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SPECIAL MEETING.

The twenty-second meeting of the Institute was held at the House of the American Society of Civil Engineers, No. 127 East 23rd Street, New York City, January 10, 1888, and was called to order at 8 p. m. by the President of the Institute, Mr. T. C. Martin.

THE PRESIDENT: The subject which we have before us this evening is of a very interesting nature. The paper is by Mr. Willard E. Case, of Auburn, N. Y., and is entitled, "Electrical Energy from Carbon without Heat." In the absence of Mr. Case, it will be read by Mr. Mailloux.

ELECTRIC ENERGY FROM CARBON WITHOUT HEAT.

BY WILLARD E. CASE.

The following experiments, undertaken by the author, may be of interest as indicating the way in which the cheap generation of electrical energy may possibly be brought about.

In the first experiment, an element was formed through which heat energy was converted into electrical energy, in which the correlation of forces is beautifully illustrated.

It is a sort of voltaic battery, in which plates of tin and platinum, forming the electrodes, are immersed in a solution of chromic chloride, which has no action on the plates at ordinary temperature, so no current is generated. The cell is hermetically sealed, and when heated the liquid becomes active, and part

of one of its elements, chlorine, leaves the chromic chloride, goes over and temporarily combines with the tin, forming a proto-chloride of tin. The chemical action generates an electric current, but soon the tin is all converted into chloride, and the current ceases. When the cell is cooled, this temporary combination of the chlorine and tin is broken up, and the chlorine returns to the chromium proto-chloride. The tin being set at liberty, falls as a metallic precipitate to the bottom of the cell in the form of crystals, ready to renew the combination when the cell is again heated. None of the materials of the element are destroyed, they last an indefinite time. The chlorine changes from chromic chloride to tin and back, as often as the cell is heated and cooled.¹

It is well known that the voltaic battery converts the potential energy of a metal directly into electricity, without heat. This cell, similar to the voltaic battery, converts heat into electricity. The voltaic battery acts at ordinary temperatures, giving up all the energy stored in the metal, and there is the end of it; while this cell acts only when heat is applied to it, converting part of this heat into electricity. After the tin has all been converted into chloride the cell becomes inert, no matter how much more heat be applied. The cell must then be cooled to get this tin back into the metallic state, so here it is necessary to have a difference of temperatures, the tin and liquid being simply a medium by which heat is transformed into electric energy.

It will probably be found that the solution of the tin absorbs heat, and so tends to cool the liquid, and the precipitation develops heat, and so tends to warm the liquid, and that the part where the solution occurs must be kept warmer than that where the tin precipitates. An investigation would probably show that when electric currents are generated the heat absorbed by the solution of the tin is in excess of that generated by the precipitation by the equivalent of the electrical energy developed, and that the possible excess is governed by the second law of thermodynamics. If the cell works between 80° and 180° F., the E. M. F. at the higher temperature is about 0.26 volt, the efficiency is less than 16 per cent., as the possible efficiency=

$$\frac{T - t}{T} \text{ reckoned from absolute zero, or } \frac{638^\circ - 538}{638^\circ} = .157.$$

In fact, this cell is a heat engine, analogous to the thermopile

¹ This cell has been described in Proc. Roy. Soc. No. 244, 1886.

which is said to convert only 2 per cent. of the energy of the coal into electric energy. In practice probably nothing like 16 per cent. could be utilized.

It is an inexorable law of nature, that under the conditions in which we live a great waste must accompany the transformation of heat into any other form of energy. In the condensing steam engine it requires to condense the steam four or five pounds of water to every pound of steam. Three-fourths the heat used goes to warm that water, and is wasted. In hot air engines or gas engines a cold water jacket must be used, and to it goes the larger share of the heat employed. In the thermopile one set of junctions must be kept cool by circulation of air or water. In Edison's pyromagnetic generator the iron tubes must be cooled by a blast of cold air.

By the second law of thermo-dynamics the minimum amount of heat that goes to this cooling agent is the fraction $\frac{t}{T}$ of the total amount employed, where t is the temperature of the cooler, reckoned from the absolute zero, and T the higher temperature of the working substance; t cannot be less than about 500° , so the numerator of the fraction is always large, and the heat wasted is the larger portion. Understand that this is a law of nature; it is inevitable under the conditions in which we live. No cunningly devised furnace, or feed water heater, or cut-off, or triple expansion apparatus, or pyro-generator can save this heat. The most that any of these devices can do is to save what would otherwise be wasted over and above the proportion $\frac{t}{T}$. But are we to go on wasting all this energy of fuel? Cannot some means be employed to utilize it? We know that the voltaic battery is not a case of the transformation of heat into electrical energy; it produces electrical energy directly. The second law of thermodynamics does not apply, as no heat appears. If we could convert the chemical energy of coal and oxygen into electric energy, directly and cheaply, we would do away with all our steam motors at once. There is no known reason why a cheap substance may not be found which will act on coal and develop electric currents in place of heat. This electric energy would be the equivalent of the heat energy that would be developed by the combustion of the same coal in the ordinary way, and could be transformed into mechanical power, heat, light, etc., with small loss.

So far, little progress has been made in this direction. Some time ago, Jablockhoff produced a battery in which plates of carbon and iron were immersed in fused nitre. The carbon being oxidized, furnished strong currents. The objection to this element is the generation of heat through local action. To it the second law does not apply. Another experiment of more interest than the first, is an illustration of an element which is not affected by the second law, as heat is not essential to its operation. The energy due to the complete oxidation of carbon is converted into electric energy directly.

In a glass cell containing sulphuric acid, C. P. Sp. Gr. 1.81, temp. 75 Fah., two electrodes were immersed, one of platinum, the other of lump graphite; only a slight E. M. F. was indicated 0.007 volt, due to the combination, the graphite acting as a positive element; on the addition of a small quantity of chlorate potassium to the acid, the E. M. F. immediately rose to 0.8 volt, the graphite being disintegrated after a time. This cell polarized rapidly, which was partially prevented by mechanical means. The reaction of chlorate potassium with sulphuric acid may be represented by the following equation: 3KClO_3 (chlorate of potassium) + $2\text{H}_2\text{SO}_4$ (sulphuric acid) = 2ClO_2 (peroxide of chlorine) + KClO_4 (perchlorate potassium) + $2\frac{1}{2}\text{KHSO}_4$ (acid sulphate of potassium) + H_2O (water).

A method of exclusion was adopted to ascertain the oxidant of this electrolyte; chlorine peroxide (ClO_2) appeared to be the only active agent. It is decomposed by the carbon, chlorine being evolved with some oxygen. It was assumed that in this cell graphic acid ($\text{C}_{11}\text{H}_4\text{O}_5$) was formed¹ as the result of the chemical actions. There is probably much waste of energy through local action, as the chemical reactions go on when the circuit is open, but to a less extent. In another experiment an electrolyte was formed of sulphuric acid and chlorine peroxide, the gas being formed in a retort by the action of sulphuric acid on chlorate potassium, and conducted over into the acid in which it was dissolved. This cell, with a positive element of graphite, opposed to platinum, gave an E. M. F. of 0.7 volt.²

¹ See Q. J. Chem. Soc. Vol. XII, 1859.

² Great care must be taken in the preparation of this gas, as it explodes at a temperature of about 140° F. It can be preserved in the dark. And is decomposed by sunlight into its component parts.

A similar combination was used with a solution of chlorine peroxide in water as the electrolyte. The E. M. F. assigned to these cells is only approximate, as it was found dependent on the quantity of chlorine peroxide in solution, which was constantly changing. The resistance also varied with the different degrees of concentration of the exciting fluid.

Different forms of amorphous carbon were substituted in place of graphite in the first form of cell. Gas carbon gave an E. M. F. 0.007 volt when opposed to platinum in sulphuric acid; on the addition of chlorate potassium the E. M. F. rose to 0.5 volt.

Carbon, produced by the action of sulphuric acid on cane sugar, in this experiment, gave an E. M. F. of 0.3 volt.

The carbon of animal charcoal, wood charcoal, coke and anthracite, gave an E. M. F. variable with each form, ranging from 0.3 volt to 1.25 volt. The measurements of E. M. F. of the various combinations were made with the electrode immersed in separate parts of the same solution, that the concentration of the liquid and quantity of gas in solution might be as nearly equal in each cell as possible. It was found when the carbon in comminuted form was contained in a porous cup, that the combination gave an E. M. F. of 1.24 volt, apparently due to the presence of the oxygen of the air.

It is impossible at the present stage of the investigation to assign any definite value of the E. M. F. to these forms of amorphous carbon. In some cases they appear to have an E. M. F. higher than that of graphite.

The energy of the combination of carbon and oxygen, when completely oxidized to (CO_2) carbonic acid gas, is stated to be 9624, foot-pounds per grain equivalent, which is 2.0594 equivalents.¹ In these carbon elements the E. M. F. is not so high, as there must be deducted the counter E. M. F. or polarization, and the energy due to the force of setting chlorine free.

A resort to chemical analysis, of the products formed by the reaction in the cell, indicates the following conclusions:

First.—Carbon produced by the action of sulphuric acid on cane sugar proved to be partially oxidized, or impure carbon.

Analysis gave the following values:

C	62.20 per cent.
H.....	1.61 per cent.
O.....	36.19 per cent.

¹ See Sprague's Electricity, p. 5, 19.

Analysis proves that ($\text{H}_2\text{SO}_4 + \text{KClO}_3$) sulphuric acid + chlorate of potassium oxidizes carbonaceous bodies, like the above product of (H_2SO_4) sulphuric acid on cane sugar, to CO_2 , and further, that such bodies first are changed to compounds soluble in the acid (caramel-like substances), which are rapidly oxidized to CO_2 .

Second.—Battery carbon of the composition :

C.....	96.20 per cent.
H_2O	70 per cent.
Residue of Fe. and SiO_2	2 30 per cent.

The fact was shown that this form of carbon can be oxidized CO_2 .

Third.—Wood charcoal, of the following composition after ignition.

C.....	94. per cent.
H_2O	5.5 per cent.
Silicious res.....	.5 per cent.

This, after repeated re-ignition, was oxidized by the electrolyte to CO_2 , no intermediate compounds being formed, and further, in case of pure amorphous carbon the oxidation is complete ; that is, that all the carbon is oxidized to CO_2 .

These analyses were made with the solution at a temperature of 122 F. to hasten the action, the carbon being in contact with the platinum. In these elements the oxidizing material is too expensive for practical use.

Undoubtedly the direction of experiments in the future will be to find some cheap substance which will absorb oxygen from the air and give it up to the carbon ; in fact, acting as a carrier of oxygen, so oxydizing it without heat ; and this is not improbable, as we already know of substances which do this, though giving a low E. M. F.; thus, for instance, the ferric salts are reduced to ferrous by agitating their solutions with carbon, being regenerated by absorbing oxygen from the air.

By pursuing this line of investigation, we can be sure we are not ignorantly striving against any law of nature when attempting to convert the whole potential energy of carbon into electrical energy.

DISCUSSION.

MR. C. O. MAILLOUX: Mr. Case also favored us by sending a sample of the battery, which you have before you. It consists of a porous cup, in which the graphite in lumps is placed, and outside of which is a sheet of platinum. Sulphuric acid, of the greatest density obtainable, chemically pure, is placed in both the inner and outer vessel. As explained in the paper, in order to render the sulphuric acid active, he puts the chlorate of potassium into the outer vessel, which gives it that light wine color. I have brought a little galvanoscope which I have calibrated for the purpose, so that it gives a rough indication of the voltage of the battery. Each division represents $\frac{5}{100}$ of a volt., and when I close the circuit you will see that it gives a deflection of about 14 degrees. That would be equivalent to about .7 of a volt. I think that Mr. Case states that the electromotive force of his battery is between .7 and of a .8 volt; but, unfortunately, as you notice, the electromotive force falls down very rapidly, owing to polarization. You will notice it is falling down. It is now only 12 degrees. It seems to stay there better, but if I let it rest a little while, it comes to more nearly the full strength, though not quite. I might add for the information of the members that Mr. Case states, in a note sent with the battery, that the internal resistance is about 2.7 ohms, and that when placed on short circuit it gives, approximately, a quarter of an ampère for a short time. He adds, by way of explanation: "You understand I am not showing a practical invention; simply showing a new principle which may be developed." I think you will all agree that undoubtedly there is here a wonderfully interesting principle and one which would be as valuable as the philosopher's stone, if ever even half of what was expected from the philosopher's stone is realized from it.

MR. TOWNSEND WOLCOTT:—I would like to ask why it polarizes so. As I understand, the oxidizing liquid is in contact with the platinum. It ought to act, I should think, like the chromic acid in a Poggendorff cell, to oxidize the hydrogen; or, is it hydrogen that polarizes it?

MR. MAILLOUX:—He states that the polarization can be prevented by mechanical means; so that it is probably due to uncombined chlorine.

MR. WETZLER:—I was about to suggest that the polarizing might be brought about by the setting free of the peroxides of chlorine; that is the gas produced, and it is probably the one that does the polarization.

MR. F. B. CROCKER:—In regard to this polarization, it is very evident that the active material is peroxide of chlorine ClO_2 following Mr. Case's nomenclature, which is in solution in the liquid. The oxygen of the ClO_2 combines with the carbon, and sets free chlorine on the platinum plate, and that, of course, polarizes the cell. I should imagine that Mr. Case's mechanical means for preventing polarization, are just the same as the mechanical means usually employed in cells which polarize by the setting free of gas on the negative plate, viz.: simply shaking them, roughening the surface of the plates, using a platinized silver plate or anything of that sort, to more or less get rid of the gas, and in that way reduce polarization. I do not see any other cause of polarization there except, perhaps, that there is also the formation of carbonic acid gas on the positive plate. That also would produce polarization.

MR. C. S. BRADLEY:—Perhaps I might be able to give you something interesting. Of course many of you are aware of this method of calculating the possible volt to be obtained from any combination. Now, this seems to me hard to understand. (Referring to equations on the blackboard.) In calculating the volts, I use the whole number; I do not use the equivalents. I use English measure, also. If anybody wishes to reduce it to French measure, or anything of that sort, he can do so. The heat units which are given out by the combination of different substances, of course, can be found in many works. In Watt's Chemical Dictionary, which I have here, you will find the heat of chemical combination and the heat of chemical action. You will find the various energies given and the various heat units given out by an atom of the various substances, and it is very fully carried out and the whole thing has been demonstrated by experiment. Now, we find, when we refer to carbon and oxygen, that carbon, in combining to form carbonic acid—12 pounds of carbon uniting with oxygen will heat 94,800 pounds of water one degree Fahrenheit. That is Andrew's determination. Favre and Silbermann give 96,960. Now, in the first place it is necessary to reduce everything to a hydrogen basis. We find that there are two

atoms of oxygen. This calls for four atoms of hydrogen. Therefore it is necessary to divide 96,960 by 4, giving 24,240. Now, the volt is about 23,030. I have tried it both experimentally and by calculation, and that is as near as I have been able to come to it. I presume that is not accurate. I do not recommend it as an accurate thing. That, you see, would give a trifle over a volt. It is, perhaps, .01 over a volt that that carbon is capable of giving theoretically. That, of course, can be determined experimentally. There is also a way of calculating it from the foot pounds and the correlation of forces, etc. You can get but a certain number of volts out of any combination of two substances, no matter what they are, and you can calculate to just the possible amount that you can get in volts, and you can get no more.

The question of resistance is one of the main points in the whole of this subject; I tried, in 1882, quite a long series of experiments with fused salts and their action upon coal. Of course the oxygen of the atmosphere is absolutely necessary. We cannot, by any means, expect to accomplish direct conversion unless we use the oxygen of the atmosphere. Otherwise, we must use a manufactured product which must be very expensive. Therefore, we have got to introduce the oxygen of the atmosphere, which is just as essential as the coal. That battery costs a great deal more to run from the chlorate of potash used there than a zinc battery. So that to get cheap power in that way, it is necessary that you should use carbon or hydrogen, or a combination of them, and the oxygen of the atmosphere; and to use the oxygen of the atmosphere, you must either supply it at the time you are operating with the coal, or from the manufactured article. Manufactured articles are dear; so it is necessary to use it at the time. Therefore, I hit upon the plan of taking manganate of sodium or potassium and putting a blast of air through the electrolyte, and by that means supplying it with air and allowing it to act on the coal which is put into another part of the vessel. The main point is the resistance. The voltage falls very little short of the theoretical. That is all right; but the resistance is too high for it to be practical. At least, I have always so regarded it. It would require a pond about ten feet in diameter per horse-power. (Laughter.) That is, if you allow two inches between the coal. Of course, coal is a rough substance. You have got to allow a considerable distance between your plate on which the oxygen supply is furnished and the coal, which of course runs up the resistance.

Then, in studying up the matter, I found in Watt's Chemical Dictionary that F. Braun had a determination of the conductivity of fused salts in the neighborhood of their melting points. Putting the conductivity of mercury at zero, that of the best sulphuric acid, is about 7,700, the following numbers were also obtained: Chloride of lead, 32,200; nitrate of soda, 11,475, and so on. But, of all the records I have ever found, and in all the experiments I have tried, chloride of lead is of the lowest resistance or the highest conductivity among the salts. It is about four times as good as the best sulphuric acid. We noticed in some of the electrical papers of a late date, mention of Mr. Acheson's device, in which he proposes to use gases in one case. Now, gases are of a great deal higher resistance than any fused electrolyte, and the fused electrolyte, of course, is, as I said before, too high. The lead chloride is the lowest. It is possible, of course, that somebody may find substances of very low resistance, but it is rather a hard job. Now, of course, I do not mean to advance this as a pessimistic view of the matter at all. It is just simply to make a statement of the conclusions which I have reached which I hope may be of benefit to other people, and perhaps save them some experiments and time.

MR. JOSEPH WETZLER:—The previous speaker, in criticizing the apparatus devised by Mr. Acheson in which gases are used as the medium between the electrodes, has remarked that they are of very high resistance. I think that is a question of relativeness merely. I do not know what the absolute resistance of the fused products is, which the previous speaker employed, but we all remember the experiments originally made by Faraday, who, after placing the points of an electric circuit apart, heated up the terminals of the platinum wires and effected the passage of the current thereby. You also know that if we heat the air sufficiently as is done in an electric arc, we get comparatively very low resistance.

MR. BRADLEY:—I also made this experiment. I employed an outer vessel of zinc in which was placed a porous cup containing a bar of zinc. The outer vessel was filled with a concentrated solution of zinc chloride, and the porous cup was fed by a constant stream of fresh water to maintain the solution within it dilute. The vessel was then heated by a Bunsen burner from below. (See illustration.)

In that way I could control it so as to keep the inner zinc cool, while the outside dish was heated.

It is well-known that chloride of zinc has a high heat of solution. My idea was that if I could keep a strong solution in the outer vessel just on the point of crystallizing in contact with the zinc, and a weak solution within the porous cup, I could cause a

BRADLEY'S EXPERIMENTAL BATTERY.

passage of the molecules of zinc across, and a current to be generated. The calculated electromotive force from the arrangement was .3 of a volt. I worked at it a good while before I got .3 volt, but I finally succeeded. The question of resistance, of course, comes in and that is the greatest difficulty in all apparatus of this kind. On weighing the outer vessel and the interior plate, the latter should have lost, and the former should have

gained. But I found that the inside one had lost, while it was hard work to find that the exterior one had gained anything. So it left me in doubt whether those .3 volts were actually due to the heat of solution or not. But it is quite interesting as an experiment.

MR. CROCKER: That question of equi-volts is rather an interesting one. I shall not go into the figures, but I think Mr. Sprague, of England, has done the subject a good deal of harm by prefixing that "equi" to the well known term "volt." People are used to that word, but the result of prefixing "equi" to it has been that they have let it alone, just as if he had attached a dynamite bomb to it. And really I do not see why it is put there. An equi-volt, as far as I can see is just as much a volt as any other volt. It is well enough, perhaps, to designate volts obtained by chemical action as equi-volts; but I do not know any reason for it. You might just as well separate volts obtained by an Edison dynamo and call them Edi-volts. Really these equi-volts are just plain, ordinary North American volts. And I think that if the calculation of the E. M. F. of chemical action was more often used—it would be of great service in a great many cases. For example, Mr. Bradley and I, before we had made any experiment whatever on the subject, calculated out what would be the electromotive force of a combination of zinc and bromine; and we calculated, just as Mr. Bradley described there, by taking the heat units produced by the combination of zinc and bromine and then going through those figures we got 1.8 volts. By a great many experiments very carefully carried out we got 1.78 volts. Now that is just .02 different from our calculations. At first we got 1.8, because, of course, the instrument would not detect that .02. It was only by continual experiments that we got the average of 1.78. Now that is close enough for all practical purposes, and you can arrive at results which are practically close enough, with a combination of zinc and iodine, for example, or any combination of two elements, or an element and a compound body. For instance, you can calculate out the electromotive force of zinc and chromic acid, or nitrate of soda or anything of that sort, and you will arrive at results which approximate plenty close enough for practical purposes with the actual electromotive force obtained by experiment.

Now, that seems to me to be a very important thing, because

very often you want to find out these facts and have not time to try them and you save yourself the experiment by calculation. Of course all kinds of short cuts like that are very often a great advantage to the investigator, and so far as I know this one is very seldom used. Mr. Sprague is about the only authority who speaks of it at all, and in practice I have never met any one who used this method. Some people doubt that you can get reliable results in this way. They claim that they are mere accidental coincidences, but I think when they occur a great many times and when you can actually prove mathematically, that there is such a relation, then there can be no longer any doubt about it.

The contact theory has also prevented the adoption of this calculation of electromotive forces. The idea is that there is a contact difference of potential; that it is not due to the chemical action, but is due to the contact; the chemical action merely keeps up the action. I never could see much in that contact theory myself. If you have a certain amount of chemical affinity and it produces so many units of energy in the form of heat in combustion, why shouldn't it produce the same amount of energy in the form of electricity in a voltaic cell? The contact theory is one of those things that you cannot see any reason for—why should zinc and bromine have a contact difference of potential of 1.8 volts? Whereas you can see a very good reason why they should have a chemical electromotive force of that amount. The contact theory is a purely arbitrary thing. A man tells you there is a contact difference of so and so. There is no reason for it that I can see, and the fact that the contact difference of potential is usually the same in liquids as in air, is due to the fact, that there is oxygen, moisture, etc., present in both cases, and you have substantially the same conditions in the air that you have in a voltaic cell.

Those two theories of contact difference of potential and the “equi” prefix to “volt” have retarded a very important branch of science, I think.

MR. WOLCOTT:—I do not understand why the zinc would be dissolved off from one electrode and deposited on the other. Does the chloride of zinc dissolve the metallic zinc?

MR. BRADLEY:—The Grotthuss hypothesis is generally understood—that there is a chain of molecules of chlorine and zinc, all the way across the electrolyte. If there is more affinity for the

zinc on one side than there is on the other, the zinc will cross over as soon as the circuit is closed.

MR. WOLCOTT:—But I do not see where you get your affinity unless there is some tendency of the chloride of zinc to attack the zinc.

MR. BRADLEY:—Here the water plays a part. Of course you could devise all sorts of theories to account for it. The water, of course, and the zinc chloride have an affinity for each other.

MR. WOLCOTT:—If you have free chlorine you are all right.

MR. BRADLEY:—If you have got free chlorine on one side and zinc on the other; here you have free chlorine on one side and free water on the other.

MR. WOLCOTT:—You have got something to attack that zinc to begin with.

MR. BRADLEY:—Not necessarily. Suppose you are transferring copper by electrolysis.

MR. WOLCOTT:—You have got the outside electromotive force to do that.

MR. BRADLEY:—Here you have got a chemical affinity or a chemical pressure.

MR. WOLCOTT:—You have got a chemical affinity, but it leaves out the zinc.

MR. BRADLEY:—It is the heat here that is doing it.

MR. CROCKER:—The chloride of zinc does dissolve the zinc off on one side.

MR. BRADLEY:—Yes, and deposits it on the other side.

MR. CROCKER:—Just the same as in the case of chlorine and zinc cell. You do not have the chlorine directly in contact with the zinc. You have chloride of zinc between.

MR. BRADLEY:—The chlorides of tin are the best to perform it with. In this case you have the stannous chloride on one side and the stannic chloride on the other, and then the chlorine runs across.

DR. GRIMSHAW:—I should like to inquire, in reference to the allusion there to the graphitic acid, if that alleged fourth condition of carbon called *graphon*, has been positively proved to exist?

MR. MAILLOUX:—I can only say that the paper was handed to me but a few minutes before the meeting began, and I must take it from Mr. Case's own statement. I can neither substantiate it nor refute it. However, as the presence of other, similar, analogous acids has been either suspected or proved, such as sili-

con into silicic acid and various others—phosphorous, for instance, and sulphur, itself an amorphous substance; while on the other hand we have plumbic, cupric and boric acids and various other acids of that character, and it does not seem to me impossible that graphitic acid could exist. As I say, I only take it on hypothesis, which is the way Mr. Case gives it to us.

DR. GRIMSHAW:—There have been cases where the existence of new compounds of that kind has been announced and the statement afterwards withdrawn. There was one time when gas-carbon was supposed to be a fourth amorphous condition of carbon, and then the name *graphon* was applied to it, as a body forming an acid of that character. Afterwards I thought there was some doubt about it. A good many of the conditions of these elements ending in “on” have been shaken up badly within a few years. For instance, the amorphous condition of boron has been decided, I believe, to be the boride of aluminium. Very often it is a question whether alleged forms of carbon are not boron instead of carbon. The silicic acid, to which Mr. Mailloux referred, used to be known as the teroxide. I believe that is now upset. The amorphous forms of these three elements are pretty badly mixed in the minds of chemists.

Adjourned.

NOTE ON THE ABOVE DISCUSSION.

BY WILLARD E. CASE.

In answer to the inquiry of Dr. Grimshaw in reference to graphitic acid, I will say that according to Brodie Phil. Tr. 1859, 249, graphite is attacked by such an oxidizing mixture, as $\text{H}_2\text{S O}_4$, and K ClO_3 , gradually oxidizing it to $\text{C}_{11}\text{O}_5\text{H}_4$ (graphic acid) a substance crystalline and insoluble in all reagents, while a mor- phous carbons are oxidized to substances soluble in the strong acid mixture, but reprecipitated by water. As shown by the first analysis amorphous carbon in contact with platinum in a mixture of $\text{H}_2\text{S O}_4$ and K ClO_3 forms (caramel like) substances soluble in the acid which are rapidly oxidized to C O_2 . Graphic acid is formed then, only from the action of this mixture on gra- phite. Berthelot in a very extensive investigation. “Recherches sur les etats du carbon ann. de chim. Phys. [4] XIX—392” verifies Brodie’s work, but says the name graphitic

oxide is better, as $C_{11}H_4O^5$ is not an acid in a strict sense. When amorphous carbons are used as the oxidizable substances, chlorine is liberated on the platinum plate and carbonic acid gas on the positive plate. I adopted the expression "equi-volt" as I preferred to follow the terminology of the authority quoted. The E. M. F. can be calculated as Thompson showed by the first law of thermodynamics in 1851, that $E = J e \theta$. θ being the thermal value of all the chemical reactions going on per gramme of some one substance acted on, when a current is produced by or passed through the cell, e being the electro-chemical equivalent of this same substance J being 42×10^6 .*

* See Jenkin Elect. Mag., 3d Edition, 1876, p. 169-170.