THE THERMOELECTRIC PROPERTIES OF CARBON.[1]

By William C. Moore.

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In an attempt to learn something of the nature of the so-called amorphous carbon, an investigation of the thermoelectric properties of commercial arc carbons was begun in this laboratory in the early part of 1914. It is true that some work of this type had been previously reported upon by others, but the work of Buchanan,[2] is open to the objection that three carbon rods were used in series in measuring the thermal electromotive force of a carbon platinum couple, thus introducing the possibility of getting potential differences between the carbon rods themselves; while Monckman[3] measured the potential set up when a hot carbon rod was touched against a cold rod of similar material, without actually measuring the electromotive force set up when his carbon rod was an element of a couple employed in the usual way.

Monckman observed a change in sign of his galvanometer deflection when the hot rod was at 480° and the cold at 16°, and, assuming a gradual regular rise and fall of the thermal electromotive force, decided that the neutral point must have been in the neighborhood of 250° and that this indicated a change in the properties of carbon at that point.

While our investigation was under way, an article by Bidwell on "The Thermojunction of Carbon and Graphite"[4] appeared. This investigator noted that heating his carbon and graphite rods to near 2000° made the thermoelectric behavior more regular and attributed this to the expulsion of impurities. Differences in the original raw materials used in the manufacture of the carbons and changes in the nature of the carbon, except graphitization, were not taken into account by Bidwell. There is abundant evidence, however, that heating does actually change the properties of carbon,[5] and there is likewise some previous evidence that some of these changes are reversible.[6]

This evidence seems to be substantiated by our experiments, which covered a period of several months. During this time a large number of measurements were made on various kinds of arc carbons. A summary

[1] Read in abstract at the New Orleans meeting of the American Chemical Society.

[2] *Phil. Mag.*, [5] **20**, 117 (1883).

[3] *Proc. Roy. Soc. London* (*A*), **44**, 220 (1888).

[4] *Phys. Rev.*, [2] **3**, 450 (1914).

[5] See Moissan, "The Electric Furnace" (Lenher's translation, p. 38, *et. seq.* (1904 ed.), as to the effect of heat on the properties of lamp black, and Buchanan, *Loc. cit.*, as to changes in carbon filaments.

[6] Manville's work on the variability of the temperature of combustion of charcoal when subjected to temperature fluctuations (*J. chim. phys.*, **5**, 297–339 (1907)), and that of Brion (*Ann. der Phys.*, **59**, 215 (1896)) on the effect of sudden changes of temperature on the resistance of carbon filaments, may be cited in this connection.

of some of our typical experiments may therefore be of interest from the light they shed on the nature of amorphous carbon.

Experimental.

In the preliminary experiments, six arc carbons were used, two of which were of the same kind of carbon. These six pieces may be designated as 1, A, B, C, D, and E, respectively. A, B, C, D, and E were clamped in turn against 1; leads were fastened to the free ends, and the circuit completed through a millivoltmeter used as a galvanometer. The clamped ends were heated by a Meker burner. In every couple, except that formed by 1 and B, which were of the same kind of carbon material, there was developed considerable electromotive force. Carbon 1 was positive at the cold end in all cases except when E was the other member of the couple. In this case E was positive, and the electromotive force was greater than with any of the other couples.

D and E were now made into a couple; after 42 minutes' heating (to low redness) in the flame of a Meker burner, the thermal electromotive force had risen to about 7.25 millivolts, E of course being positive. A number of runs were then made, using various combinations of carbon to make the thermojunctions. The couple burned very rapidly at the higher temperatures. From carbon-carbon couples it was a natural step to carbon-copper couples. The burning of the carbon and the oxidation of the copper were so serious, however, that it was finally decided to make up couples by inserting the carbon into a long copper tube, $^7/_8$ inch internal diameter, and closed at the end to be heated. Contact between the carbon and copper was secured by flattening the closed end of the tube and forcing the wedge-shaped end of the carbon into this angle. The carbon was held in place by a brass rod which passed through a rubber stopper closing the copper tube. This rod was soldered at its inner end to a brass cap which made a tight contact over the end of the carbon, and served as a terminal for the carbon cold junction. The cold junction was kept cool by a stream of water playing over the copper tube. In making an experiment the air was continuously exhausted by means of a water pump. The copper tube showed a little leakage in some of the experiments but, even when leaking a little, protected the carbon from burning. It was noted that at the higher temperatures, the carbon became "copper plated" over a large portion of its length. The thermal electromotive force was measured by means of a high resistance Siemens-Halske[1] millivoltmeter; furnace temperatures by a bare base metal thermocouple. Above 600° these temperatures are accurate to within about

[1] In order to guard against changes of contact resistance, special care was taken to see that all contacts were well made, and in one case it was found that the resistance of a carbon-copper couple changed from 0.306 ohms at room temperature to 0.27 ohms at 720°.

15°; below that temperature, probably within 5 to 8 degrees. A Hoskins FB 204 electric furnace was used as the heating device. The copper tube and the thermocouple were in close proximity; each was immersed ten inches in the furnace.

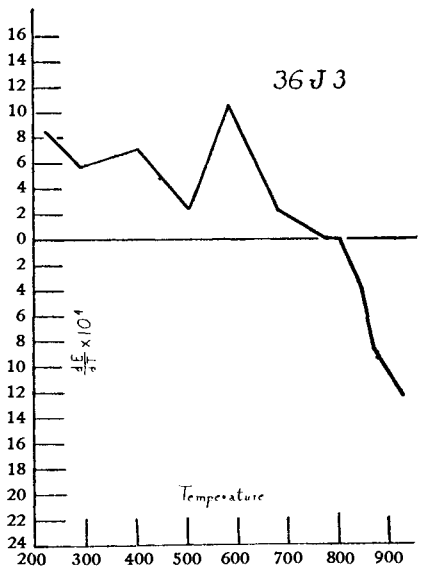
Table I gives a summary of the results obtained. The carbon used in Experiment 36J3 was of a different composition from the carbons used in 36J4 and 36J5. The thermal histories of these three carbons were different, but each carbon had been previously heated to a temperature higher than that finally reached in the experiments. We might also add that the maximum temperatures recorded below were purely fortuitous.

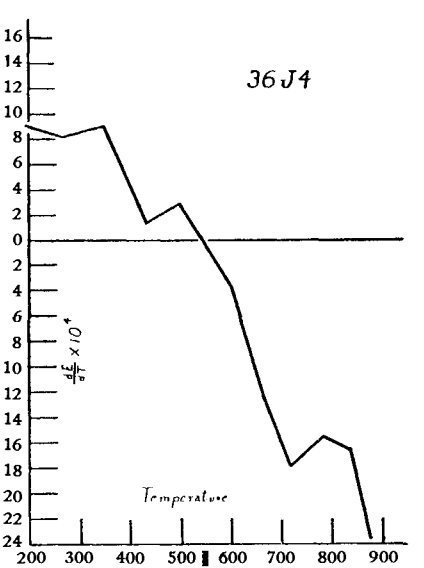
TABLE I.

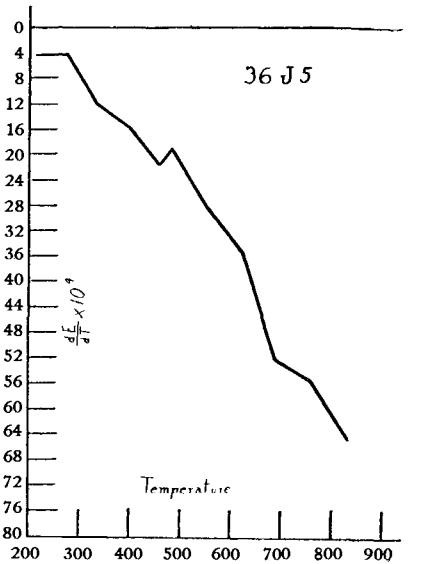
Expt. No.	Initial furnace temp.	Initial E. M. F. (M. V.)	Temp. difference at point max. E. M. F.		Fur. temp. at max. E. M. F.		Max. E. M. F. millivolts.
			Beginning.	Ending.	Begin.	Ending.	
36J3	157°	+0.08	717°	784°	741°	816°	+0.41
36J4	157°	+0.09	478°	528.5°	514°	565°	+0.30
36J5	169°	—0.06	..	..	..	..	—2.18

Expt. No.	Polarity.		Max. fur. temp.	E. M. F. at max. fur. temp. (millivolts).
	Initial.	Final.		
36J3	Cu.+	Cu.+	945°	+0.32
36J4	Cu.+	Cu.−	910°	—0.21
36J5	Cu.−	Cu.−	878°	—2.18

Explanation of Table and Discussion of Results.—The first three columns need no explanation. The fourth column shows the differences in temperature, of the hot and cold carbon-copper junctions, when the thermal electromotive force reached a maximum. This occurred only in Expts. 36J3 and 36J4. This maximum electromotive force *remained constant* over a considerable temperature range, and began to decrease when the temperature differences between the hot and cold carbon-copper junctions reached the values shown in the fifth column. The sixth and seventh columns show the actual furnace temperatures (± about 8°), at the beginning and end of this constant temperature interval, respectively. The other columns need no especial comments. This table shows most of the striking features exhibited by various carbon-copper thermocouples. It should be added, that the readings obtained with an individual carbon are approximately reproduceable. For instance, in Expt. 36-2-A in which a carbon-copper couple was used, several runs were made with the same couple, readings being taken both with rising and falling temperatures. Here, readings of 3.24 millivolts were obtained at the following temperature differences, the starred values being for falling temperatures in the furnace: 321°, *314°, 323°; and readings of 2.40 millivolts at temperature differences of 256° and *258°. In 36J3, after 945° was reached, the furnace was allowed to cool and the electro-


36 J 3
16 14 12 10 8 6 4 2 0 2 4 6 8 10 12 14 16 18 20 22 24
$\frac{dE}{dT} \times 10^4$
Temperature
200 300 400 500 600 700 800 900


36 J 4
16 14 12 10 8 6 4 2 0 2 4 6 8 10 12 14 16 18 20 22 24
$\frac{dE}{dT} \times 10^4$
Temperature
200 300 400 500 600 700 800 900


36 J 5
0 4 8 12 16 20 24 28 32 36 40 44 48 52 56 60 64 68 72 76 80
$\frac{dE}{dT} \times 10^4$
Temperature
200 300 400 500 600 700 800 900

motive force rose. When the temperature difference was 839° the electromotive force was 0.40 as against the same value, for a temperature difference of 847°, on the rising temperature.

If a carbon-carbon couple be set up, using different kinds of carbon, we may get very high electromotive forces. One couple of this type gave 14.59 M. V. when the cold junction was at 55.5° and the hot junction was at 707°.

It will be noted in the above table that there was a considerable temperature interval over which the electromotive force remained constant, in the two experiments, 36J3 and 36J4. This means, that the temperature coefficient of the thermal electromotive force remains at zero throughout a considerable temperature range. The attempt was made to plot the temperature coefficient of the potential, against temperature. The potential in most cases was so small, however, that steps of 50° or more were necessary to get any curve at all, and after plotting, the curves were very irregular, especially at the lower temperatures. For 36J3 the temperature interval for zero temperature coefficient was from 775° to 805°, while for 36J4, the *point* of zero coefficient was at 540°. It may be said, however, that the general directions of the temperature-coefficient temperature curves change for these two experiments, after passing through the zero point. For 36J5 all the potential values were such that the temperature coefficient was entirely negative, and the rough curve for this experiment was more nearly a straight line than with 36J3 and 36J4. These rough curves are shown in the appended figures.

The thermoelectric properties of various kinds of arc carbons are thus seen to differ considerably. These differences are in general due to two causes, (*a*) difference in raw materials used, and (*b*) differences in manufacturing history.

The general change of direction of our temperature-coefficient temperature curves mentioned as being noted in Experiments 36J3 and 36J4, taken with the long temperature interval of constant electromotive force for these couples, suggests that possibly some constituent of our carbon, may have passed through a transition interval in the temperature regions noted. Whether this constituent is a form of carbon or a complex compound of carbon is of course unknown.

Summary.

This study of the thermoelectric properties of carbon offers evidence from a new viewpoint that amorphous carbon is not a single definite substance. The thermoelectric properties of this material are reproduceable for any one carbon, but they may vary with the temperature, and are determined by the kind of raw material used and the manufacturing history of the carbon. The fact that with some varieties of arc carbons a considerable temperature range of constant electromotive

force was found, indicates the possibility of a transition interval for these carbons.

The author's thanks are due his assistant, Mr. J. B. Davies, for much of the painstaking experimental work involved, and Mr. W. R. Mott for aid in looking up the literature.

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A NEW CRYSTALLINE VARIETY OF SILVER.

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Various modifications of silver, many of them of somewhat ill-defined character, have, from time to time, been described.[1] Carey Lea has carried out an extensive series of researches on the properties of silver precipitated from a solution of its salts by ferrous citrate, ferrous tartrate, etc., in the presence of alkalis. His colloidal silver, which is held to be an allotropic modification of the metal, displays almost every shade of color—blue, red, green, purple and golden; some of his "precipitates" are very soluble in water and very sensitive to light. According to Lüdkte,[2] however, the mirror and the black silver, obtained by the reduction of silver nitrate with zinc, are allotropic modifications, while the work of Kohlschütter and Fischmann is an attempt to explain the way in which the specular form of native silver, known as hair-silver, is formed.

Experimental.

Spongy silver[3] was first prepared by igniting pure and dry precipitated silver tartrate in a crucible. Nitric acid, diluted with an equal volume of water, dissolved the silver completely. Strong nitric acid (sp. gr. 1.42), however, from which lower oxides of nitrogen were removed by boiling with carbamide, was allowed to act on the spongy silver at the ordinary temperature. At first some action took place with the formation of silver nitrate, nitrous acid and oxides of nitrogen; but after a time the solution of silver stopped, and on allowing the mixture to stand with occasional shaking for about a fortnight, the remaining silver was converted into long needle-shaped crystals—easily visible to the naked eye.

At first a few thin, needle-shaped crystals appeared floating on the surface of the acid liquid which was being shaken; the test tube being allowed to stand again for some time, the crystals gradually increased in quantity, the larger needles remaining at the bottom of the tube. The nitric acid was decanted off and the crystals were thoroughly washed with

[1] Carey Lea, *Am. J. Sci.*, **37**, 476; **38**, 47, 129 (1889); *Phil. Mag.*, **31**, 238, 320, 497; **32**, 337 (1891); *Am. J. Sci.*, **48**, 343 (1894); Lüdtke, *Wied. Ann.*, **92**, 152, 1056 (1894); Kohlschütter and Fischmann, *Ann.*, **387**, 86 (1912).

[2] *Wied. Ann.*, **50**, 678 (1883).

[3] The spongy silver examined under the microscope showed no crystalline structure.