical furnace, even when using crucibles of quicklime.

Fused potassium nitrate attacks chromium energetically at a dull red heat. The experiment is much more brilliant if the chlorate be substituted for the nitrate ; the chromium floats on the liquid as potassium does on water, producing a vivid incandescence. Fused potash has no appreciable action on chromium at a dull red heat.

Refining commercial ferro-chromium in the electric furnace.—The use of fused lime for the refining of the metal rich in carbon may be adopted for technical purposes. If a commercial ferro-chromium containing 60 per cent. of chromium be taken, it is easy to deprive it of its carbon by fusing it in a bath of molten lime in the electric furnace.

The following analyses show this. A ferro-chromium from Saint-Chamond gave a total of 7·3 per cent. of carbon by combustion in oxygen. After a first fusion under molten lime it

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[1] *C. R.*, xcii. 792 (1881).

contained but 5 per cent. Finally, after a second fusion, it contained but 0·1 per cent. of carbon; it could be used technically to introduce a considerable amount of chromium into steel without increasing the percentage of carbon.

A second series of experiments was carried out on a similar product, which was crystalline and gave on analysis:

Chromium	61·81
Iron	30·02
Total carbon	7·53
Slag	0·33
	99·69

This sample, broken up into fragments and fused in a bath of molten lime, yielded a fine-looking metallic regulus, close grained, and containing now a total of 4·2 per cent. of carbon.

The operation was repeated, taking care not to continue too long the refining process, and the metal then gave the following figures:

Chromium	64·00
Iron	35·12
Total carbon	0·70
Slag	0·22
	100·04

It is clear that fused lime, which so easily forms calcium carbide in presence of carbon, may thus be used to refine a metal by removing the contained carbon. It would seem as though these reactions might be used technically.

Treatment of chrome iron ore in the electric furnace.—The easy reduction of chromium oxide in the electric furnace allows us to treat similarly certain minerals rich in chromium, such as chrome iron ore, found native in well-crystallized masses, and corresponding to the formula FeO, Cr_2O_3.

It is sufficient to powder the mineral finely, to add to it an amount of carbon corresponding to the oxygen, and then to heat the mixture in the electric furnace. Using a mass of 2 kilos. and a current of 1,000 amperes at 60 volts, we obtained in a few minutes a perfectly fused mass of ferro-chromium containing:

Chromium	60·9
Iron	31·6
Total carbon	6·1
Silicon	1·1
	99·7

This preparation might doubtless be used, as we observed as far back as February, 1893, for the preparation of alkaline chromates. It would be sufficient to throw the coarsely powdered alloy into a bath of fused sodium or potassium nitrate; insoluble iron sesquioxide would be formed, and an alkaline chromate soluble in water, which might be separated and purified by re-crystallization.

Conclusions.—To resume, impure chromium may be prepared in large quantities by using the intense heat of the electric arc. The crude metal which corresponds nearly to Cr_4C, may be refined by molten lime or by the double oxide of calcium and chromium. The metal obtained is more infusible than platinum; it may be filed, assume a fine polish, and is not attacked in air. It is but slightly attacked by acids and withstands aqua regia and fused alkalies.

This preparation of chromium will enable one to deal successfully with the alloys of the metal. With copper, for example, it gives interesting results. Pure copper, alloyed with 0·5 per cent. of chromium, doubles in strength, and this alloy, which may be highly polished, does not alter in moist air as readily as copper alone.

B. **Manganese.**

The use of the electric furnace has so simplified the long and difficult reduction of manganese oxide that it may be demonstrated in a lecture experiment[1].

Pure manganous oxide is mixed with carbon and heated in the arc. With 300 amperes at 60 volts reduction is complete in five to six minutes. There remains at the bottom of the crucible a mass of manganese carbide weighing 100 to 120 grms.

The reduction may be carried out more slowly by means of a voltaic arc of 100 amperes at 50 volts. In this case it takes ten to fifteen minutes.

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[1] The oxides of nickel and cobalt are also reduced quickly by carbon in the electric furnace. We obtained samples of crude metal of the following composition:

	1	2	3
Nickel . .	86·10	87·62	94·40 per cent.
Total carbon .	13·47	11·90	6·19 ,,

A sample of cobalt prepared with an excess of oxide gave in three successive analyses:

Carbon (per cent.) .	0·726	0·732	0·741

In presence of excess of carbon, the metal becomes saturated with it and samples are obtained giving the following figures on analysis:

	1	2	3	4	
Manganese .	85·00	85·82	90·60	94·06	per cent.
Carbon . .	14·59	13·98	10·20	6·35	„

If the reduction take place in presence of an excess of oxide the amount of carbon is largely diminished, and only 4 to 5 per cent. of carbon is found in certain masses. When crude manganese so prepared contains but little carbon the metal may be kept in open vessels, but as soon as the quantity of carbon increases, decomposition is readily brought about by the moisture of the air. Small fragments placed in water are oxidized in 24 hours, yielding a gaseous mixture of hydrogen and hydrocarbons.

The ease with which the moisture of the air brings about decomposition is the greater, the nearer the percentage of carbon approaches the carbide Mn_3C discovered by Troost and Hautefeuille. We shall refer subsequently to the properties of this carbide.

The preparation of large amounts of metallic manganese by means of a more powerful arc is complicated by the ready volatilization of manganese, leading to very small yields.

To guard against too intense a heating the mixture to be reduced is heated in a carbon crucible closed by a lid. Under these conditions we obtained metallic ingots weighing 400 to 500 grms., yielding the figures:

Manganese	95·20	96.12	per cent.
Carbon	4·50	3·60	„

This crude metal, heated in a brasque made of oxide, is refined superficially, yielding a very soft metal which may be filed with ease. Manganese free from carbon does not scratch glass.

Starting with the purest pyrolusite obtainable (97·5 per cent.), which was first calcined in a Perrot furnace, and heating it with carbon in a closed crucible (500 amperes at 50 volts), we obtained a crude metal of the following composition:

	1	2	
Manganese	89·78	91·13	per cent.
Total Carbon	7·59	6·41	„
Ash	2·06	1·78	„

The yield was 96 per cent. of the oxide used. I believe that this reaction may be easily applied to the industrial production of metallic manganese; as the refining of the liquid metal takes place easily in presence of an excess of oxide, manganese may thus be obtained free from carbon and silicon.

C. Molybdenum.

Molybdenum may be obtained, as a powder, by heating the dioxide to dull redness in pure hydrogen, and then heating the metal obtained in a current of hydrochloric acid gas.

Molybdenum has hitherto been looked upon as infusible. Debray, using the oxyhydrogen blowpipe, was able to melt, with difficulty, molybdenum containing 4 to 5 per cent. of carbon[1].

Preparation of molybdenum.—We started from pure ammonium molybdate, which was powdered and placed in a crucible of refractory material capable of taking 1 kilogrm. The closed crucible is heated for an hour and a half in a Perrot furnace. After cooling, the oxide appears as a dense violet grey powder, corresponding to the formula MoO_2 (Bucholz's preparation). One experiment yields from 760 to 770 grms. of oxide. This oxide mixed with carbon is heated in the crucible of the electric furnace. In some preliminary experiments carried out with an excess of carbon we obtained, on heating for five to eight minutes (350 amperes at 70 volts), samples containing:

	1	2	3
Carbon (per cent.)	9·77	9·88	9·90

The preparation was then repeated as follows. The calcined oxide was mixed with finely powdered sugar carbon[2] in the proportion of:

Oxide	300 grms.
Carbon	30 „

This mixture contains a considerable excess of oxide in relation to the carbon. The powdered mass is carefully heaped up in a carbon crucible and submitted to the heating action of the arc for six minutes (800 amperes at 60 volts). The metal must not be fused completely, so that a solid layer of the mixture may line the crucible; otherwise, the latter would be vigorously attacked by the liquid molybdenum.

Under these conditions, one obtains a metal quite free from

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[1] H. Debray, *C. R.*, xlvi. 1098 (1858).

[2] In repeating this and similar experiments where the work is of a less delicate nature than that here described, some more readily available form of carbon, such as petroleum coke, may be used with advantage. Its purity, however, should always be ascertained by analysis.

carbon and over two kilograms may be prepared with ease in an hour.

If the preparation last more than six minutes, the molybdenum is liquefied, eats into the crucible, and there results a grey mass which is very hard and brittle.

In another experiment, using a furnace with a cavity of 5 to 6 litres capacity, we obtained in one operation 8 kilos. of molybdenum which were run out with ease. In another case we obtained an ingot weighing 10·2 kilos.

Finally, since the publication of my researches in the *Comptes rendus de l'Académie des Sciences*[1], one of my students, M. Guichard, has obtained considerable quantities of crude metal by the reduction of native molybdenite[2] with carbon, in the electric furnace. The metal thus obtained contained no sulphur. It gave on analysis:

Molybdenum	91·80	per cent.
Iron	2·10	,,
Total carbon	6·64	,,

This new reduction is of importance, for it will enable one to obtain molybdenum, containing more or less carbon, by the direct treatment of the mineral in the electric furnace.

Crude molybdenum.—The crude metal has a density of 8·6 to 8·9 according to the percentage of carbon. When saturated with carbon it is far more fusible than the pure metal. If rich in carbon, it is grey and brittle; when containing 2·5 per cent. it becomes white and is then very difficult to break on the anvil. It has all the characteristics of the molybdenum studied by Debray. Carbon is rapidly dissolved and, on cooling, is given up as graphite, molybdenum behaving exactly like cast iron. However, when saturated with carbon, it yields a crystalline carbide in fine needles. The grey crude metal is very hard; it marks steel and quartz. On fusion it yields a very mobile liquid which may be cast, with the production of vivid sparks and abundant fumes of molybdic acid.

These samples gave on analysis:

	White crude metal.			Grey crude metal.		
	1	2	3	4	5	
Molybdenum .	95·83	—	—	—	92·46	per cent.
Combined carbon .	3·04	3·19	2·53	4·90	5·50	,,
Graphite . .	0·00	0·00	0·00	0·00	1·71	,,
Ash . . .	0·74	0·53	0·62	—	—	,,

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[1] Moissan, *C. R.*, cxvi. 1225 (1893); cxx. 1320 (1895).

[2] Guichard, *C. R.*, cxxii. 1270 (1896).

Molybdenum carbide.—This compound may be prepared by heating molybdenum dioxide in the electric furnace with excess of carbon. The best proportions are—dioxide 250 grms., carbon 50 grms. The heating lasts eight to ten minutes (800 amperes at 50 volts). When excess of carbon is used, it is found in the mass as graphite. The mass obtained has a crystalline fracture of a bright white colour and it cleaves easily. It may be readily broken up on the anvil and small and well-defined elongated prisms may be picked out. The carbide has a density of 8·9 and corresponds to the formula Mo_2C.

Analysis.—In the different samples studied, the molybdenum after treatment with nitric acid was precipitated as mercurous molybdate, and finally estimated as dioxide. When the carbide contained no graphite, the carbon was separated by means of pure dry chlorine, and then estimated by weighing the carbon dioxide produced by its combustion in oxygen. The results for carbon are always a little low by this method. We obtained the following figures:

	6	7	8	Theory for Mo_2C.
Molybdenum .	93·82	—	—	94·12 per cent.
Combined carbon.	5·62	5·53	5·48	5·88 ,,
Graphite . .	—	—	—	— ,,
Ash . . .	0·17	—	—	— ,,

If the carbide contains graphite it is attacked by nitric acid in a flat-bottomed flask through which a current of oxygen passes. The evolved gases then pass into a tube containing copper oxide; the water vapour is retained by sulphuric acid and the carbon dioxide by caustic potash. From the increase in weight of the potash tube is deduced the amount of carbon dioxide and hence of carbon. The acid liquid in the flask yields the graphite after filtration and washing, and the molybdenum is then determined by means of mercurous nitrate. This new method gave:

	9	10
Molybdenum	92·60	91·90 per cent.
Combined carbon . . .	5·15	5·43 ,,
Graphite	1·61	1·98 ,,

Taking into account the graphite, one obtains for the ratio of metal to carbon:

	9	10	Theory for Mo_2C.
Molybdenum . . .	94·45	94·10	94·12 per cent.
Combined carbon . .	5·55	5·90	5·88 ,,

Pure fused molybdenum.—Pure molybdenum has a density of 9·01. It is as malleable as iron and may be filed and polished with ease. It may be worked when hot. It scratches neither quartz nor glass. If quite free from carbon and silicon it is scarcely oxidized in air below a dull red heat. It may be kept unaltered for several days in ordinary water or water containing carbon dioxide. In air, above a dull red heat, it becomes covered with an iridescent film, in the manner of steel. At about 600° C. it begins to oxidize, yielding molybdic acid which is slowly volatilized.

A fragment of molybdenum heated for some hours in a porcelain tube placed in an inclined position in a combustion furnace, yields, in the upper part of the tube, a felting of crystals of molybdic acid. The metal is not coated with any other oxide and even disappears finally, yielding fine crystals of molybdic acid. Heated with a gas blowpipe, a fragment of molybdenum evolves vapours of molybdic acid in considerable quantity. With the oxyhydrogen flame it burns without melting, yielding copious vapours of molybdic acid and a blue fusible oxide.

Finally, heated in a current of pure oxygen, it burns between 500 and 600° C., and, if the current of oxygen be rapid, the combustion proceeds without the aid of external heat. This combustion takes place with vivid incandescence and furnishes an effective lecture experiment.

Fused potassium chlorate attacks molybdenum violently. If the chlorate is melted, on throwing a fragment of molybdenum on to the surface of the liquid, the metal becomes incandescent and assumes a rotatory motion. The temperature rises rapidly; the molybdenum burns with flame production, and abundant white vapours of molybdic acid are given off which remain suspended in the air as light, white filaments. Sometimes the temperature of the fragment of molybdenum is so high as to pierce the wall of the dish, which melts in contact with the metal.

Fused potassium nitrate gives an identical though somewhat less violent reaction under the same conditions, yielding an alkaline molybdate.

A mixture of molybdenum and pure oxide of lead heated in a test-tube produces a marked evolution of heat and light.

Sulphur has no action at 440° C., but sulphuretted hydrogen at 1,200° C. converts molybdenum into an amorphous, bluish-grey sulphide, having the properties of molybdenite and leaving a black mark on paper.

Fluorine does not attack molybdenum in lumps in the cold, but if the metal be roughly powdered, a volatile fluoride is formed without incandescence.

Chlorine attacks the metal at a dull red heat without incandescence. With bromine action takes place at a bright heat without any great intensity. Iodine does not react at the softening-point of glass.

The fluorides of silver, zinc, and lead are decomposed without formation of volatile fluorides.

Phosphorus pentachloride, if slightly heated, attacks molybdenum yielding a volatile chloride, which is altered in moist air assuming a fine blue colour. This reaction takes place with most molybdenum compounds: with the metal, oxides, sulphide, molybdic acid and molybdates; it may be used as a rapid test for the metal and its compounds.

The test is carried out as follows: Place in a test-tube some of the substance to be examined, add a little phosphorus pentachloride and warm. Red fumes of molybdenum chloride and oxychloride are formed which condense in a brown ring more or less of a dark shade. The latter may be scarcely visible if the amount of molybdenum is very small. On leaving it exposed to moisture for a few minutes it is seen to become intensely blue owing to the formation of the hydrated chloride.

The action of hydracids on pure molybdenum resembles their action on the crude metal. These experiments have already been described by Bucholz, Berzelius, and Debray. We need only recall that though hydrofluoric acid does not attack molybdenum, the addition of a drop of nitric acid causes an action to begin, which goes on energetically. Solution is complete in a mixture of equal parts of the two acids; there remains a pinkish liquid, which gives no precipitate with potassium ferrocyanide, but only an intense reddish-brown coloration. After a few hours, the whole passes into a jelly.

In a current of nitrogen at 1,200° C. molybdenum, whether in fragments or as powder, yields no nitride. Phosphorus heated up to the softening-point of glass does not combine with the metal.

Boron and molybdenum unite at the temperature of the electric furnace, yielding a molten iron-grey mass containing geodes lined with prismatic needles. Under the same conditions silicon yields a crystalline silicide, infusible in the oxyhydrogen flame.

The action of carbon is sufficiently important to be mentioned at greater length. We have already described the action of this element on liquid molybdenum. Pure molybdenum, as already mentioned, is a fairly soft metal which is easily filed and which does not even scratch glass. If a fragment of the metal be heated for some hours in contact with powdered carbon at about 1,500° C., cementation takes place, a small quantity of carbon is absorbed, and its hardness is increased.

Pure molybdenum heated in a current of oxygen causes no milkiness in baryta water. After cementation the metal, heated in a stream of oxygen at a red heat, causes the formation of barium carbonate. It then marks glass. By heating it up to 300° C. and plunging it suddenly into cold water it is tempered, becomes brittle and sufficiently hard to scratch quartz.

Conversely, if crude molybdenum containing 4 per cent. of carbon be taken, this form being very hard and brittle, and if a fragment of this be heated for several hours in a brasque of molybdenum dioxide, the crude metal is refined and its surface may then be filed and polished. I ascribe this removal of carbon from the solid metal, at a temperature very distant from its melting-point, to the ease with which the vapours of molybdic acid pass through the metal.

I believe that these properties may find some application in metallurgy.

When it is required to remove oxygen from a metal saturated with it, such as is obtained in the first part of the Bessemer process, manganese is added, which is oxidized more easily than iron, and then passes into the slag (Troost and Hautefeuille). Aluminium has also been employed with good results, because it is very combustible, that is, it readily combines with oxygen; but this metal has the drawback of producing a solid oxide. It seems to me that molybdenum might be used under the same conditions; it would have the advantage of yielding a volatile oxide, molybdic acid, which would be evolved at once as a gas, stirring up the whole mass. Further, using a slight excess of the metal, there would remain in the bath a metal as malleable as iron and capable of being tempered.

Powdered molybdenum, which one has hitherto attempted to use industrially, does not act in the same way, for it burns rapidly in contact with air on the surface of the bath with no useful result.

Analysis of pure molybdenum:

	11	12	13	14	
Molybdenum .	99·98	99·37	99·89	99·78	per cent.
Carbon . .	0·00	0·01	0·00	0·00	„
Ash . . .	0·13	0·28	0·08	0·17	„

Conclusions.—Pure fused molybdenum may be obtained in the electric furnace. When pure it has a density of 9·01. It is as malleable as iron and may be filed when cold and forged when hot. Heated in a carbon brasque it undergoes cementation, and by sudden cooling it yields a steel which is much harder than pure molybdenum.

Conversely, crude molybdenum heated in contact with oxide loses its carbon, is refined and assumes the properties of the pure metal.

In presence of excess of carbon, molybdenum yields in the electric furnace a definite carbide Mo_2C, which is stable and crystalline.

D. **Tungsten.**

We showed in May, 1893[1], that it was an easy matter to prepare large amounts of crude tungsten in the electric furnace, and that this might be refined by remelting the metal in presence of an excess of tungstic acid.

Preparation of crude tungsten.—The mixture of tungstic acid and carbon is placed in the crucible of the furnace and after heating for about ten minutes, with a current of 350 amperes at 70 volts, one obtains a metallic ingot weighing about 120 grms. The bright metal thus prepared is very hard, has a white colour, and a very fine-grained texture if there be no excess of carbon. On the contrary, samples 3 and 4 had a micaceous appearance and contained lamellae of graphite. Four samples gave us:

	1	2	3	4	
Total carbon .	0·64	2·74	4·56	6·33	per cent.

Preparation of the pure metal.—Pure tungsten may be obtained by heating directly in the electric furnace a mixture of tungstic acid and sugar carbon in the following proportions: pure tungstic acid, 800 grms.; powdered sugar carbon, 80 grms.

This mixture contains an excess of tungstic acid.

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[1] H. Moissan, *C. R.*, cxvi. 1225 (1893). Ed. Defacqz, *Ann. de Ch. et de Ph.*, sér. 7, xxii. 238 (1901).

Tungsten being a difficultly fusible metal, the heating must last some ten minutes with a current of 900 amperes at 50 volts. An ingot is obtained, parts of whose surface are well fused, but the interior is porous and the mass touches the carbon crucible only at a few points. By thus avoiding the complete fusion of the metal, the carbon of the crucible does not interfere and the excess of the tungstic acid is volatilized.

Physical properties.—Tungsten prepared in the manner described may be absolutely free from carbon. M. Deslandres, who has kindly examined it spectroscopically, reports that the metal is very pure. It only yielded a few faint lines due to calcium.

When porous it may be welded together like iron by hammering, at a temperature much below its melting-point. It may be filed with ease, and when free from carbon it does not mark glass.

A piece of malleable tungsten was heated in a charcoal brasque at a forge temperature for an hour and a half. The crucible containing the metal was surrounded by a titaniferous brasque to prevent the action of nitrogen. After cooling the outer crust of the metal contained carbon, and was sufficiently hard to mark the ruby. Pure tungsten thus readily undergoes cementation, and this explains the varying results hitherto obtained in attempting to melt the metal. Riche had succeeded in melting tungsten by causing it to take up carbon, in the arc produced by 200 Bunsen elements[1]. Similarly, Siemens and Huntington[2] fused very small quantities of crude metal containing 1·8 per cent. of carbon in their electric furnace.

Pure tungsten is more infusible than chromium and molybdenum. The density of the pure metal is 18·7, and it has no action on a magnetized needle.

Chemical properties.—Fluorine attacks tungsten at ordinary temperatures, yielding a volatile fluoride with incandescence. The action of the hydracids was studied in detail by Riche and reinvestigated by Roscoe in 1872[3]; it need not be discussed here.

Nitrogen and phosphorus do not combine with tungsten at a red heat.

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[1] Riche, *Ann. de Ch. et de Ph.*, sér. 3, vol. l. 5 (1857).

[2] Brit. Assoc. Southampton, 1882, 496; *Ann. de Ch. et de Ph.*, sér. 5, vol. xxx. 465 (1883).

[3] Manchester, *Lit. Phil. Soc. Proc.*, xi. 79.

When heated with silicon and boron in the electric furnace, tungsten yields crystalline, metallic-looking compounds which scratch the ruby easily. At 1,200° C. it reduces carbon dioxide, forming a blue oxide without deposition of carbon.

Fused tungsten is not sensibly altered in moist air, but it is attacked if left for a long time in contact with water containing carbon dioxide. It is but very slightly attacked by hydrochloric and sulphuric acids, as also by hydrofluoric acid, but a mixture of hydrofluoric and nitric acids dissolves it rapidly. Some oxidizing agents, such as lead peroxide and fused potassium chlorate, attack the powdered metal with incandescence.

Fused sodium carbonate dissolves it slowly, but the change is fairly rapid with a mixture of carbonate and nitrate.

Analysis.—The metal was attacked by the mixture of alkaline carbonate and nitrate and the tungsten separated as mercurous tungstate.

We obtained the following results with samples which could be filed easily and did not scratch glass.

	1	2	3	
Tungsten . .	99·76	99·82	99·87	per cent.
Carbon . .	0·00	0·00	0·00	„
Ash . .	0·18	0·09	0·00	„

Tungsten carbide.—If, in the preparation of tungsten, the heating be prolonged, the metal fuses completely and comes into intimate contact with the carbon crucible; it takes up carbon at once and yields a carburized metal. Analyses of various samples have already been given. In presence of excess of carbon, tungsten yields a definite carbide, W_2C. This carbide has an iron-grey colour, is very hard and marks corundum with ease.

At 18° C. it has a density of 16·06. It behaves in much the same way as the metal, although more readily attacked. It ignites in fluorine in the cold; at about 500° C. it burns in oxygen yielding tungstic acid and carbon dioxide, and when molten it readily dissolves carbon which is given up as graphite on cooling.

Like the metal it is but very slowly attacked by acids, except in the case of nitric acid, which, when boiling, dissolves it readily.

It is oxidized with bright incandescence by fused potassium chlorate or a mixture of carbonate and nitrate. At a red heat it burns also in nitrous oxide and in nitrogen peroxide.

Analysis.—The total carbon was estimated by means of chlorine, and the graphite, separated from the amorphous carbon by means of fuming nitric acid, was weighed on a tared filter. Finally, the tungsten was separated off as mercurous tungstate.

	1	2	3	Theory for W_2C.
Combined carbon .	3·22	3·05	3·09	3·16 per cent.
Tungsten . . .	96·60	96·78	96·95	96·84 „

Williams[1] has shown the presence of a definite carbide, having the formula WC, in the mass obtained by heating the following mixture in the electric furnace:

Tungstic acid	120 grms.
Petroleum coke.	20 „
Iron	150 „

This carbide was mixed with much iron and double carbide. The iron was removed by a magnet, the graphite by reason of the difference of densities, and the last traces of impurity by means of chlorine.

The following figures were obtained on analysis:

	1	2	3	Theory for WC.
Tungsten . . .	93·55	93·52	93·60	93·88 per cent.
Carbon . . .	5·87	6·20	6·08	6·12 „

Iron-tungsten double carbide[2].—By the above process Williams obtained a certain amount of some double carbides of iron and tungsten. Some crystals may be separated from the mixture by the action of a magnet. On treating these with aqua regia, one half disappear and there remains a metallic-looking powder which corresponds fairly exactly to the formula $2Fe_2C.3W_2C$. The differences in the analyses are due to the fact that it was not possible to remove altogether a second double-carbide.

The analyses gave:

	1	2	3	Theory for $2Fe_3C.3W_2C$.
Tungsten . . .	72·00	71·40	71·30	73·60 per cent.
Iron	23·18	23·50	23·80	22·40 „
Carbon . . .	3·80	4·20	—	4·0 „

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[1] P. Williams, *C. R.*, cxxvii. 410 (1898).

[2] Moissan and Kowznetzow have described a double carbide of tungsten and chromium $W_2C.3Cr_3C_2$, *C. R.*, cxxxvii. 292 (1903).

Conclusions.—Tungsten is readily prepared by the reduction of tungstic acid by carbon in the electric furnace. The metal may be obtained in a very pure state, if its melting-point be not reached.

By working with an excess of carbon, or by fusing the metal in a carbon crucible, a definite carbide W_2C is obtained which dissolves carbon, giving it up subsequently as graphite.

Pure tungsten may be filed and welded; it readily undergoes cementation, has no action on a magnetic needle, and it melts at a higher temperature than chromium and molybdenum.

E. Uranium.

Metallic uranium was first obtained by Péligot[1] by reducing uranium chloride by potassium in a platinum crucible. In this way one obtains a grey powder in which are found a few metallic globules.

Other workers have slightly modified this method, and in 1883 Zimmermann[2] restudied the properties of uranium, obtaining the metal by the reduction of the chloride with sodium.

The metallic globules obtained by this method were but few. Their fusion was due to the intense heat resulting from the action of the alkali metal on the chloride. We have repeated all these experiments. Whenever a platinum crucible is used the uranium is contaminated by this metal. With Zimmermann's method the uranium contains about 2 per cent. of iron and a small amount of sodium.

Further, whatever be the method employed, all these pulverous forms of uranium contain nitrogen and often oxygen.

As we shall show later, uranium possesses a very great and hitherto unsuspected affinity for nitrogen. It seemed to us that the action of the alkali metals might be studied under better conditions by using a double compound of sodium and uranium.

Preparation of the double chloride of uranium and sodium, UCl_4, 2 NaCl.—When a current of gaseous uranium chloride acts on sodium chloride at a dull red heat, there is formed

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[1] *Ann. de Ch. et de Ph.*, sér. 3, vol. v. 5 (1842).

[2] *Liebig's Ann.*, ccxvi. 14 (1883).

a double chloride which assumes a crystalline state on cooling; and has an apple-green colour; it melts at about 390° C., is soluble in cold water and is decomposed by alcohol.

This preparation is easily carried out in a tube of Bohemian glass, by forming uranium chloride at one end, by the action of chlorine on uranium carbide, and allowing the gaseous chloride to pass over fragments of sodium chloride heated to dull redness at the other end. The solid sodium chloride first becomes coloured and retains all the vapour of uranium chloride, then finally it melts quickly.

As one knows, uranium chloride UCl_4 is a hygroscopic substance fuming in air and difficult to handle. On the contrary, the double crystalline chloride is far less hygroscopic and unstable. When fused it yields a very stable liquid, giving off practically no vapour.

Reduction of the double chloride by the alkali metals.— The reduction was carried out in a strong iron cylinder closed with a screw stopper. 300 grms. of the double chloride and 100 grms. of freshly cut sodium were introduced in alternate layers. After closing the cylinder it is heated for twenty-five minutes in a brightly burning wood fire. The heat of the reaction is such as to raise the vessel to a white heat in a few moments. After cooling, the cylinder was opened and the powdery contents first treated with alcohol at 96° C. in order to remove the excess of sodium, then washed quickly with cold boiled water, and finally with alcohol and ether.

Preparation of uranium in the electric furnace.—The oxides of uranium are not reduced by carbon at the highest temperatures obtainable with ordinary furnaces. This is no longer the case at the high temperatures available in the electric furnace.

To obtain the metal, uranium nitrate, which may be prepared in a very pure state, is calcined in a porcelain crucible. There remains a green oxide having approximately the composition U_3O_8. To this is added sugar carbon and the whole is strongly compressed into a carbon crucible. Reduction takes place in a few moments under the action of a current of 450 amperes at 60 volts. After cooling, a metallic ingot possessing a bright fracture is found in the crucible.

The yield of uranium by this method is considerable. An experiment lasting twelve minutes yields a mass of 200 to 220 grms. A crude metal is obtained in this way, the percentage of contained carbon depending on whether the oxide or the carbon is in excess in the mixture.

The qualitative analysis of these first samples showed that uranium, carbon and a little nitrogen were alone present. Various analyses gave:

	1	2	3	4	5	
Uranium .	86·25	89·46	89·10	95·70	97·60	per cent.
Carbon .	13·50	11·03	10·24	5·02	2·06	„

In a new series of experiments, we used the following mixture:

Uranium oxide	500 grms.
Sugar carbon	40 „

Some 500 grms. of this mixture are placed in a carbon crucible and the heating is continued for seven to eight minutes with a current of 800 amperes at 45 volts. A fused mass weighing 350 grms. is obtained. Thus prepared, under good conditions, the metal contains but very little carbon and may even contain none at all. On the other hand, one may find a small quantity of oxide which causes the formation of a burnt metal whose physical properties are sensibly altered. If the heating be too long, the metal takes up carbon readily, yielding a carburized metal and eventually the crystalline carbide U_2C_3.

In order to prevent the action of nitrogen, it is advisable to carry out the experiments in a carbon tube closed at one end, in the manner already described.

Refining of crude uranium.—Uranium prepared by the above method and containing 0·1 to 0·5 per cent. of carbon may be superficially refined by heating the fragments in a brasque of green uranium oxide for several hours in a forge fire. To ensure success the crucible containing the oxide of uranium and the metal must be carefully placed inside a second crucible containing a finely powdered titaniferous brasque. Should this be omitted, the resulting metal is yellow in colour and is covered with nitride.

Preparation of metallic uranium by electrolysis.—The double chloride of uranium and sodium already described is very easily electrolysed. Spongy uranium often containing small crystals of the metal is deposited at the cathode. A potential difference of 8 to 10 volts is sufficient to ensure a regular working. We employed as a rule a current of

50 amperes. The bath is kept in a liquid state by the heating action of the current itself.

The electrodes were made of pure carbon and the chloride was placed in a cylindrical porcelain vessel. The latter was closed by means of a ground porcelain plate through which passed the two electrodes and a glass tube bent at right angles. Through this tube was introduced, above the fused salt, a current of hydrogen free from nitrogen.

When quite cold, the contents of the crucible are treated with ice-cold water; they are then quickly washed with alcohol, for finely divided uranium decomposes water at ordinary temperatures. The uranium obtained is crystalline; some of the crystals in the neighbourhood of the electrode are even fairly well defined and may be 1 mm. long.

With an iron electrode this method yields alloys of uranium and iron which are silver white, very fine grained, and which may be filed with ease.

Physical properties.—When pure, uranium is quite white and has a fainter bluish tint than iron to whose polish it may attain. If the metal have a yellowish colour, one can always detect the presence of nitrogen.

Pure uranium is easily filed; it does not mark glass; it takes up a small amount of carbon when heated in a carbon brasque and may then be tempered.

It is not magnetic when quite free from iron; this has already been mentioned. Uranium may be distilled in the electric furnace and by condensation of the vapour one obtains small metallic spheres free from carbon and non-magnetic.

Chemical properties.—Finely powdered uranium as obtained by electrolysis catches fire in fluorine, burning brilliantly and producing a volatile fluoride which is green. Chlorine attacks it at 180° C., bromine at 210° C., in both cases with incandescence. The same reaction takes place at 260° C. in iodine vapour with the formation of an iodide. These reactions are all complete.

The metal obtained by Zimmermann was not attacked by iodine vapour, and the reaction in a stream of chlorine was not complete, a bulky residue being left in the boat.

Hydrochloric acid gas attacks uranium with incandescence at a dull red heat yielding a stable chloride which gives a green solution with water. Hydriodic acid attacks it at a red heat.

Finely powdered uranium burns in pure oxygen, already, at 170° C., forming a very dark green oxide.

If molten uranium be dropped on to porcelain, or if fragments be shaken up in a glass vessel, brilliant sparks are obtained owing to the combustion of a small amount of the metal. There results, but with far greater brilliancy, a phenomenon analogous to that of the combustion of iron particles which catch fire by simple friction in the air. The metal might be adapted with ease to the making of percussion caps, but, when it gives very good sparks, it contains a good deal of carbon and is on that account somewhat friable. It might be better to use an alloy of iron and uranium containing a small quantity of carbon.

Uranium reacts with sulphur at about 500° C., yielding a black sulphide which is slowly attacked by hydrochloric acid with evolution of sulphuretted hydrogen. It combines with selenium with incandescence.

As already noticed uranium combines very easily with nitrogen. Fragments of the metal heated up to 1,000° C. in a stream of nitrogen became covered with a yellow layer of nitride.

Powdered uranium reacts with ammonia gas above dull redness without incandescence, causing an evolution of hydrogen and leaving behind a black crystalline powder which is being studied further.

Pure uranium in a very fine state of division decomposes water slowly at ordinary temperatures, more quickly at 100° C. This property brings it very near to iron. Troost and Hautefeuille have shown that reduced iron decomposes water at its boiling-point.

Fused uranium becomes covered with a layer of oxide when in contact with water, and the action is considerably quickened by the presence of carbon dioxide.

Analysis.—In all these researches the uranium was separated and estimated as the oxide U_3O_8, and the carbon was weighed as carbon dioxide.

The double chloride of uranium and sodium gave on analysis:

	1	2	3	Theory	
Uranium . .	47·9	47·7	48·20	48·08	per cent.
Sodium . .	—	—	10·10	9·21	,,
Chlorine . .	42·3	42·4	42·01	42·68	,,

Metallic uranium, prepared by means of sodium, gave:

	1	2	
Uranium	99·40	99·28	per cent.

The samples always contained traces of the alkali metal. The metal prepared in the electric furnace contained:

	1	2	3	4	
Uranium .	99·121	99·106	98·021	99·520	per cent.
Carbon .	0·168	0·601	1·356	0·005	,,
Ash . .	0·187	0·204	0·303	0·421	,,

Finally, as prepared by electrolysis:

	1	2	
Uranium	99·27	99·48	per cent.
Insoluble in nitric acid .	0·52	0·27	,,

Conclusions.—Metallic uranium is easily obtained either by decomposing the double chloride of uranium and sodium by means of sodium, or by the electrolysis of this double salt, or better, by the reduction of uranium oxide by carbon in the electric furnace. These three methods give good yields, and we have had occasion in these researches to prepare 15 kilogrms. of metallic uranium.

Uranium may be obtained crystallized; the pure metal resembles iron very closely in some of its properties; it may be filed, it takes up carbon and may be tempered, and it oxidizes like iron. It combines more readily than iron with oxygen; if finely powdered it decomposes water slowly in the cold. Similarly, its action with hydracids is more energetic. It has a powerful affinity for nitrogen and, unless great care be taken during its preparation to avoid the action of this gas, the metal always contains a certain amount.

The metal, if quite free from iron, has no action on a magnetic needle and it is considerably more volatile than iron in the electric furnace.

F. **Vanadium**[1].

The important researches of Sir Henry Roscoe[2] have shown how difficult it is to prepare this element. He proved for instance that, by the reduction of vanadic acid by carbon, one had never yet obtained anything but a silicide scarcely fusible at the temperature of a wind furnace. Roscoe was finally able to overcome the numerous difficulties in this preparation and he obtained metallic vanadium by reducing the dichloride with pure dry hydrogen. He pointed out, however, that the

[1] *C. R.*, cxvi. 1225 (1893); cxxii. 1297 (1896).

[2] *Phil. Trans.*, clviii. 1 (1868); clix. 679 (1869); clx. 317 (1870).

metallic powder thus obtained still contains a very small amount of oxygen and 1·8 per cent. of hydrogen. The preparation of metallic vanadium is one of the most difficult we have had to deal with in the electric furnace. We started from pure ammonium metavanadate which, on calcination, yielded a brownish-yellow vanadic oxide which is fairly easily fusible. This oxide was then mixed with sugar carbon and when placed a few centimeters from the arc (350 amperes at 70 volts) no reduction took place. The arc had to play in contact with the powder and the heating to last twenty minutes in order to obtain, at the surface of the mixture, small metallic granules of the size of a lentil.

We then had to work with far greater power. By using an arc produced by a 150 H.P. machine, measuring 1,000 amperes at 70 volts, we were able to reduce the oxide completely and to fuse the carbide in a few moments.

The samples prepared under these conditions, which contained graphite, gave the following percentages of total carbon:

	1	2	3
Carbon . .	25·47	25·68	17·56

Thanks to the kindness of M. Heeren, who placed at our disposal a considerable amount of ashes from a vanadiferous coal[1], we have been able to continue and extend these researches.

Treatment of vanadiferous ashes.—The ashes mixed with fragments of coal which were handed over to us contained from 8 to 10 per cent. of vanadic acid. They were roasted in a muffle in order to remove all carbonaceous particles. The residue then contained 38 per cent. of vanadic acid; 500 grms. of ashes were placed in a two-litre flask on a sand-bath and attacked by nitric acid to which is added from time to time a

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[1] Mourlot has given the following analysis of these ashes, *C. R.*, cxvii. 546:

Part soluble in acids.		*Part insoluble in acids.*	
Vanadic acid . . .	38·5	Silica	13·6
Sulphuric acid . . .	12·1	Alumina	5·5
Phosphoric acid . . .	0·8	Iron sesquioxide . .	9·4
Iron sesquioxide . .	4·1	Magnesia	0·9
Alumina	4·0		
Lime	8·44		29·4
Potassium oxide . . .	1·8		
	69·74		

small amount of hydrochloric acid. The whole is then taken up with water and the insoluble residue washed. After filtering through a cloth all the liquids are mixed together and evaporated to dryness; the residue is treated with ammonium hydrate (one-tenth strength), and one obtains a first solution of ammonium vanadate which is concentrated and then precipitated by nitric acid, yielding raw vanadic acid.

The insoluble residue is extracted by means of one-tenth ammonium hydrate; this yields a further amount of vanadate which is also treated with nitric acid. The raw acid thus obtained is purified by the method of L'Hôte[1]. The vanadium is converted into vanadyl chloride and the latter is decomposed by water. Vanadyl chloride was obtained at 250° C., and 150 grm. fractions were rectified by means of a distillation column with beads. The substance distils at 126·5° C., as indicated by L'Hôte. By decomposing it with water one obtains pure vanadic acid which is then carefully dried.

Preparation of crude vanadium.—Vanadic anhydride was mixed with finely powdered sugar carbon in the following proportions:

Vanadic anhydride	182 grms.
Sugar carbon	60 ,,

300 grms. of this mixture were heated in the electric furnace by means of a current of 900 amperes at 50 volts. The experiment lasted five minutes. There resulted a vanadium rich in carbon, which gave on analysis:

	1	2	3	4	5
Carbon (per cent.)	10·5	13·8	11·6	16·2	15·9

In another series of experiments we used: vanadic anhydride, 100, carbon, 20, and we obtained samples which contained:

	1	2	3
Carbon (per cent.) . .	9·9	9·2	9·83

All these experiments were carried out in carbon tubes. In this preparation one must use intense currents for a very short time, because the anhydride melts easily and wets the entire tube, when carburation becomes very rapid.

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[1] *Ann. de Ch. et de Ph.*, sér. 6, xxii. 407 (1891).

When we attempted to refine the metal so obtained this easy liquefaction of vanadic acid rendered all our efforts useless. The notable researches of Roscoe have shown that the preparation of vanadium is one of the most difficult in mineral chemistry.

The strong affinity of vanadium for nitrogen renders the preparation still more difficult. It is advisable to obtain at the outset a very high temperature in order to destroy the nitride.

By heating, for two minutes only, pure vanadic acid in a carbon tube by means of a current of 1,000 amperes at 60 volts, and by passing a constant supply of hydrogen, we were able to obtain vanadium containing but 5·3 to 4·4 per cent. of carbon.

Another sample, heated for three minutes, contained 7·42 per cent. of carbon.

Properties of carburized vanadium.—Vanadium containing 5 per cent. of carbon is white, has a bright, metallic fracture, is not oxidized in air and has a density of 5·8 at 20° C. Roscoe obtained 5·5 for vanadium containing traces of oxygen and 1·3 per cent. of hydrogen.

This metal burns in oxygen at a red heat with incandescence. Chlorine attacks it at a dull red heat without incandescence. It combines readily with nitrogen, and, generally speaking, the crude metal is more easily attacked by acids than the definite carbide of which we shall speak later. Hydrochloric acid does not attack it, either in the cold or on heating, while boiling concentrated sulphuric acid attacks it but very slowly. Its other properties resemble those of the vanadium described by Roscoe, and we shall not mention them here.

Preparation of vanadium carbide.—By heating in the electric furnace vanadic anhydride mixed with sugar carbon, in a carbon tube, for nine or ten minutes (900 amperes at 50 volts) one obtains a metallic regulus consisting of a definite carbide of vanadium, which gives up a little graphite at the moment of solidification[1].

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[1] In a crucible experiment a piece of lime from the roof of the furnace fell into the crucible and there was formed a mixture of vanadium and calcium carbides. The latter was decomposed by standing in air, and there remained isolated and well defined crystals of vanadium carbide. The excess of lime was removed by means of acetic acid, and the dried mixture was then treated with methylene iodide, which rendered it possible to remove some crystals of graphite owing to the difference of densities.

Properties of vanadium carbide.—This carbide VC is volatile when strongly heated in the electric furnace. Its melting-point is somewhat higher than that of molybdenum. When liquid it has a metallic appearance. Its density is 5·36, and it scratches quartz with ease. It occurs in fine well-defined crystals.

Chlorine attacks it with incandescence above 500° C., yielding a readily volatile liquid chloride. It burns in oxygen at a dull red heat with bright incandescence. It does not combine with sulphur at the softening-point of glass. Nitrogen and ammonia acting at a red heat form the nitride. It does not react at a dull red heat with gaseous hydrochloric acid, water vapour and sulphuretted hydrogen.

Hydrochloric and sulphuric acids do not attack it, whereas it reacts with nitric acid in the cold.

Oxidizing agents such as fused nitrate and chlorate of potassium decompose it at dull redness. With the chlorate there results a vivid incandescence.

Analysis.—Vanadium carbide gave on analysis:

	1	2	Theory for VC.
Carbon . . .	18·39	18·42	18·98 per cent.
Vanadium . .	81·26	80·79	81·01 ,,

Alloys of vanadium.—Vanadium, in spite of its high melting-point, readily forms alloys. Some of these we have studied.

By heating together for three minutes, in the electric furnace (900 amperes at 50 volts), a mixture of oxide of iron, of vanadic anhydride and sugar carbon so as to give a 20 per cent. vanadium alloy, one obtains a homogeneous whitish-grey mass, with a crystalline fracture. It is hard, but may be filed and contains:

Iron	72·96 per cent.
Vanadium	18·16 ,,
Carbon	8·35 ,,

A mixture of vanadic anhydride, copper oxide and carbon calculated to give a 5 per cent. vanadium alloy gave, under the same conditions, a well-fused regulus of a bronze colour, very malleable, easily filed, and harder than copper. It contained 96·52 per cent. of copper and 3·38 per cent. of vanadium.

An alloy of aluminium and vanadium may be prepared by keeping molten aluminium at the bottom of a fire-clay crucible and throwing on to its surface a mixture of vanadic acid and aluminium filings. The latter metal acts as reducing agent. There results a vivid incandescence, and, by shaking up the mass, one obtains an alloy of the two metals which is very malleable and rather soft, sticking to the tool when filed. This alloy contained 2·5 per cent. of vanadium.

In another experiment we heated a mixture of reduced silver and the calculated amounts of vanadic anhydride and carbon for a 10 per cent. vanadium alloy. The experiment lasted three minutes (900 amperes at 50 volts). A metallic ingot was thus obtained consisting of two superposed parts; above, the vanadium without a trace of silver, and below, the silver with its fine white colour giving, after solution, no single reaction of vanadium. These two elements thus exert no action on one another.

Conclusions.—By reducing vanadic acid with carbon in the electric furnace one may easily obtain large yields of a metal containing 4 to 5 per cent. of carbon. If the heating be prolonged, there is always obtained a new crystalline and well-defined carbide, having the formula VC. This compound does not act on water at ordinary temperatures, and is more stable in presence of acids than crude vanadium.

Vanadium unites with iron, copper and aluminium at the temperature of the electric furnace, but does not form an alloy with silver.

Considering its properties as a whole, vanadium more closely resembles the metalloids than the metals; its carbide is like those of titanium and zirconium, which possess the same formula.

G. **Zirconium.**

Fused zirconia is easily reduced by carbon in the electric furnace. If a considerable amount of zirconia be placed in a carbon crucible, one finds after the action of the arc, below the molten zirconia, a metallic mass of zirconium containing neither carbon nor nitrogen, but containing varying amounts of oxide.

On the other hand, by mixing zirconia with an excess of carbon, one obtains a metallic-looking body possessing a bright fracture and containing no nitrogen. On analysis it gave:

	1	2	3
Carbon	4·22	4·60	5·10 per cent.

Metallic zirconium is readily obtained from this carbide by fusing it up again in presence of an excess of liquid zirconia. It is a very hard substance easily marking glass and the ruby. It has a density of 4·25 which is very near the value obtained by Troost who gave 4·15 as the density of this element. The properties of the metal have been very well studied by this worker, and we have nothing to add to his important communications on this subject[1].

Zirconium carbide.—We have studied with F. Lengfeld a definite crystalline compound of zirconium and carbon.

Preparations of Zirconia.—The methods hitherto given for the preparation of pure zirconia present great difficulties when one attempts to work with large quantities of zircon (zirconium silicate). We have modified the preparation as follows.

The selected zircon is powdered, mixed with sugar carbon, and heated in a carbon crucible in the electric furnace for ten minutes (1 000 amperes at 40 volts). Silicon being far more volatile than zirconium, as previously demonstrated, is first evolved and there remains a metallic looking mass which is well fused and consists chiefly of zirconium carbide with a small amount of silicon. This impure carbide is attacked by a stream of chlorine at a dull red heat. There results a mixture of the chlorides of zirconium, iron and silicon. The quantity of silicon chloride is so small that one observes no condensation of a liquid substance.

These chlorides are then treated with boiling concentrated hydrochloric acid; zirconium chloride separates out in an almost pure condition. It is collected and washed with concentrated hydrochloric acid; it is then dissolved in water, treated with hydrochloric acid and evaporated to dryness. One must be careful not to raise the temperature too high. The residue is taken up with distilled water and finally precipitated by ammonia. One obtains in this way a perfectly white hydrate, free from iron and silicon, which is then calcined in a Perrot furnace.

The anhydrous oxide is mixed with sugar carbon and with oil, then made into cylinders and gently calcined. This mixture is placed in a carbon tube closed at one end, and is heated for ten minutes with a current of 1,000 amperes

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[1] *C. R.*, lxi. 109 (1865).

at 50 volts. Part of the zirconia is volatilized and begins to fuse. As is seen, the heating must be intense and it is only in the hottest part, that is at the bottom of the tube, that one finds a small ingot or metallic globules.

It happens frequently that the carbon tubes are unable to withstand this high temperature; holes or cracks are developed and the zirconium carbide obtained under these conditions contains some calcium carbide, derived from the interior of the furnace; it deliquesces in the air.

This reduction has been carried out with varying quantities of carbon, and has always yielded the same product. If the mixture be heated with a less powerful current, the carbide obtained contains nitrogen.

Properties.—This new carbide of zirconium has a grey colour, a metallic appearance and does not deliquesce in air, even at 100° C.; it marks glass and quartz with ease, but has no action on the ruby.

The hydracids readily attack this carbide; fluorine acts in the cold and chlorine at 250° C. with incandescence, bromine at 300° C., and iodine at 400° C.

It burns vividly in oxygen at dull redness. Heated with sulphur, the latter volatilizes before any reaction takes place. In sulphur vapour at a dull red heat it yields a small amount of sulphide.

Zirconium carbide kept liquid in the electric furnace dissolves carbon which it gives up as graphite on cooling.

Water and ammonia are without action both at ordinary temperatures and at dull redness.

Hydrochloric acid, whether dilute or concentrated, has no action, even at its boiling-point. Dilute nitric acid has but little action, but the concentrated acid reacts at once, and with violence if the temperature be raised. Concentrated sulphuric acid and aqua regia decompose the carbide slowly in the cold, more readily on warming.

Oxidizing agents such as potassium nitrate, permanganate or chlorate attack it energetically; the chlorate may even react explosively.

Potassium cyanide is without action at its melting-point, while fused caustic potash dissolves it fairly readily.

Analysis. **Estimation of zirconium.**—The zirconium was determined by the following methods:

1. The carbide was attacked by a mixture of fused hydrate and

nitrate of potassium. Taken up with water, hydrochloric acid added and the oxide precipitated with ammonia, calcined and weighed.

2. The carbide is burnt in a stream of oxygen and the zirconia weighed directly.

Estimation of carbon.—The carbide is heated to redness in a stream of chlorine and the residue weighed, the amount lost representing the amorphous carbon. The residue which is not attacked consists of pure graphite, and the difference between its weight and that of the carbon gives the amount of combined carbon[1].

The following figures were obtained:

	1	2	3	
Zirconium . .	83·00	82·8	86·1	per cent.
Combined carbon .	10·70	10·3	—	„
Graphite . . .	6·00	8·76	—	„

Taking into account the graphite, the proportions of zirconium and combined carbon become:

	1	2	Theory for ZrC.	
Zirconium . .	88·6	88·7	88·3	per cent.
Combined carbon .	11·14	11·3	11·7	„

Conclusions.—Pure zirconia and carbon when heated together outside the arc in the electric furnace yield a carbide of formula ZrC,[2] well crystallized and not decomposed by water at 0° or at 100° C. This fact is interesting, for zirconium, which is not far from thorium in Mendeleeff's grouping of the elements, differs from it in some respects, since its carbide is very stable, while thorium carbide is decomposed by cold water with evolution of acetylene, ethylene, methane and hydrogen.

H. Titanium.

Titanium has hitherto been better known in a state of combination than in the free state. It has only been obtained as an amorphous powder whose appearance and properties varied with every preparation. In the first method, due to

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[1] We attempted to determine the combined carbon by treating the carbide with fuming nitric acid and allowing the evolved gases to pass over a copper column heated to redness; the carbon dioxide was absorbed in potash bulbs and weighed. The figures obtained were not concordant, for organic compounds are always formed which are only slowly decomposed by fuming nitric acid.

[2] We gave an account of our first researches on zirconium to the Académie des Sciences on May 29, 1893 (*C. R.*, cxvi. 1222). At the same sitting Troost gave an account of his work on the same subject and signalled the existence of a carbide ZrC_2 obtained with a weak current (35 amperes at 70 volts), but operating in the middle of the arc.

Berzelius, potassium was made to react with an alkaline fluotitanate. Under these conditions one obtained a reddish powder, subsequently shown to be but a nitride.

Wöhler[1], and later Wöhler and Deville[2], by causing sodium to act on potassium fluotitanate in a stream of hydrogen, prepared another powder, grey in colour, which they considered to be titanium and which decomposed water at 100° C.

Finally, more recently, S. Kern[3], by carrying the vapour of titanium chloride in a stream of hydrogen over sodium heated to redness in a boat, obtained another grey powder which only decomposed water at 500° C. Moreover, none of these workers published any analysis of the titanium which, in general, was always obtained by the reduction of a titanium compound by means of an alkali metal.

The very strong affinity of titanium for nitrogen and the great difficulty of getting a continuous stream of hydrogen absolutely free from nitrogen tended to complicate this preparation in a remarkable manner. All the samples hitherto obtained contained either potassium or sodium, silicon, oxygen, nitrogen, and hydrogen.

Following up the reduction of the oxides of uranium, silicon, and vanadium by means of carbon in the electric furnace, we took up again the study of titanium.

By heating titanic acid in a carbon crucible or boat by means of a current of 100 amperes at 50 volts, one always obtains, either fused or crystallized, an oxide of titanium of an indigo blue colour. If the experiment be repeated with a current of 300 to 350 amperes at 70 volts, one obtains a perfectly fused mass of a bronze yellow colour. This is the titanium nitride Ti_2N_2 described by Friedel and Guérin.

To prepare titanium a far higher temperature is required. With a 45 H.P. engine, and varying the form of the experiment, we never obtained anything but the nitride. The preparation only becomes possible when sufficient heat is developed to raise the temperature above the decomposition point of this nitride.

By heating a mixture of titanic acid and carbon in a carbon crucible, by means of an arc of 1,200 amperes at 70 volts (in the furnace for tubes), there results a fused mass which after

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[1] *Ann. de Ch. et de Ph.*, sér. 3, xxix. 166 (1850).

[2] ibid., sér. 3, lii. 92 (1858).

[3] *Chem. News*, xxxiii. 57 (1876).

cooling has a distinct crystalline appearance, and consists of a titanium carbide TiC absolutely free from nitrogen.

Finally, by heating with the same arc, but this time in a crucible, a mixture of titanic acid and carbon containing no excess of carbon one obtains, after cooling, a metallic mass, the upper part of which is fused to a depth of 2 to 3 cm.; it consists of titanium possessing a bright fracture and containing varying quantities of carbon.

Titanium nitride can no longer exist under these conditions and titanium containing more or less carbon is alone present.

This progressive action of an increasingly powerful current on a mixture of titanic acid and carbon seems to me to prove decisively that the rise of temperature of the electric arc is a function of the current. This study, while demonstrating the simultaneous increase of current intensity and heating power of the arc, adds largely to the number of experiments to be carried out in this way.

Preparation of titanium.—One may use as titanic acid the rutile from Limoges, well crystallized and carefully chosen. It contains but a very small amount of silica and iron. In this case the titanium obtained is not pure but contains from 1 to 2 per cent. of iron and a little silicon.

It is advisable to substitute titanic acid prepared in the laboratory for the natural product. The titanic acid is then intimately mixed with carbon, compressed and carefully dried. The mixture is pressed tightly into a cylindrical carbon crucible some 8 cm. in diameter, and the whole is placed in the middle of the electric furnace. 300 to 400 grms. are thus worked up at one time.

The arc resulting from a current of 1,000 amperes at 60 volts is allowed to play for ten to twelve minutes; the current is then stopped, the apparatus allowed to cool, and then the furnace is opened. The crucible contains a homogeneous mass which has only been liquefied to a depth of a few centimeters. This mass is covered with a yellow glaze of fused titanic acid.

With a current of 2,200 amperes at 60 volts, the yield of titanium is larger, but the fusion of the mixture in the crucible is not complete. Each experiment yields about 200 grms. of titanium. Below the fused titanium is found a yellow layer of nitride more or less crystalline and, at the bottom of the crucible, another layer of blue titanium oxide bristling with small crystals. These different layers of varying composition are a proof of the rapid lowering of the temperature from the surface to the bottom of the crucible. The metal obtained under these conditions contains more or less carbon according to the proportions of titanic acid and carbon used. We have thus obtained the following figures:

	Amperes.	Volts.	Duration in minutes.	Carbon.	Ash.	
Rutile + carbon .	1,000	70	15	15·3	3·3	per cent.
" " .	1,200	70	12	11·2	2·0	"
" " .	1,000	60	12	8·2	2·4	"
Titanic acid + carbon	1,100	70	10	7·7	4·5	"
Titanium carbide + titanic acid .	2,000	60	9	4·8	2·1	"

The carburized metal may be mixed with titanic acid and heated again in the electric furnace with as powerful a current as before. Under these conditions, especially if the process be rapid in order to avoid the carburizing action of the arc, one obtains a titanium free from nitrogen and silicon and containing, as impurity, some 2 per cent. of carbon. We have not yet been able to lower this percentage.

Properties.—Titanium prepared under these conditions occurs in fused masses possessing a bright white fracture, sufficiently hard to mark quartz and steel with ease; they are nevertheless friable and may be easily powdered in an agate mortar. The density of the metal is 4·87.

Chlorine attacks titanium at 350° C. with incandescence, forming the liquid chloride $TiCl_4$. Bromine at 360° C. gives a dark-coloured bromide. Iodine acts at a still higher temperature, without noticeable incandescence, giving a solid iodide, which Hautefeuille has prepared in a pure state.

Titanium burns in oxygen at 610° C. with incandescence, leaving a residue of amorphous titanic acid. It is slowly attacked by sulphur at the softening-point of glass. A dark-coloured body is produced which is not attacked by cold hydrochloric acid, but gives off sulphuretted hydrogen with the boiling concentrated acid.

Powdered titanium is converted into the nitride by heating at 800° C. in a stream of nitrogen. Heat is evolved in this reaction and the boat is raised to a temperature higher than that of the tube. This is the first clearly established case of the vivid combustion of an element in nitrogen.

Phosphorus vapour reacts at about 1,000° C. yielding a dark coloured phosphide, but the action is only superficial.

Carbon dissolves in molten titanium and combines to form a definite carbide. The excess of dissolved carbon crystallizes out as graphite.

Silicon and boron unite with titanium in the electric furnace giving fused or crystalline borides and silicides, which are as hard as the diamond.

Titanium readily dissolves in molten iron and the alloy formed may be filed with ease. It dissolves also in lead. With copper, tin and chromium it gives alloys which we are studying further.

Boiling concentrated hydrochloric acid attacks titanium slowly with evolution of hydrogen and production of a violet solution. With hot nitric acid, the action is slow yielding titanic acid. Solution is far more rapid with aqua regia, but the titanic acid formed soon retards the reaction.

Dilute sulphuric acid dissolves titanium more easily, even in the cold; heating is however required for a continuous action. Hydrogen is evolved and a violet solution formed. With boiling concentrated acid, sulphur dioxide is evolved. Titanium dissolves in a mixture of nitric and hydrofluoric acids with violent effervescence. The action is as energetic as with silicon.

Oxidizing agents act on titanium fairly readily. Fused potassium nitrate attacks it without apparent evolution of heat; but if powdered titanium be thrown into potassium chlorate at its decomposition temperature, there results a vivid incandescence. The fused alkaline carbonates attack it in the same way as does a mixture of potassium nitrate and carbonate.

Pyrophoric titanium heated in a current of steam begins to decompose the gas only at 700° C., and the decomposition is not continuous till about 800° C. Titanic acid is formed and hydrogen may be collected. Silver fluoride is reduced by powdered titanium at 320° C. with incandescence.

Analysis.—The powdered titanium is attacked by a fused mixture of carbonate (2 parts) and nitrate (8 parts) of potassium. The resulting white mass is taken up with cold water; the residue of insoluble titanate is dissolved in cold hydrochloric acid and added to the first solution. Titanic acid is then precipitated by ammonia, observing the rules given for this analysis.

To determine the carbon, the titanium is removed at dull redness by means of a stream of pure dry chlorine, and by combustion of the black residue in oxygen the carbon dioxide formed and the residual ash may be estimated. We obtained the following figures:

	1	2	3	
Titanium . .	94·80	96·11	96·69	per cent.
Carbon . .	3·81	2·82	1·91	„
Ash . .	0·60	0·92	0·41	„

Titanium carbide TiC.—By heating a mixture of titanic acid (160 parts) and carbon (70 parts) in the electric arc for ten minutes (1,000 amperes at 70 volts), one obtains a definite carbide according to the equation

$$TiO_2+3C=TiC+2CO$$

The carbide occurs in well-fused masses with a crystalline fracture or in crystal aggregates; it contains a slight excess of carbon which crystallizes out as graphite. This graphite retains tenaciously traces of titanium and, after combustion in oxygen, there remains a yellowish-white ash in which titanic acid is easily detected.

Titanium carbide has a density of 4·25. It is not attacked by hydrochloric acid which enables one to separate it with ease from any excess of titanium. It is slowly attacked by aqua regia. Water vapour has no action at 700° C. In its other reactions it resembles titanium. It burns, however, far more easily in oxygen. At an incipient red heat it catches fire in this gas, and the heat evolved is sufficient to raise the substance to a white heat. Powdered and thrown into a burner flame, it yields vivid sparks which are far brighter than those of titanium.

Analysis:

	1	2	3	Theory for TiC.	
Carbon . .	20·06	19·40	19·18	19·36	per cent.
Titanium .	—	79·94	80·41	80·64	„

Titanium nitride.—The nitride may be obtained by heating titanic acid, with or without carbon, by means of a current of 300 amperes at 70 volts; it occurs in bronze-coloured fused masses, not easily powdered, very hard, marking the ruby and slowly cutting the diamond. The density is 5·18. On analysis it gave 78·3 and 78·7 per cent. of titanium. This compound, free from carbon, thus corresponds to that described by Friedel and Guérin, who gave the density as 5·28 and the percentage of titanium as 78·1.

Titanium oxide.—The blue oxide obtained by the action of a weak current on titanic acid has much the appearance of the suboxide mentioned by Laugier and Karsten, the existence of which is, however, still doubtful.

The oxide we obtained has a deep indigo colour, and is made up of a mass of crystals.

Conclusions.—By the action of the heat produced by an arc of variable intensity on a mixture of titanic acid and carbon, one obtains:

1. The blue suboxide of titanium.
2. The fused nitride Ti_2N_2.
3. Fused titanium or a crystalline carbide TiC.

Fused titanium is the most refractory body we have as yet prepared in the electric furnace; it is more infusible than vanadium and leaves far behind such metals as pure chromium, tungsten, molybdenum, zirconium. It could only be prepared at a temperature higher than the temperature of decomposition of its nitride and by means of the arc produced by a 100 H.P. machine. The fused metal has a lesser affinity for nitrogen than the powders obtained by the action of the alkali metals on the fluotitanates; however, when powdered, this titanium burns in nitrogen at 800° C.

The whole of the properties of titanium bring it clearly near to the metalloids and more especially to silicon.

I. Silicon.

We have already shown that silica is easily volatilized in the electric furnace. With a current of 1,000 amperes at 50 volts there is a copious formation of silica vapour. One is surrounded in a few moments with very light filaments of silica which float about and remain suspended in the air for a long time. Examined under the microscope these filaments are seen to consist of very small spherules of silica which possess a very distinct brownian movement in water.

If the experiment be stopped before the silica is completely volatilized, the mass taken out of the crucible presents occasionally on its lower part very characteristic crystals of silicon, similar to those described by de Senarmont. This first experiment shows that silica may be reduced by carbon at a high temperature.

The phenomenon is far more distinct if a mixture of quartz and powdered carbon is placed in a carbon cylinder closed at one end and heated in the electric furnace. The aperture of the tube is lined with flaky silica; below are found very definite crystals of carbon silicide which are scarcely coloured, and a little lower, a complete ring of bright, black crystals, through which are scattered fused globules[1]; these black crystals are only attacked by the mixture of nitric and hydrofluoric acids. They catch fire in fluorine in the cold and burn brightly forming silicon fluoride.

Some of the crystals show very clearly the superposed structure of the crystals obtained by solution in molten zinc. They always contain carbon silicide, but the crystalline dust collected in all parts of the tube contained from 28 to 30 per cent. of crystallized silicon.

This experiment, which has been repeated several times, shows that silica is reduced to silicon by carbon under the action of the electric arc. If the temperature be not too high, part of the silicon is not acted on by carbon and may be found in crystals or as fused globules. By cooling the vapour of silicon at the moment of its formation, this method might be adapted to the preparation of silicon[2].

E. Vigouroux[3], using our furnace, has shown that liquid silica might be easily reduced by aluminium, giving a good yield of crystallized silicon.

J. Aluminium.

Alumina had hitherto been looked upon as an irreducible oxide; such is not the case.

If perfectly transparent crystals of corundum be placed in a boat inside a carbon tube in the electric furnace, and the whole heated by means of a current of 1,200 amperes at 80 volts, the alumina is volatilized in a few minutes. The boat is entirely converted into graphite and contains no trace of ash, and from either side of the tube may be detached a crystalline felting of graphite and alumina, further than which are found spheres of metallic aluminium 2 to 3 mm. in diameter, which are easily identified.

The experiment may be varied by using a carbon tube closed at one end and placed in the furnace in such a manner that the closed end is heated most strongly. This tube is 40 cm.

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[1] Some of the silicon globules contain small crystals of carbon silicide which are transparent and have a fine yellow tint.

[2] Silicon is now technically prepared by the reduction of silica by carbon in the electric furnace.

[3] Thesis, *Faculty of Science*, Paris, 1896, p. 59.

long and has an inside diameter of 40 mm. 100 grms. of alumina are placed at the bottom of the tube, which is heated for fifteen minutes with a current of 300 amperes at 65 volts.

Towards the end of the experiment abundant fumes are evolved from the tube, and if condensed on a cold surface they give a white deposit of alumina. This substance is heated with cold dilute acetic acid which removes any traces of iron and lime, and is then washed with distilled water and dried; among the irregular particles are seen very small spheres of fused alumina.

After cooling, one finds in the upper part of the tube a white deposit of alumina, and, in the lower part, an ingot of fused alumina which varies in appearance according as the oxide was in the cooler or hotter part.

The most strongly heated part is covered with a film of graphite resulting from the condensation of the carbon vapour which filled the tube. On the wall are seen small white or slightly yellow globules consisting of a mixture of aluminium and its carbide.

The experiment is far more conclusive if an intimate mixture of alumina and starch be heated under the same conditions, the starch providing by its decomposition the necessary carbon.

In an experiment which lasted eighteen minutes (300 amperes at 65 volts) a certain quantity of aluminium was obtained containing fine lamellae of the carbide Al_4C_3, to be described later.

The experiment was repeated four times with identical results; and in every case the cooled mixture was covered with graphite resulting from the condensation of carbon vapour.

Another series of experiments carried out in crucibles at a lower temperature showed that alumina alone may be fused and kept liquid in a carbon crucible without reduction.

In one preparation carried out with a tube closed at one end, it happened that the other end became stopped up by a plug of alumina and carbon. This experiment, which had not been as prolonged as the former ones owing to short circuiting, gave, in the heated part, a felting of graphite and of very thin hexagonal crystals consisting entirely of alumina and showing iridescence phenomena. The tube contained no trace of metallic aluminium. The production of this mixture of corundum and crystalline graphite shows that the vapour of alumina, which is so easily formed, and the vapour of carbon may come in contact without producing aluminium. A far higher temperature is required to bring about this reduction.

To resume, alumina is not reduced by carbon in the electric furnace, but reduction takes place when the vapours of these two bodies are subjected to a very high temperature. In this case the alumina loses its oxygen, yielding the metal which is partially converted into carbide.

Impurities of aluminium [1].—The above experiments, together with the discovery of crystallized aluminium carbide, to be described later, led us to take up again the analytical study of aluminium prepared by electrolysis.

The aluminium industry, founded in France by Henri Sainte-Claire Deville in 1854, is undergoing a very rapid development. Now that it has become possible to decompose alumina by intense currents, the preparation of the metal has become commercially successful and the price has sunk to four francs a kilogram. The rapid progress of this industry leads one to hope that this price will be lowered further still [2]. It is probable that the properties of this light metal will enable it to find many applications.

The secondary points which require fresh investigation, such as the refining of aluminium or the cheap preparation of pure alumina from bauxite or kaolin, will doubtless soon be worked out.

Commercial aluminium is already used in several ways; it is used for the refining of steel and iron [3], and further, several of its alloys possess very interesting properties.

The different workers who have investigated the properties of aluminium have often arrived at different results. The same has been the case when, owing to its lightness, different countries have tried to use the metal for the making of parts of a soldier's outfit, such as drinking-cups, flasks, saucepans, in order to lighten the weight of his knapsack. Occasionally the metal has behaved satisfactorily and has been valued for its qualities, at other times it has failed completely. These difficulties arise chiefly from the differences in the composition of commercial aluminium.

We may add that the aluminium produced by the various electrolytic processes is never pure, and that its composition varies considerably; all metallurgists know how traces of

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[1] *C. R.*, cxix. 12 (1894).

[2] Aluminium is now about two shillings a kilo.

[3] This has been studied by R. A. Hadfield in England and by Le Verrier in France.

foreign substances affect the physical and chemical properties of a metal. It would therefore be all to the advantage of manufacturers to obtain aluminium as pure as possible, so that its properties would become constant and the metal would always yield the same results.

The impurities of commercial aluminium hitherto detected are two in number: iron and silicon.

The iron comes from the ore, from the electrodes and from the crucibles. The purity of the alumina and the careful manufacture of the electrodes and the crucibles will tend to remove this. A. Minet has published some interesting experiments on this subject, and has clearly demonstrated the bad effects produced by a small amount of iron.

The silicon is also derived in part from the electrodes and from the crucibles, but chiefly from the alumina used. It is more difficult to avoid the presence of this element. Although in certain cases it has no detrimental effect, we have been able to diminish its amount easily by simply fusing the metal under a layer of alkaline fluoride [1].

But, in addition to iron and silicon, there are usually present two other hitherto unobserved impurities; these are nitrogen and carbon.

When a fragment of commercial aluminium is treated with a 10 per cent. solution of caustic potash the metal is quickly attacked, and the hydrogen which is vigorously evolved carries along with it a very small amount of ammoniacal vapours. This may be demonstrated by bubbling the gas through a Nessler's reagent. A coloration is soon produced, and eventually a more or less bulky precipitate. It is highly important to use absolutely pure potash in this experiment.

When a current of nitrogen is passed into molten aluminium it becomes saturated with the gas, and the metal so obtained shows a slight diminution in its tensile strength and its

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[1] The sample of aluminium used in this experiment had the following composition:

Aluminium	98·02
Iron	0·90
Silicon	0·81
Carbon	0·08
Nitrogen	Traces
	99·81

After one fusion beneath a layer of alkaline fluorides, it contained but 0·57 per cent. of silicon.

ductility. The presence of nitrogen thus alters the physical properties of aluminium[1].

Professor J. W. Mallet, of the University of Virginia, had indicated, as far back as 1876, the existence of a nitride of aluminium; it is to this body, which is slightly soluble in aluminium, that these changes of properties are due[2].

We have detected carbon as a constant impurity in commercial aluminium, and in larger amounts than nitrogen. When 100 grms. of aluminium are acted on by a stream of hydrochloric acid or hydriodic acid gas free from oxygen there remains a grey residue. This matter taken up with dilute hydrochloric acid yields a very light amorphous carbon, maroon in colour, burning completely in oxygen to carbon dioxide; this carbon contains no trace of graphite. It may be estimated by treating some ten grammes of aluminium with a concentrated solution of potash. The residue is taken up with water, dried, and finally burnt in a stream of oxygen. The weight of carbon is easily deduced from that of the carbon dioxide. We obtained in this way the following percentages of carbon: 0·104, 0·108, and 0·080.

The effect of this element on the physical properties of aluminium seems to us very characteristic. To demonstrate this we melted a good quality aluminium in a crucible; part of this was run into a mould; crystallized aluminium carbide was dissolved in the other still molten part. A few moments later this was also run into a mould, and one obtained in this way two samples, one of fused aluminium, the other of aluminium containing carbide. Samples were cut out of these ingots, and while the fused aluminium had a tensile strength of 11·1 kilos. per square millimeter and an extension of 9 mm. per 100, the carburized aluminium broke with a weight varying from 8·6 to 6·5 kilos., and had an extension of 3 to 5 mm. per 100[3].

	Elastic limit per sq. mm.	Tensile strength per sq. mm.	Elongation per cent.
[1] Fused aluminium	7·5 kilos.	11·102 kilos.	9
Aluminium saturated with nitrogen	6·5 ,,	9·6 ,,	6

[2] *J. C. S.*, xxx. 349 (1876).

[3] These experiments were carried out directly on the fused metal without conversion into sheet metal or re-heating. After a first formation into sheets, without re-heating, the following figures were obtained:

Carburized aluminium . .	20 kilos.	20·793 kilos.	2·5
After conversion into sheet .	7·7 ,,	13·8 ,,	26·5

Having had occasion to analyse aluminium from the three great works, at La Praz (France), Neuhausen (Switzerland), and Pittsburg (U.S.A), we detected another impurity, which seems to us to be very important from the point of view of the permanence of the metal. We refer to the presence of sodium in commercial aluminium.

The presence of sodium may be demonstrated in some samples as follows: 250 grms. of carefully prepared filings are placed in an aluminium bottle in presence of 300 cc. of distilled water obtained from a metal retort. The mixture is left to itself for a fortnight, taking care to boil it up every day. It is then poured on to a filter[1], washed with boiling water, and the collected liquid, which is faintly alkaline, is evaporated to dryness in a platinum dish. On heating to dull redness the mass becomes brown; pure hydrochloric acid diluted with water is added, and an unmistakable evolution of carbon dioxide takes place. Evaporate again to dryness, heat at 300° C. to expel the excess of hydrochloric acid, when there is left a residue possessing all the properties of sodium chloride. Take up with water and determine the chlorine as silver chloride; from the weight of the latter is estimated the amount of sodium removed from the aluminium filings by water.

On making a complete analysis of the metal we found sodium in a number of samples. The amount varied from 0·1 to 0·3 per cent. In one sample, prepared some time ago by the firm of Bernard, the percentage was 0·42[2].

When aluminium contains a small amount of sodium it is first attacked slowly by cold water, and then the action becomes more energetic.

If, for instance, a small unchanged volume of water be left in contact with a strip of aluminium of this type, a thin layer of alumina is seen to form at first on the metal. After a few days the liquid is distinctly alkaline when tested with litmus.

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[1] There is often obtained in this experiment a small amount of soluble alumina doubtless analogous to colloidal alumina, which passes through the filter and is then precipitated.

[2] The presence of sodium in commercial aluminium shows that the electrolysis of the mixture of cryolite and alumina gives rise to a number of secondary reactions in which sodium plays a varying part according to the composition of the bath and the intensity of the current.

From this point the decomposition is more rapid. At all the points where the aluminium contains sodium a little alkali is produced, which reacts on the metal to form an aluminate. The latter then dissociates by contact with water to form sodium hydrate, depositing alumina; it will be readily understood that the decomposition becomes more rapid as the liquid becomes slightly alkaline.

The alloys of aluminium which may be prepared will thus have very different properties according as they contain or do not contain a small amount of sodium[1].

Thus in a research on the alloys of aluminium and tin Riche showed that these alloys decomposed water at ordinary temperatures[2].

I was able to get a similar alloy containing 6 per cent. of tin with aluminium quite free from sodium, and under these conditions, after a stay of two months in ordinary water, the metal became pitted at several points, and small deposits of alumina were formed, but there was no evolution of gas. This experiment was carried out as follows: sodium-free aluminium was alloyed with 6 per cent. of tin, avoiding the action of nitrogen and of the fire gases, for Franck has shown that at redness aluminium decomposes carbon dioxide and even carbon monoxide.

An alloy was thus obtained which was rolled out under strong pressure and then gave—

	Re-heated.		Rolled in the cold.
Tensile strength . .	17·6	Tensile strength . .	28·43
Elastic limit . . .	8·20	Elastic limit . . .	22·90
Elongation . . .	20·0	Elongation . . .	6·0

A leaf of this metal was divided into two parts; the first was placed in Seine water which was aerated every day by shaking; the second was placed in a vessel of Bohemian glass in presence of Seine water covered by a layer of oil several centimeters deep. The mean temperature of the laboratory was about 20° C. The experiment, begun on September 30, lasted two months. The metal became covered with a white efflorescence; it developed pits over nearly the whole surface, but no single bubble of hydrogen was evolved. The sample

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[1] It is thus essential, in all work on this subject, to determine at the outset the exact composition of the aluminium used.

[2] *Journ. de Pharm. et de Ch.*, sér. 6, i. 5 (1895).

placed in the water, which was shaken daily, was the more quickly attacked.

This experiment was only done with an alloy poor in tin. Riche has shown that with higher percentages of tin the decomposition of water became very active, and he has thus shown why all attempts to bind aluminium with a tin solder must be rejected.

Moreover, aluminium is a metal which, carefully re-heated, may very well be stamped out or worked into sheets. One must only expect from it what it can give.

M. Riche, to whom I communicated these results before publication, has also detected the presence of sodium in some aluminium samples.

M. Moissonnier, who has carried out a lengthy research on this subject, has also come across a sample of aluminium containing 0·4 per cent. of sodium.

There is another point which we think it important to emphasize in connexion with the alloys of aluminium, and more especially that with copper. It is very difficult to preserve any alloy which is not homogeneous.

In his memoir on the equivalent of aluminium Dumas had drawn attention to the non-homogeneous nature of the aluminium prepared by Deville's method[1].

We have often observed the bad influence of this want of homogeneity in the case of stamped-out aluminium objects. If distilled water be allowed to stand in such a vessel for fifteen days, small white dots of hydrated alumina are seen to form; the dots are surrounded by a bright ring and go on growing. After cutting out the attacked part and removing the hydrated alumina one finds, under the microscope, that there is in that spot a small particle of carbon or of some other substance, which has acted as one of the elements of a couple, and which has led to the destruction of the metal over a smaller or larger surface. If instead of water a concentrated solution of common salt be left in contact with the non-homogeneous metal, this behaviour is accentuated and each carbon particle acts in a manner sufficient to make a hole in the aluminium sheet.

This formation of small electrical couples on the surface of the metal is the cause of its alteration. On the contrary, with

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[1] 'But I recognized subsequently the uneven distribution of iron and silicon in impure aluminium.' *Ann. de Ch. et de Ph.*, sér. 3, lv. 153 (1859).

a homogeneous metal containing neither nitrogen, carbon, nor sodium, no points of attack are produced, and the water which has been in contact with the metal retains all its limpidity and contains no alumina.

The same behaviour is observed with alcohol diluted with water, as, for example, with rum, and, in the case of poor quality aluminium it explains the alteration of certain flasks, which sometimes takes place very energetically.

Finally, it may be pointed out that aluminium, which has a strong tendency to form an electrical couple with any other metal, should always be used alone.

Iron or brass in contact with aluminium will always bring about in a short time the oxidation of the metal to alumina. All manufacturers who have had to work with large surfaces of aluminium have found out, by experience and to their cost, the prevalence of this corrosion.

In recapitulation, commercial aluminium contains, in addition to iron and silicon, a small amount of carbon, traces of nitrogen, and sometimes sodium. These different substances modify considerably the properties of aluminium, but it is to be hoped that electro-metallurgy will soon produce a purer metal of constant composition[1].

It is not the place to point out in a chemical work the importance of re-heating in the rolling and the stamping-out of aluminium. It is known that without this precaution the metal rapidly crinkles and becomes unfit for use.

New method for the preparation of aluminium alloys[2].—The method already described for the making of a vanadium-aluminium alloy starting from vanadic acid, may be applied to a certain number of oxides. It depends on the powerful affinity of aluminium for oxygen. The researches of C. Winkler and others have already shown how readily magnesium reduces certain oxygenated compounds. Aluminium may also be used in certain cases. Making use of this property, I have been able to obtain alloys of aluminium with most of the

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[1] We may add that commercial aluminium often contains a small amount of alumina totally devoid of crystalline form. Finally, in certain samples, on examining under the microscope the residue left after treatment with hydrochloric acid, we found very definite crystals of carbon boride. The boron was derived from the boric acid used in the cementing of the carbon of the electrodes.

[2] *C. R.*, cxxii. 1302 (1896).

refractory metals, isolating them by means of the electric furnace.

The preparation of these alloys is an easy one. It consists in throwing a mixture of the oxide to be reduced and of aluminium filings on to the surface of a bath of molten aluminium. The combustion of part of the aluminium in air, at the surface of the bath, produces so much heat that the most refractory oxides are reduced. The metal passes continuously into the aluminium bath and raises the melting-point of the alloy. This preparation is carried out in the dry way without the addition of any flux.

There have thus been obtained alloys of aluminium with nickel, molybdenum, tungsten, uranium and titanium. It happens frequently that the heat evolved by the reaction is so intense that the eye cannot bear it. We have prepared several times alloys containing 75 per cent. of tungsten which were only kept liquid thanks to this large evolution of heat. 10 per cent. alloys are easily obtained. It must be borne in mind that the reaction is sometimes an explosive one.

These different alloys seem to us to be of some interest. For they render it possible to pass these refractory metals, whose melting-point is above the temperature of our ordinary furnaces, into a given metal, even when it has a fairly low fusion-point. When, for instance, metallic chromium is brought into contact with molten copper, the latter dissolves but a very small amount, about ½ per cent., and one cannot go any further. But an aluminium-chromium alloy dissolves in molten copper in all proportions, forming a mixed alloy of copper-chromium-aluminium. It is easy to extract the aluminium from this alloy by spreading over the liquid bath a thin layer of copper oxide. As one knows, the latter dissolves readily in the copper and burns the aluminium which rises to the surface as alumina.

This process might be used equally to introduce tungsten or titanium into a bath of steel kept liquid in a Siemens-Martin oven. The excess of aluminium would be rapidly burnt and would pass into slag. It might be destroyed by the addition of a small amount of iron oxide.

We believe that this is a general method and that it will enable one to obtain many new alloys.

Analysis of aluminium and its alloys[1].—The impurities met

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[1] *C. R.*, cxxi. 851 (1895).

with in commercial aluminium have a great influence on its properties and it is therefore important to analyse it as thoroughly as possible.

The commercial methods hitherto employed are not generally satisfactory, whether the ferruginous residue left by aluminium after treatment with dilute hydrochloric acid be looked upon as silicon, or whether the aluminium be estimated by difference.

Preliminary tests.—The aluminium must first of all be tested for copper. About 2 grms. of the metal are dissolved in dilute hydrochloric acid and a stream of sulphuretted hydrogen is passed into the solution. When the percentage of copper is very small, it is advisable to heat the solution slightly and to keep it tepid for several hours after the passage of the gas.

Filter and test qualitatively for copper in the residue. Then test qualitatively for silicon, iron, carbon, nitrogen, titanium, and sulphur[1].

Analysis of aluminium free from copper.

Estimation of silicon[2].—About 3 grms. of the metal are weighed out and attacked with pure dilute hydrochloric acid (1:10). When a grey residue is obtained (containing silicon, iron, aluminium, and carbon), it is separated off and attacked by fusion with a small amount of sodium carbonate in a platinum crucible.

Take up the contents of the crucible with dilute hydrochloric acid and add this solution to the first. The liquid is placed in a porcelain dish and evaporated to dryness on the water bath. Then heat the residue to 125° C. in an air bath; it must then be quite white, powdery, and must no longer adhere to a stirrer. To obtain this result it is advisable to scratch the sides of the dish with a spatula and to crush the lumps formed by means of an agate pestle. The dish is removed after twelve hours' heating when one has observed that a glass rod moistened with ammonia and placed above the residue no longer causes the formation of white fumes, showing that all the hydrochloric acid has been expelled.

Take up the residue with tepid distilled water to which is

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[1] We have already shown how the presence of nitrogen might be detected in aluminium. *C. R.*, cxix. 12 (1894).

[2] Cf. H. Goldschmidt, *Zeit. für Elektrochem.*, viii. 123 (1902).

added a mere trace of hydrochloric acid. Boil for a few minutes, when the silica remains insoluble, and filter. After washing and drying the silica is calcined and weighed[1].

Estimation of aluminium and iron.—The original solution of the aluminium in one-tenth hydrochloric acid, after removal of the silica, is diluted with water up to 500 c.c. 25 c.c. of this solution, corresponding to 0·15 grm. aluminium, are taken and neutralized with ammonia in the cold, and the two oxides are precipitated by means of freshly prepared ammonium sulphide. Digest the mixture for an hour. Filter, wash, dry, calcine, and weigh.

We have not used ammonia for this precipitation, for, in order that it may be complete, the solution must not be too dilute, and must contain a fair quantity of ammoniacal salts and very little free ammonia. One may of course remove the excess of ammonia by boiling, but, in this case, one must stop the moment the solution is only feeble alkaline; should one go further, the alumina reacts slowly on the ammoniacal salt and the liquid becomes acid. On this ground we preferred the precipitation by means of ammonium sulphide.

Precipitated alumina is, as one knows, very difficult to wash. It is essential that the washing should be done by decantation with boiling water in a cylindrical Bohemian glass vessel. The washing is complete when the supernatant liquid no longer contains chloride. The precipitate is filtered off, dried, calcined, and weighed. This gives the weight of alumina and iron sesquioxide contained in the aluminium. The iron, which is precipitated as hydrated sulphide, oxidizes rapidly on washing and calcining.

It is also important to dry the alumina carefully before heating it to redness. Further, the calcination must be proceeded with slowly, for dried alumina occasionally decrepitates when strongly heated. Finally, the calcination must be prolonged because alumina loses its contained water only at a high temperature.

Estimation of iron.—Take 250 c.c. of the original solution after removal of the silica. Evaporate down to about 100 c.c. Add caustic potash quite free from silica, which first precipi-

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[1] To make sure that this silica contains neither alumina nor iron oxide, pour some pure hydrofluoric acid into the platinum dish used for the last calcination. After evaporation on the sand bath there should be no residue.

tates the iron and the aluminium and then dissolves the alumina when excess is added. Keep the mixture near its boiling-point for ten minutes.

The precipitate is washed five or six times by decantation with boiling water and then filtered off. Take up the precipitate with dilute hydrochloric acid and re-precipitate with an excess of potash. Wash and filter, dissolve once more in hydrochloric acid and now precipitate with ammonia. Filter, wash, calcine and weigh the ferric oxide.

The calculated proportion of iron oxide is subtracted from the weight of the two oxides obtained above, and the difference represents the alumina.

Estimation of sodium.—The method depends on the fact that aluminium nitrate is destroyed by heating yielding alumina at a temperature lower than that of the decomposition of sodium nitrate.

Take 5 grms. of aluminium (the presence of copper does not interfere) as turnings or in strips in a conical flask. Add nitric acid[1] diluted with its own volume of water. The attack does not take place in the cold, but the temperature must be raised with care, because the heat of the reaction may be such as to cause a violent evolution of gas.

The solution is concentrated in a platinum dish on the water bath, and evaporated to dryness on a sand bath or over a free flame; powder the residue with an agate pestle.

Heat at a temperature lower than the point of fusion of sodium nitrate, till nitrous fumes are no longer evolved. Take up the residue with boiling water, decant off the liquid and repeat three or four times the washing of the alumina[2].

The dish and the pestle are then washed and all the washings, to which a few drops of nitric acid are added, are evaporated to dryness. Wash three times with boiling water to eliminate each time a fresh quantity of alumina which is mixed with the sodium nitrate. Finally treat with boiling water; evaporate down in a porcelain dish, filter, add to the liquid a small excess of pure hydrochloric acid, and take down to dryness. Add a fresh amount of hydrochloric acid and, after evaporation, heat to 300° C. to expel the excess of acid;

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[1] It is advisable to invert a small funnel over the mouth of the flask to catch the spray formed by the evolution of gas and vapours.

[2] The first filtrate often deposits on cooling a varying amount of alumina in a gelatinous form.

the remaining sodium chloride is estimated as silver chloride. From the latter is calculated the amount of chlorine and hence of sodium[1].

Estimation of carbon.—Take 2 grms. of the metal as turnings or filings and pound them in a mortar with 10 to 15 grms. of powdered mercuric chloride, to which is added a small quantity of water. Evaporate the mixture on the water bath in a dish, then place it in a porcelain boat and heat in a stream of pure hydrogen. The boat is then placed in a tube of Bohemian glass through which passes a stream of oxygen free from carbon dioxide, and heated to redness. The issuing gas is made to pass through Liebig potash bulbs and two small U tubes containing pieces of fused potash. The increase of weight of these tubes gives, as carbon dioxide, the amount of carbon contained in the aluminium.

Analysis of copper-aluminium alloys.

Estimation of copper.—When the alloy contains up to 6 per cent. of copper, 0·5 grm. of the metal is dissolved in nitric acid free from chlorine and the solution is made up to 50 c.c. The estimation is carried out by means of the electrolytic method due to Lecoq de Boisbaudran, using the arrangement devised by Riche. The current used measured 0·1 ampere; the operation lasts twelve hours at 60° C., and twenty-four hours in the cold. When the electrolysis is finished, the copper is washed, dried, and weighed as such.

Estimation of silicon, aluminium, and iron.—The copper is first eliminated by sulphuretted hydrogen, and the alumina, iron, and silicon determined in the manner described above.

Conclusions.—We give as an example the analysis of a sample of aluminium from Pittsburg:

Aluminium	98·82
Iron	0·27
Silicon	0·15
Copper	0·35
Sodium	0·10
Carbon	0·41
Nitrogen	traces
Titanium	,,
Sulphur	,,
	100·10

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[1] During the whole of the analysis the vessels must be carefully sheltered from the glass dust which may exist in the atmosphere of the laboratory.

The aluminium industry has made great progress during the last few years from the point of the purity of the metal. The analysis just given is a good example of this since it contains but 0·27 of iron and 0·15 of silicon. Three years ago a flask manufactured at Karlsruhe from Neuhausen aluminium gave on analysis:

Aluminium	96·12
Iron	1·08
Silicon	1·94
Carbon	0·30
	99·44

A comparison of these two analyses shows that it is now possible to produce a purer metal.

If aluminium could be obtained by electrolysis, free from sodium and carbon, we believe that it would be far more permanent.

It must be pointed out in conclusion, that the figures given by analysis are insufficient alone to fix the value of the metal; the mechanical properties such as elongation, elastic limit, and breaking stress must also be taken into account.

CHAPTER IV

STUDY OF CARBIDES, SILICIDES, BORIDES, PHOSPHIDES, AND ARSENIDES

METALLIC CARBIDES

Metallic carbides had hitherto been but little studied. It had long been known that certain metals, when molten, could dissolve varying amounts of carbon, but, previous to my researches, the class of carbides consisted almost entirely of compounds obtained as a rule by the solution of carbon in a large excess of metal.

The direct preparation of crystalline carbides is not possible in the ordinary laboratory furnaces, for the heat they produce is wholly insufficient.

The electric furnace, in which temperatures of 3,500° C. and even above can be easily obtained, enabled us to take up this study under better conditions. The results of these researches are as interesting from the point of view of industrial applications as from that of the classification of the various elements. For the carbides, which were formerly looked upon as badly defined compounds, have such new and distinct properties that they are very valuable for the natural classification of the elements and must be taken into account by chemists. The property of decomposing water in the cold with production of pure acetylene is for instance characteristic of neighbouring metals such as calcium, barium, and strontium. Under the same conditions, the carbides of aluminium and beryllium produce pure methane. These are new and important properties.

We had noticed at the very outset of our researches with the electric furnace that, if the electrodes were in contact with the fused lime, a dark-coloured compound was formed possessing a crystalline fracture and consisting of carbon and calcium. This new body gave off rapidly, in contact with water, a gas possessing a peculiar odour recalling that of acetylene.

After our first communications on the production of the diamond and on the preparation of various refractory metals, we resumed this study and its results were first published in the *Comptes rendus de l'Académie des sciences.* They are gathered together in this chapter.

Up to the present we have prepared but few double carbides, but there doubtless exist others whose study might well repay research.

Carbides of the alkali metals.

A whole series of crystalline carbides have been prepared in the electric furnace by the reduction of metallic oxides or carbonates by means of carbon. This method cannot, however, be employed for the preparation of certain carbides, such for example as those of the alkali metals (lithium excepted). It was of interest to seek out the reason for this remarkable difference.

Berthelot[1], in a paper on the existence of a new group of metallic radicles, had pointed out the existence of the compounds $NaHC_2$ and Na_2C_2, formed by heating sodium in an atmosphere of acetylene. Sodium carbide Na_2C_2, prepared in this way, is analogous in all its properties to calcium carbide, which is easily prepared in the electric furnace and led to the foundation of an acetylene industry.

A. Lithium carbide.

Preparation.—Heat in the electric furnace a mixture of carbon and lithium carbonate in the proportions required by the equation:

$$Li_2CO_3 + 4C = Li_2C_2 + 3CO.$$

This is carried out in a carbon tube closed at one end.

At the outset, only a small amount of metallic vapour is evolved, then the reaction becomes violent, finally stopping almost completely.

If the preparation be stopped at the moment when the metallic vapours begin to come off more abundantly, one finds at the bottom of the tube a white substance possessing a crystalline fracture; this is lithium carbide. If, on the other hand, the heating be prolonged till all reaction has ceased, one finds fused drops of carbide in the upper part of the tube,

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[1] *Ann. de Ch. et de Ph.*, sér. 4, ix. 385 (1866).

and the more strongly heated part contains graphite only. The temperature employed has a great influence on the yield of carbide. Lithium carbide is volatilized or decomposed into its elements at a high temperature; it is far more easily decomposed than calcium carbide. The temperature of decomposition is between that of sodium carbide and those of the carbides of the alkaline earths.

With a current of 350 amperes at 50 volts, the heating lasts ten to twelve minutes. On the other hand, with 950 amperes at 50 volts, copious metallic vapours are given off at the end of the fourth minute, and the operation must be stopped at once if any carbide is to be found in the hottest part of the tube.

The carbide, mixed with a little carbon, may also be obtained by heating lithium in a stream of acetylene at the temperature of a good coke fire.

Properties.—Lithium carbide occurs as a crystalline mass which is as transparent as an alkaline fluoride or chloride; bright crystals may be seen under the microscope and these alter very quickly in moist air. Its density is 1·65 at 18° C.; it is fairly brittle and does not scratch glass.

It is a very powerful reducing agent; it is also the carbide richest in carbon which we have prepared, since it contains 69 per cent. of its weight of carbon.

It catches fire in fluorine and chlorine in the cold, and burns brightly forming the fluoride and chloride of lithium. Slight heating brings about its incandescence in bromine or iodine vapour.

It burns brightly below a red heat in oxygen, and in the vapours of sulphur and selenium. It burns energetically in phosphorus vapour, yielding a phosphide which is decomposed by cold water with evolution of phosphuretted hydrogen. Arsenic reacts at a red heat.

Potassium chlorate and nitrate oxidize it at their melting-points with bright incandescence. Fused potash attacks it with a large evolution of heat while concentrated acids attack it but slowly.

Lithium carbide decomposes water in the cold, evolving pure acetylene. This reaction, which is rapid at ordinary temperatures, becomes violent at 100° C. It is precisely similar to the reaction with the crystalline carbides of calcium, barium, and strontium.

One kilogram of lithium carbide decomposed by water yields 587 litres of acetylene.

Analysis.—A known weight of the carbide was decomposed by water in a graduated tube over mercury. The volume of acetylene evolved is measured, allowance being made for its solubility in water. The alkali in the water is then determined by a simple titration, and from this the amount of lithium is calculated. We obtained the following figures :

	1	2	3	Theory for Li_2C_2
Carbon	62·85	62·92	62·97	63·15 per cent.
Lithium	36·31	36·29	36·40	36·84 „

B. Sodium carbide.

No carbide is formed by the action of a powerful current (1,000 amperes at 70 volts) on a mixture of pure sodium carbonate and carbon. If, on the other hand, a mixture of caustic soda and sugar carbon be heated in a closed crucible placed inside a carbon crucible, by means of a weaker current, one obtains a black powder which evolves a little acetylene in contact with water.

Acetylene is far more slowly absorbed by sodium than by potassium. In consequence of this behaviour[1] the experiment was modified as follows: sodium and liquid acetylene were sealed up in a tube and allowed to remain at the laboratory temperature. The reaction is slow at first, but after a few days the surface of the sodium loses its brightness and becomes covered with a yellowish-white layer which increases in thickness till the metal is completely transformed.

The tube is then strongly cooled and opened and the gases extracted by means of a mercury pump. Hydrogen was easily detected among the excess of acetylene. The yellowish-white product was analysed as follows :

A weighed amount was decomposed by water and the acetylene evolved was measured and analysed in order to make sure of its purity. The sodium was found by a titration of the resultant alkaline liquid. This compound, prepared in the cold, corresponds to the formula $NaHC_2$; it is thus sodium

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[1] The fact that potassium acetylide is more easily formed explains why Berthelot detected traces of acetylene in the hydrogen produced by the action of potassium on water, whereas he could detect no such traces in the case of sodium.

acetylide, the intermediate compound between acetylene and sodium carbide.

Liquid acetylene is not absolutely necessary for this reaction; it takes place at ordinary temperatures with gaseous, compressed acetylene. The velocity of the reaction seems to stand in some definite relation to the pressure.

It has already been observed that the union of sodium and gaseous acetylene takes place with great difficulty at ordinary pressures, and is only detected after several months. Under a pressure of one atmosphere the compound is formed more readily and by heating gently, even under reduced pressure, the conversion is still more rapid. It is distinct at 50° C.; a small piece of sodium was completely converted into $NaHC_2$ by allowing it to remain for fifteen days in contact with acetylene at 70° C.

Dissociation of the compound $NaHC_2$.

The white compound obtained by the action of acetylene on sodium at ordinary temperatures was placed in a Bohemian glass tube, closed at one end and connected at the other with a mercury pump.

By gently heating the compound $NaHC_2$ in vacuo it becomes brown, and then gives off pure acetylene. On heating further the colour darkens and, while acetylene is still evolved, a small amount of liquid hydrocarbons is condensed in the colder part of the tube. If the experiment be stopped before the softening-point of glass is reached and cold water added to the solid residue, pure acetylene is evolved. This body is the sodium carbide Na_2C_2 discovered by Berthelot. By heating the residue to redness in vacuo instead of treating it with water, no more gas is evolved; black carbon remains at the bottom of the tube, and above the heated part is found a bright ring of sublimed sodium. So that sodium carbide is decomposed into its elements, in vacuo, at a temperature which is barely that of the softening-point of Bohemian glass. This explains the failure of all efforts to reduce sodium hydrate or carbonate by means of carbon. The temperature of the electric furnace is much too high to render possible the existence of sodium carbide. The above reactions find expression in the equations:

$$2\,NaHC_2 = C_2H_2 + Na_2C_2$$

$$Na_2C_2 = Na_2 + C_2$$

C. **Potassium carbide.**

This compound was obtained by Berthelot by acting on potassium with acetylene at a red heat.

On heating a mixture of potassium carbonate and carbon ($K_2CO_3 + 2C$) by means of a current of 900 amperes at 45 volts, there is obtained a black powdery mass which consists of nearly pure carbon, containing but traces of the alkali metal and evolving no gas on treatment with water. So that no carbide is formed with a current of this intensity.

In a second experiment the mixture was placed in a carbon tube closed at one end and heated for eight minutes in the electric furnace with a weaker current (350 amperes at 45 volts). After cooling, one finds in the tube a coarse-grained product, parts of which seemed to be fused. On treatment with water, gas is at once evolved; if only moistened with water, the mass glows and evolves a gas which burns with a reddish-violet flame; this is occasionally accompanied by a small explosion.

By causing water to act on this substance in a tube filled with mercury, there is produced a slight evolution of gas. The black residue consists of carbon and the aqueous filtrate has a yellowish colour; it has a strongly alkaline reaction and contains a small amount of carbonate and cyanide. The evolved gas consists of hydrogen, acetylene, and a little nitrogen. In two experiments the amount of acetylene was found to be 70 and 66·6 per cent.

The volume of gas evolved and therefore the amount of carbide formed by this process is very small.

The temperature of the electric furnace is thus seen to be too high for the preparation of potassium carbide.

It was observed further that potassium is slowly attacked by acetylene at ordinary temperatures and pressures, and that in time a complete transformation could be brought about. For these experiments a small piece of potassium was placed in a tube 50 cm. long containing acetylene over mercury. The level of the mercury was seen to have risen considerably on the second day. The absorption went on slowly and when at the end of forty-nine days the experiment was finished, there remained a mixture of 3·87 c.c. of acetylene and 4·48 c.c. of hydrogen (at 0° C. and 760 mm.), being a total of 8·35 c.c., whereas the original acetylene measured 17 c.c. under the same conditions. So that about 8·65 c.c. of acetylene were absorbed, as is required by the following equation:

$$\underset{\text{2 vols.}}{C_2H_2} + K = KHC_2 + \underset{\text{1 vol.}}{H}.$$

There is formed in this way a white substance which only sticks slightly to the tube and which is decomposed at once by cold water with evolution of pure acetylene. The volume evolved measured 7 c.c., or less than is required by theory. This small difference is accounted for by the polymerization of part of the acetylene.

Thus, potassium acetylide is formed by the action of potassium on acetylene at ordinary temperatures, as was discovered by Berthelot, and this substance KHC_2 is intermediate between acetylene C_2H_2 and potassium carbide K_2C_2.

Carbides of the alkaline earth metals.

Historical.—In 1863 Berthelot[1], in a masterly research, gave the properties of acetylene obtained by the action of hydrochloric acid on copper acetylide.

At the end of the same year, Wöhler[2] showed that by the action of carbon on an alloy of zinc and calcium there was formed a black powdery mass, containing an excess of carbon, and evolving a mixture of gases by treatment with cold water. Wöhler was able to detect acetylene in the mixture, but the latter was not fully analysed.

We may recall also that, along another line of research, Winkler[3] had observed the reduction of the carbonates of the alkaline earths by magnesium at a red heat.

Maquenne[4] took up the work in 1892 and, by studying the reaction more fully, prepared a carbide of barium as an amorphous, impure powder, which by treatment with water evolved acetylene containing only 3 to 7 per cent. of hydrogen.

This black powder gave off about 50 litres of gas per kilogram. It was found impossible, as reported by Maquenne, to prepare calcium carbide by this method[5].

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[1] *Ann. de Ch. et de Ph.*, sér. 3, lxvii. 52 (1863).

[2] *Liebig's Ann.*, cxxiv. 220 (1862).

[3] *Berichte*, xxiii. 120 (1890); xxiv. 1966 (1891).

[4] *Ann. de Ch. et de Ph.*, sér. 6, xxviii. 257 (1893).

[5] 'I would draw attention to the fact that barium carbonate is the only

The following year, Travers (London, February, 1893), by heating in a Perrot furnace a mixture of calcium chloride, powdered charcoal, and sodium, obtained a grey mass containing about 16 per cent. of calcium carbide, decomposable by water[1]. He made use of this method of preparing acetylene gas in the preparation of the acetylides of mercury[2].

The question had reached this stage, when in a note appearing in the *Comptes rendus* for December 12, 1892, I published for the first time an account of the formation in the electric furnace of a calcium carbide fusible at a high temperature. This is what was written on the matter: 'If the temperature reaches 3,000° C., the very substance of the furnace, the quicklime casing, runs like water. At this temperature calcium oxide is rapidly reduced by carbon, and the metal is set free in large quantities ; it combines readily with the carbon of the electrode forming a calcium carbide liquid at a red heat, so that it is easily collected.' Following up these investigations, I presented to the Académie des Sciences a further note on calcium carbide on March 5, 1894, followed, on March 19, by another note on the carbides of barium and strontium. In this work it was shown that at the high temperature of the electric furnace, there can exist but a single compound of carbon and calcium, and that this compound is crystalline.

Its formula was established by analysis and in studying its properties it was seen that this body decomposes cold water with the evolution of absolutely pure acetylene gas, this being the origin of the industrial manufacture of acetylene. With regard to this, mention should be made of the technical research of an American experimenter, T. L. Willson.

At the end of a patent, taken out by him in the United States on February 21, 1893 (No. 492,377), for the preparation of aluminium bronzes, reference was made to an uninvestigated carbide of calcium as well as to a large number of other bodies, simple or compound. This mention, however, has no scientific value, because Willson does not give the analysis of the product

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compound of the alkaline earths which is converted into the carbide by magnesium ; the others, and more especially calcium carbonate, are only partially attacked, and give, on treatment with water, a mixture of hydrogen and a little acetylene' (Maquenne).

[1] *Proc. Chem. Soc.*, Feb. 1893, 15.

[2] R. T. Plimpton and M. W. Travers, *J. C. S.*, 1894, vol. lxv. 264.

obtained; he did not even notice that this product decomposed cold water with the evolution of some gas.

Further, the publication of this patent is later than that of our first note on the electric furnace in which the formation of this fused carbide of calcium[1], deposited along the electrodes, was pointed out.

Willson, who avoided with the greatest care any possible 'fusion bath,' was really striving to prepare metallic calcium.

If it was not his good fortune to discover the crystalline calcium carbide, it is to him, however, to a great extent, that this new compound owes its reputation in North America.

D. Preparation of calcium carbide.

An intimate mixture is made of 120 grms. of lime, made from marble, and 70 grms. of sugar carbon[2]; part of this mixture is placed in the crucible of the electric furnace, and heated for 15 minutes with a current of 350 amperes at 70 volts. Under these conditions a carbide of calcium is obtained, corresponding to the formula CaC_2, according to the following equation:

$$CaO + 3\,C = CaC_2 + CO.$$

A slight excess of lime is purposely allowed, since the crucible supplies the quantity of carbon necessary to the formation of a definite carbide.

The yield is from 120 to 150 grms.

Calcium carbonate might be substituted for the lime in the mixture, but not with advantage because of the large volume of the substances employed.

The necessary proportions in this case are readily seen from the equation:

$$CaCO_3 + 4\,C = CaC_2 + 3\,CO.$$

The product obtained by the two methods was the same in appearance, viz.:—a black homogeneous mass which melted and preserved the shape of the crucible in which it was formed. In this preparation it is important that the mixing of the lime and carbon should be thorough. The use of an excess of sugar carbon must also be avoided, otherwise, the fused lime reacts less easily with the carbon and only very little carbide is produced. If a liquid bath be not obtained,

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[1] Moissan, *C. R.*, cxv. 1031 (1892).

[2] See footnote, p. 152.

the preparation is bad, and the resulting powder gives with water but a very feeble evolution of gas.

On several occasions, even, none at all was obtained. These experiments have been repeated on a larger scale, using a current of 1,000 amperes at 60 volts, and a kilogram of the mixture of lime and carbon. If an excess of lime be employed, metallic calcium is chiefly produced, as is shown by the following experiment. In a cavity in the quicklime bed of the electric furnace is placed a mixture of lime and charcoal in the proportions required by the equation,

$$CaO + C = CO + Ca.$$

The furnace possessed, in the middle of a horizontal face, a circular aperture 2 cm. in diameter, into which was fitted an iron tube, the latter being surrounded externally by a lead coil carrying a current of cold water.

The furnace having been set going, with a current of 350 amperes at 50 volts, after seven or eight minutes' heating, vapours are vigorously given off, whilst very bright white flames emerge from the furnace along the electrodes.

The vapours on passing along the cooled iron tube leave behind a grey deposit, which, in contact with water, evolves large quantities of hydrogen containing traces of acetylene.

The water became milky and contained calcium hydrate.

As has already been stated, it was found impossible to convert this finely divided calcium into a regulus.

In our first experiments very pure lime made from marble was used.

If the lime contain sulphates, phosphates, or silicates, the results are rather different. A certain amount of these impurities are found again in the acetylene gas. The sulphur appears even to occur as an organic sulphur compound. In order to ascertain the influence of these compounds, a mixture of sugar carbon and calcium sulphate was heated in the electric arc, the mixture corresponding to the formula

$$CaSO_4 + 4\,C.$$

After complete dehydration in a Perrot furnace, the mixture was placed in the electric furnace in a carbon tube closed at one end and heated for five minutes by a current of 900 amperes at 60 volts.

The product which collects at the bottom of the tube is well fused; it presents a crystalline fracture, but is only slowly decomposed by water with a very slight evolution of gas.

The gas yields on analysis 99·2 per cent. of acetylene. When treated with dilute hydrochloric acid this mixture gave a rapid evolution of gas, which after absorption by potash and then by cuprous ammonium chloride gave the following figures:

	1	2
Sulphuretted hydrogen .	56·20	57·00 per cent.
Acetylene	43·30	42·60 „

On repeating the experiment, using barium sulphate and carbon in the same proportions, a well-fused crystalline mass was obtained, which in contact with water evolved very little gas. On the other hand, when treated with dilute hydrochloric acid it was rapidly attacked, evolving a mixture of gases yielding on analysis:

	1	2
Sulphuretted hydrogen .	88·20	86·90 per cent.
Acetylene	11·40	12·80 „

Finally barium phosphate, mixed with sufficient sugar carbon for complete reduction, was heated for three minutes in a carbon tube using a current of 950 amperes at 70 volts. It produced similarly a well-fused crystalline mass of a dark brown colour.

This substance was decomposed by cold water, with a plentiful evolution of a gas smelling of garlic.

In order to remove the hydrogen phosphide so formed it was treated with a solution of copper sulphate.

The acetylene in the residual gas was absorbed by cuprous ammonium chloride.

The following figures were obtained:

	1	2
Acetylene	89·00	88·50 per cent.
Hydrogen Phosphide (PH_3) .	10·90	11·30 „

The same experiment has been repeated with the three sulphates and phosphates of the alkaline earths; the results have been similar, except that the volume of gas evolved by the action of water varied. If, however, these mixtures be heated in the electric furnace for a longer time, or by a more powerful arc, all the sulphur or phosphorus can be driven off as a volatile compound, and the carbide of the alkaline earth obtained, which is alone stable at a very high temperature[1].

These experiments show that in the industrial preparation of calcium carbide one must avoid, above all, lime containing phosphates. The latter are readily reduced by carbon, yielding a phosphide which is decomposed by water with the formation of hydrogen phosphide.

In conclusion, a last remark must be added on this point. A lime mixed with magnesia yields carbide of calcium only with difficulty. The explanation seems to be simply that in the electric furnace the magnesia does not yield a carbide of magnesium. It thus behaves as inert matter and retards the fusion of the mixture.

Physical properties.—Carbide of calcium cleaves very readily, and shows a distinctly crystalline fracture. The crystals which can be detached have a reddish-brown colour, are opaque and bright.

The thin plates, examined under a microscope, are transparent and of a dark red colour.

These crystals do not belong to the cubical system. Their density determined in benzene at 18° C. is 2·22; this carbide is insoluble in all reagents, in carbon bisulphide, in petroleum, and in benzene.

Chemical properties.—Carbide of calcium is unaffected by hydrogen either in the cold or on heating.

Calcium carbide, at room temperature, takes fire in fluorine gas with the formation of calcium fluoride and carbon tetrafluoride. Dry chlorine is without action in the cold. At a temperature of 245° C. the carbide becomes incandescent in an atmosphere of chlorine; chloride of calcium and carbon are produced, but the weight of the carbon is smaller than the weight of the carbon in the acetylide. Bromine reacts at 350° C., and iodine vapour also decomposes the carbide with incandescence at 305° C. Calcium carbide burns in oxygen at a dull red heat, forming calcium carbonate. In sulphur vapour incandescence occurs at about 500° C., with the formation of calcium sulphide and carbon bisulphide.

No reaction with pure dry nitrogen was observed even at

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[1] Similar experiments have been carried out using the arsenates of calcium and barium, and at continually increasing temperatures, obtaining firstly a mixture of carbide and arsenide, and finally a carbide free from arsenide.

1,200° C[1]. Phosphorus vapour at a red heat changes calcium carbide into calcium phosphide without incandescence.

Arsenic vapour, on the other hand, reacts with considerable evolution of heat, forming calcium arsenide.

At a white heat silicon and boron are without action on this compound (calcium carbide).

Calcium carbide, on fusion, dissolves carbon, which it deposits afterwards as graphite.

Carbide of calcium does not react with most metals.

It is not decomposed by sodium and magnesium at the softening temperature of glass. With iron there is no action at a red heat, but at a high temperature a carburized alloy of iron and calcium is formed.

Tin appears to have no action at a red heat, whilst antimony forms at the same temperature a crystalline alloy containing calcium. The most interesting reaction of calcium carbide is that taking place with water. If a fragment of this carbide be passed into a eudiometer tube filled with mercury, and then a few cubic centimeters of water introduced, a violent evolution of gas is produced, which only ceases when all the carbide is decomposed, calcium hydroxide remaining suspended in the liquid. The gas evolved is pure acetylene, completely absorbed by ammoniacal cuprous chloride, and leaving an almost imperceptible trace of impurity at the top of the tube. This decomposition by water takes place with evolution of heat, but without ever reaching the point of incandescence. It is nevertheless as vigorous as the reaction between sodium and water.

From the weight of the carbide taken in the experiment and the volume of gas produced, the reaction appears to be represented by the following equation :

$$CaC_2 + H_2O = C_2H_2 + CaO.$$

This decomposition occurred in our work whenever the carbide came in contact with a liquid containing water.

The carbide or acetylide of calcium furnishes thus an easy means of preparing pure acetylene, in addition to those described by Berthelot in his classic work on this compound.

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[1] Cf. however, Erlwein—Frank—Caro, *Zeitschrift für angew. Chemie*, xvi. 520, 533, 536 (1903).

That the gas obtained is very pure acetylene is shown by the following figures :

Volume of gas analysed	1·28
Oxygen added	15·15
Total volume	16·43
After sparking	14·50
After potash	11·98
Contraction	1·93
Carbon dioxide by difference	2·52

If the gas were pure acetylene we should have theoretically a contraction of 1·95 and carbon dioxide 2·56.

Another analysis yielded a result identical with the above.

This proof was sufficient to establish the purity of the gas, but we proceeded to determine its density.

Two experiments gave the figures 0·907 and 0·912. Berthelot has given 0·92 as the density of acetylene, and the theoretical value is 0·90. If water vapour is allowed to act on calcium carbide at a dull red heat the action takes place much less vigorously. The carbide is soon covered in fact by a layer of carbon and carbonate, which limits the action of the steam, and the evolution of gas, consisting chiefly of hydrogen and acetylene, is much less rapid. Acids act best on the carbide when they are dilute. With fuming sulphuric acid the evolution of gas is quite slow, and it appears to be absorbed to a great extent.

The ordinary acid produces a more rapid decomposition, giving a marked odour of aldehyde.

With fuming nitric acid there is no action in the cold, and the carbide is scarcely sensibly attacked on boiling. Very dilute nitric acid causes the evolution of acetylene. A dilute solution of hydriodic acid also gives off pure acetylene, and the same is the case with dilute hydrochloric acid. On the other hand, if the carbide be heated to bright redness in dry hydrochloric acid gas strong incandescence is produced, and a mixture of gases evolved very rich in hydrogen.

Certain oxidizing agents act with great energy on this compound. Fused chromic anhydride becomes incandescent in contact with calcium carbide, evolving carbon dioxide. An aqueous solution of chromic acid only evolves acetylene.

Potassium chlorate and potassium nitrate do not appreciably attack the carbide on fusion. At a red heat, however, decomposition takes place with the formation of calcium carbonate.

Lead dioxide oxidizes it with incandescence below dull redness, and the lead formed by the reduction contains calcium. If ground with lead fluoride at the ordinary temperature calcium carbide becomes incandescent.

Heated with anhydrous alcohol in a sealed tube to 180° C. the carbide produces acetylene and calcium ethylate:

$$2\,C_2H_5OH + CaC_2 = C_2H_2 + (C_2H_5O)_2Ca.$$

The acetylene obtained in this reaction is completely absorbed by ammoniacal cuprous chloride, but it yields a black acetylide which seems to indicate the presence of hydrocarbons of the acetylene series.

The violent action of chlorine on acetylene, pointed out by Berthelot[1], may be shown in the following way.

A few fragments of calcium carbide are allowed to fall into a flask containing cold water well saturated with chlorine. Bubbles of acetylene are at once formed which take fire in contact with the chlorine, the odour of the carbon chlorides being easily detected at the same time.

In this form the reaction furnishes an interesting lecture experiment.

Analytical.—The determination of the calcium was easily made after the decomposition of the carbide by water, allowing for a small amount of graphitic carbon which remained behind in numbers three and four.

The carbon was determined by difference, the loss of gaseous acetylene being estimated by means of a small apparatus similar to that used in the analysis of carbonates.

It was also easily determined by collecting over mercury the gas evolved from a known weight of the acetylide, when acted upon by a little water in a graduated tube. This method yielded the following figures:

(1) 0·1895 grms. of the carbide evolved 64 c.c. of gas in the presence of 4 c.c. of water. The liquid dissolves its own volume of acetylene so that there are 68 c.c. of gas produced. Theoretically 0·1895 grm. of the carbide CaC_2 should yield 68 c.c. at 15° C., and 760 mm. pressure.

(2) 0·285 grm. of the carbide yielded with 4 c.c. of water a total volume 96·5 + 4 = 100·5 c.c. Theoretically 102 c.c. should be obtained. The determinations of carbon and calcium, in the crystalline compound already described, gave the following figures:

	1	2	3	4	Theoretical.
Calcium .	62·7	62·1	61·7	62·0	62·5 per cent.
Carbon .	37·3	37·8	—	—	37·5 ,,

Conclusions.—In short, at a sufficiently high temperature,

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[1] Berthelot, 'Recherches sur l'acétylène,' *Ann. de Ch. et de Ph.*, sér. 3, vol. lxvii. 52 (1863).

metallic calcium or its compounds readily form in contact with carbon a carbide or acetylide of the formula CaC_2.

This reaction may perhaps be of a certain geological importance.

It is easily conceivable that in the early geological periods the carbon of the vegetable and animal kingdoms existed in the form of carbides. The large quantity of calcium distributed in the crust of the earth, its diffusion in all formations whether recent or ancient, the ease with which the carbide is decomposed by water, all would lead one to believe that it has played a part in this fixing of carbon in a metallic form.

Moreover, Berthelot[1] has already argued that the action of water vapour on the acetylides of the alkalies, or of the alkaline earths, could readily explain the generation of hydrocarbons and other carbonaceous compounds.

It might be added that the action of air on this carbide of calcium, producing at a red heat carbon dioxide, would explain the passage of the carbon from a solid carbide to the gaseous form of carbon dioxide. The latter can then be assimilated by vegetable matter.

Dissociation of calcium carbide.—A number of experiments have shown that calcium carbide may be decomposed in the electric furnace by means of a strong current.

On attempting the preparation of small quantities of calcium carbide by means of a current of 1,200 amperes at 60 volts, it sometimes happened that after ten minutes there was obtained a product consisting almost entirely of powdered graphite and containing but traces of carbide. It cannot be assumed that the compound has been volatilized, for the carbon remains behind in the crucible. It is more probable that the carbide has been dissociated, the calcium readily distilling off, and the carbon being left behind as a powder.

Using the cooled tube proposed by Deville for the condensation of carbon vapour, we were never able to observe the condensation of any calcium carbide. If fused carbide be heated in the electric furnace, the only products found on the water-cooled copper tube are graphite dust, powdered lime, and calcium, which evolves hydrogen on treatment with water; the purity of the hydrogen may be demonstrated eudiometrically.

So that calcium carbide, like the carbides of lithium and

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[1] Berthelot, *Ann. de Ch. et de Ph.*, sér. 4, vol. ix. 481 (1866).

sodium, may be broken up into its elements, only at a much higher temperature.

The colour of calcium carbide.—The crystals of calcium carbide have already been described (p. 208). Later researches tend to show that the metallic sheen and the colour of the crystals are due to impurities. Calcium carbide is as transparent as sodium chloride, if quite free from iron. The following experiments support this view.

Heat to redness some metallic calcium in a crucible of pure amorphous carbon, obtained by the sudden decomposition of acetylene. There is formed a white carbide which is decomposed by cold water to form calcium hydrate and acetylene; under the microscope it is seen to consist of a mass of transparent crystals[1].

By heating calcium hydride CaH_2, obtained by direct union of its elements, in a crucible of pure amorphous carbon, one obtains a white carbide CaC_2, thin plates of which are perfectly transparent. The same results are obtained by repeating the experiments with crystalline calcium nitride, Ca_3N_2.

The compound $CaC_2 . C_2H_2 . 4NH_3$ may be obtained by the action of acetylene on calcium-ammonium at −60° C.; on decomposition it yields a white transparent carbide. Finally, the following experiment was carried out.

The white carbide was mixed with a small amount of iron oxide in a crucible of pure graphite, and heated in the electric furnace. On cooling there is obtained a carbide having the same lustre and general appearance as the commercial product.

So that perfectly pure calcium carbide is transparent. The brown colour and lustrous appearance are due to the presence of iron, of which a mere trace is sufficient.

Examination of samples of commercial calcium carbide.—The preparation of calcium carbide in the electric furnace has developed very much of late years, and large quantities are now produced.

Although the method is a simple one, the preparation of the carbide on a large scale presented special difficulties. Many points had to be gradually investigated: the conditions to be maintained during the mixing, the quality of the lime and of the carbon, the manipulation of very large electrodes

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[1] This synthesis may be brought about by the heat of a spirit-lamp. The heat of the reaction is sufficient to cause the fusion of the carbide formed, hitherto only carried out in the electric furnace.

in connexion with powerful currents. Most of these problems have now been solved. The removal and the utilization of the hot gases which are abundantly evolved during the process still present some difficulties, which seem, however, to be partially removed by the processes most recently introduced.

Sufficient care was not exercised, in the earlier stages of the industry, in the choice of raw materials such as lime and carbon. In the first works for the production of carbide, coke, rich in ash and containing sulphur and phosphorus, was used as the source of carbon. Further, any available lime was used, which of course nearly always contained aluminium silicate, phosphate and sulphate. It is not to be wondered at, that the heating of such a mixture in the electric furnace produced a very impure calcium carbide. This carbide contained calcium phosphide, aluminium sulphide, and silicides, some of which were decomposable by water. So that on treatment with water, there was obtained a supply of very impure acetylene containing phosphuretted and sulphuretted hydrogen.

Ignorance or a desire for profit led these works to place an impure carbide on the market, yielding an impure acetylene. This state of things explains the difficulties encountered in the application of acetylene to illumination purposes. It was soon recognized that pure lime and coke as free from ash as possible were necessary as raw materials.

The preparation of carbide is now carried out under better conditions. One can now obtain commercially a well-fused, homogeneous carbide possessing a crystalline fracture and the very characteristic gold-like lustre. This carbide should always be employed for the technical production of acetylene. It is, however, advisable to submit the carbide to analysis and not to rely implicitly on its appearance, characteristic though it may be.

Of the many analytical methods proposed, that of Lunge and Cederkreutz[1] is the only one which seems to give good results. It consists in treating a known weight of carbide with excess of water. The chief difficulty consists in getting a thoroughly average sample, especially from a large mass, because of the great hardness of the carbide.

Theoretically, 1 kilogram of calcium carbide should yield

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[1] *Zeitschrift für angew. Chemie*, 1897, 651.

349 litres of acetylene. The following volumes (at 0° C. and 760 mm.) were obtained by treating various samples with lime-water previously saturated with acetylene:

	1	2	3	4	5	6	7
Litres	292·81	294·10	301·30	304·61	307·72	316·41	318·77

The yield of gas is always much smaller when the carbide is unfused and without crystalline structure, porous and grey in colour. Such samples gave the following figures:

	1	2	3
Litres .	228·60	250·40	260·30

The question of the impurities of acetylene need not be discussed here, as it has already been thoroughly studied[1].

We may mention that some samples contain fairly large quantities of ammonia. E. Chuard[2], who made the observation, got the following figures:

Ammonia in the gas . . .	0·03 to 0·06 per cent.
Nitrogen in residue . . .	0·24 to 0·40 ,,

We got the following figures with four different samples:

	1	2	3	4
Total nitrogen	0·02	0·12	0·15	0·31 per cent.

Some of the samples yielded a small amount of phosphuretted hydrogen, others none.

The insoluble residue left after decomposing the carbide with water was of special interest to us. For the investigation of this residue the carbide was decomposed by means of a sugar solution, the lime then remaining in solution as calcium saccharate. The small residue (starting with 10 grms. of carbide) was filtered off and washed, first with a sugar solution and then with water, care being taken that neither of these liquids contained carbon dioxide. The washing was continued with alcohol and then with ether, and the residue was dried in vacuo at 40° C.

Examined under the microscope the residue was seen to consist chiefly of carborundum, calcium, and iron silicides, and

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[1] C. Willgerodt, *Berichte*, xxviii. 2107 (1895); de Brevans, 'L'éclairage à l'acètylène,' 2nd Internat. Congress of Applied Chemistry (Paris, 1897), iv. 506; E. Hubou, ibid., 516; Giraud, ibid., 574; Bergé et Reychler, *Bulletin de la Soc. Chim.*, xvii. 218 (1897).

[2] *Bulletin de la Soc. Chim. de Paris*, xvii. 678 (1897).

of white particles rich in lime; among these a little calcium sulphide and graphite were found.

The residue loses a little in weight by treatment with 10 per cent. hydrochloric acid; in the solution are found iron, lime, and a little alumina and phosphorus. The carborundum and the graphite remain unaltered, but the calcium sulphide is decomposed. By further treatment with concentrated acid silica is dissolved, together with more lime and iron. There is no fixed proportion between the volume of acetylene evolved and the amount of insoluble residue.

The various operations were carried out with a number of samples and the following figures obtained:

	1	2	3	4	5
Treatment with sugar solution . . .	3·4	5·3	3·2	3·9	3·4
„ „ 10 per cent. hydrochloric acid	2·1	1·9	1·5	2·4	1·4
„ „ concentrated acid . . .	1·7	1·7	1·4	2·2	1·1

The nature of most of the impurities can be ascertained by means of the above method and by a microscopic examination of the residues.

Silicon.—This is found chiefly as carborundum. This compound is readily recognized under the microscope, the green or blue hexagonal crystals being very characteristic. It is easily separated from other substances by reason of its high density (3·12) and of its stability.

After treating the calcium carbide residue successively with boiling sulphuric acid and hydrofluoric acid there remain but carborundum and graphite, which are separated by means of bromoform (density 2·9).

Silicon has also been found as calcium silicide, as was observed by Le Chatelier[1]. Small spheres possessing a metallic fracture are sometimes met with, consisting of iron, carbon, and silicon. Finally, the presence of the superposed crystals of silica of Marsden[2] has been observed.

We have not come across samples of calcium carbide catching fire in the air owing to the evolution of silicon hydride produced by the action of small quantities of water. But we have often observed the evolution of this gas on treating the residue with concentrated hydrochloric acid, and thus decomposing any calcium silicide present.

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[1] *Bulletin de la Soc. Chim. de Paris*, xvii. 793 (1897).

[2] *Proc. Royal Soc., Edinburgh*, xi. p. 20 (1880–81).

Sulphur.—In the samples we examined sulphur occurred as calcium or aluminium sulphide.

Calcium sulphide was repeatedly detected in the residue obtained by treating the carbide with sugar solution; some of this was placed under the microscope and treated with a few drops of an acid solution of lead acetate, when the white particles of calcium sulphide became quite black. No sulphuretted hydrogen is evolved by the action of water on this calcium sulphide when in presence of calcium hydrate.

Further, no sulphuretted hydrogen is found in the acetylene evolved by decomposing the carbide with an excess of water, as any which might be formed is retained by the calcium hydrate present.

Any sulphates present in the lime used for the preparation of the carbide are reduced, and thus calcium sulphide is formed. If the lime contain aluminium silicate the silicon and the carbon unite to form carborundum, and if sulphur be present, as sulphate or sulphide, aluminium sulphide may be formed, which is decomposed by cold water with evolution of sulphuretted hydrogen.

By heating together antimony sulphide and aluminium in the electric furnace, Mourlot obtained a perfectly fused aluminium sulphide, possessing a crystalline fracture and stable at a high temperature. Calcium carbide prepared under these conditions may therefore contain aluminium sulphide which evolves sulphuretted hydrogen on treatment with cold water.

Sulphur cannot be present as silicon sulphide for the following reasons: If aluminium containing silicon be placed in a boat and heated to redness in a stream of sulphuretted hydrogen, one obtains in the boat a fused mass of aluminium sulphide, and in the cold part of the tube a deposit of silicon sulphide. The latter is therefore readily volatile and cannot occur in calcium carbide which is prepared in the electric furnace. When the carbide contains a certain amount of calcium sulphide, the action of traces of water brings about the formation of an organic compound containing sulphur, which is easily distinguished from sulphuretted hydrogen. This was proved as follows: The carbide was decomposed with excess of water, and the acetylene evolved was passed through two sets of Liebig bulbs filled with a solution of copper nitrate, of lead nitrate, or of caustic alkali. The unabsorbed gas was burnt and the products of combustion aspirated through a small quantity of distilled water at 0° C. In three different cases a small amount of sulphuric acid was formed during the combustion and could be easily detected. The smallest trace of sulphuretted hydrogen was retained in the absorption bulbs, and yet a compound containing sulphur was unabsorbed[1]. An experiment carried out under similar conditions with the air of the laboratory gave a negative result.

The most distinct reaction was obtained when the acetylene was first washed by means of an alkaline solution. In this case the solution of the copper or lead salt in the first bulb was turned black by the action of phosphuretted hydrogen, but on examination was found to contain but traces of sulphur and often none at all. There was therefore no sulphuretted hydrogen contained in the gas.

The total sulphur was determined in three samples:

	1	2	3
Sulphur .	0·37	0·43	0·74 per cent.

The analysis was carried out as follows: A few grams of carbide were decomposed by means of a small amount of sodium hydrate solution, and the whole then evaporated to dryness. The residue was then treated with a mixture of alkaline carbonate and nitrate. Take up with water and filter, acidify with hydrochloric acid, and add ammonium hydrate and filter again, then determine the sulphur. F. J. Pope[2] had previously suggested a somewhat different method.

Iron.—This is found as silicide or carbo-silicide. The amount contained varies greatly and depends on the purity of the carbon used.

Phosphorus.—Phosphorus is the most troublesome impurity in calcium carbide. It is found chiefly as calcium phosphide, which is decomposed by water. Phosphorus is also found in the small metallic spherules which contain iron and silicon.

Carbon.—Some samples of carbide were found to contain a certain amount of graphite in very thin plates, a few of which were hexagonal though the majority were irregular and distorted. This graphite is not intumescent and retains silica and calcium tenaciously.

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[1] Lunge and Cederkreutz obtained the same result by passing the acetylene through a solution of lead acetate and then oxidizing it by means of sodium hypochlorite. A white precipitate was formed on adding barium chloride.

[2] *Journal of the Amer. Chem. Soc.*, xviii. 740 (1896).

Finally, the possibility of the occurrence of diamonds in commercial carbide having been pointed out, special experiments were made on this point. After treating the carbide with water and concentrated hydrochloric acid the residue was submitted to the method of separation already given when dealing with the separation of diamonds (Chap. II).

In this way were obtained a few transparent, rounded particles, which showed not the faintest crystalline structure and which did not burn in oxygen. None of the samples examined contained diamonds.

Action of calcium carbide on oxides.—Fused calcium carbide reacts energetically with oxides[1]. If the metal does not combine with carbon, as in the case of lead, tin and bismuth, it is liberated and may be separated, or it may combine with other substances which may be present.

If the metal combines with carbon a double decomposition takes place according to the equation

$$RO + CaC_2 = CaO + RC_n,$$

where R is the metal and n represents the number of carbon atoms with which it combines.

In this way were obtained the carbides of aluminium, chromium, manganese, tungsten, and silicon, which had already been obtained by direct union or by reduction of the oxides by carbon.

The two other metals of the alkaline earths, barium and strontium, readily form carbides or acetylides which possess similar properties.

E. Preparation of barium carbide.

The carbon crucible of the electric furnace is filled with an intimate mixture of dry barium monoxide (50 grms.) and sugar carbon (30 grms.). It is then heated for fifteen to twenty minutes with a current of 350 amperes at 70 volts.

After cooling a black mass retaining the shape of the crucible is obtained, which is readily broken, showing after fracture large crystalline plates.

Barium carbonate may be substituted for barium oxide if one wishes to avoid the preparation of the latter compound in a pure state.

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[1] Moissan, *C. R.*, cxxv. 839 (1897); Fröhlich, *Z. für angew. Chem.*, 1899, 1179; K. Geelmuyden, *C. R*, 1026 (1900); F. von Kügelgen, *Z. für Elektrochemie*, vii. 541, 557, 573 (1901).

In this case 150 grms. of pure barium carbonate are added to 25 grms. of sugar carbon, the whole well mixed, and heated as before. The yield is slightly less than by the previous method, but the same product is obtained corresponding to the formula BaC_2.

We have already mentioned, in dealing with calcium carbide, that Maquenne, by the action of magnesium on barium carbonate, obtained impure barium acetylide capable of giving a 4 to 7 per cent. yield of acetylene on treatment with water.

F. Preparation of strontium carbide.

Strontium carbide can be obtained under the same conditions, and with the same ease, by heating in the electric furnace 30 grms. of sugar carbon with 120 grms. of pure strontium oxide, or 150 grms. of strontium carbonate with 50 grms. of sugar carbon. Strontium carbide appears also as a black mass with a crystalline brown red fracture. Like the other acetylides of the alkaline earths it decomposes slowly in damp air.

Properties.—Barium carbide is the most easily fusible of the alkaline earth carbides; its density is 3·75. The density of strontium carbide is 3·19.

These carbides are attacked by fluorine with incandescence and the fusion of the fluoride produced.

Like calcium carbide, they are instantly decomposed by water yielding the hydroxide of the metal and pure acetylene gas.

Acids, whether concentrated or dilute, act exactly as described for calcium carbide.

The action of the halogens is also energetic. In the presence of the gaseous halogen, the reaction takes place with incandescence when the temperature is sufficiently high.

We cannot do better than compare the different results obtained when the temperature at the moment of incandescence is determined by a thermo couple and thermometer.

	Temperature of incandescence in		
	Dry Chlorine.	Bromine Vapour.	Iodine Vapour.
CaC_2 .	245° C.	350° C.	305° C.
SrC_2 .	197° C.	174° C.	182° C.
BaC_2 .	140° C.	130° C.	122° C.

This action of the halogens is interesting since barium acetylide, which combines readily with chlorine, bromine, and iodine, combines with the last element at a lower temperature than that at which it is attacked by bromine or chlorine. This is the reverse of what takes place with calcium carbide.

The action of oxygen is also very energetic, but at a much higher temperature; a temperature at which glass softens is required, the experiment being particularly fine in the case of barium carbide. A vivid incandescence is produced, fused barium oxide being produced at the same time. Barium carbide is decomposed with incandescence by sulphur at a temperature slightly above the melting-point of the latter, barium sulphide and carbon disulphide being produced. A similar reaction occurs with strontium carbide at about 500° C.

Similarly, selenium reacts with vivid incandescence producing the selenides of carbon and of the alkaline earths.

No action could be detected with nitrogen at 1,200° C.[1], but phosphorus vapour reacts vigorously at a dull red heat with brilliant incandescence and the formation of a phosphide. With arsenic the reaction is less vigorous and requires a higher temperature.

At 1,000° C. silicon and boron have no action on the carbides of the alkaline earths.

Analytical results.—The determinations of carbon, barium, and strontium were carried out by the methods already mentioned under calcium carbide.

These analyses yielded the following figures:

	1	2	Theoretical.
Strontium . .	77·96	78·32	78·47 per cent.
Carbon. . .	21·55	21·41	21·52 „

	1	2	Theoretical.
Barium . .	85·30	85·10	85·00 per cent.
Carbon. . .	15·10	14·87	15·00 „

These new compounds correspond therefore to the formulae SrC_2 and BaC_2.

Conclusions.—In short, the metals of the alkaline earths, calcium, barium, and strontium, unite readily with carbon at the temperature of the electric furnace producing crystalline carbides. These bodies are instantly decomposed by cold water with formation of the metallic hydroxide and evolution of pure acetylene gas.

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[1] The residue treated with boiling water after the evolution of acetylene, furnishes, however, some ammoniacal vapours.

This new method of preparing the carbides of the alkaline earths in the electric furnace has already been applied industrially, since the publication of our early work.

It makes it possible to obtain acetylene easily, and the first application of acetylene gas for lighting purposes seems to have yielded good results.

The manufacture of calcium carbide has been studied in Europe and America by a large number of engineers and chemists.

The easy preparation of the carbides of the alkaline earths in the electric furnace may also produce certain changes in the manufacture of baryta and strontia. These two oxides and their salts may be readily obtained, starting with the carbides formed by the action of carbon on the naturally occurring carbonates of barium and strontium.

These carbides would be easily decomposed by water with the evolution of acetylene, yielding the hydroxides of barium and strontium which in turn could be readily converted into the chloride, chlorate, or nitrate.

G. **Beryllium carbide.**

Beryllium carbide Be_4C_3 has been obtained by Lebeau[1] by the action of carbon on pure beryllia obtained from beryl.

Treatment of beryl in the electric furnace.—By heating beryl for eight to ten minutes in a carbon tube by means of a current of 950 amperes at 45 volts, most of the silica is volatilized, and, in the heated part, there remains a fused metallic-looking mass consisting of a mixture of aluminium carbide, beryllium carbide, iron silicide and carborundum. The mass is attacked with dilute acid and a solution of alumina and beryllia obtained. By using hydrofluoric acid one obtains directly a solution of fairly pure beryllia, the alumina remaining as the insoluble fluoride. A better yield of beryllia is obtained by using a powerful reducing agent such as calcium carbide, instead of carbon.

About 50 kilograms of finely powdered beryl are mixed with 50 kilograms of calcium carbide, and the mixture heated for one and a half hours, in the furnace used for the preparation of calcium carbide, by means of a current of 1,500 amperes.

The fused mass remaining in the furnace weighed 31 kilograms. In addition to this, there remained some of the

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[1] *C. R.*, cxxi. 496 (1895); cxxvi. 1202 (1898).

powdered mixture which had not been heated sufficiently. The fused mass was broken up and allowed to remain in the moist air, when it decomposes and falls to powder. Beryllium and aluminium are then present as carbides or hydroxides. A considerable quantity of beryllia may be extracted by digesting with ammonium carbonate. This treatment, however, is a lengthy one. By using sulphuric or hydrofluoric acid, one can obtain in a short time 90 to 95 per cent. of the beryllia contained in beryl.

Preparation of beryllium carbide.—Pure beryllia is mixed intimately with half its weight of sugar carbon, stirred round with a little oil and compressed into small cylinders. These are heated at a dull red heat and then transferred to a carbon tube and placed in the hottest part of the electric furnace (950 amperes at 45 volts). A product containing nitrogen is obtained with a weaker current.

If the operation has been successful, one finds inside the tube a fused mass with a crystalline fracture, covered with graphite and having a reddish colour. This product contains no nitrogen, and in fact the only impurity is a little graphite.

One of the characteristic reactions of this compound, wherein it resembles aluminium carbide, is its decomposition by water with evolution of methane. This reaction, which takes place very slowly in acid solution, goes on rapidly and completely in hot concentrated alkaline solution.

Different analyses yield the figures:

	1	2	3	4	
Beryllium . .	59·53	59·17	60·91	59·76	per cent.
Carbon . .	40·47	40·83	39·09	40·24	„

Taking the atomic weight of beryllium as 13·8, the percentages required for the formula Be_4C_3 are:

Beryllium	60·52	per cent.
Carbon	39·47	„

H. Magnesium carbide.

On heating magnesium powder carefully in a stream of acetylene (Berthelot), one obtains an impure carbide mixed with carbon, but evolving acetylene distinctly on treatment with water.

This carbide was placed in a double-walled crucible of pure graphite and heated for six minutes in a carbon tube closed at one end, by means of a current of 600 amperes at 60 volts. After cooling, there was not the slightest evolution of gas on treating the black residue left in the crucible with water. So that magnesium carbide is completely decomposed at a high temperature. This explains why magnesia may be fused and kept liquid in a carbon crucible without being reduced. Magnesium carbide cannot exist at the fusion-point of magnesia.

I. Cerium carbide.

Our work on the alkaline earth carbides has led us to study the compounds of carbon with the metals of the cerium earths. We should here mention that O. Petterson, in a paper entitled 'Contributions à la chimie des éléments des terres rares[1],' has, by applying our method, obtained the carbides of lanthanum, yttrium, ytterbium and holmium. He has given, however, no analyses of the hydrogen carbides produced by the action of water. It is, on the other hand, to this point, that our experiments have been particularly directed.

Preparation of cerium carbide.—Pure cerium dioxide CeO_2,[2] white in colour, is mixed intimately with sugar carbon in the following proportions:

Sugar carbon	48
Cerium dioxide	192

These proportions correspond to the equation:

$$CeO_2 + 4\,C = CeC_2 + 2\,CO.$$

The reduction takes place in the electric furnace at a comparatively low temperature. The oxide first fuses, and then ebullition occurs owing to the evolution of carbon monoxide. The heating is stopped when the mass is in a state of quiet

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[1] Petterson, *C. R.* (Sweden), sér. 2, ii. 1895; *Ber.* xxviii. 2419 (1895).

[2] In order to prepare the dioxide we started with cerite, which was first of all treated with sulphuric acid. The sulphates so obtained were converted into oxalates, which were finally converted into nitrates. By applying to these nitrates the method of Debray, or rather by fusing them in a bath of sodium-potassium nitrate at a lower temperature, we could precipitate the cerium as ceric oxide mixed with the basic nitrates of lanthanum and didymium. On taking up the nitrates by dilute sulphuric acid, there remained cerium oxide, pale yellow in colour, which could be rendered sufficiently pure by repeating the same process three or four times.

fusion. This preparation is carried out in a carbon tube closed at one of its extremities. With a current of 300 amperes at 60 volts the complete reduction of 100 grms. of the oxide requires 8 to 10 minutes. 600 grms. require 3 minutes with a current of 900 amperes at 50 volts. During the course of the work more than 4 kilos. of cerium carbide were prepared.

Properties.—The cerium carbide appears as a homogeneous mass with a crystalline fracture. It readily breaks up in presence of air, being covered by a yellowish powder, evolving at the same time a characteristic odour resembling that of allylene. When examined under the microscope in benzene, the finely powdered carbide appears in crystalline fragments, among which are found parts of well-marked hexagons, transparent and of a reddish-yellow colour. When free from graphite these small coloured crystals are quite transparent. The density of cerium carbide taken in benzene is 5·23.

Fluorine does not attack cerium carbide in the cold, but, on raising the temperature slightly, a bright incandescence ensues with the evolution of a white volatile fluoride.

Chlorine attacks this compound at about 230° C., forming cerium chloride which adheres to the graphite contained in the carbide.

Bromine and iodine react similarly with incandescence but at higher temperatures. In oxygen cerium carbide burns with evolution of light and heat, forming a crystalline residue of the oxide and giving off carbon dioxide. The reaction is quantitative and enabled us to determine the total metal and carbon. Similarly, sulphur vapour produces a sulphide of cerium with incandescence, the sulphide evolving sulphuretted hydrogen in contact with acids. Selenium acts similarly below a red heat. Nitrogen and phosphorus are without action on the carbide at the softening-point of glass.

Carbon dissolves in fused cerium carbide and crystallizes from the mass in the form of graphite.

Hydrochloric acid gas attacks cerium carbide at 650° C. with incandescence producing a mixture of the chloride and finely divided carbon, hydrogen being evolved at the same time. Hydriodic acid under the same conditions yields an iodide at a dull red heat.

At a red heat sulphuretted hydrogen yields a mixture of graphitic carbon and cerium sulphide.

At a temperature of 600° C. ammonia did not produce a nitride.

Oxidizing agents act vigorously on this compound.

Potassium chlorate attacks it, as soon as fused, with incandescence.

The reaction is less vigorous with potassium nitrate.

Caustic potash and potassium carbonate decompose cerium carbide on fusion, with evolution of heat, forming hydrogen and a yellowish white oxide.

Concentrated sulphuric acid has no action in the cold; on heating sulphur dioxide is given off.

Fuming nitric acid has no action, and the action of the dilute acid is chiefly that of the water it contains.

The most characteristic reaction of cerium carbide is that taking place in contact with water. If water be allowed to drop on a fragment of the carbide, the temperature is raised sufficiently to cause the evaporation of the liquid. In presence of excess of water the reaction, violent at first, soon slows down but is only complete after ten or twelve hours.

Cerium carbide produces, by its decomposition, a white hydroxide of cerium which in contact with air acquires the colour of wine sediment. The gases evolved consist chiefly of acetylene and methane, yielding the following figures on analysis:

	1	2	3	4	5	
Acetylene .	75·00	75·00	76·69	76·42	75·64	per cent.
Ethylene .	3·52	4·23	—	—	—	,,
Methane .	21·48	20·27	—	—	—	,,

These figures were obtained using carbides quite free from calcium, and treating with water at the ordinary temperature.

This decomposition, yielding a practically constant proportion of acetylene and methane, led us to think that we were dealing with two bodies simply related, one of which yields acetylene and the other methane, such as is produced, for example, from the mixed carbides of aluminium and calcium. Following up this idea attempts were made to fractionate the cerium carbide by the action of water, very dilute mineral acids, and organic acids under different conditions, but without result[1].

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[1] In order to separate these carbides the method of Berthelot was followed. Details are given under lanthanum carbide.

By subjecting cerium carbide to the high temperature of the electric furnace, in such a way as to produce partial distillation, we hoped to concentrate one of the carbides in the distillate or the residue, but this yielded no better results[1]. From these different experiments the following conclusions have been drawn.

When cerium carbide is decomposed by ice-cold water, the proportion of the gaseous hydrocarbons varies in a well-defined manner, as is shown by the following figures:

	1	2	3	
Acetylene .	78·47	79·7	80·00	per cent.
Ethylene .	2·63	—	—	,,
Methane .	18·90	—	—	,,

If the cerium carbide be decomposed no longer by water, but by dilute acids, the proportion of acetylene is still more variable. A sample of carbide yielding with excess of pure water, at room temperature, 71 per cent. of acetylene, only yielded 65·8 per cent. with dilute hydrochloric acid, but 83 per cent. with dilute nitric acid.

Further, if the residue left on decomposing cerium carbide with water be examined, on extracting the liquid with ether one recovers in the form of hydrocarbons 3 or 4 per cent. of the combined carbon. One obtains, therefore, a mixture of saturated and unsaturated liquid hydrocarbons. The decomposition of cerium carbide by water is as complex as that of uranium carbide, which is described later, but takes place without evolution of hydrogen. This complexity is due to secondary reactions which vary with the temperature and medium employed.

Analytical.—The cerium was determined as oxide CeO_2 by roasting the nitrate or sulphate, or by the direct combustion of the carbide in oxygen. The figures showed little difference whichever method was employed; they have always been slightly higher than the theoretical value, owing probably to the value of the atomic weight (141) which was used.

According to several writers who have worked on cerium, and according to Schützenberger, the oxide CeO_2 does not always possess a constant composition. The total carbon was determined by direct combustion in oxygen and weighing as carbon dioxide.

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[1] It should not be forgotten that in the experiments of long duration made with the electric furnace, the cerium may take up a small quantity of calcium carbide. One must always make certain that the cerium carbide used contains no calcium.

The samples containing graphite were acted on by nitric acid, and the residual graphite finally determined by weighing as carbon dioxide after combustion in oxygen.

The formula CeC_2 requires theoretically:

Cerium	85·46 per cent.
Carbon	14·54 „

The following figures were obtained experimentally:

	1	2	3	4	5	6	
Cerium .	86·46	85·99	85·37	85·74	86·12	85·93	per cent.
Carbon .	14·90	14·81	—	—	—	—	„

Conclusions.—Cerium forms with carbon in the electric furnace a crystalline carbide CeC_2, analogous to calcium carbide.

The carbide is decomposed by cold water yielding a gaseous mixture of acetylene, ethylene, and methane, and of liquid and solid carbides more or less complex.

J. Lanthanum carbide.

Preparation.—The oxide of lanthanum is readily reduced by carbon in the electric furnace, requiring however a higher temperature than cerium dioxide.

The oxide of lanthanum is mixed with finely powdered sugar carbon in the following proportions:

Lanthanum oxide	100
Sugar carbon	80

This mixture is placed in a carbon tube closed at one end, and is heated in the electric furnace for twelve minutes using the arc produced by a current of 358 amperes at 56 volts.

Properties.—In this way a homogeneous ingot is obtained, well fused, possessing a crystalline fracture, and lighter in colour than cerium carbide. Small fragments examined under the microscope are seen to be transparent, yellowish in colour, and possessing very marked crystalline structure.

The density of crystalline lanthanum carbide has been found to be 5·02 at 20° C.

This value is a little higher than that given by Petterson (4·71).

Fluorine does not attack lanthanum carbide, even when finely powdered, at ordinary temperature. On gently heating the formation of the fluoride takes place with incandescence. Chlorine attacks this compound at 250° C., producing lanthanum chloride with incandescence.

Bromine furnishes similar results at 255° C.

Iodine reacts similarly with incandescence.

Carbide of lanthanum burns in oxygen less readily than cerium carbide. The combustion is complete, however, at a red heat, and the reaction renders possible the separation of lanthanum as oxide and the determination of the total carbon as carbon dioxide.

Sulphur reacts with lanthanum carbide only with difficulty. The carbide may be heated in sulphur vapour to a temperature at which glass softens without any appreciable formation of sulphide. If the reaction product be treated with water a hydrocarbon is formed, and with hydrochloric acid only a trace of sulphuretted hydrogen is evolved.

Selenium vapour reacts more vigorously, forming a selenide which is decomposed by dilute hydrochloric acid with the evolution of hydrogen selenide.

Nitrogen and phosphorus do not appear to react at a temperature of 700° to 800° C. Lanthanum carbide which has been heated in nitrogen yields, however, a trace of ammonia on fusion with potash.

Carbon dissolves in fused lanthanum carbide, and on cooling is deposited in the form of well-crystallized graphite.

Dilute acids attack lanthanum carbide readily; fuming nitric acid, corresponding exactly to HNO_3, has however no action. On the other hand, concentrated sulphuric acid decomposes it with the evolution of heat forming sulphurous acid. Lanthanum carbide, when heated in a stream of ammonia gas, decomposes at a red heat with slight incandescence forming a nitride which evolves ammonia on fusion with potash. There exists therefore a nitride of lanthanum which we shall study further.

Hydrochloric acid gas attacks lanthanum carbide considerably below a red heat, forming lanthanum chloride and hydrocarbons.

This carbide, when heated in a stream of nitrous or nitric oxide to a temperature below redness, burns with bright incandescence.

Oxidizing agents such as powdered potassium permanganate, potassium chlorate, or potassium nitrate, attack it with considerable evolution of heat.

Similarly, fused potash decomposes it with evolution of hydrogen.

Water rapidly decomposes lanthanum carbide at the ordinary temperature, forming the hydrated oxide and evolving a mixture of hydrocarbons containing acetylene, ethylene, and methane. The acetylene and ethylene were determined by absorption by ammoniacal cuprous chloride and bromine respectively, and the composition of the residual methane determined by the eudiometer. In order to make sure that the last gas was pure methane, it was treated with absolute alcohol free from air, as recommended by Berthelot[1]. After the removal of the liquid, the alcohol vapour was absorbed by sulphuric acid, and on analysis the residual gas yielded the same figures as before. One is not dealing therefore with a mixture of hydrogen and ethane, and the last gas is undoubtedly methane.

The following figures were obtained:

	1	2	3	4	
Acetylene .	71·15	70·18	71·17	70·71	per cent.
Ethylene .	1·93	1·15	0·95	2·01	„
Methane .	27·22	28·67	27·88	27·98	„

The gaseous products contain almost the whole of the carbon combined with the lanthanum.

An experiment was carried out with a known weight of carbide containing 5 per cent. of graphite. The gas evolved yielded the figures of analysis 4, which correspond to 11·66 per cent. combined carbon. Theoretically we should obtain 13·7 per cent. This slight difference in carbon is explained by the formation of small quantities of liquid and solid hydrocarbons.

We were able to separate these by extracting with ether the water used to decompose the metallic carbide.

Analysis.—The total carbon was determined directly by combustion in oxygen. For the rest a known weight of the carbide was acted on by dilute nitric acid, the graphitic carbon weighed on a tared filter and the lanthanum determined by evaporating and igniting the nitrate solution.

	1	2	Theoretical for LaC_2	
Lanthanum . .	85·42	85·80	85·23	per cent.
Carbon . .	14·59	14·07	14·77	„

Conclusions.—Lanthanum oxide mixed with carbon and heated in the electric furnace readily produces a transparent,

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[1] Berthelot, *Ann. de Ch. et de Ph.*, sér. 4, xx. 392 (1870).

crystalline carbide of the formula LaC_2. This carbide is decomposable by water at the ordinary temperature, yielding a mixture of acetylene and methane accompanied by traces of ethylene. The proportion of methane is slightly greater than in the case of cerium carbide.

At the moment of its decomposition by water this compound also yields traces of liquid and solid hydrocarbons.

K. Yttrium carbide.

The study of the carbides of yttrium and thorium was carried out in conjunction with A. Etard.

Preparation of yttria.—A certain number of minerals such as gadolinite, euxenite, and monazite contain the rare earths of the yttrium group. The usual method of treating these rare earths is to dissolve the powdered mineral in sulphuric acid and to precipitate the oxides by oxalic acid.

The oxalates are washed, dried at 400° C., and then decomposed by dilute sulphuric acid, and the clear solution is saturated with potassium sulphate crystals. It is known that the double sulphates of the cerium group (lanthanum, didymium) are insoluble in a solution of potassium sulphate, whilst the double sulphates of the yttrium group, such as ytterbium, holmium, &c., remain in solution. When the sulphate solutions no longer show the characteristic spectra of neodymium and praseodymium (the old didymium), it is certain that the cerium and lanthanum are completely precipitated. The mother liquors are now treated with oxalic acid, and one obtains as oxalates the whole of the rare earths of the yttrium group containing ytterbium, holmium, thulium, &c.

It was necessary to separate the yttria from the other oxides, and with this end in view the following method was proposed: viz. the fractional precipitation of the complex mixture of rare earths, previously neutralized by sulphuric acid, by potassium chromate.

If a small quantity of potassium chromate, about one-tenth of that required, be added, a basic precipitate of chromates is produced in which ytterbium, holmium, thulium, and the other elements predominate. The precipitate being basic, the solution becomes rich in chromic acid and acquires a beautiful red colour. The magma which is deposited under these conditions soon crystallizes. It can be separated, washed easily, and then reduced in acid solution by alcohol so as to obtain first of all the oxalate, and finally the oxide by calcination.

The red mother liquor is treated with another tenth of potassium chromate, adding at the same time just enough ammonia to make the solution neutral, as can be easily ascertained by its yellow colour. A new deposit, at first flocculent, but afterwards crystalline, is produced.

By continuing the operation methodically, the tenth precipitate consists of basic yttrium chromate. The rare earth so separated shows no absorption bands and its atomic weight is 89. If necessary one can work up the fractions in series by the same method, and with patience a few hundred grams of yttria can be obtained showing none of the absorption bands of neodymium, praseodymium, ytterbium, holmium, thulium, and samarium.

This method, which is more rapid than any previously described, furnished the yttria used in this research.

Preparation of yttrium carbide.—Finely powdered yttria is intimately mixed with sugar carbon, and just sufficient oil of turpentine added to form a thick paste.

The whole is strongly compressed, and then the lumps calcined in a Perrot furnace. The mixture is heated in a carbon cylinder, closed at one end. The reduction of the yttria requires a higher temperature than does that of cerium oxide. With 900 amperes at 50 volts it is necessary to heat for five or six minutes. During the reduction metallic vapours are evolved which burn at the mouth of the tube with a white flame tinged with purple.

Yttrium and cerium evolve metallic vapours under similar conditions to those of the metals of the alkaline earths.

Properties.—Yttrium carbide, YC_2, appears as a well-fused regulus, friable, and presenting a distinct crystalline fracture. Under the microscope yellow transparent crystals can be clearly seen, sometimes mixed with graphite. The density of yttrium carbide in benzene at 180° C. is 4·13. Petterson gives 4·18.

Several new properties of yttrium carbide will be described below.

It is attacked by fluorine in the cold.

It burns in chlorine below a red heat with bright incandescence, and a similar reaction takes place in bromine vapour

It burns with even greater ease in iodine vapour, forming a stable iodide.

It burns in oxygen and in the vapours of sulphur and selenium.

It is only attacked with difficulty by concentrated acids.

Sulphuric acid causes no evolution of gas in the cold, but on heating sulphur dioxide is evolved.

Water decomposes it in the cold forming a white hydrated oxide, and a mixture of hydrocarbons giving the following analyses:

	1	2
Acetylene	71·7	71·8 per cent.
Methane	19·0	18·8 ,,
Ethylene	4·8	4·45 ,,
Hydrogen	4·5	4·95 ,,

The proportions of the different gaseous hydrocarbons are therefore similar to those furnished by cerium carbide. Acetylene is the chief product and hydrogen is found in small quantities.

Analysis.—The method employed was the same as that described under cerium, and yielded the following figures:

	1	2	Theoretical for YC_2
Yttrium . . .	78·5	78·72	78·76 per cent.
Carbon . . .	21·4	21·55	21·23 ,,

L. Thorium carbide.

Preparation of thorium oxide.—Thorium oxide occurs in thorite or in its richest form, orangite. These minerals are hydrated silicates of thorium containing also iron, calcium, the metals of the cerium group (lanthanum, didymium), and those of the yttrium group (ytterbium, &c.).

The powdered mineral is treated with boiling hydrochloric acid, and the solution of chlorides precipitated by oxalic acid, the thoria and rare earths being deposited from the acid solution. The precipitate is washed to remove iron, calcium, and magnesium. The mixture of oxalates is then treated with a saturated solution of ammonium oxalate, which possesses the well-known property of dissolving thorium oxalate, without touching the oxalates of the true rare earths.

The filtered liquid is then treated with nitric acid to precipitate the thorium oxalate. This process of alternate solution and precipitation is repeated until a pure product is obtained.

Thorium oxide so obtained shows no absorption bands in the spectroscope when a 20 per cent. solution is used in a tube 20 cm. long. It is absolutely white and gives an atomic weight of 232. Finally, when heated on a platinum wire it gives only a dull, almost non-luminous flame, of a lilac colour. As is now known, this is the most delicate test for pure thoria.

Preparation of the carbide.—We should mention in the first place that Troost[1] obtained in the electric furnace a fused mass with thorium, the composition of which approached the formula ThC_2. This mass possessed the property of changing in moist air with increase in size.

In order to obtain the crystalline carbide a mixture of 72 grms. of thoria and 6 grms. of carbon, compressed into small cylinders, as in the case of yttrium, was heated in the electric furnace. With a current of 900 amperes at 50 volts the reduction was complete in four minutes.

Properties.—Pure thorium carbide ThC_2 appeared as a homogeneous mass, well fused, crystalline in fracture and easily split. When observed under the microscope it was seen to consist of small yellow transparent crystals mixed with some laminae of graphite. The density of thorium carbide at 18° C. is 8·96. The action of acids on this compound is similar to that described under yttrium.

When slightly heated in oxygen, thorium carbide burns with dazzling brightness. Heated in sulphur vapour it causes another beautiful incandescence, forming a dark coloured sulphide, which is attacked by hydrochloric acid, differing in this respect from the sulphide described by Chydenius.

It burns in selenium vapour below a red heat with vivid incandescence, forming a selenide which is attacked by dilute hydrochloric acid with the evolution of hydrogen selenide. Hydrochloric acid gas attacks thorium carbide at a dull red heat, causing incandescence, and forming a chloride which is but slightly volatile. With sulphuretted hydrogen at a red heat the reaction proceeds slowly and without incandescence. When heated to about 500° C. in ammonia gas, thorium carbide evolves hydrogen, and the residue yields ammonia gas on fusion with potash.

A nitride of thorium is therefore formed.

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[1] *C. R.*, cxvi. 1227 (1893).

Concentrated acids have little action on this compound, dilute acids, however, attack it rapidly.

Potash, potassium chlorate, and potassium nitrate decompose this carbide on fusion, with incandescence.

Thorium carbide decomposes readily when thrown into cold water, yielding a mixture of gases giving the following figures on analysis[1]:

	1	2	
Acetylene . . .	47·05	48·44	per cent.
Methane	31·06	27·69	„
Ethylene	5·88	5·64	„
Hydrogen . . .	16·01	18·23	„

We have further proved the formation of liquid and solid hydrocarbons in small quantities.

Analysis.—The following results were obtained:

	1	2	Theoretical for ThC_2	
Thorium . .	89·70	89·53	90·62	per cent.
Carbon . .	10·30	10·47	9·37	„

Summarizing, yttria, as indicated by Petterson, forms a carbide of the formula C_2Y. This carbide may be obtained in transparent crystals, decomposable by cold water with the formation of a gaseous mixture rich in acetylene, containing in addition methane, ethylene, and a little hydrogen. Similarly, thorium yields a crystalline, transparent carbide of the formula ThC_2, which in contact with water also produces a mixture of gaseous hydrocarbons containing less acetylene and more free hydrogen.

M. Aluminium carbide.

Hitherto no compound of carbon and aluminium was known, and the solubility of carbon in this metal has been called in question by several chemists[2].

We have prepared, in the electric furnace, a well-crystallized carbide of the formula Al_4C_3, using the following method.

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[1] The acetylene was determined by ammoniacal cuprous chloride. On treating the residue with bromine in a tube over water, the volume of ethylene was obtained. Finally, the eudiometric analysis of the residual gas shows whether it does or does not contain a mixture of hydrocarbons, $C_{2n}H_{2n+2}$ and hydrogen. If hydrogen be present, the gas is treated with boiled alcohol, the alcohol vapours are removed by boiled sulphuric acid and the residue consisting of pure hydrogen is exploded in the eudiometer. *C. R.*, cxix. 16 (1894).

[2] According to Mallet aluminium does not combine with carbon; on the other hand Franck, by calcining a mixture of aluminium and lamp-black, obtained a metallic substance yielding hydrogen contaminated with acetylene when treated with hydrochloric acid.

Preparation.—In order to obtain this new compound, use was made of the electric furnace for tubes described at the beginning of this work. Fairly thick carbon tubes are filled with aluminium and placed in the carbon tube, which is traversed by a stream of hydrogen. Each boat contains 15 to 20 grms. of aluminium, and the heating is continued for five or six minutes, using a current of 300 amperes at 65 volts. After cooling in a current of hydrogen the boats are found to contain a grey metallic mass, on the surface of which metallic globules are found which are formed in consequence of an expansion at the moment of solidification.

When this mass is broken, the aluminium is seen to be packed with brilliant crystals of a fine yellow colour.

A similar product is obtained when aluminium is heated in the electric furnace in a carbon crucible, except that in this preparation the yellow crystals of aluminium carbide are contaminated by a trace of nitrogen.

A similar result is obtained by heating in the electric furnace a mixture of kaolin and carbon. A considerable amount of vapour is evolved and the residue consists of a metallic mass, yellow in colour and presenting a distinct crystalline fracture.

In order to separate the carbide from the excess of metal, the mass is broken up into fragments of 1 to 2 grms., and treated with concentrated hydrochloric acid, in a test-tube packed in ice. It is essential to carry out the operation as rapidly as possible, and to avoid any rise of temperature, since the water present reacts with the aluminium carbide even in the cold, as we shall see later.

Since the action is slowed up by the formation of aluminium chloride, sparingly soluble in hydrochloric acid solution, it is necessary to wash with iced water, and then, after decanting the liquid, to add a fresh quantity of acid. As soon as hydrogen is no longer evolved, the residue is rapidly washed with iced water, then with absolute alcohol, and finally after washing with ether it is dried in the air-bath.

In order that this preparation may be successful it should be completed in about half an hour. A series of test-tubes is used, which are looked after at the same time.

The use of weaker acid causes a much less vigorous action, which, however, is more prolonged, the product obtained being already partially decomposed.

Properties. — Aluminium carbide prepared in this way appears in fine yellow transparent crystals, some of which are as much as 5 or 6 mm. in diameter. Some of the crystals have the shape of regular hexagons, and possess a definite thickness. Their density determined in benzene is 2·36. They are decomposed at the highest temperature of the electric arc.

Chlorine attacks the carbide at a dull red heat, forming aluminium chloride and a deposit of amorphous carbon which retains the shape of the original crystals, containing however no trace of graphite. Bromine is without action at the ordinary temperature, but at about 700° C. it reacts with incandescence forming aluminium bromide and leaving a residue of carbon. Iodine appears to have no action at a bright red heat.

Oxygen at a dull red heat only attacks aluminium carbide superficially, showing that the alumina formed at first forms a film which protects the carbide from further action.

Sulphur, on the other hand, attacks it at the same temperature, with considerable evolution of heat forming aluminium sulphide and traces of carbon disulphide. Most of the carbon, however, remains behind in the form of thin plates.

Nitrogen and phosphorus have no action on aluminium carbide at a dull red heat.

Certain oxidizing agents attack the carbide vigorously. When mixed with dry potassium permanganate and heated slowly, vivid incandescence occurs, and aluminium is formed with the evolution of carbon dioxide. With potassium bichromate and chromic anhydride it burns slowly at a dull red heat; lead dioxide and massicot are reduced with incandescence, whilst potassium chlorate and nitrate have no action.

A solution of an alkaline bichromate, to which sulphuric acid has been added, attacks it slowly both in the cold and on boiling. Fuming nitric acid has no action either in the cold or on heating, but the addition of a few drops of water starts an action after a few moments. Concentrated hydrochloric acid only attacks it slowly, the dilute acid, however, dissolves it in a few hours. Concentrated sulphuric acid is reduced to sulphurous acid on boiling; the dilute acid acts on the carbide at about 100° C.

Fused potash attacks this carbide vigorously at about 300° C.;

the alkaline carbonates, on the other hand, produce only partial decomposition at a bright red heat.

The most interesting reaction shown by aluminium carbide is the slow decomposition produced by water at the ordinary temperature. We have previously shown that the crystallized carbides of the alkaline earths, e.g. CaC_2, are decomposed by water yielding pure acetylene gas. The yellow aluminium carbide, Al_4C_3, decomposes in the presence of water forming methane. To see this evolution of gas it is sufficient to place a few crystals of the carbide in a tube filled with mercury and add a small quantity of water. After twelve hours 0·145 grm. of the carbide yielded 7·5 c.c. of gas, and after seventy-two hours 35·5 c.c. Complete decomposition requires ten or twelve days. The action is accelerated by heat, but light appears to have no effect. Analyses showed the reaction to be expressed by the following equation:

$$Al_4C_3 + 12\,H_2O = 3\,CH_4 + 2\,Al_2(OH)_6.$$[1]

Analysis.—The analysis of this carbide of aluminium presented numerous difficulties on account of its easy decomposition with water. If the samples obtained are not absolutely pure, they contain aluminium hydroxide, which complicates the analysis considerably. The formula Al_4C_3 requires theoretically Al 75·4 per cent., C = 24·6 per cent.

Determination of the aluminium.—Two methods were used to determine the aluminium.

I. A known weight of the carbide is left in contact with dilute hydrochloric acid for some hours until completely dissolved. If the body is absolutely pure, there is no residue, if not, the solution has to be filtered from a small quantity of carbon and insoluble matter. The clear liquid containing aluminium chloride is evaporated to dryness, and then carefully ignited. The light residue of alumina is weighed and the amount of aluminium present in the compound calculated.

This method gave

Al	75·48	75·12 per cent.

II. A known weight of aluminium is fused with potash in a silver crucible, the residue taken up with water and a slight excess of hydrochloric acid added. The solution, heated to boiling, is treated with

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[1] According to this equation 0·100 gram of carbide should yield 48·8 c.c. of methane. The results of two experiments are given below:

(i) 0·070 gram yielded 31·5 c.c. Theory 32·6.

(ii) 0·145 gram yielded 69·1 c.c. Theory 70·90.

That the gas collected under these conditions is methane, is shown by the following analyses:

Original vol. 1·6 c.c., oxygen added 8·5 c.c. After explosion 7·1 c.c. Contraction 3 c.c. After potash 5·6 c.c. Carbon dioxide 1·5 c.c.

sodium thiosulphate, a precipitate of alumina and sulphur being formed. After filtering and ignition this is weighed—

Al . . .	74·7	74·9	75·7 per cent.

Determination of carbon.—When aluminium carbide is treated with chlorine, the whole of the metal is converted into chloride, the carbon remaining behind. Excess of chlorine is removed by heating in a current of hydrogen, the residue being then burnt in a stream of oxygen and the carbon dioxide absorbed and weighed. This method always yielded low results, even with perfectly dry chlorine. This was probably due to the presence of traces of carbon dioxide and oxygen in the chlorine, and to the presence of a trace of alumina in the carbide; this mixture of carbon and aluminium being acted on by the chlorine with the production of carbonic oxide. The best figure obtained by this method was 23·5, whilst the formula Al_4C_3 requires 24·6.

The only method yielding comparable results consists in decomposing a known weight of carbide with water at the ordinary temperature and measuring the volume of methane produced. From this volume the weight of carbon contained in the aluminium carbide can easily be calculated. The following figures were obtained:

Carbon .	24·2	24·7	24·8 per cent.

Conclusions.—Carbon can combine with aluminium to produce a yellow crystalline carbide of the formula Al_4C_3. This new compound is a powerful reducing agent; its most interesting reaction is its slow decomposition by cold water, with the evolution of methane CH_4. It is the first example of this kind of decomposition. It is possible that this carbide plays a part in the geological phenomena which have produced for centuries the evolution of methane.

N. Manganese carbide.

In the calorimetric researches of Troost and Hautefeuille[1], on the carbides of iron and manganese, mention is made of a carbide Mn_3C, which was prepared in the blast furnace, and which on slow cooling yielded true cleavage solids.

We have obtained the same compound in the electric furnace, and have studied its decomposition by water.

Preparation.—To prepare this carbide a mixture of 200 grms. of the pure oxide Mn_3O_4 and 50 of sugar carbon was heated.

The reduction is best carried on in a carbon tube closed at one end, on account of the ready volatility of manganese at the temperature of the electric furnace. With a current of 350 amperes at 50 volts the heating is continued for five

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[1] *C. R.*, vol. lxxx. 909 (1875).

minutes; with 900 amperes at 50 volts the reduction is almost instantaneous.

Properties.—This carbide if exposed to the air for several days readily breaks up, as shown by Troost and Hautefeuille.

Its density is 6·89 at 17° C. In the cold, fluorine attacks it causing incandescence, and forming a violet-coloured fluoride, which we are studying further. Chlorine decomposes it at a slightly higher temperature, the incandescence which commences is, however, not maintained.

When gently heated it burns in oxygen, also in nitrous oxide, and nitrogen peroxide.

Ammonia gas reacts with manganese carbide at a dull red heat with the liberation of hydrogen and the formation of a metallic nitride.

Dilute acids readily attack manganese carbide; hydrochloric acid in particular forming liquid hydrocarbons, a reaction analogous to that studied long ago by Cloëz with cast iron.

Gaseous hydrochloric acid yields, below a red heat, manganese chloride with the evolution of hydrogen containing a small quantity of gaseous hydrocarbons.

The action of water on manganese carbide was particularly interesting. When placed in a tube over mercury, in the presence of excess of water, decomposition sets in with the formation of a hydrated oxide and the production of a gas burning with a practically non-luminous flame.

The analysis of this gas showed that it contained neither acetylene nor ethylene, but consisted of a mixture of methane and hydrogen. By using carbides more or less rich in carbon, and prepared at different temperatures, combustion in the eudiometer yielded the following figures:

	1	2	3
Methane .	51·00	51·32	50·60 per cent.
Hydrogen .	49·00	48·68	49·40 „

When the carbide contains an excess of metallic manganese, the latter decomposes the water, and a much larger quantity of hydrogen is obtained. Such a sample[1] yielded in fact the following figures:

Methane	43·57 per cent.
Hydrogen	56·43 „

[1] This sample of manganese carbide was prepared in the wind furnace.

The carbide, well saturated with carbon, always gives almost exactly the same proportion of methane and hydrogen. Further, no liquid or solid hydrocarbons are found in the water used for its decomposition.

By measuring the gas evolved by a known weight of carbide it has been possible to establish the following equation[1]:

$$Mn_3C + 6\,H_2O = 3\,Mn(OH)_2 + CH_4 + H_2.$$

Analysis.—The determination of carbon and manganese, allowing for the graphitic carbon present, yielded the following figures for Mn = 55:

	1	2	Theory for Mn_3C.
Manganese .	93·5	93·22	93·23 per cent.
Carbon . .	6·5	6·78	6·77 „

Conclusions.—The carbide Mn_3C discovered by Troost and Hautefeuille can be obtained between 1,500° C. and 3,000° C. When pure, it decomposes water at the ordinary temperature, forming a mixture of equal volumes of methane and hydrogen. This reaction can therefore be represented by a simple equation.

O. **Uranium carbide.**

Commercial uranium oxide contains as impurities a small amount of iron and a considerable proportion of alkali. In fact, it is an indefinite compound of uranium oxide with soda, potash, or ammonia.

The commercial oxide is dissolved in pure nitric acid, and the salt obtained recrystallized twice. The crystals, dried in air, are dissolved in ether (Peligot's method[2]), and the mixture is distilled on the water bath after having added to it its own volume of water. The distillation is carried out in a glass flask. The addition of water is necessary in order to avoid

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[1] We have decomposed by water 0·585 grm. of a manganese carbide containing 2·3 per cent. graphite, and therefore equivalent to only 0·5726 grm. Mn_3C. From this we collected 136 c.c. of gas at 761 mm., and 12° C. The gas contained 51 per cent. methane, that is 69·3 c.c. Reduced to 0° and 760 mm., this becomes 66·17 c.c., and contains 0·0354 grm. of carbon. According to the above equation, one should obtain 72·4 c.c. of methane, i.e. 0·0388 grm. of carbon, a figure near to that experimentally obtained. Hence this experiment verifies our equation.

[2] Peligot, *Ann. de Ch. et de Ph.*, sér. 3, v. 7 (1842).

too vigorous a reaction at the end of the operation, with the carrying over of part of the liquid, on account of the sudden evolution of golden red vapours.

The aqueous solution of uranium nitrate is evaporated to dryness, and the residue after ignition consists entirely of the yellow uranium oxide. By a further ignition in a Perrot furnace for two hours, it is converted into the green oxide, which is used directly for the preparation of the carbide.

Preparation.—The green uranium oxide is mixed with finely powdered sugar carbon in the following proportions:

Uranium oxide	500 grms.
Sugar carbon	60 „

About 800 grms. of the mixture are placed in a carbon crucible and heated in the electric furnace for eight to ten minutes using a current of 900 amperes at 50 volts. After about five minutes reduction takes place, and bright sparks are thrown out from the furnace. Some minutes later the sparks disappear, and there remains in the crucible a liquid uranium carbide, which is allowed to cool and solidify in the furnace.

Properties.—The carbide appears in dense fragments, metallic in appearance, crystalline in fracture and resembling bismuth in colour. It contains more or less graphite, proceeding partly from the carbon absorbed from the crucible. The fragments examined under the microscope are distinctly crystalline, reflecting light well, and sometimes showing regular quadratic surfaces. Its density, taken in benzene, is 11·28 at 18° C.

Its hardness is not very great, it scratches glass and quartz but not corundum; like metallic uranium, it emits brilliant sparks when struck by a hard body. When quickly powdered in a mortar it takes fire and continues to burn.

Fluorine has no action on it in the cold, but on gentle heating it burns in the gas with a bright light. Chlorine attacks it at 350° C. with incandescence, forming a volatile uranium chloride. Bromine reacts at 390° C. producing a slight incandescence. Finally, iodine attacks it without incandescence below a red heat. With this last element uranium carbide forms an agglomerated mass, slightly volatile and soluble in water, to which it imparts a green colour.

Uranium carbide burns brightly in oxygen at 370° C. The reaction having once started, passes through the whole mass without any further heating. Carbon dioxide is evolved copiously, and a dark violet oxide remains, which leaves a green stain on porcelain.

With potassium nitrate or chlorate, a vivid incandescence occurs with the formation of an alkaline uranate.

Uranium carbide burns in sulphur vapour with incandescence at the melting-point of glass, forming uranium sulphide and carbon bisulphide.

Selenium reacts at a lower temperature, with incandescence, forming the selenide of uranium.

Nitrogen attacks uranium carbide at 1,100° C. but the conversion to nitride is incomplete. The residue yields ammonia distinctly on treatment with potash. Uranium carbide becomes incandescent in nitric oxide at 370° C., leaving a black residue of complex composition.

Dilute hydrochloric, nitric, and sulphuric acids attack it slowly in the cold, yielding a solution green at first, and afterwards becoming yellow.

Concentrated acids, except nitric acid, act only with difficulty in the cold, but on heating, rapid decomposition takes place.

Hydrochloric acid gas reacts with incandescence, at about 600° C., producing a chloride which forms with water an unstable brown solution.

Sulphuretted hydrogen at the same temperature forms a sulphide of uranium.

Ammonia gas gives a nitride at a red heat, but the decomposition is not complete.

The most interesting reaction of this new compound is that taking place with water.

When fragments of the carbide are brought in contact with water at the ordinary temperature, a slow evolution of gas takes place, which is accelerated if the quantity of water present be small or if the temperature be slightly raised. If the experiment be carried out in the absence of air, there is formed at the same time a green hydrated oxide of uranium. In contact with air, it takes a dark grey colour.

The gas evolved from uranium carbide does not consist of any single hydrocarbon. On analysis it was found to possess the following composition:

	1	2	
Acetylene . . .	0·17	0·72	per cent.
Ethylene . . .	6·77	5·16	„
Methane . . .	78·05	80·60	„
Hydrogen . . .	15·01	13·52	„

One obtains then in this case a complex mixture of gaseous hydrocarbons, and if one calculates the total carbon so recovered from a known weight of carbide, it is at once seen that it falls short by about two-thirds of the combined carbon in the carbide. The reaction being complete, the water used was extracted with ether. After separating the ethereal solution and distilling we obtained the whole of the missing carbon in the form of liquid and solid carbides. After evaporating the ether, the liquid was distilled off between 70° and 200° C., a tarry residue being left behind. The distillate was found to be rich in hydrocarbons. Its investigation is not yet completed, but we have already proved that it contains unsaturated hydrocarbons because it readily reduces silver nitrate in the presence of ammonia or potash, forming a mirror on the tube. This reaction could not be due to an aldehyde because the liquid gives no coloration with Schiff's reagent.

At a dull red heat, this carbide is decomposed by steam with incandescence forming a black oxide and evolving carbon dioxide.

Analysis. **Determination of total carbon.**—The total carbon has been determined after the action of chlorine, or by direct combustion. The figures obtained by the first method have always been a little high; the combustion of the carbon obtained, after the action of chlorine, left a residue of 2 to 3 per cent.

The following figures were obtained by this method :

Carbide A	1	2	3	4	
Residue after chlorine and then ignition in hydrogen	12·062	13·009	11·781	10·475	per cent.
Residue after combustion in oxygen . . .	2·670	3·036	2·382	1·550	„
Carbon burnt (by difference)	9·392	9·973	9·399	8·925	„

In using the second method, the carbon burns readily in oxygen, the combustion being complete, and yielding the green uranium oxide and carbon dioxide. This method has the advantage that both carbon and uranium are determined in the same specimen.

By absorbing the carbon dioxide in potash and weighing, the following figures were obtained :

	Carbide A.		Carbide B.
	1	2	
Total carbon . .	8·67	9·02	8·38 per cent.

Determination of combined and graphitic carbon.—The combined carbon has been determined by difference, subtracting the weight of graphite from that of the total carbon.

The graphite was determined in two ways.

(1) By acting on the carbon remaining after treatment with chlorine with boiling nitric acid, and weighing on a tared filter.

	Carbide A.		Carbide C.	
Graphite . .	1·3	1·1	1·2	1·08 per cent.

(2) The carbide was attacked with dilute boiling nitric acid, and the graphite collected either on a tared filter or on glass wool. In the latter case it was burnt and weighed as carbon dioxide.

	Carbide A.	Carbide B.
Graphite (on tared filter) . .	1·6 per cent.	——
Graphite (by combustion) . .	1·58 „	1·6

Determination of uranium.—The method of precipitation by ammonia yielded figures which were rather low ; the best results were obtained by burning the carbide directly in oxygen, and weighing the residue after ignition in a stream of hydrogen.

	Carbide A.		Carbide B.	Carbide C.
	1	2		
Uranium per cent. . .	90·3	91·1	91·3	91·13

Determination of nitrogen.—The specimens of carbide prepared in the electric furnace all contained a small quantity of nitrogen, easily detected by fusion with potash. It was determined (volumetrically) by Dumas' method.

Nitrogen . . . . 0·4 to 0·2 per cent.

Calcium.—Some specimens formed after prolonged heating contained 0·1 to 0·2 per cent. of calcium. It is probable that the acetylene evolved is due to the presence of this calcium in the form of carbide.

Allowing for the nitrogen and graphite one obtains the following figures for the relative proportions of combined carbon and uranium.

	A 1.	A 2.	A 3.	Theory.
Combined carbon . .	7·6	7·5	6·9	6·97 per cent.
Uranium	92·4	92·5	93·1	93·02 „

This corresponds to the formula U_2C_3 for U=240 ; and U_4C_3 for U=120.

In some further experiments, made with a carbon tube closed at one end and traversed by a continuous stream of hydrogen, we have been able to obtain a pure uranium carbide, free from nitrogen and giving the following figures on analysis:

	1	2	
Combined carbon	7·20	7·16	per cent.
Uranium	92·86	92·79	„

Summary.—When uranium is heated in the electric furnace with excess of carbon, it yields a definite crystalline carbide of the formula U_2C_3.

This new body is decomposed by cold water, and about one-third of its carbon appears in the form of gaseous hydrocarbons rich in methane. The remainder of the carbon produces a mixture of liquid and solid hydrocarbons and tarry matter. It is probable that this complex reaction is due to polymerization phenomena, analogous to those described by Berthelot in his work on the pyrogenetic decomposition of hydrocarbons. The presence of hydrogen in the gaseous mixture may be due, on the other hand, to a secondary reaction of a hydrated uranium oxide which would be a powerful reducing agent. Péligot has already shown in fact, that the anhydrous protoxide of uranium has a great affinity for oxygen, that it is pyrophoric, and that there exists a suboxide which has the property of decomposing water.

One sees then, from these experiments, that the reaction of certain carbides with cold water may be rather complex. This decomposition seemed to us the more interesting, that it enables one to obtain gaseous, liquid, and solid hydrocarbons, the fundamental organic compounds, by the simple action of water on a metallic carbide at ordinary temperature.

P. Iron carbide.

The action of carbon on iron.—The investigation of iron carbide has long attracted the attention of chemists. Many papers have been published on this subject, and we may mention more especially the work of Sir F. Abel and During, Müller, Osmond and Werth (1885); Arnold and Read (1894); that of Mylius, Foerster, and Schoene[1], which is a model of thorough and skilful research; the work of E. D. Campbell (1896), who studied more especially the decomposition of iron carbide by means of dilute hydrochloric acid, and the formation of gaseous and liquid hydrocarbons; and finally that of H. von

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[1] *Z. für anorg. Chem.*, xiii. 38 (1897).

Jüptner (1896) on the saturation capacity of iron by carbon. The many other researches cannot be enumerated here.

All these researches go to prove clearly that fused or hardened steel contains a crystalline carbide corresponding to the formula Fe_3C, which is very easily prepared.

Pig iron.—Before studying the subject further, we wished to examine a variety of samples of pig iron which, according to different workers, contains iron carbides of very varying composition.

1. We examined first a pig iron from a furnace in Denain, much of which was kindly placed at our disposal by M. Meteyer.

This pig iron was crystalline and was obtained from furnace No. 3.

The pieces, which were several cubic centimeters in volume, seemed at first sight to be crystalline, but on closer examination it was seen that the angles along corresponding edges showed no regularity, and that the faces were more or less bent. The analysis of sample gave:

Iron	87·99	per cent.
Carbon . . .	8·75	„
Silicon . . .	2·17	„

The percentage of carbon varies considerably on analysing other parts of the same piece. The crystalline appearance was due to the fact that the iron had been compressed between large plates of graphite and the seeming crystals belonged to no system. The residue obtained after destroying the graphite contained no diamonds.

2. The second samples came from a furnace (No. 3) belonging to Metz & Co. (Luxemburg).

Sample A.—This consisted of compact, non-homogeneous pieces and came from a crystalline part of the pig containing but little cast iron. The mass was completely decomposed by hydrochloric acid; there remained a considerable residue, transparent in part and containing much graphite. The residue was treated alternately with hydrofluoric and sulphuric acids, and the graphite destroyed by means of potassium chlorate and nitric acid. The small residue left was fused with potassium bisulphate and then with the double potassium hydrogen fluoride, and finally treated with boiling sulphuric acid. Nothing remained after this treatment which could be recognized under the microscope. The residue therefore contained no diamonds.

Sample B.—This consisted of 58 grms. of non-homogeneous substance, containing reddish-purple crystals of titanium nitride, octahedral crystals of titanic acid and some red and black crystals, which had only here and there a metallic appearance. The mass had no definite formula. After the treatment described above, there was no residue observable under the microscope.

Sample C.—A piece of 42 grms. contained no trace of diamond.

These samples were of special interest, as Rossel had drawn attention to the occurrence of transparent diamonds in the pig iron from these works. We could not detect any in the samples we examined.

During the investigations of metallic carbides, which I and my pupils have carried on for some years, the necessity of investigating the action of carbon on pure iron at increasingly high temperatures became apparent. If Swedish iron or pure iron obtained by the reduction of iron oxide in hydrogen be fused with sugar carbon in the electric furnace, it is found that the fused mass becomes thicker as the temperature rises. At a temperature near the melting-point of titanium, the contents of the crucible have become so viscous that the latter may be turned upside down without loss. As the temperature sinks, the metal becomes after a few moments as mobile as water. The mass solidifies on cooling to a lump of iron which is covered with graphite and has all the characteristics of grey cast iron. On examining this metal, especially if one has used pure iron, one finds but little combined carbon, about 1 per cent., but numerous crystals of graphite.

It follows from this and from the analyses of pig iron that iron, cooled in an ordinary manner, contains more or less graphite, but only a little combined carbon. On treating such a fused mass with dilute acids, a large part of the carbon is evolved in the form of gaseous hydrocarbons, while the other part remains in the form of more or less complex compounds, which have only been imperfectly investigated.

In the preparation of transparent or crystalline diamonds by the sudden cooling of cast iron in water, we often observed radiated particles looking like iron boride or silicide, possessing a definite composition and crystallization. We thought at the time that iron carbide might exist at a high temperature, but that on cooling to the solidifying point of iron it decomposed almost entirely. Other examples of this behaviour are known. Sainte-Claire Deville and Debray have proved that by suddenly cooling the vapour from boiling silver in the air, one obtained metallic silver containing silver oxide. This oxide was thus obtained at a temperature far above its decomposition temperature.

Troost and Hautefeuille have also shown that ozone, which is so easily decomposed by raising the temperature slightly, could be formed between 1,300 and 1,400° C. We believe that the direct preparation of iron carbide is another example of this remarkable behaviour.

By suddenly cooling iron saturated with carbon, one obtains a lump of metal containing a considerable quantity of carbide, up to 5·25 per cent. of combined carbon.

Preparation of iron carbide.—If a very pure carbide is to be obtained, one must avoid the complete saturation of the iron by carbon and restrain the formation of graphite. To this end one heats in the electric furnace 500 grms. of Swedish iron in a carbon crucible, which gives up the necessary amount of carbon, for three minutes with a current of 900 amperes at 65 volts. The crucible is then withdrawn with a pair of tongs and dipped into water, that is, the experiment used in the production of diamonds is repeated. Some carbide is always formed whether the fusion has been good or bad, and whether pressure has been developed or not.

The iron obtained in this way is very hard and brittle, has often a distinct crystalline appearance and contains no trace of graphite, but from 3 to 4 per cent. of combined carbon, as is shown by the following analyses:

	1	2	3	4
Combined carbon . .	3·31	3·49	3·68	3·92 per cent.

The crystals of iron carbide, which could be seen distinctly among the metal, were separated by the method described by Mylius, Foerster, and Schoene in their work on the carbide occurring in steel.

A few modifications were introduced in order to obtain a very pure product.

1. Two pieces of iron were placed in a solution of 7 per cent. hydrochloric acid in a crystallization dish and joined up to

the positive pole of two Bunsen cells. The two negative poles were connected up with a plate of carbon placed vertically in the middle of the dish. The pieces were taken out after 24 hours and any adhering substance, consisting of a mixture of carbide and amorphous carbon, was brushed off.

2. The pieces of iron, together with a very dilute acid solution, were placed in a drawn-out glass tube for three weeks, keeping out the air.

If only a little carbide is to be obtained in one operation, one may use strong acids and warm. The iron is generally more easily attacked than the carbide, so that the latter remains in the residue after treating not too energetically with mineral acids, organic acids, aqueous iodine, chromic acid, &c.

By treating finely powdered iron with normal nitric acid, one obtains a carbide containing a little light carbon. Semi-normal nitric acid yields, after a few hours, almost pure carbide.

Purification.—Whatever be the method of preparation used, the carbide always contains a varying amount of free carbon and liquid or solid hydrocarbons which are only slightly soluble in ether. A pure product, corresponding exactly to the formula Fe_3C, may be obtained by treating the impure carbide with anhydrous fuming nitric acid. Iron carbide is not attacked in the cold, but only at the boiling-point of the acid.

By leaving the carbide for two hours in fuming nitric acid at 35° C. the free carbon and the hydrocarbons are converted into soluble compounds. The mixture is then poured into an excess of water, the liquid decanted off and the residue washed with alcohol and ether, and dried at 100° C. in an atmosphere of carbon dioxide; the carbide should be perfectly dry before being brought into the air.

This purification by nitric acid may be accelerated by the addition of a small amount of potassium chloride. Instead of this mixture one may use an aqueous 10 per cent. solution of chromic acid, which is allowed to act at its boiling-point, till the crystals assume a bright glistening appearance.

Properties.—This carbide, whose formula is Fe_3C (see analyses), has the same appearance as the product obtained from steel, only the crystals are larger. It has a bright white colour; the crystals are partly broken up, but some are fairly regular. They have a density of 7·07 at 16° C.

Iron carbide is not attacked in the cold by dry oxygen, but it is decomposed fairly quickly in moist air containing carbon dioxide. It burns in oxygen on heating, the readiness with which it burns depending on its state of division. If very finely divided, it may catch fire in moist air below 150° C.

The carbide becomes red-hot in sulphur vapour at 500° C., and burns in chlorine below 100° C. with incandescence, the same happening in bromine vapour at about 100° C. On the other hand, iodine vapour only acts at a red heat and then without incandescence.

Hydrochloric acid gas acts at 600° C., forming iron chloride and hydrogen, the latter containing a small quantity of hydrocarbons.

Fuming nitric acid has no action in the cold, even when the carbide is finely divided or when one introduces a platinum wire. But decomposition takes place at once on the addition of only a small amount of water.

All the dilute acids attack iron far more readily than the carbide. A complete decomposition takes place at once on boiling.

By heating iron carbide with dilute hydrochloric acid in a sealed tube, one obtains hydrogen and methane.

Hydrogen . . .	86·3 c.c.
Methane . . .	13·7 „

Under the same conditions, using concentrated acid, there were evolved:

Hydrogen . . .	73·5 c.c.
Methane . . .	26·5 „

Pure water has no action on iron carbide between 0° and 150° C., the same being true of saturated solutions of sodium and manganese chlorides.

Considering its properties as a whole, this carbide bears a close resemblance to the carbide obtained from steel.

Analyses.

1. Carbide purified electrolytically:

	1	2	3	Theory.
Iron . . .	93·40	93·22	93·14	93·33 per cent.
Carbon . . .	6·47	6·67	6·67	6·66 „

2. Carbide purified by means of aqueous iodine:

	1	2
Iron	93·10	93·25 per cent.
Carbon	6·66	— „

3. Carbide purified with dilute acids:

	1	2
Iron	93·17	93·56 per cent.
Carbon	6·58	6·61 „

CLASSIFICATION OF CARBIDES

New theory of the formation of paraffins.—We shall review in these conclusions the whole of our work on the new class of metallic carbides. At the high temperature of the electric furnace a certain number of metals, such as gold, bismuth, and tin, do not dissolve carbon.

Liquid copper only takes up a very small quantity, which is, however, sufficient to change its properties and greatly modify its malleability.

Silver, at its boiling-point, dissolves a small quantity of carbon, which it afterwards deposits as graphite on cooling.

This carburized silver, obtained at a very high temperature, presents a curious property, viz. that of expanding on solidifying. This phenomenon is analogous to that met with in the case of iron. Pure silver and pure iron contract on sodidification. Cast iron and carburized silver, on the other hand, expand under the same conditions.

Aluminium possesses similar properties.

The metals of the platinum group readily dissolve carbon at their boiling-point, depositing it after solidification in the form of graphite. This graphite is intumescent.

A large number of metals give, however, at the temperature of the electric furnace, definite crystalline compounds.

By passing acetylene gas over the alkali metals, Berthelot[1] has prepared the carbides of sodium and potassium.

By heating lithium oxide or carbonate with carbon in the electric furnace, we have been able to obtain readily lithium carbide in transparent crystals, evolving 587 litres of pure acetylene gas per kilogram.

Similarly, by heating in the electric furnace a mixture of the oxide with carbon, we have been able, for the first time, to prepare by a general method, the carbides of calcium[2],

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[1] Berthelot, *Ann. de Ch. et de Ph.*, sér. 4, vol. ix. 385 (1866).

[2] The carbides of calcium and barium had hitherto been obtained as black amorphous powders, very impure.

barium, and strontium in a pure, crystalline form and in considerable quantity.

All these carbides are decomposed in contact with water with the evolution of acetylene. The reaction is quantitative, and the gas obtained perfectly pure. The three carbides of the alkaline earths correspond to the formula RC_2, and the carbides of the alkali metals to formula R_2C_2.

The industrial preparation of acetylene is based on this reaction.

Another type of carbide crystallizing in hexagonal plates, 1 cm. in diameter, was furnished by aluminium. This metal, when heated strongly in the electric furnace in presence of carbon yields yellow plates of the carbide, which can be isolated by a somewhat delicate method, viz. treatment with dilute hydrochloric acid, cooled to the temperature of melting ice. This metallic carbide is decomposed by water, at the ordinary temperature forming alumina and pure methane. It corresponds to the formula Al_4C_3.

Lebeau has obtained, under the same conditions, the carbide of beryllium which also evolved pure methane in contact with cold water[1].

The metals of the cerium earths also give crystalline carbides, the formula of which appears to be similar to that of the alkaline-earth carbides RC_2.

We have especially studied the decomposition by water of the carbides of cerium CeC_2, lanthanum LaC_2, yttrium YtC_2, and thorium ThC_2.[2]

All these bodies decompose water, yielding a gaseous mixture rich in acetylene and containing some methane. In the case of thorium carbide, the proportion of acetylene is less and that of methane greater.

Our first experiments with iron never yielded crystalline compounds. By the slow cooling of cast iron saturated with carbon at 3,500°, the iron did not yield a definite compound. This is no longer the case if the cooling be rapid; it is then possible to obtain a crystallized carbide.

It has been known for a long time, thanks to the work of Troost and Hautefeuille, that manganese produces a carbide Mn_3C. This carbide can be prepared in the electric furnace

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[1] P. Lebeau, *C. R.*, cxxi. 496 (1895).

[2] Moissan and Etard, *C. R.*, cxxii. 573 (1896).

with the greatest ease, and in contact with water is decomposed, yielding a mixture of equal volumes of methane and hydrogen.

Uranium carbide, U_2C_3, which was obtained by the same method, presented a more complex reaction. This carbide, which is well crystallized and transparent when in thin plates, is decomposed in contact with water yielding a gaseous mixture containing chiefly methane, and also hydrogen and ethylene.

The most interesting fact, however, presented by this carbide is the following: the action of cold water yields not only gaseous, but also liquid and solid hydrocarbons. About two-thirds of the carbon is recovered in this form.

The carbides of cerium and lanthanum yield in the same way liquid and solid hydrocarbons, only in smaller quantity, when decomposed by water.

The whole of these carbides, decomposable by water at the ordinary temperature with the production of hydrocarbons, form the first class of compounds in the family of metallic carbides.

The second class consists of those carbides which do not decompose water at the ordinary temperature, such as the carbides of molybdenum Mo_2C, tungsten W_2C, and chromium Cr_4C and Cr_3C_2.

These latter compounds are crystalline, not transparent, and possess a metallic lustre. They are very hard and fuse only at a very high temperature. We have been able to prepare them all in the electric furnace, details and analyses being given in preceding chapters.

The metalloids also give definite crystalline carbides with carbon at the temperature of the electric furnace. We shall mention, as examples, the carbide of silicon, obtained in the amorphous state by Schützenberger[1] and prepared later in fine crystals by Acheson; the carbide of titanium, TiC, which is so hard that it will scratch diamond; the carbide of zirconium, ZrC,[2] and the carbide of vanadium, VC.

A general fact appears from the numerous researches carried out with the electric furnace, viz. that those compounds which are formed at a high temperature have always very simple formulae and that, as a rule, only a single compound exists.

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[1] *C. R.*, cxiv. 1089 (1892).

[2] Moissan and Lengfeld, *C. R.*, cxxii. 651 (1896).

The reaction which appears to us the most interesting in the whole of this work is the ready production of gaseous, liquid and solid hydrocarbons by the action of cold water on certain metallic carbides. It seems to us that this might be of interest to geologists.

The evolution of more or less pure methane, which is met with in certain soils, and which has existed for centuries, might have its origin in the action of water on aluminium carbide.

A reaction of the same order might explain the formation of the liquid and solid hydrocarbons. As is well known the various theories with regard to the formation of petroleum are as follows:

1. Production by the decomposition of organic matter, vegetable or animal.
2. Formation of the petroleum by purely chemical reactions; a theory first brought forward by Berthelot[1], and which has been the subject of an important communication by Mendeleef.
3. Production of the petroleum through the agency of volcanic phenomena, a hypothesis first suggested by Humboldt in 1804.

By the decomposition of 4 kilos. of uranium carbide we have obtained, in a single experiment, more than 100 grms. of liquid carbides.

The mixture so obtained consisted chiefly of hydrocarbons of the ethylene series together with small quantities of acetylene homologues and of saturated hydrocarbons. These carbides being formed in the presence of a large proportion of methane, at the ordinary temperature and pressure, we have been led to think that when the decomposition takes place at a higher temperature, only saturated hydrocarbons like the paraffins would be produced.

Berthelot has shown in fact that the direct addition of hydrogen to an unsaturated hydrocarbon may be brought about by the action of heat alone.

The existence of these new metallic carbides, decomposable by water, may then modify the theoretical hypotheses brought forward up to the present to explain the formation of petroleum. One thing is very certain, we must be on our guard against too hasty generalizations.

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[1] *Ann. de Ch. et de Ph.*, sér. 4, ix. 481 (1866).

It is probable that there exist petroleums of different origin. At Autun, for example, the bituminous shales appear to have been produced by the decomposition of organic matter.

On the other hand, in Limagne, bitumen occurs in all the fissures of the freshwater limestone, which is very poor in fossils. This bitumen is directly connected with volcanic veins (basaltic), therefore it is obviously connected with the volcanic eruptions of Limagne.

A recent boring, made at Riom to a depth of 1,200 meters, produced a flow of several litres of petroleum. The formation of this liquid carbide in the earth might be due to the action of water on metallic carbides. We have shown, under calcium carbide, the conditions under which this compound can burn to form carbon dioxide.

It is conceivable that in the first geological periods of the earth, almost the whole of the carbon was present in the form of metallic carbides. When water began to play a part in the reactions, the carbides yielded hydrocarbons, and these last carbonic acid by oxidation. One might find an example of this reaction in the neighbourhood of Saint-Nectaire. The granites which there form the edge of the tertiary basin, allow the continuous escape of considerable quantities of carbon dioxide.

We believe also that certain volcanic phenomena might be attributed to the action of water on easily decomposable metallic carbides. All geologists know that the last sign of a centre of volcanic activity consists in the emanation of various hydrocarbons, yielding bitumen and petroleum, and, at the final stage of complete oxidation, carbon dioxide.

A movement of the soil bringing water in contact with metallic carbides would produce the violent evolution of a volume of gas. At the same time, the temperature rising, the phenomena of the polymerization of the carbides would intervene, giving rise to complex products. The hydrocarbons would thus be produced first of all, the phenomena of oxidation appearing later, and rendering the reactions more complex.

In certain places a volcanic fissure might act as a powerful draught chimney.

One knows that the nature of the gas collected varies according as the volcano is submarine or terrestrial. At Santorin, for instance, Fouqué has collected free hydrogen at the mouths of submarine volcanoes, whilst in terrestrial fissures he has only found water vapour. The existence of these metallic carbides, easily formed at a high temperature, and which must occur in all probability in the deeper formations of the earth[1], may explain then, in some cases, the formation of gaseous, liquid, and solid hydrocarbons, and may be the cause of certain volcanic eruptions.

SILICIDES

The new method, which has enabled us to obtain definite crystalline metallic carbides, may be extended to the preparation of the silicides.

These compounds were previously but badly characterized and little known.

We shall give as examples of this work the action of silicon on iron, chromium, and silver; these three metals having been chosen for further investigation after some preliminary experiments.

A. **Silicides of iron**[2].

Researches on cast iron containing silicon have been numerous enough, but very little work exists on the crystalline silicides of iron. By the action of silicon tetrachloride on iron heated to redness, Frémy[3] obtained crystals of a silicide SiFe; Hahn[4] has pointed out the existence of an amorphous silicide, $SiFe_2$, which, treated with hydrofluoric acid, leaves a residue of silky crystals of SiFe. Finally, we should mention the thermochemical work of Troost and Hautefeuille[5].

We have been able to obtain a crystallized iron silicide by the direct union of iron and silicon, either by heating with gas carbon in a reverberatory furnace, or in the electric furnace.

Preparation.—1. One places, in a porcelain boat, a 'brasque' of crystallized silicon, corresponding to about one-tenth of the weight of metal used. On this is placed a cylinder of soft iron, and the boat is placed in a porcelain tube traversed by a slow stream of pure, dry hydrogen. The tube is heated by gas carbon to a temperature at which the tube is slightly

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[1] The difference between the average density of the earth and that of the superficial layer seems to suggest the existence of a central mass rich in metals.

[2] See P. Lebeau, *Ann. de Ch. et de Ph.*, sér. 7, xxvi. 5 (1902).

[3] *Encyclopédie chimique.*

[4] *Liebig's Annalen*, cxxix. 57 (1864).

[5] *C. R.*, lxxxi. 264 (1875).

deformed, but which is, however, lower than the fusing-point of soft iron, determined by a preliminary experiment.

A silvery-white ingot is obtained after heating, which consists of a crystallized iron silicide contaminated by excess of metal.

In this experiment, where two solid bodies, silicon and iron, are heated to a temperature of about 1,200° C., considerably below the melting-point of either, there is produced a fused metallic ingot. This shows, we think, that the action is due to the vapour pressure of the solid silicon which brings about combination with the iron, yielding a silicide more easily fusible than the metal itself. We have previously established the existence of similar phenomena with boron, and it seems to us that one can give the same explanation for the absorption of carbon by iron. At this temperature, 1,200° C., silicon, boron and carbon already exert a vapour pressure which, although very small, is sufficient to cause the formation of liquid or solid compounds with the iron before the temperature of fusion is reached.

2. In the crucible[1] of the electric furnace are placed 400 grms. of soft iron in small cylinders, and 40 grms. of crystallized silicon, which are then heated for four minutes with a current of 900 amperes at 50 volts. The experiment must be carried out quickly in order to avoid the formation of the silicide of carbon.

If the proportion of silicon be increased, the product will be attacked by acids only with difficulty, and it is almost impossible to separate the silicide formed.

3. One can heat, in the electric furnace, a mixture of iron oxide and crystallized silicon, which readily yields volatile silica, and an ingot of iron silicide containing excess of the metal.

In an experiment carried out at the temperature of a good forge, we heated cylinders of soft iron, surrounded by crystallized silicon. As is always the case under these conditions, each crystal of silicon was covered with a fine layer of nitride and oxide which prevented complete fusion of the metalloid into one mass. After the experiment, the iron cylinders withdrawn from the mass had preserved their form and had not been fused at all. They were transformed into silicide even to the axis of the cylinder, and one could by chemical

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[1] The carbon of the crucible plays no part in this reaction, because we have clearly shown that silicon will readily displace carbon from fused cast iron.

means separate and isolate as silica the silicon which they contained to the extent of 2 per cent. This is a new example of the vapour-pressure of silicon and silica below their melting-points.

The metallic masses, obtained by any of these methods, are attacked by nitric acid diluted with four times its volume of water. The action, very rapid at first, slows down little by little in proportion as the metal disappears.

After decantation and washing, there remains a crystallized silicide of the formula $SiFe_2$.

Physical properties.—Iron silicide appears in small prismatic crystals, bright, and possessing a metallic lustre; its density is 7·00 at 22° C.; its melting-point is lower than that of iron and higher than that of cast iron. It affects the magnetic needle.

Chemical properties.—Iron silicide is completely dissolved by aqueous hydrofluoric acid, and the reaction soon becomes very vigorous. This result does not agree with the experiments of Hahn who has mentioned the existence of a silicide of iron unacted upon by hydrofluoric acid. When reduced to a fine powder the silicide is slowly attacked by hydrochloric acid. Nitric acid has no appreciable action on this compound, but water brings about its decomposition with the formation of silica.

The gaseous hydracids attack iron silicide at temperatures varying from a dull red to a bright red heat.

Fused nitrate and chlorate of potassium are without action. The fused alkaline carbonates attack it slowly, whilst a mixture of nitrate and carbonate decomposes it readily.

Analysis.—The silicide was fused with a mixture of alkaline carbonate and nitrate; the iron determined as Fe_2O_3, and the silicon as SiO_2. In this way the following figures were obtained:

	1	2	3	4	Theory.
Iron .	79·20	81·10	82·12	81·43	80·00 per cent.
Silicon .	20·95	19·04	18·02	18·59	20·00 „

Lebeau[1], by allowing iron silicide to crystallize from an excess of copper silicide, obtained the compound SiFe, already prepared by Frémy and Hahn.

A mixture of coarsely powdered commercial copper silicide, with 10 per cent. of its weight of clean iron filings, is placed in a carbon tube and heated for four to five minutes in the electric

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[1] *C. R.*, cxxviii. 933 (1899).

furnace with a current of 950 amperes at 50 volts. There is thus obtained a fused mass which has a homogeneous crystalline appearance and a white metallic fracture, recalling that of copper silicide. After treatment with nitric acid and then with sodium hydrate to remove the gelatinous silica formed, one obtains an iron silicide of the formula SiFe in crystals possessing a metallic lustre.

This method may also be used for the preparation of the silicides of nickel, cobalt, and chromium.

B. **Chromium silicide**[1].

1. If a few fragments of crude chromium containing about 2 per cent. of carbon—a metal more infusible than iron—be placed in a boat made of a brasque of silicon, one can, by heating to a temperature of 1,200° C. in a stream of hydrogen, bring about the fusion of the chromium as silicide of chromium. Here again, owing to its vapour-pressure in the solid state, the silicon has passed into the chromium, and brought about fusion.

To carry out this experiment it is important to arrange the reverberatory furnace with care, and to increase the draught by a flue 10 to 12 meters long. In some of the experiments the porcelain tube was flattened and the two walls became fused together.

2. A mixture of chromium, containing no carbon, with 15 per cent. of silicon by weight, was heated in the carbon crucible of the electric furnace for nine minutes, using a current of 900 amperes at 50 volts.

One obtains in this way a mass showing a crystalline fracture and containing the silicide dissolved in excess of the metal.

3. A mixture of 60 parts of silica, 200 parts of chromium sesquioxide, and 70 parts of sugar carbon, was heated in the electric furnace for ten minutes, using a current of 950 amperes at 70 volts. One obtains in this way a well-fused mass, brittle and distinctly crystalline. Several cavities which were found in the interior of the metallic mass were lined with needles of chromium silicide.

The coarsely powdered metallic masses were treated by cold concentrated hydrofluoric acid. After a few moments a vigorous action sets in; this action is moderated by adding small quantities of water so as to avoid any rise in temperature which would bring about the decomposition of the silicide. It

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[1] See also P. Lebeau and J. Figueras, *C. R*, cxxxvi. 1329 (1903).

is next washed with water and again treated with cold concentrated hydrofluoric acid until all action just ceases. One finally obtains the silicide $SiCr_2$ in small prisms, isolated or fused to each other.

This silicide is often contaminated by a small quantity of a crystalline silicide of carbon, from which we have not been able to separate it, and which must be allowed for in the analysis.

Its chemical properties are very similar to those of iron silicide. It reacts similarly with acids. Chlorine attacks it with incandescence at a red heat. Hydrochloric acid gas converts it at about 700° C. into the chlorides of silicon and chromium. Fused potassium nitrate reacts rapidly, yielding a silicate and a chromate; finally, fused potassium attacks it slowly. We should add that this silicide scratches quartz and corundum with the greatest ease. Most of the silicides moreover possess a much greater hardness than the corresponding carbides. One finds amongst the compounds bodies harder than carbon silicide.

Analysis.—The analysis of chromium silicide presented certain difficulties. The silicide was first fused with a mixture of 2 parts of potassium carbonate and 8 of potassium nitrate. The whole was then taken up with hydrochloric acid. The separation of the silica, rendered insoluble in acid by two successive evaporations on the sand bath, is always complete. The presence of carbon silicide which was separated by further action of the acid, and the existence in some samples of a carbosilicide of chromium made the analysis still more complex.

The following figures were obtained :

	1	2	3	Theory.
Chromium . .	80·22	79·83	80·36	78·79 per cent.
Silicon . . .	19·60	21·08	19·92	21·21 ,,

Action of silicon on silver[1].

When a mixture of crystallized silicon and silver is heated in the electric furnace one obtains, if the temperature be very high, a metallic mass which is covered with fine crystals. These might at first sight be taken for silver silicide. By dissolving away the silver with nitric acid one obtains a residue consisting of yellow, transparent hexagons, the analysis of which shows that they consist entirely of silicide of carbon. When the temperature of the electric furnace is less high, the silicon leaves the silver before solidification ; it crystallizes partly in the form of crystals transparent under the microscope, analogous to

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[1] See also Moissan and Siemens, *C. R.*, cxxxviii. 657 (1904).

those described by Vigouroux[1]. The silver which surrounded the crystals did not yield any trace of silicon on analysis.

The same experiment has been made with a reverberatory furnace as described above, and the silver again retained no silicon. The same was the case with some trials made in the forge, and in some experiments carried out in the Perrot furnace, in which the silicon, prepared by the method of Deville (action of sodium on the fluosilicate), was heated in contact with fused silver.

In these different experiments the liquid silver dissolved silicon, but deposited it in the crystalline form, at the moment of solidification.

This phenomenon appears to be comparable to the behaviour of phosphorus and silver. The metal dissolves in fact an appreciable quantity of phosphorus below 1,000° C., and at the exact point of passage from the solid to the liquid state, one sees the sudden spurting due to phosphorus vapour, as is the case with oxygen[2]. Vigouroux, in an important research on amorphous silicon and its compounds, has followed up this study of the preparation of silicides in the electric furnace[3]. He has obtained in this way crystallized silicides of nickel, cobalt, manganese, copper, platinum, and tungsten.

C. **Manganese silicide**[4].

Vigouroux[5] obtained a silicide of the formula Mn_2Si:

(1) by the direct action of silicon on manganese;
(2) by the action of silicon on the oxide;
(3) by the action of carbon on a mixture of silica and the oxide.

One obtains a definite silicide which is very hard and brittle and has a metallic lustre. It has a density of 6·6 at 15° C. and a light yellow colour. It remains unchanged in the air and melts at the temperature of an ordinary cupel oven.

D. **Silicides of nickel and cobalt**[6].

Vigouroux[7] heated together 10 parts of silicon and 90 parts of the metal in the electric furnace.

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[1] *C.R.*, cxx. 1161 (1895).

[2] Hautefeuille and Perrey, *C.R.*, xcviii. 1378 (1884).

[3] *Ann. de Ch. et de Ph.*, sér. 7, xii. 5, 153 (1897).

[4] Other silicides of manganese have been studied by P. Lebeau, *Ann. de Ch. et de Ph.*, sér. 8, i. 553 (1904).

[5] *C. R.*, cxxi. 771 (1895).

[6] See also P. Lebeau, *Ann. de Ch. et de Ph.*, sér. 7, xxvii. 271 (1902).

[7] *C. R.*, cxxi. 686 (1895).

A reaction takes place at once and the excess of metal distils off. There are thus obtained greyish-white fused masses, which are very hard and brittle and consist of the silicides of the respective metals. The following figures were obtained:

	1	2	Theory for Ni_2Si.
Silicon	18·36	19·25	19·28 per cent.
Nickel	81·66	81·00	80·72 ,,

	1	2	Theory for Co_2Si.
Silicon	20·04	19·12	19·25 per cent.
Cobalt	80·70	80·28	80·75 ,,

E. **Copper silicide.**

Vigouroux[1] obtained a silicide of the formula Cu_2Si by heating together, in the electric furnace, 10 parts of silicon and 90 parts of copper, and driving away the excess of metal by raising the temperature. This substance is very hard and brittle and a fresh fracture shows a steel grey colour which gradually becomes reddish. The compound was analysed by treatment with a mixture of alkaline carbonate and nitrate. and further treatment with hydrochloric acid.

F. **Tungsten silicide.**

This was obtained by Vigouroux[2] by heating a mixture of tungsten oxide and silicon in the electric furnace. One obtains a well-crystallized body corresponding to the formula W_2Si_3.

Conclusions.—In short, the action of silicon on the metals may yield three different results.

1. The solid silicon may, owing to its vapour-pressure, combine with the metal and yield, by an action similar to that of cementation, a true silicide, the melting-point of which is lower than that of the metal.
2. The liquid silicon may unite with the fused metal in the electric furnace.
3. The silicon dissolves in the liquid metal, forming however no compound with it, or a very unstable one, and is deposited as crystallized silicon at the moment of solidification of the metal.

G. **Silicide of carbon**[3].

The amorphous silicide of carbon of the formula SiC was discovered by Schützenberger[4].

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[1] *C. R.*, cxxii. 318 (1896).

[2] ibid., cxxvii. 393 (1898).

[3] Moissan, ibid., cxvii. 425 (1893).

[4] ibid., cxiv. 1089 (1892).

By heating in the electric furnace a mixture of silica, coke, alumina, and sodium chloride, E. G. Acheson has obtained a crystalline carbon silicide coloured blue by iron. He has since realized the commercial preparation of this compound, which is of use on account of its great hardness, and to which the name carborundum has been given.

In the researches which I have carried out on the crystallization of carbon, I had occasion to find in 1891, in the masses of silicon fused in the blast furnace, small crystals of a silicide of carbon in the middle of a brasque of carbon. I did not, however, publish anything on this subject at the time, and the discovery of the crystallized carbon silicide really belongs to Acheson.

The study of the action of the electric arc on silicon has led us to prepare this silicide, finely crystallized, in four different ways.

1. **Direct combination of silicon with carbon.**—In attempting to make carbon dissolve in silicon kept at its melting-point in a wind furnace, we obtained this compound in fine crystals the length of which sometimes reached several millimeters; these crystals were detached by dissolving the mass of silicon in a boiling mixture of pure HNO_3 and hydrofluoric acid. This first preparation showed us that the silicide of carbon is readily formed in presence of a solvent at a temperature of 1,200°–1,400° C.

2. **Preparation in the electric furnace.**—The same compound may be obtained much more simply, by heating in the electric furnace a mixture of 12 parts of carbon and 28 of silicon. Under these conditions a mass of crystals is obtained which are well purified first of all by a boiling mixture of pure HNO_3 and hydrofluoric acid, and then by treating with the oxidizing mixture of Berthelot, nitric acid and potassium chlorate. The crystals are most often coloured yellow, but may be quite transparent, and sometimes show a sapphire blue colour. The transparent crystals are obtained by carrying out the preparation quickly in a crucible of compressed carbon, and using silicon as free as possible from iron.

3. **Crystallization from molten iron.**—Silicide of iron is heated in the electric furnace with excess of carbon. The regulus, remaining after the experiment, is treated with aqua regia to remove the whole of the iron. The crystalline residue is then heated for several hours with a mixture of anhydrous

nitric acid and hydrofluoric acid, and finally treated eight or ten times with the potassium chlorate oxidizing mixture. One obtains similarly a metallic regulus containing crystals of carbon silicide by heating in the electric furnace a mixture of iron, silicon, and carbon, or more simply a mixture of iron, silica, and carbon.

4. **Reduction of silica by carbon.**—The same compound may be obtained by reducing silica by carbon in the crucible of the electric furnace. The crystals of carbon silicide so obtained are less coloured than those obtained by solution in iron, if care be taken to use pure silica and carbon.

5. **Action of carbon vapour on silicon vapour.**—A more novel method of preparing carbon silicide consists in allowing the vapours of carbon and silicon to react on one another. The experiment is carried out in a small elongated carbon crucible, containing a fused mass of silicon. The bottom of the crucible is heated to the highest temperature of the electric furnace. At the end of the experiment one finds in the apparatus prismatic needles of carbon silicide, which are almost colourless, very hard, and brittle.

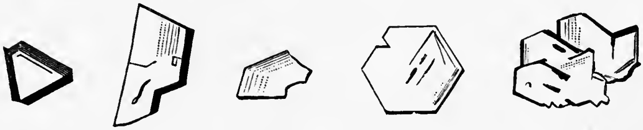

FIG. 42.—Carbon silicide. × 10.

Properties.—The crystallized silicide of carbon is, as we have seen, a compound formed at a high temperature. Its stability is very great, since it is unaffected by the most powerful reagents. This property had previously been clearly demonstrated for the amorphous compound by Schützenberger.

Carbon silicide, when free from traces of iron, is colourless; its well-defined crystals sometimes appear as regular hexagons (Fig. 42).

Some of the crystals show, but rarely, triangular markings and parallel striae; the practised eye can distinguish them at once from those of the diamond. Further, these crystals affect polarized light, showing beautiful iridescent colours.

Their density is 3·2, they are extremely hard, scratching both chrome steel and the ruby. It is sufficient to rub the polished surface of a ruby with some powdered carbon silicide on a hard wood point to cause deep and well-defined scratches. Heated in oxygen to a temperature of 1,000° C. the crystals are unchanged. Similarly they may be calcined in air by means of the Schloesing blowpipe without any trace of oxidization. Sulphur vapour does not attack them at 1,000° C.

Heated to 600° C., in a current of chlorine for one and a half hours, the crystals are only superficially acted on[1]. The reaction is complete at a temperature of 1,200° C. Fused potassium chlorate and potassium nitrate have no action at all. The same is the case with boiling sulphuric and hydrochloric acids. The mixture of mono-hydrated nitric acid with hydrofluoric acid, which dissolves silicon so readily, is without action on crystals of carbon silicide. Lead chromate oxidizes this compound, but in order to bring about complete combustion in a glass tube, the operation must be repeated several times on the same sample.

Fused caustic potash disintegrates this silicide, causing it first of all to cleave in a regular manner and then, after heating to dull redness for an hour, it dissolves it with the formation of potassium carbonate and silicate. This last reaction may be used to determine the silica, whilst the carbon may be weighed as carbon dioxide after combustion with lead chromate.

Analysis.—The carbon was determined in 0·1 to 0·2 gram of the silicide, which was heated with lead chromate in a platinum boat to a temperature a little above 1,000° C. The experiment was conducted in a tube of Berlin porcelain traversed by a continuous stream of oxygen. The silicon, weighed as silica, was obtained by fusing 0·2 gram of the silicide with a mixture of potassium nitrate and carbonate; the residue was taken up by hydrochloric acid, and then evaporated to dryness. After the fusion, the analysis is carried out in the same way as the determination of silica in a silicate. The following figures were obtained in this way:

	1	2	Theory.
Silicon	69·70	69·85	70·00 per cent.
Carbon	30·00	29·80	30·00 ,,

These analyses show that the crystals of carbon silicide, obtained by the various methods described above, all correspond to the formula SiC.

At the temperature of the electric arc, there is produced only a single compound of silicon and carbon, the simplest

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[1] Under these conditions the loss of weight on 0·28 gram was only 0.012.

possible, containing a molecule of each element. This silicide, possessing such great stability, is a type of these new compounds prepared with the aid of the electric furnace.

BORIDES

Boron is capable of yielding, like silicon and carbon, several series of well-defined crystalline compounds. The study of these new bodies will enrich the chemistry of bodies which are sometimes very stable, and some of which will probably find various industrial applications.

Further, they will furnish useful criteria for the classification of the elements and the establishment of their valencies.

A. Boride of iron.

We shall study first of all the preparation of iron boride, which may serve as a type for the preparation of a certain number of metallic borides.

Moreover, this preparation followed quite naturally from the action of boron on the carbides of iron, and it has enabled us, in collaboration with G. Charpy[1], to take up the study of boron steels.

Preparation of boride of iron.—This new compound may be obtained 1. By the action of chloride of boron on reduced iron. 2. By the direct action of boron on iron.

1. **Action of chloride of boron on reduced iron.**—Pure reduced iron is placed in a porcelain tube traversed by a slow current of boron trichloride vapour, and heated to dull redness. The volatile ferric chloride is at once produced and there remains in the tube a grey, amorphous boride of iron.

2. **Action of boron on iron.**—This preparation may be carried out in a tube furnace heated by a good coke fire. A porcelain boat is lined with the necessary quantity of boron, and on this is placed either Swedish iron, or reduced iron. A slow current of hydrogen is passed through the tube, which is heated to between 1,100 and 1,200° C.

After cooling in a stream of hydrogen, one obtains a metallic regulus which, when the proportion of boron is about 9 per cent., has a well-marked crystalline texture, and breaks easily along certain well-defined planes of cleavage. The mass is traversed by long needles which often show iridescent colours.

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[1] *C. R.*, cxx. 130 (1895).

When a cylinder of soft iron is placed on pure amorphous boron, under the conditions just described, the boron brings about true cementation, and long before the melting-point of iron, which could not be reached in this apparatus, the fusion of the boron cast iron takes place readily. This boron cast iron, when it contains 8 to 9 per cent. of boron, fuses at a temperature much below that of ordinary cast iron. This temperature has been found by the Le Châtelier thermo-electric couple to be about 1,050° C. If the proportion of boron reaches 15 per cent., the fusion becomes much more difficult, the regulus shows a conchoidal fracture and the crystalline structure is not clear. A mixture containing 20 per cent. of boron is only fused with difficulty by a good coke fire, or even by a furnace heated with gas carbon; it is better under these conditions to use the electric furnace.

Boron cast iron may also be obtained by heating, in the electric furnace, fragments of good soft iron, in a carbon crucible lined with boron. The reaction can then be carried out with larger quantities, and, with a current of 300 amperes at 65 volts, the heating need only last five to six minutes. If the temperature be too high, the carbon of the crucible takes part in the reaction, and the boron cast iron contains a variable quantity of the crystallized boride of carbon. The metallic ingots, prepared either in the tube furnace or in the electric furnace, are crushed and treated with hydrochloric acid diluted with two to three times its volume of water. In this way the excess of iron is dissolved and there remains behind a crystalline mass, which is washed with water and then with alcohol and ether to avoid the simultaneous action of carbon dioxide and moisture during drying. The crystals obtained in this way have a constant composition corresponding to the boride of iron BFe.

Properties.—Iron boride appears in bright crystals of a yellowish grey colour, several millimeters in length. Its density is 7·15 at 18° C. These crystals remain unchanged in dry air or oxygen. In moist air they are rapidly covered with a yellowish deposit[1]. Heated to redness in a stream of chlorine, they are attacked with incandescence, chlorides

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[1] If one uses a tube over mercury, a small quantity of water and a known quantity of air, it is found after twenty-four hours that there is a marked diminution in the quantity of oxygen, and that each particle of boride is covered with a gelatinous deposit having the appearance of rust.

of iron and boron being formed; bromine attacks this compound more easily and there appears to be formed a double bromide of boron and iron. Both iodine and hydriodic acid are without action at 1,100° C.

Iron boride burns brightly when heated in oxygen, and the combustion, when once started, is complete without any further heating. In all these experiments, the amorphous boride was found to be more readily attacked than the crystalline form. Since this action of oxygen is increased when the powdered boride is brought in contact with moisture and carbonic acid, the phenomenon of incandescence sometimes observed during the drying of impure boron, prepared by the action of sodium on boric acid, is to be attributed to the existence of this boride of iron.

Amorphous boron is attacked by sulphur at a temperature slightly above its melting-point. The crystallized boride is similarly attacked, with incandescence, but at a higher temperature. At a red heat phosphorus yields a mixture of the phosphides of iron and boron. Potassium chlorate at its melting-point does not attack iron boride, but on raising the temperature, action commences which goes on with incandescence. The same is the case with fused potassium nitrate.

The fused alkaline carbonates decompose iron boride rapidly, the reaction being complete in a few moments.

Fused potash attacks it vigorously, but without incandescence.

Sulphuric acid, concentrated or dilute, is without action in the cold; on boiling, it decomposes the boride with evolution of sulphur dioxide and formation of anhydrous ferrous sulphate. Concentrated hydrochloric acid acts slowly on heating, whilst the dilute acid has no action at all. As was shown above, this renders possible the separation of the boride from excess of iron. Hydrofluoric acid solution only acts slowly, both in the cold and on heating. The best solvent for iron boride is nitric acid, and consequently, aqua regia. Dilute nitric acid only dissolves it on heating, but fuming nitric acid attacks it violently.

Analysis.—The iron has always been determined as Fe_2O_3; it was not possible to use permanganate solution with this compound. The boron was determined as calcium borate, using Gooch's method of separating the boric acid with methyl alcohol.

In this analysis the iron boride was acted on with nitric acid in a special apparatus, designed for the purpose, which has previously been described[1]. After the evolution of gas had ceased, the boric acid was distilled off with methyl alcohol and the distillate treated with quicklime. From the increase of weight of the lime the percentage of boron was calculated. In this way the following figures were obtained:

	1	2	3	Theory for FeB.
Iron . .	84·15	84·48	83·86	83·58 per cent.
Boron . .	15·18	14·94	15·19	16·42 ,,

The slight excess of iron shown in these analyses is due to the fact that the boride crystals always retain a trace of enclosed iron. The amorphous boride, obtained by the action of boron trichloride on reduced iron, furnished more exact figures (analysis 3). These analyses fix the formula of this crystalline compound as FeB.

By raising the temperature of the electric furnace at the moment of the formation of the boron cast iron, we have never been able to obtain any other compounds. At these high temperatures chemistry seems to become simpler, and one obtains only a single compound, always possessing a very simple formula.

B. Borides of nickel and cobalt.

The borides of nickel NiB and cobalt CoB may be obtained in a pure crystalline state by the methods which have already served for the preparation of iron boride, viz. by the direct combination of boron with the metal. The experiment may be carried out either in the electric furnace or in an ordinary reverberatory furnace heated by gas carbon.

Preparation in the electric furnace.—The metal is placed in a carbon crucible lined with powdered boron, and heated for five minutes using a current of 300 amperes at 50 volts.

Preparation in the reverberatory furnace.—A porcelain boat is lined with 10 to 12 grms. of powdered boron. On this is placed 100 grms. of the metal, and the boat is then heated in a porcelain tube in a very slow stream of pure, dry hydrogen.

Whichever method of heating be employed, a brittle metallic regulus is obtained, consisting of the crystalline boride together with the excess of the metal. When the electric furnace is used the crystalline structure is less well

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[1] *C. R.*, cxvi. 1087 (1893).

defined. These metallic ingots are crushed and attacked by nitric acid diluted with its own volume of water. In the case of cobalt one can even use the commercial concentrated acid.

When the action is over, a crystalline boride remains, as a rule in the form of prisms, and closely resembling in appearance the corresponding iron compound. The boride is then washed with distilled water, alcohol, and ether, and finally dried rapidly in the oven, since these compounds readily change in moist air.

Physical properties.—The borides of nickel and cobalt appear in brilliant prisms, several millimeters in length. The density of cobalt boride at 18° C. is 7·24. That of nickel is 7·39. These two compounds scratch quartz with difficulty and are magnetic.

Chemical properties.—Chlorine attacks these two borides with incandescence below a dull red heat; boron trichloride is given off and a sublimate is formed which is yellow in the case of nickel, and blue with cobalt.

With bromine the action takes place without incandescence just below a red heat. Boron tribromide distils over and a residue green in the case of cobalt and yellow with nickel remains behind. The borides of nickel and cobalt prepared in the electric furnace are scarcely attacked by iodine at the melting-point of glass. On the other hand, the same compounds prepared in the reverberatory furnace are distinctly attacked under identical conditions.

At the ordinary temperature these borides are not decomposed by oxygen or by dry air, but they change rapidly in moist air, more especially in presence of carbonic acid. Below dull redness these borides burn brightly in pure oxygen. They are attacked by sulphur vapour at about 700° C. with incandescence. At its melting-point, potassium chlorate is without action, but if the temperature be raised, the borides are attacked with considerable evolution of heat. Potassium nitrate behaves similarly, but reacts less vigorously and without incandescence.

A mixture of sodium nitrate and carbonate causes a complete conversion into the black oxide and the alkaline borate. The alkaline carbonates and alkalies when fused dissolve the borides without incandescence.

When heated in a current of steam to dull redness, the borides of nickel and cobalt are decomposed forming an oxide, the boric acid being carried off by the steam.

Hydrochloric acid, especially when dilute, has little action.

Nitric acid, on the contrary, attacks them vigorously and the action of a mixture of nitric and hydrochloric acids is very violent. Dilute sulphuric acid has no action at all, whilst strong sulphuric acid on boiling causes the evolution of sulphur dioxide.

Analysis.—1. The boride was acted on by dilute nitric acid in the apparatus already described for the determination of boron. The boric acid driven off with methyl alcohol was weighed as calcium borate, using the same method as before. The nickel and cobalt left in the nitric acid solution were precipitated as oxide by potash, washed by decantation with boiling water, and weighed as metal after reduction in a stream of hydrogen.

2. The boride was fused with a mixture of potassium nitrate and carbonate; on taking up with water, the cobalt or nickel remains insoluble as oxide, and is weighed as metal. The potassium borate is introduced into the apparatus for the determination of boric acid, nitric acid is added and the analysis continued as above.

We have obtained in this way the following figures, using the atomic weights, nickel = 58·6, and cobalt = 58·7.

	1	2	3	Theory for NiB.
Nickel . .	85·45	85·11	84·12	84·19 per cent.
Boron . .	14·51	14·88	14·43	15·81 ,,

	1	2	3	4	Theory for CoB.
Cobalt .	83·68	84·06	83·85	85·37	84·22 per cent.
Boron .	15·89	16·04	—	—	15·78 ,,

Conclusions.—The borides of nickel NiB and cobalt CoB are readily obtained in a crystalline form at 1,200° C. The properties of these new compounds are analogous to those of iron boride already described. These borides permit the taking up of boron by a metal such as iron, since, as we have shown[1], at a high temperature, boron and silicon displace carbon from molten cast iron.

C. Boride of carbon.

When dealing with the action of the electric arc[2] on boron, silicon, and carbon, we have already called attention to the existence of new crystalline compounds formed at very high temperatures, which are unaffected by most reagents, and possess very great hardness equalling, and in some cases exceeding, that of the diamond.

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[1] *C. R.*, cxix. 1172 (1894).

[2] ibid., cxvii. 423 (1893).

Several methods have already been described for the preparation of carbon silicide[1], and we shall now describe a similar compound, boride of carbon.

Wöhler and Deville[2] pointed out in 1857 the existence of a variety of boron to which they gave the name of 'adamantine boron.' W. Hampe[3], on repeating the work, showed that one was dealing with a mixture of different compounds containing in particular a boride of aluminium and a carbo-boride of aluminium, both being definite crystalline compounds.

In his more recent work on this subject, A. Joly[4] has been able to isolate from this mixture a small quantity of boride of carbon, the determination of the carbon in which, after treating with chlorine, led him to ascribe to it the formula B_6C. When boron and carbon are caused to react at the temperature of the electric furnace two borides are formed; the one acted upon by a mixture of potassium chlorate and nitric acid, the other unacted upon. The latter corresponds to the formula B_6C; it is this compound which we shall now describe.

Formation.—This boride of carbon may be obtained:

1. When an electric arc is caused to pass between two poles of carbon agglomerated with a mixture of boric acid and aluminium silicate. Under these conditions it is always contaminated with carbon silicide.

2. When a small quantity of boron is placed in the middle of the electric arc playing between two carbon poles.

3. By heating pure boron to about 3,000° C. in the electric furnace, in a small carbon crucible fitted with a lid.

4. This boride is also formed in the interior of fused metals. It is produced when a boride of iron rich in boron is heated in a carbon crucible in the electric furnace. The fused regulus obtained is treated first with hydrochloric and then with aqua regia, and one obtains in this way a black residue consisting of graphite and of boride of carbon. If for this experiment one uses siliceous cast iron the residue obtained, after treatment with acids, consists of boride of carbon and carbon silicide.

5. By dissolving a mixture of sugar carbon and pure boron in silver or copper heated in the electric furnace; very well-defined crystals of carbon boride are obtained by this method.

1. **Preparation by the direct union of boron and carbon.**—Sixty-six parts of amorphous boron and twelve parts of sugar

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[1] *C. R.*, cxvii. 425 (1893).

[2] *Ann. de Ch. et de Phys.*, sér. 3, lii. 63 (1858).

[3] *Liebig's Ann.*, clxxxiii. 75 (1876).

[4] *C. R.*, xcvii. 456 (1883).

carbon are heated in the electric furnace, in a carbon crucible using a current of 250–300 amperes at 70 volts. The reaction is complete in six or seven minutes. After cooling the crucible, a black mass is obtained resembling graphite in appearance, showing a bright fracture and evidence of the beginnings of fusion. After prolonged treatment with fuming nitric acid, the mass disintegrates and a crystalline powder is left which is treated six times with potassium chlorate and anhydrous nitric acid, washed with water and then dried.

2. **Preparation by dissolving in iron boride.**—Iron combines readily with boron producing definite borides which have been already described. When iron is heated in the electric furnace with excess of carbon and boron, under the conditions described above, a regulus is formed showing a very bright fracture.

After removing the excess of metal with aqua regia, the residue consists almost entirely of boride of carbon. The crystals in this case are badly defined; after being treated six times with potassium chlorate they are free from graphite, and their analysis leads to the formula B_6C.

3. **Preparation by dissolving in copper and in silver.**—Since iron readily dissolves a considerable excess of boron, we have endeavoured to employ, in this preparation, metals which at the moment of cooling do not form definite compounds with this metalloid. Silver and copper, particularly the latter, have yielded the best results.

The boride of carbon obtained in silver is, after the removal of the metal by nitric acid, very pure, but its crystallization is not definite.

With copper, on the other hand, brilliant crystals are obtained which are very well defined. An intimate mixture of boron and sugar carbon is prepared as described above (boron 66, carbon 12), and 15 grms. are placed in a carbon crucible with 150 grms. of pure copper turnings[1]. The mixture is heated for six to seven minutes using a current of 350 amperes at 70 volts. After a few moments a malleable ingot is withdrawn from the furnace, which has retained the appearance of metallic copper, but is slightly blackened on the surface. The process of fusion is so rapid that in three hours a number of these ingots sufficient for the preparation of about 200 grms. of the boride can readily be obtained.

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[1] Care must be taken that the copper turnings are free from sand which would form the crystallized carbon silicide.

By simple treatment with ordinary nitric acid, the well-crystallized boride is obtained, containing only a trace of graphite. To remove the latter body, the mixture is treated six to eight times with dry potassium chlorate and concentrated nitric acid, then boiled with sulphuric acid for several hours. Finally it is again digested with the mixture of potassium chlorate and nitric acid, then washed with water and dried.

Properties.—As we have said above, this boride belongs to the same class of compounds as carbon silicide. Like it, it possesses great stability and great hardness; carbon boride occurs in brilliant black crystals of density 2·51. As was noticed by Joly, chlorine attacks it below 1,000° C. without incandescence. Boron trichloride is formed and very bright porous carbon remains. Bromine and iodine are without action. Heated in oxygen to 500° C. it does not yield carbon dioxide, but at 1,000° C. it burns brightly, but with more difficulty than the diamond, yielding carbon dioxide and a black residue covered with fused boric acid. Sulphur does not react with carbon boride at the melting-point of glass. The same is the case with phosphorus and nitrogen at 1,200° C. This compound is unacted on by all acids. Concentrated hydrofluoric acid, anhydrous nitric acid, or a mixture of the two have no action even when boiling. Heated with fuming nitric acid for four hours at 150° C. in a sealed tube, nothing goes into solution. Concentrated solutions of iodic and chromic acids are without action, either on boiling or on heating in sealed tubes to 150° C. At a dull red heat it is attacked by fused potash, and by a fused mixture of sodium and potassium carbonates.

The most interesting property of this new compound is its excessive hardness; whilst carbon silicide will scarcely polish a diamond and will not cut it, we have been able to produce facets on a diamond by using powdered carbon boride. This compound is in fact very friable; a fine powder can be obtained in a steel crushing mortar, and mixed with oil it may be used in place of diamond powder on a steel wheel for cutting diamonds. It appears to be less hard than the diamond, because the grinding is slower, but the facets are very sharply cut; this compound and titanium carbide are the first examples of definite bodies which will grind the diamond. This compound is thus considerably harder than carbon silicide.

Analysis. **Determination of carbon.**—The carbon was determined by two different methods. 1. By acting on the boride with chlorine, heating the resultant mass in a boat in a stream of hydrogen, and finally burning the carbon in oxygen; from the weight of carbon dioxide absorbed the percentage of carbon was calculated.

2. A known weight of the boride was mixed with large excess of lead chromate, and heated to a high temperature in a porcelain tube. The carbon dioxide was absorbed and weighed and the percentage of carbon calculated.

Determination of boron.—The boride of carbon is fused with a mixture of sodium and potassium carbonates in a platinum crucible; taken up with water, nitric acid added and the boron determined by methyl alcohol and lime by Gooch's method[1], using the apparatus which we have previously described[2].

The following figures were obtained[3]:

	1	2	3	Theory.
Boron . .	84·57	84·19	84·52	84·62 per cent.
Carbon . .	15·60	14·91	15·55	15·38 ,,

BORIDES OF THE ALKALINE EARTH METALS[4]

An intimate mixture of 10 grms. of pure boron and 50 grms. of quicklime was placed in a carbon tube closed at one end and heated for seven minutes in the electric furnace (900 amperes at 45 volts). After cooling, there was found in the tube a fairly hard, brittle, fused mass with no crystalline structure. This substance is only slowly attacked by water, but dissolves almost completely in hydrochloric acid, leaving a very small residue. The latter, examined under the microscope, was found to contain graphite and some cubic crystals which are yellow when small, but darker coloured if large. These crystals, which are not attacked by hydrochloric acid, dissolve quickly in nitric acid and contain only boron and calcium.

The yield being very small, the reaction was carried out in another way. A mixture of 10 grms of calcium carbide and 1 grm. of pure boron is heated in the furnace. The boron does not seem to displace the carbon from the carbide; a small amount of calcium boride is formed, but this seems to be due to the dissociation of the carbide rather than to any definite action of boron on the carbide.

The same result is obtained by acting on calcium borate

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[1] *Amer. Chem. Journal*, ix. 23 (1887).

[2] *C. R.*, cxvi. 1087 (1893).

[3] Cf. H. Gautier. Atomic weight cf Boron. *Ann. de Ch. et de Ph.*, sér. 7, xviii. 352 (1899).

[4] Work done in conjunction with P. Williams.

with sugar carbon or with calcium carbide at the temperature of the electric furnace.

To increase the yield the boron must be produced in the midst of the mixture. This result is achieved as follows.

D. Preparation of calcium boride.

A mixture is made of 1,000 grms. of perfectly dry calcium borate, 630 grms. of pure aluminium in pieces, and 200 grms. of finely powdered sugar carbon, both being carefully dried. The borate is first mixed with the carbon and then the aluminium is added. The whole is heated for seven minutes in a carbon crucible by means of a current of 900 amperes at 45 volts. The amount of aluminium is sufficient to reduce the borate completely. The addition of carbon prevents the formation of alumina, which is very difficult to separate from the calcium boride. Part of the aluminium is found afterwards as carbide, which is easily decomposed by water and dilute acids.

The length and the regularity of the heating exert a great influence on the yield of calcium boride.

The fused lumps obtained on cooling are homogeneous, crystalline, and metallic-looking. They are broken up into small pieces and treated with dilute hydrochloric acid till nothing more dissolves out. Large volumes of unpleasant smelling gases are evolved during the process, consisting of hydrogen, acetylene, methane, and boron hydride. The residue is treated with boiling concentrated hydrochloric acid and then washed with water. The residue then obtained contains chiefly calcium boride together with a small amount of organic matter of low density obtained by the action of hydrochloric acid on the fused mixture. The latter may be separated by reason of its low density. On treating the residue with ether and toluene, these liquids assume an intense colour due to the extraction of another organic substance which may be obtained by evaporating off the solvent. It is a brown gummy substance, which gives with fuming nitric acid a pale yellow nitro-derivative easily soluble in ether. We are investigating this substance further.

After washing repeatedly with ether and toluene, the calcium boride is heated with hydrofluoric acid. The residue is washed with water, dried and digested with ether till the latter remains uncoloured. The crystalline powder so obtained is washed with water, then with alcohol, and finally dried in vacuo.

This crystalline powder is not absolutely pure, but still contains a small amount of graphite and carbon boride.

Physical properties.—Calcium boride is a black, shining, crystalline powder, seen under the microscope to consist of right-angled or cubic crystals which, when very thin, are transparent or faintly yellow.

The compound marks quartz with ease and is hard enough to scratch the ruby. It has a density of 2·33 at 15° C. On heating in the electric furnace it fuses to a homogeneous mass, possessing a crystalline fracture.

Chemical properties.—Calcium boride may be heated to redness in hydrogen without change. Fluorine attacks it in the cold with incandescence; chlorine acts at a red heat, evolving a considerable amount of heat and forming the chlorides of calcium and boron. Bromine and iodine react at the same temperature, but more slowly.

On heating in the air, calcium boride only catches fire at a bright red heat. Sulphur vapour acts at the same temperature. The compound is not decomposed on heating to 1,000° C. in a stream of nitrogen.

Water exerts no action at ordinary temperatures, and the compound in this behaves quite differently from calcium carbide. It may be heated in water, under pressure, up to 250° C. without change. The change is very slow in steam at even higher temperatures; the heating must be continued up to 1,000° C. to obtain any considerable quantity of gas.

As already noticed, calcium boride may be fused in the electric furnace. In this fused condition, it is acted on by water with evolution of hydrogen and hydrogen boride.

This reaction seems to point to the existence of a second boride containing less boron which is decomposed by water.

The halogen hydracids in the gaseous state act slowly on calcium boride at dull redness. Ammonia is without action at the softening-point of glass.

Aqueous hydracids have no action, nor has dilute sulphuric acid, while the concentrated acid acts with production of sulphur dioxide. Nitric acid, whether dilute or concentrated, acts energetically.

Oxidizing agents, such as lead peroxide or fused nitre, react violently at a red heat. Bromine water or a mixture of potassium chlorate and hydrochloric acid decompose the boride slowly. The carbonate, bisulphate, and fused hydrate of potassium react vigorously at a red heat.

Analysis.—The calcium boride is treated with nitric acid directly in the vessel used for the estimation of the boron, the latter carried out by the method of Gooch[1]. The boric acid is expelled by methyl alcohol and the calcium in the residue is converted into the oxalate, the latter is calcined and the oxide formed is weighed.

In order to determine the small amount of carbon present as impurity, the substance was decomposed by means of pure chlorine; the residue is taken up with water to remove the soluble calcium chloride, the solution filtered, the residue washed and finally burnt in oxygen. The carbon dioxide formed is absorbed in potash bulbs and weighed.

The residue insoluble in nitric acid is washed, dried at 110° C. and weighed. It consisted of small, unattacked crystals of carbon boride B_6C.

The following figures were obtained:

	1	2	
Calcium . . .	36·22	36·03	per cent.
Boron	57·43	57·30	,,
Carbon	2·66	2·82	,,
Insoluble . . .	1·21	1·02	,,

By working out the figures obtained for calcium and boron for 100 parts of pure boride, one obtains:

	1	2	
Calcium . . .	38·66	38·61	per cent.
Boron	61·33	61·39	,,

These figures are not far from those required by the formula CaB_6, these being

Calcium . . .	37·86	per cent.
Boron . . .	62·14	,,

E. Strontium boride.

This was obtained in the manner described for calcium boride, by fusing together strontium borate, aluminium, and carbon in the electric furnace. This compound is very dense and may be obtained in a pure state by removing most of the impurities by treatment with bromoform.

Physical properties.— Strontium boride is obtained as a black powder, consisting of small crystals which, under the microscope, are seen to be transparent if not too thick, and of a reddish-brown tint. The crystals are larger than those of calcium boride and scratch quartz easily. Their density is 3·28 at 15° C.

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[1] *Amer. Chem. Journal*, ix. 23 (1887).

Chemical properties.—These are very similar to those of calcium boride; it does not, however, catch fire in fluorine in the cold, but requires to be first heated gently.

Analysis. This was carried out as for calcium boride:

	1	2	Theory for SrB_6.
Strontium . . .	56·33	56·56	57·10 per cent.
Boron . . .	43·38	43·00	42·90 „
Carbon . . .	0·67	0·63	— „
Insoluble . .	trace	trace	— „

F. Barium boride.

This compound was obtained by the above method, but is more easily prepared than either of the two preceding borides. The yield is larger and purer, thanks to the high specific gravity of the compound.

Properties.—These are similar to the properties of the borides just described. The crystals are small but very regular and have a density of 4·36 at 15° C. The chemical properties are identical with those of the borides of calcium and strontium. The compound is very hard, scratching quartz and the ruby but not the diamond.

Analysis.

	1	2	Theory for BaB_6.
Barium . . .	67·20	67·09	67·57 per cent.
Boron . . .	32·25	32·28	32·43 „
Carbon . . .	0·29	0·31	— „
Insoluble . .	trace	trace	— „

G. Beryllium borocarbide.

This compound, obtained by P. Lebeau[1], seems to us to be of great interest, as it is an example of the double compounds one may expect to prepare with ease in the electric furnace.

A mixture of 75 parts of beryllia and 45 parts of boron, moistened with a little alcohol, is compressed and dried at 150° C. It is placed in a carbon tube and heated for seven or eight minutes in the electric furnace by means of a current of 980 amperes at 45 volts. One obtains a metallic-looking mass which gave on analysis:

	1	2	Theory for $Be_6B_6C_4$.
Beryllium . .	32·83	32·54	32·33 per cent.
Boron . . .	39·18	39·12	39·17 „
Carbon . . .	27·99	28·34	28·49 „

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[1] *C. R.*, cxxvi. 1347 (1898).

METALLIC PHOSPHIDES

The compounds consisting of phosphorus and a metal were hitherto not well characterized and of doubtful composition. The use of the electric furnace has led to a general method of preparation of well-defined phosphides, stable at high temperatures.

Phosphides of the metals of the alkaline earths.—As far back as 1845, Paul Thénard[1] obtained an amorphous, vermilion red product by the action of phosphorus vapour on red-hot lime, for which he gave the formula $P_2.CaO$. This phosphide of lime was decomposed by water and this reaction led to the preparation and characterization of the different hydrides of phosphorus.

Before this, Dulong had given a general method for the preparation of phosphides by the action of phosphorus vapour on metals. The work was subsequently repeated by P. Vigier.

This method could only be used when pure metallic calcium was available; but this was not obtainable previous to our researches.

Preparation of crystalline calcium phosphide.—Calcium phosphide may be obtained by the reduction of tricalcium phosphate by carbon in the electric furnace. The preparation requires some care, as this compound is comparatively easily decomposed at high temperatures. The pure phosphate was obtained by precipitation, dried and ignited in a Perrot furnace, it was then powdered and mixed with carbon in the following proportions:

Tricalcium phosphate . .	310 parts.
Lampblack	90 ,,

The mass was ground with a little turpentine and compressed into small cylinders, which were then placed in a tube covered with carbon and heated once more in a Perrot furnace. The mixture is then placed in a crucible in the electric furnace and heated for four minutes by means of a current of 950 amperes at 45 volts.

After cooling, one finds in the crucible a fused mass which should not adhere to the sides, this only happening when the heating has been too prolonged. In this case the outer layers of the calcium phosphide are contaminated with some

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[1] *Ann. de Ch. et de Ph.*, sér. 3, xiv. 12 (1845).

calcium carbide. When the heating has been too short, the phosphide is mixed with fused unreduced phosphate and its red crystals are distinctly seen in the mass.

Only a very small quantity of phosphorus vapour is evolved during the preparation. If, however, the heating be continued after the reduction is complete, the calcium phosphide is decomposed and the phosphorus distils off in large quantities and burns as it issues from the furnace. Finally, the calcium and the carbon unite and there remains calcium carbide alone, containing but traces of phosphide.

So that it is extremely important not to prolong the heating if one wishes to prepare pure calcium phosphide in this way.

Fused calcium phosphide may also be obtained from the lime phosphide of Thénard, this being obtained by acting on red-hot lime with an excess of phosphorus vapour. This compound is placed in a carbon crucible and heated for seven to eight minutes by means of a current of 800 amperes at 50 volts. One obtains in this way a well-fused, dark red mass which is contaminated with calcium carbide.

Properties. — Calcium phosphide, prepared in the electric furnace, occurs in reddish-brown pieces, whose colour recalls that of calcium nitride. The fracture is crystalline, and, when the reduction is not complete, one finds well-defined dark red crystals amongst the fused phosphate.

This phosphide is very refractory and could not be fused except in the electric furnace.

It decomposes slowly in vacuo at the softening-point of Bohemian glass, and the evolution of a small amount of phosphorus vapour may be distinctly observed. The dissociation pressure reaches only a few millimeters. The density of the compound is 2·51 at 15° C. It is apparently undecomposed by heating to 900° C. in hydrogen. Chlorine has no action in the cold; on heating gently to 100° C., the reaction begins and goes on with incandescence, with production of calcium chloride and vapours of phosphorus chloride. Bromine behaves similarly while iodine reacts at a dull red heat. Calcium phosphide burns brilliantly in oxygen at 300° C., forming lime and phosphoric anhydride. Sulphur also reacts at 300° C., decomposition taking place with considerable evolution of heat, forming a yellow sublimate and calcium sulphide.

The action of nitrogen on calcium phosphide seemed to be of special interest. For, if nitrogen could replace phosphorus in this compound, this would be a convenient method of passing from the phosphide to the nitride. As one knows, calcium nitride is decomposed by water, evolving ammonia, and this reaction might find some technical application. But the heat of formation of calcium phosphide seems to be greater than that of calcium nitride, as all efforts failed to bring about this reaction, even at 900° C. At 1,200° C., the calcium takes up a certain amount of nitrogen, and, at the same time, some phosphorus is evolved; but the reaction is far from being complete. The residue gives, on treatment with water, a mixture of ammonia and phosphuretted hydrogen, but the latter is in large excess. One is dealing here with the dissociation of calcium phosphide. No reaction takes place on heating the compound in arsenic vapour at the softening-point of glass. Boron and carbon have no action at 700° C.; but, in the electric furnace, carbon replaces the phosphorus, forming fused calcium carbide.

The halogen hydracids in the gaseous state act violently; hydrochloric acid gas decomposes the compound at a red heat, with incandescence.

Neither sulphuretted hydrogen nor ammonia seems to react at 700° C.

The reaction of calcium phosphide with water is of special importance; the compound is decomposed at once by cold water, forming calcium hydrate and phosphuretted hydrogen. The presence of calcium hydrate retards the action when the phosphide is in crystalline masses, but it becomes very energetic if the phosphide is powdered.

If the heating in the electric furnace has been sufficiently long, the phosphuretted hydrogen formed by the action of water on the phosphide is not spontaneously inflammable. This is a characteristic difference from the body prepared by Thénard. The decomposition is, however, a complex one, for the phosphorus of the calcium phosphide is not all obtained as the hydride PH_3. Some samples, which had been heated for a shorter time, gave phosphuretted hydrogen containing free hydrogen. When, on the other hand, the phosphide had been strongly heated it no longer gave hydrogen with water, but a little acetylene could be detected. Acids act on calcium phosphide according to the proportion of water they contain.

Even with concentrated nitric acid, there is scarcely any reaction in the cold; there is a slow action on warming. Oxidation takes place rapidly in the cold with ordinary nitric acid; red fumes are evolved and a gas which is spontaneously inflammable.

Similarly, fuming sulphuric acid has no action in the cold, while the dilute acid reacts energetically. Absolute alcohol, ether, benzene, and turpentine have no action at ordinary temperatures.

Oxidizing agents react vigorously. Fused potassium chlorate or bichromate react with incandescence.

By heating a mixture of the phosphide and potassium permanganate, a violent reaction takes place accompanied by incandescence and explosions.

Nitrous oxide and nitrogen peroxide have an oxidizing action on warming. Lime and a small amount of nitride are formed with incandescence.

Analysis of calcium phosphide.—The phosphide was decomposed by oxidation with fuming nitric acid. The metal was precipitated as calcium sulphate in alcoholic solution, and the phosphoric acid determined as ammonium magnesium phosphate. Results:

	1	2	3	4	Theory for Ca_3P_2.
Calcium .	65·82	65·71	65·38	65·40	65·93 per cent.
Phosphorus	—	33·79	33·92	33·85	34·06 ,,

Phosphides of strontium and barium.—A. Jaboin[1] has obtained by the above method the phosphides of strontium and barium Sr_3P_2 and Ba_3P_2.

These bodies, which have a density of 2·98 and 3·18 respectively, have the same general properties as calcium phosphide.

Phosphides of iron, nickel, cobalt, and chromium.—On reducing the phosphates of these metals in the electric furnace, one only obtains as a rule fused masses of varying composition containing phosphorus.

G. Maronneau[2] obtained the phosphides by a modification of the method used by Lebeau for the preparation of iron silicide, FeSi. He heated a mixture of copper phosphide and filings of one of the above metals, and separated the phosphide by means of nitric acid which dissolved away the excess of copper.

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[1] *C. R.*, cxxix. 762 (1899).

[2] *C. R.*, cxxx. 656 (1900).

Iron phosphide Fe_2P exists in bright greyish-white needles, whose density is 6·57. They gave on analysis:

	1	2	Theory for Fe_2P.
Iron . . .	77·80	78·10	78·31 per cent.
Phosphorus . .	21·45	21·17	21·69 ,,

Nickel phosphide Ni_2P and cobalt phosphide Co_2P occur also in bright needles, and are not attacked by acids. They gave on analysis:

	1	2	Theory for Ni_2P.
Nickel . . .	78·60	79·40	79·20 per cent.
Phosphorus . .	20·90	20·30	20·80 ,,

	1	2	Theory for Co_2P.
Cobalt . . .	79·41	79·61	79·20 per cent.
Phosphorus . .	20·09	20·20	20·80 ,,

Chromium phosphide CrP has a dull grey colour resembling that of graphite and it is not dissolved by acids. Analysis results:

	1	2	Theory for CrP.
Chromium . .	63·02	62·92	62·93 per cent.
Phosphorus . .	36·35	36·87	37·07 ,,

Copper phosphide.—Phosphides of copper of varying composition have been described by several investigators. The compound Cu_2P was obtained by G. Maronneau[1] on reducing copper phosphate by means of carbon in the electric furnace. There results a black crystalline powder, from which the graphite may be separated by means of bromoform. The crystals gave on analysis:

	1	2	Theory for Cu_2P.
Copper . . .	80·55	79·95	80·38 per cent.
Phosphorus . .	18·40	19·32	19·62 ,,

METALLIC ARSENIDES

The arsenides hitherto described were, like the phosphides, compounds of composition varying with the method of preparation. P. Lebeau[2] has applied the method used for the preparation of the phosphides, that is, the reduction of an oxygenated compound by carbon, to the preparation of the arsenides of the alkaline earth metals, and he has obtained perfectly definite compounds which are stable at the temperature of the electric furnace.

Calcium arsenide.—An intimate mixture of 100 parts of

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[1] *C. R.*, cxxviii. 936 (1899).

[2] *C. R.*, cxxviii. 95 (1899).

calcium arsenate and 30 parts of petroleum coke is ground up with a little turpentine and compressed into a compact mass. This is calcined and then heated for two to three minutes in the electric furnace by means of a current of 950–1,000 amperes at 45 volts. The crucible is at once withdrawn from the furnace and covered with a carbon lid in order to prevent oxidation. The reaction product is taken out while still hot and enclosed in glass tubes. The fused mass consists of calcium arsenide nearly always contaminated by traces of calcium carbide and graphite.

The fused mass seems to have a crystalline structure. Under the microscope, it is seen to consist of reddish-brown particles, resembling calcium phosphide.

The most interesting reaction of this new compound is its decomposition by water, which begins in the cold, forming calcium hydrate and pure arseniuretted hydrogen. This is a very good method for preparing this gas.

Analysis.

	1	2	Theory for Ca_3As_2.
Calcium . . .	45·18	44·83	44·44
Arsenic . . .	54·83	55·17	55·55

Strontium and barium arsenides.—These arsenides are prepared like calcium arsenide, and possess similar properties. They are decomposed by water, forming pure arseniuretted hydrogen, and they correspond to the formulae Sr_3As_2 and Ba_3As_2.

METALLIC SULPHIDES

In view of the general extension of reactions at high temperatures, it was interesting to investigate the behaviour of sulphides in the electric furnace.

A. Mourlot[1], by heating mixtures of sulphates and carbon in the electric furnace, has obtained the sulphides of lithium, of the alkaline earth metals, and of magnesium in a crystalline form; these compounds had hitherto only been obtained as amorphous powders. This general method has made it possible to prepare crystalline sulphides of zinc, cadmium, lead, manganese, and antimony. These sulphides are stable at a high temperature. The sulphides of zinc, cadmium, lead, and tin are volatile and crystallize on cooling. The sulphides are reduced by carbon, producing either the corresponding carbide or the metal.

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[1] *Ann. de Ch. et de Ph.*, sér. 7, xvii. 510 (1899).

CHAPTER V

RECENT RESEARCHES ON CARBIDES, SILICIDES, AND BORIDES

A. The carbides of neodymium and praseodymium.

Preparation of neodymium carbide.—The neodymium oxide used, Ne_2O_3, had the mauve colour indicated by Demarçay. We prepared an intimate mixture of this oxide with sugar carbon in the following proportions: oxide 250 grms., carbon 20 grms. To this is added as small an amount as possible of turpentine, and the mass is compressed into small cylinders; the latter are gently calcined in a porcelain crucible placed in a Perrot furnace, till combustible gases are no longer evolved. They are then, while still warm, sealed up in bottles, all moisture being carefully excluded. The mixture is heated up in the electric furnace for four minutes (900 amperes at 50 volts), when there is found in the crucible a fused mass which, as a rule, is very easily detached. Under these conditions, the mass consists of almost pure neodymium carbide. If the heating be too prolonged, the carbide attacks the crucible dissolving varying amounts of carbon and adheres to its walls.

Preparation of praseodymium carbide.—The oxide used was brown and corresponded to the formula PrO_2. The mixture of oxide and carbon was prepared as already described, in the following proportions: oxide 250 grms., carbon 32 grms. The length of the heating was the same and the product had much the appearance of neodymium carbide.

Properties.—We have studied in detail several of the reactions taking place between these new carbides and various elements and compounds in order to add to our knowledge of these rare earths.

Neodymium carbide is seen under the microscope to exist in hexagonal lamellae of a somewhat deeper yellow colour than aluminium carbide. Its density is about 5·15.

Praseodymium carbide has the same colour and is also crystalline. It has a density of 5·10.

Both carbides are unreduced by hydrogen at a red heat. No reaction takes place with fluorine at ordinary temperatures but, on heating slightly, a vivid incandescence is produced and the reaction goes on unaided in a current of the gas. The fluorides produced are insoluble in water; neodymium fluoride is greenish-white and praseodymium fluoride has the colour of sulphur. The heat of the reaction is not sufficient to melt them and they are not easily volatilized.

No reaction takes place in a stream of chlorine in the cold, but, at a dull red heat, the carbides become incandescent and anhydrous chlorides are formed which dissolve in water with considerable evolution of heat. We have already drawn attention several times to this ready preparation of chlorides by the action of chlorine on metallic carbides.

Bromine acts like chlorine, while iodine vapour at a dull red heat reacts far less energetically, without any incandescence, producing one or more iodides soluble in water.

On heating in a rapid stream of oxygen at 400° C., a vivid incandescence takes place and the carbides are completely oxidized. Neodymium carbide yields a mauve oxide while praseodymium gives a black oxide. We have used this reaction for the estimation of the carbon.

Sulphur reacts slowly at its boiling-point. The resulting sulphides are decomposed by dilute acids; they are readily attacked by boiling water, but only very slightly in the cold. The reaction with sulphur is not complete till the temperature has risen to 1,000° C.

Nitrogen reacts at 1,200° C., but the change is only superficial and the amount of nitride formed is very small. However, ammonia is distinctly evolved when the product is treated with water. Experiments to be described later prove the existence of the nitrides of neodymium and praseodymium.

Carbon dissolves readily in the fused carbides, as has already been remarked. At the moment of solidification, graphite crystallizes out and carbides are obtained possessing a grey metallic fracture.

These carbides are decomposed by water as rapidly as those of cerium, lanthanum, and yttrium. A large volume of gas is evolved and a hydrated oxide is left behind, which is greenish-white in the case of neodymium and violet in that of praseodymium. There are formed in addition, liquid and solid hydrocarbons. The gases evolved consist chiefly of acetylene, of a small quantity of ethylene and of its homologues, and of hydrocarbons of the methane series.

Decomposition by water of neodymium carbide:

	1	2	3	4	
Acetylene . . .	66·22	65·42	65·80	67·20	per cent.
Ethylene hydrocarbons	6·34	5·92	6·90	5·95	„
Methane „ .	27·44	28·66	27·30	26·85	„

Decomposition by water of praseodymium carbide:

	1	2	
Acetylene	67·50	68·31	per cent.
Ethylene hydrocarbons .	2·50	3·57	„
Methane „ .	30·00	28·32	„

The action of acids on the two carbides varies with their state of dilution. Concentrated nitric acid has no action, while the dilute acid causes the evolution of hydrocarbons whose composition may vary owing to the oxidizing action of the acid.

Similarly boiling concentrated sulphuric acid is reduced to sulphurous acid, while the dilute acid reacts by virtue of the water it contains.

Gaseous hydrochloric acid has no action in the cold, but an energetic reaction takes place at dull redness. The products are soluble in water, neodymium yielding a pink solution and praseodymium a green solution.

Both carbides are attacked at a red heat by sulphuretted hydrogen without incandescence; the products obtained are the same as with sulphur.

Ammonia reacts distinctly at 1,200° C. Neodymium carbide becomes black and praseodymium yellow. The residue on treatment with water yields hydrocarbons, and ammonia is abundantly evolved. There is no doubt that both these metals can form nitrides.

Analysis.—The fused carbide was attacked with dilute nitric acid which dissolves it readily. Any contained graphite is separated off by filtration and weighed. The nitrate formed is evaporated to dryness and calcined, and the amount of metal in the carbide is calculated from the weight of oxide obtained. In some cases ammonium oxalate was added to the solution containing but little nitric acid and the oxalate obtained was calcined. This method yielded somewhat lower figures.

The carbon was estimated as carbon dioxide obtained by direct combustion in a stream of oxygen. The combustion must be a very active one to ensure a complete oxidation of the carbide. This method yielded the best results, though they were still a little too low[1].

	Neodymium carbide. 1	2	3	Theory for NeC_2.
Percentage of metal	84·24	85·73	85·90	85·68
„ carbon	14·08	14·27	13·37	14·32

	Praseodymium carbide. 1	2	3	Theory for PrC_2.
Percentage of metal	84·60	85·10	84·91	85·41
„ carbon	14·40	13·79	14·29	14·58

Conclusions.—The oxides of neodymium and praseodymium, when heated with carbon in the electric furnace, yield crystalline carbides of the formulae NeC_2 and PrC_2 respectively. They are decomposed by water in the cold, yielding a mixture of hydrocarbons and the hydrated oxide.

We have already shown that the carbides of the three alkaline earth metals yield pure acetylene on treatment with water; aluminium carbide yields pure methane. Neodymium and praseodymium belong to the cerium group of the elements, which comes between the group of the alkaline earths and aluminium.

It is, therefore, of interest to note that these two new carbides yield with water a mixture of hydrocarbons rich in acetylene and in methane. It may be remarked, further, that the percentage of acetylene diminishes in passing from cerium to neodymium, and that the latter metal and praseodymium, so alike as to have been known for a long time under one name, yield hydrocarbon mixtures of very similar composition.

Finally, all the carbides of the cerium group correspond to the general formula RC_2.

B. Samarium carbide[2].

Preparation.—200 grms. of samarium oxide, Sa_2O_3, were mixed with 20 grms. of sugar carbon and agglomerated by pressure. On heating for four minutes in the electric furnace (900 amperes at 45 volts), we obtained a fused regulus weighing 150 grms.

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[1] Atomic weights taken were Ne=143·6, Pr=140·5.

[2] *Ann. de Ch. et de Ph.*, sér. 7, xxii. 110 (1901).

Properties.—This carbide has a more distinctly metallic aspect than those just described. Some small pieces examined under the microscope were seen to be transparent, of a yellow tint, and some particles showed a hexagonal form. It has a density of 5·86.

This carbide is not reduced by hydrogen at 1,000° C. If slightly heated in a stream of fluorine or chlorine it becomes incandescent, forming the corresponding compounds. Bromine and iodine react at dull redness.

Complete combustion takes place in oxygen at 400° C., if the carbide be sufficiently finely divided, yielding a yellowish-white oxide. Sulphur reacts also, but at a far higher temperature.

The carbide is decomposed by cold water, as are the other carbides of this series already described, yielding liquid and solid hydrocarbons and a gaseous mixture which gave on analysis:

	1	2	
Acetylene	70·1	71·2	per cent.
Ethylene hydrocarbons . . .	7·6	8·1	„
Hydrogen and methane hydrocarbons	22·3	20·7	„

This mixture is very similar to that evolved from yttrium carbide, which contained a percentage of 71·7 to 71·8 of acetylene, while cerium carbide gave 78·47 to 80 per cent.

Boiling concentrated sulphuric acid is reduced by samarium carbide. With dilute acids, the decomposition is the more energetic the more water they contain.

Sulphuretted hydrogen reacts at a red heat without incandescence, forming the sulphide.

Gaseous hydrochloric acid reacts very energetically at a dull red heat. The black product obtained is far more bulky than the original carbide. With cold water, this substance yields a colourless solution and a precipitate of the oxide, but no gas is evolved.

Analysis.—The method adopted was that already described for the carbides of neodymium and praseodymium. The following figures were obtained[1]:

	1	2	3	4	Theory for SaC_2.
Percentage of metal	85·80	85·90	85·98	86·65	86·20
„ carbon	13·50	13·46	—	—	13·80

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[1] Atomic weight of samarium, 150.

Conclusions.—Samarium oxide heated in presence of carbon in the electric furnace yields a crystalline carbide SaC_2, which is analogous in composition to the carbides of cerium, lanthanum, neodymium, and praseodymium. This carbide, like many others, is decomposed by cold water, yielding a mixture of hydrocarbons rich in acetylene.

This reaction shows samarium to be more closely related to yttrium than to the cerium metals.

C. Silicides of vanadium[1].

The vanadic acid used as starting-point was prepared by the method already described, or by igniting pure ammonium metavanadate. Before being used, the acid was fused in a platinum dish in order to dehydrate it completely. It may be repeated here that this substance is very volatile at the temperature of the electric furnace; so that in many of the experiments we preferred using the oxide V_2O_3, obtained by reducing vanadic acid by heating it to redness in a stream of pure dry hydrogen.

Preparation of the silicide VSi_2.—1. In a series of preliminary experiments we heated vanadic acid with varying amounts of silicon in the electric furnace. The mass fuses rapidly and the presence of different silicides is easily recognized by treating the product with a weakly alkaline solution. A variable equilibrium is set up depending on the temperature and the amount of fused silicon present. To obtain the compound VSi_2, we heated a mixture of the oxide V_2O_3 with rather more than five times its weight of pure crystalline silicon, when the following reaction takes place:

$$2\,V_2O_3 + 11\,Si = 4\,VSi_2 + 3\,SiO_2.$$

Under these conditions there remains an excess of fused silicon in the bath, and VSi_2 is the only compound to crystallize out. These experiments were done with a current of 600 amperes at 50 volts, and the heating, which lasted four to five minutes, was somewhat difficult to control because of the great volatility of the vanadium compounds. Later we preferred a more powerful current acting for a shorter period, and we used 1,000 amperes at 50 volts in an experiment lasting two minutes.

The metallic regulus obtained under these conditions was

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[1] This work was carried out in conjunction with A. Holt, Jr. *Ann. de Ch. et de Ph.*, sér. 7, xxvii. 277 (1902).

treated with a ten per cent. solution of potash on the water bath till gas was no longer evolved.

The crystalline residue is then washed by decantation, and heated on the water bath with 50 per cent. nitric acid or with concentrated sulphuric acid. It is advisable to repeat the whole treatment some five or six times in order to obtain a pure product. It is occasionally necessary to remove a few lamellae of graphite by means of bromoform, on whose surface it swims.

2. This silicide may be also obtained by reducing a mixture of vanadic acid and silicon by means of magnesium powder. An intimate mixture is made of 10 grms. of vanadic acid, 10 grms. of silicon and 5 grms. of magnesium powder free from oil and iron. The mixture was ignited by Vautin's method[1], using barium peroxide and a little magnesium. There is found in the crucible a mass of well-fused silicide, which is treated with 10 per cent. nitric acid first in the cold and then at its boiling-point. The crystalline product is separated by levigation and then heated on the water bath with a ten per cent. solution of potash. The residue is then washed and dried and heated on the sand bath with concentrated sulphuric acid to remove a few fragments of fused magnesia. These various treatments must be repeated till all action has ceased.

Properties.—This silicide occurs in bright metallic-looking prisms. It has a density of 4·42, marks glass, and is fusible and volatile in the electric furnace. It is very stable, insoluble in water, benzene, alcohol, and ether. The only solvents we have found are fused silicon, from which it crystallizes on cooling, and fused copper silicide.

Aqueous potash and ammonia, together with nitric, sulphuric, and hydrochloric acids, have no action, nor is it attacked by mixtures of acids. On the other hand, dilute hydrofluoric acid attacks it readily in the cold.

Vanadium silicide is not attacked by fluorine at ordinary temperatures; it requires to be heated to redness, when it burns with incandescence yielding a greenish-brown residue. With chlorine there is no incandescence, and there results a dark brown liquid which solidifies at 38°C. to a red crystalline mass. The liquid is decomposed at once by water, giving hydrated silica and a blue solution of vanadium oxide and of

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[1] Similar to Goldschmidt's Alumino-thermic processes.

hydrochloric acid. This is the behaviour of a mixture of the chlorides of silicon and of vanadium.

Bromine attacks the silicide at redness without incandescence, producing a black amorphous sublimate of the bromide VBr_3, a slight orange sublimate decomposable by water and possessing all the properties of vanadyl bromide $VOBr_3$, and finally a yellowish residue which remains in the boat and which has the properties of the bromide of silicon Si_2Br_4.

Iodine vapour has but a superficial action at a red heat. Similarly oxygen, sulphur, and sulphuretted hydrogen exert but a slight action at the softening-point of glass.

Vanadium silicide heated in a current of gaseous hydrochloric acid is attacked without incandescence, yielding a colourless liquid boiling at 3° C. which is silico-chloroform, a green sublimate giving the reactions of the chloride VCl_2, and a very deliquescent reddish-brown residue, soluble in water, and giving the reactions of the chloride VCl_3.

Treated with fused potash the silicide is decomposed, gases are evolved, and a mixture of potassium silicate and vanadate is left behind. The reaction is not complete till after some considerable time. If it last but a short time there is formed an insoluble residue rich in vanadic acid. Caustic soda behaves similarly.

Ammonia gas exerts but a superficial action at 1,000° C.

The metals when fused behave differently according as to whether they form, more or less readily, compounds with silicon or with vanadium. Copper, for example, decomposes completely a small quantity of the silicide forming copper silicide and a copper-vanadium alloy. On the other hand, it is but partially decomposed by silver, yielding silicon and vanadium, which may be obtained from the silver ingot. Tin behaves similarly.

Analysis.—The analysis of this compound is somewhat difficult, and we have been unable to estimate silicon and vanadium in the same sample.

To estimate the vanadium a known weight of the silicide is attacked with pure 5 per cent. hydrofluoric acid. After filtration the liquid is evaporated to dryness, a small quantity of pure nitric acid having been added. The vanadic acid thus obtained is fused and weighed.

The silicon was determined by acting on a known weight of the silicide with fused potash. After taking up with water, hydrochloric acid is added and the liquid evaporated to dryness. This is repeated three times. Finally, the silica is determined in the usual way by evaporating to dryness and taking up with dilute sulphuric acid. The following results were obtained:

	1	2	3	Theory for VSi_2.	
Vanadium	47·98	48·25	48·30	47·80	per cent.
Combined silicon. .	51·75	51·60	52·02	52·20	,,
Free silicon	0·50	0·02	nil	—	,,

We obtained a second silicide of the formula V_2Si by using an excess of vanadium in the preparation; the experiment is a difficult one because both vanadic acid and the oxide V_2O_3 are volatile at high temperatures.

By heating in the electric furnace a mixture of excess of the oxide V_2O_3 and silicon we obtained a mixture of several silicides, among which were the compounds VSi_2 and V_2Si; but as the silicide rich in vanadium, V_2Si, is less fusible than the other, the heating must be more prolonged. The excess of oxide V_2O_3 then tends to volatilize away and the conditions are those for the formation of the compound VSi_2, which is stable in presence of excess of silicon.

A number of experiments were carried out by action with magnesium on an excess of vanadic acid in presence of silicon. This mixture is explosive when in contact with a flame, but yields no vanadium silicide.

Preparation of the silicide V_2Si:

1. We have succeeded in preparing this silicide by heating in the electric furnace a mixture of 120 grms. V_2O_3 and 14 grms. Si (1,000 amperes at 50 volts). The amount of oxide used is four times that required by the equation:

$$2\,V_2O_3 + 5\,Si = 2\,V_2Si + 3\,SiO_2.$$

If vanadic acid be used the weight taken must be ten times that required by the equation:

$$2\,V_2O_5 + 7\,Si = 2\,V_2Si + 5\,SiO_2.$$

Most of the vanadium is volatilized during the experiment, and there remains but a small ingot of the silicide V_2Si. On the top part of this there is always found a small quantity of a black amorphous substance which is not attacked by acids or alkalies, and which is easily separated from the white metallic-looking silicide beneath. The silicide is broken up into small pieces and then heated for two hours with concentrated sulphuric acid. The residue is washed with water and then treated with a boiling solution of 10 per cent. potash. Any graphite present is separated by means of bromoform.

2. This silicide was also obtained by the action of silicon on vanadium carbide (p. 170). The latter compound is stable and not readily volatile, so that an excess of vanadium may be heated in presence of fused silicon. We heated up a mixture of the oxide V_2O_3, silicon and carbon, when the following reaction took place:

$$2\ V_2O_3 + 2\ Si + 3\ C = 2\ V_2Si + 3\ CO_2.$$

The weight of V_2O_3 used was one-tenth larger than the theoretical amount. The mixture is heated for four minutes in a carbon crucible (500 amperes at 50 volts). The fused mass obtained consisted of a mixture of the silicide V_2Si and of the carbide VC. To obtain the pure silicide the mass is powdered and heated for several hours with 50 per cent. nitric acid, which destroys the carbide, and then with a ten per cent. solution of potash.

3. Finally, we used copper silicide kept at its boiling-point to allow silicon to react with an excess of vanadium. The following mixture was prepared: vanadium oxide, V_2O_3, 15 parts; silicon, 7 parts; copper, 2 parts. It was heated for four minutes in a carbon crucible (700 amperes at 50 volts). The liquid bath then contains a solution of the silicide V_2Si in a mixture of copper silicide and copper-vanadium alloy. The homogeneous and well-fused mass was then roughly powdered and heated for several hours on the water bath with 50 per cent. nitric acid. The copper silicide and the vanadium alloy are destroyed and the residue is then treated with a boiling ten per cent. solution of potash, graphite being separated by means of bromoform. The silicide obtained in this way always contains a certain amount of carborundum.

Properties.—This new silicide crystallizes in prisms and has a silver white colour. The crystals are very bright and have a metallic appearance; they are brittle and easily scratch glass and their density is 5·48 at 17° C. This silicide melts at a higher temperature than the compound VSi_2, and it is insoluble in water, alcohol, ether, and benzene.

Fluorine has no action in the cold, but on heating gently a feeble incandescence is observed and a greenish-brown substance is formed.

Chlorine acts readily at a red heat, forming a liquid which is a mixture of the chloride VCl_4 and of silicon chloride $SiCl_4$. Bromine acts similarly, yielding a black amorphous sublimate of vanadium bromide VBr_3 and a residue left in the boat of silicon bromide Si_2Br_6. Iodine exerts but a superficial action at the same temperature.

At 1,000° C. water vapour acts superficially and the crystals acquire a bluish tint; on then treating with nitric acid there is obtained a blue liquid containing the oxide V_2O_4. Sulphur vapour and sulphuretted hydrogen exert but a superficial action at a red heat. Ammonia does not react at this temperature.

On the other hand, hydrochloric acid gas reacts completely at 800° C. without incandescence, producing a mass of small bright crystals of a reddish-brown colour. These crystals are readily decomposed by water, forming a brown solution which becomes greenish-blue on the addition of nitric acid. The crystals are similarly decomposed by hydrochloric and nitric acids with evolution of gas and formation of a solution rich in vanadium. With hydrochloric acid there is formed a double chloride of silicon and vanadium.

Vanadium silicide heated in the electric furnace in presence of carbon is partially decomposed and an equilibrium is set up between the silicide and the carbide, as already mentioned. The silicide V_2Si is stable in presence of an excess of fused carbide. Heated in contact with fused silicon at its boiling-point, the silicide melts, dissolves, and then decomposes; it is completely transformed into the silicide VSi_2 which was analysed. One silicide may thus be converted into the other.

The silicide V_2Si is decomposed by sodium when heated to redness. In presence of a large excess of copper it forms copper silicide and a silicon-vanadium alloy. Silver at its boiling-point has but a slight action, but on cooling it gives up a small quantity of amorphous silicon. Tin behaves similarly. This silicide is not soluble in molten aluminium and dissolves but slightly in fused copper silicide. Hydrochloric, nitric, and sulphuric acids have no action, whether singly or mixed. Dilute hydrofluoric acid reacts readily in the cold.

Solutions of potash, soda, or ammonia have no action, but fused potash reacts readily. A mixture of potassium nitrate and sodium carbonate acting at a red heat gives vanadates and silicates.

Analysis.—The method adopted was that already described for the silicide VSi_2. The following figures were obtained:

	1	2	3	Theory for V_2S_2.
Vanadium per cent. .	78·52	79·12	77·60	78·46
Silicon „ .	20·90	21·51	21·88	21·54

Sample 1 contained 1·9 per cent. of carborundum; No. 2, 4·22; and No. 3, 2·80.

Conclusions.—We have prepared a second silicide of vanadium V_2Si, less readily fusible than VSi_2. It differs from the latter in composition, density, and colour, and reacts more readily with fluorine, chlorine, and in particular with bromine; it is only slightly attacked by fused silicon. These experiments show further that the laws of equilibrium, which are obeyed in solutions at ordinary temperatures, hold good in the case of the reactions which take place in the electric furnace between silicon, copper silicide, and vanadium carbide.

D. **Cerium silicide**[1].

A body corresponding to the formula Ce_2Si has been accidentally obtained by Ulik[2] in the electrolysis of the double fluoride of cerium and potassium.

Preparation of the silicide $CeSi_2$.—An intimate mixture was made of 172 grms. of cerium oxide[3] and 85·2 grms. of pure powdered silicon, placed in a graphite boat and heated in a tube of the same substance (600 amperes at 100 volts). The reaction starts at once, and is complete when the mass is fused. The mass obtained is mechanically separated from ash, and there are obtained fused homogeneous lumps, each weighing several grams. The lumps are broken up and treated on the water bath with a five per cent. solution of potash to remove the free silicon. The mass consists of microscopic crystals of a steel colour. The crystals are purified by levigation and dried at 100° C. They are very brittle, yielding a black powder, and they have a density of 5·67 at 17° C.

Properties.—Opaque microscopic crystals of the colour of steel. Insoluble in water, which reacts but very slowly in presence of air; insoluble in organic solvents.

Hydrogen does not react, while fluorine reacts with incan-

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[1] Work done by M. Sterba.

[2] *Chemisches Central-Blatt*, 1885, p. 1045.

[3] For preparation see Moissan, *C. R.*, cxxiv. 1233 (1897).

descence in the cold. Chlorine, bromine, and iodine react with incandescence on heating.

Air and oxygen have no action in the cold; oxidization takes place at a red heat with incandescence. Cerium silicide gives brilliant sparks if thrown into a flame.

Sulphur and selenium react with slight incandescence at their boiling-points. Heated with magnesium in an atmosphere of hydrogen, there is formed a magnesium silicide which on treatment with hydrochloric acid evolves spontaneously inflammable silicon hydride. Gaseous hydrochloric acid reacts at a red heat, while aqueous hydrochloric and hydrofluoric acids attack the silicide with evolution of hydrogen. The organic acids only react on warming. Aqueous alkalies have practically no effect, but when fused they react with incandescence. Ammonia gas reacts at a red heat.

Heated in the electric furnace, the crystalline silicide fuses to a mass having the appearance of silver.

Analysis.—A qualitative analysis showed the presence of cerium, silicon, with traces of carborundum and iron. For the quantitative analysis the silicide was treated several times on the water bath with hydrochloric acid to dissolve the cerium and render the silica insoluble. The latter was attacked by hydrofluoric acid and the residue weighed as carborundum.

We obtained the following figures:

	1	2	3	4	Theory for $CeSi_2$.	
Cerium .	71·17	70·70	70·81	71·42	71·16	per cent.
Silicon .	28·97	28·60	28·86	28·67	28·83	,,

The quantity of carborundum varied from 3·5 to 6·64 per cent. The silicides analysed came from different preparations.

Conclusions.—We have prepared a silicide of the formula $CeSi_2$, differing from that obtained by Ulik. The stability of this compound allows of its preparation in the electric furnace. Its properties differ from those of calcium silicide and resemble more those of the silicides of the heavy metals.

E. Borides of Silicon[1].

Schützenberger discovered a silicide of carbon of the formula SiC, and obtained it in the amorphous state[2]. The same compound was obtained in crystals by Acheson, and was the start-

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[1] This work was done in conjunction with Alfred Stock. *Ann. de Ch. et de Ph.*, sér. 7, xx. 433 (1900).

[2] *C. R.*, cxiv. 1089 (1892).

ing-point of the carborundum industry. One of us has shown that carbon boride B_6C, whose composition was established by Joly[1], could be prepared on a large scale in the electric furnace[2]. The boride and the silicide of carbon have similar properties — their characteristic appearance, their stability towards reagents, and their hardness. Carbon silicide marks the ruby but not the diamond, whereas carbon boride may cut into a diamond of minimum hardness.

The numerous analogies existing between the compounds of carbon and silicon led one to expect similar compounds with boron.

Silicon borides SiB_3 and SiB_6.

Preparation.—We tried at the outset to prepare these new borides by direct union of their elements. But boron and silicon only combine at a very high temperature, and our first attempts in the electric furnace were fruitless.

Under these conditions, the experiment is complicated by the presence of the substance of which the vessels are made. With a carbon crucible, there are formed carbon boride and silicide. Further, it must not be forgotten that, at this high temperature, carbon dioxide and nitrogen easily react with boron and silicon. We had thus to devise a special apparatus. We took a tube made of refractory material 20 cm. long and 45 mm. in diameter, whose ends were closed by stoppers of the same material. Through these passed two carbon electrodes 3 cm. in diameter which were kept 12 cm. apart. The tube was provided with a lateral opening which rendered it possible to introduce a well-dried mixture of five parts of crystallized silicon and one part of pure boron. Some 120 grms. of the mixture were used at one time. The silicon was prepared by the method due to Vigouroux[3], and the boron in the manner described by one of us[4].

The electrodes were joined by thin copper wires to ensure the passage of the current at the outset of the experiment. The lateral opening of the tube was closed by a lid of the same material and then covered, together with the stoppers at the ends, with a thin layer of fire-clay; finally, the whole apparatus was placed in a box of sheet iron and surrounded with dry sand.

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[1] *C. R.*, xcvii. 456 (1883).

[2] *ante*, p. 263.

[3] *Ann. de Ch. et de Ph.*, sér. 7, xii. 153 (1897).

[4] Moissan, *C. R.*, cxiv. 394 (1892).

We used an alternating current at 45 volts which could be regulated at will by means of a metallic resistance. The heating lasted from 50 to 60 seconds and the maximum current attained was 600 amperes. As it was of importance to avoid the formation of an arc inside the apparatus, the electrodes were gradually brought nearer together as the volume of the mixture diminished owing to its fusion. The borides of silicon were really formed in a bath of fused silicon, the latter serving to conduct the current.

On cooling, when the heating had been sufficiently prolonged, there was found in the apparatus an elongated mass completely fused and rich in silicon, covering the whole length of the tube.

The surface of the latter was attacked, but only slightly, as the heating was very short; this has no effect on the final result. The surface of the mass is cleaned and the ends which touched the electrodes are cut off as they contain some carbon silicide. The remainder is then roughly powdered; the fragments look like fused silicon and often contain geodes lined with small crystals which are very brilliant.

The mass is then treated with a mixture of hydrofluoric and nitric acids which dissolves out the silicon. The mixture must be kept cold during the attack and only a small amount should be worked up at a time. Should the temperature rise, the borides enter into solution.

As soon as ruddy vapours are no longer evolved, the unattacked residue is separated by decantation, washed with water and dried; there are thus obtained dark-coloured crystals which are more or less contaminated with impurities. The crystals are separated off by means of a sieve and purified by means of fused potash in a silver crucible. Ordinary non-dehydrated potash is used and the temperature must not rise much above the fusion-point of the alkali.

Half an hour is usually sufficient to dissolve out all the amorphous matter, if the mixture be stirred with a spatula. The crystals are then washed with water, with dilute nitric acid, finally with boiling water, and dried at 130° C. So obtained, they are black and very bright; even under the microscope they seem to be perfectly homogeneous. They contain, however, two different compounds of boron and silicon, as we found out after numerous analyses.

No separation could be affected by means of difference of density, but using different reagents one or other of the borides could be destroyed. On treating the mixture with a large excess of boiling nitric acid, one boride remains behind of constant composition, corresponding to the formula SiB_3.

On the other hand, by fusion with anhydrous potash at a high temperature, this first compound is destroyed, and there remains a second boride whose formula is SiB_6. The latter occurs in larger quantities than the first (80 to 90 per cent.).

Properties.—These two new borides of silicon belong to the class of substances of which carbon silicide and boride had hitherto been the sole representatives. Like the latter, these borides are very hard and they scratch quartz and even the hardest ruby with ease; they are probably less hard than carbon boride for they left no mark on the polished face of a diamond. We did not attempt, however, to cut diamonds by means of powder placed on a steel wheel.

The boride SiB_3 has a density of 2·52; it occurs usually in black rhombic lamellae, which are transparent when very thin, becoming at the same time yellow or brown. On the other hand, the boride SiB_6 always occurs in stout, opaque crystals whose faces are rather irregular. Its density is 2·47.

Both compounds conduct electricity. They are attacked by fluorine on warming slightly, much heat and light being evolved. Chlorine reacts at a red heat with incandescence, bromine slowly at the softening point of glass, while iodine has no action at this temperature.

They are difficult to oxidize, whether heated in air or in oxygen, owing to the protecting layer of silica and boric acid which is formed on the surface. Nitrogen has no action at 1,000° C.

Both borides are unattacked by the halogen hydracids, and are only very slowly decomposed by boiling concentrated sulphuric acid. As already observed, concentrated nitric acid acts fairly quickly on the boride SiB_6, but only very slowly on the compound SiB_3.

Fused anhydrous potash attacks the boride SiB_3 very readily, occasionally with incandescence. Under these conditions the boride SiB_6 is only slowly decomposed and then at a higher temperature.

Fused potassium nitrate has no action, but the alkaline carbonates, alone or mixed with nitre, attack both borides energetically at a red heat.

Analysis.—The borides were treated with fused potash in a silver crucible. The undecomposed part was separated by filtration through a Gooch crucible, weighed and used for a later determination. The boride used was not considered to be of definite composition unless two or three successive analyses were concordant.

The filtrate was divided into two parts, silica being estimated in one and boric acid in the other. The latter was determined by titration with caustic soda in presence of mannitol[1]. The boride SiB_6 contained a little iron, probably as silicide.

Analyses of different samples gave:

	1	2	3	Theory for SiB_3.	
Boron . . .	54·38	53·10	54·43	53·75	per cent.
Silicon . . .	45·86	46·44	46·01	46·25	,,

	1	2	3	4	Theory for SiB_6.	
Boron .	69·07	69·36	69·09	—	69·91	per cent.
Silicon .	29·89	30·30	29·45	—	30·09	,,
Iron . .	—	—	—	0·99	—	,,

Conclusions.—Boron and silicon combine directly at a high temperature to produce two crystalline borides SiB_3 and SiB_6. These two compounds are soluble in molten silicon from which they may be obtained by treatment with hydrofluoric and nitric acids.

The densities are nearly alike and both compounds are extremely hard, marking the ruby with ease. They are unaffected by most reagents, but the boride SiB_3 is more readily attacked by potash, while the boride SiB_6, much richer in boron, is far more readily decomposed by concentrated nitric acid.

It is of interest to compare this simultaneous formation of the two borides of silicon with the case of the two borides of carbon which are produced in a very similar manner by the action of boron on carbon.

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[1] L. C. Jones, *American Journal of Science*, ser. 4, vii. 147 (1899); A. Stock, *C. R.*, cxxx. 516 (1900).

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