On the Thermoelectric Position of Carbon

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in some photographic researches. These results are not yet ripe for publication ; but I have thought it might be well to publish the method employed, as it is one of great convenience, and very easily carried out by any one who has a spectroscope and a photographic camera.

XXIV. *On the Thermoelectric Position of Carbon.*

By JOHN BUCHANAN *.

[Plate II.]

IN the very interesting paper read by Dr. J. A. Fleming before this Society on March 14, 1885, whilst discussing the question of the life of incandescent lamps, the author remarks that quite a large proportion of the carbon filaments are found to break at the negative end, that is near the point where the current passes from carbon to platinum. It seemed to me not improbable that the negative end of the carbon might be subjected to a heating action due to the operation of the "Peltier effect." The local excess of temperature thus produced might possibly account for the observed result. In any case the determination of the position of the carbon line on the thermoelectric diagram was of interest. I am not aware that this has been done before.

Result.—For the specimen of carbon I have tried, the Thomson effect is of the same sign as in copper, and about twice the value for that metal given by Prof. Tait, as quoted in Everett's "Units and Physical Constants," § 186. The thermoelectric power of carbon is given by my experiments,

$$e_c = -390 - 1.87t \text{ C.G.S. units,} \quad . \quad . \quad . \quad (1)$$

where t denotes, as usual, the mean temperature of the junctions. The neutral point of carbon with lead is therefore about -209°C .

Thermo-couple of Platinum-Carbon.—As I have mentioned, the series of experiments described below were undertaken with the object of finding the magnitude of the Peltier effect in incandescent lamps. I therefore examined specially the behaviour of a thermoelectric couple of platinum-carbon.

* Read June 27, 1885.

The platinum was a piece of ordinary commercial wire procured from Messrs. Johnson and Matthey. The carbon was in the form of rods 12 millim. diam., such as are made for use in arc lamps. The direction of the current in such a couple is from platinum to carbon across the hot joint. The thermo-electric power at the mean temperature t is

$$e_{pt-c} = +566 + 3.94t \text{ C.G.S. units.} \quad . \quad . \quad (2)$$

Due, therefore, to the "Peltier effect," heat will be generated at the negative end of the carbon filament of an incandescent lamp when the current is passing. We can now calculate what proportion the heat thus generated locally bears to the whole quantity of heat generated in the filament.

If T denote the neutral point of a thermo-couple, then the Peltier effect for the absolute temperature θ at one joint is given by

$$\pi = (K_1 - K_2)(T - \theta)\theta, \quad . \quad . \quad . \quad (3)$$

where K_1 and K_2 are the numbers that express for each material the ratio that the Thomson effect bears to the absolute temperature. (See Tait's 'Heat,' §415.)

Hence for a platinum-carbon couple,

$$\pi = 3.94 (144 + \theta)\theta. \quad . \quad . \quad . \quad (4)$$

As a specific example, take the case of a 100-volt lamp, with the filament at a temperature of 2400°C . We get the ratio

$$\begin{aligned} \frac{\text{Heat due to Peltier effect}}{\text{Whole heat in filament}} &= \frac{3.94 \times 2673(144 + 2400)}{100 \times 10^8}, \\ &= \frac{2.7 \times 10^7}{10^{10}}, \\ &= .0027. \end{aligned}$$

The local heating at the negative end of the filament is therefore only about one quarter per cent. of the whole heat. This is too small to have any appreciable influence on the life of the lamp. It does not appear therefore that the Peltier effect accounts for the giving way of the carbon-filament at one end rather than at the other. In the course of these experiments one phenomenon was forced on my attention, the details of which are given below. It seems that con-

tinuous heating alters the thermoelectric properties of carbon. This alteration must be the result of molecular change in the material. That this has any bearing on the destruction of the filament that ensues, by keeping it for a long time at a high temperature, my experiments are not extended enough to decide.

Experimental Details.

The E.M.F. at various temperatures was determined by the null method known as Poggendorff's.

The primary circuit contained a constant cell A, a graduated wire BC, and a box of resistance-coils R.

On the graduated wire were placed sliding pieces *e* and *f*, which served as the terminals of the secondary circuit. In the secondary circuit were a galvanometer G, and the thermo couple T whose E.M.F. was to be measured, and a key K.

Fig. 1.

The arrangement of the apparatus used in the platinum-carbon experiments has now to be described.

Three rods of carbon of 1.2 centim. diameter, such as are manufactured for use in arc-lamps, were taken. One of these was thinned down into a conical form at the end destined to go into the hot bath. This end, and that of another rod intended to go into the cold bath, were electroplated with a thin shell of copper. To this copper shell were soldered the platinum wires, whose behaviour with the carbon I wished to examine. These two rods were then placed vertically and clamped in position with coppered ends dipping into their respective baths. The upper ends of these carbon rods were cut off square and the third rod laid horizontally, so as to

form with the vertical rods the third side of a vertical rectangle.

To ensure good contact one end of this third rod was bound by a number of turns of clean iron wire to the upper end of the rod whose lower end dipped into the cold bath. The other end of this third rod rested on the top of the rod the lower end of which dipped into the hot bath. The surfaces of contact were here scraped flat and kept pressed together by a weight of 3 or 4 pounds.

The platinum wires that formed the other element of the thermo-couple were of ordinary commercial material, as was mentioned above.

The galvanometer used in the secondary circuit is a very delicate mirror instrument of about $\frac{1}{4}$ ohm resistance.

The cell used in the primary circuit as a standard was a Daniell. The graduated wire (BC in fig. 1) was of German silver.

The baths, both hot and cold, were oil-baths.

The ends of the platinum wires of the thermo-couple that were exterior to the baths were joined by binding-screws to copper wires. These joints were insulated from one another by several layers of calico, and then tightly wrapped up together. Thus in the secondary circuit the only exposed contacts of dissimilar conductors were those of the copper wires joined up with the brass binding-screws of the key, of the galvanometer, and of the sliding piece on the graduated wire. During the experiment, care was taken to screen these exposed contacts as much as possible from external radiation. Moreover, all the apparatus was set up the night before, so that on the days of the experiments no metal joints whatever in the secondary circuit were touched by hand.

Some preliminary experiments I had made showed the necessity for adopting the arrangements just described. The results of these preliminary trials exhibited very curious irregularities, not altogether got rid of even by those latest arrangements. By using the precautions detailed above, I ensured, however, that the place of any disturbances that might come into play should be located with certainty in the thermo-joints under examination.

The proper amount of resistance to be inserted in the

primary circuit having been determined beforehand, the primary circuit was closed. The current was allowed to flow during the whole time the experiment lasted. The temperature of the hot bath was raised very slowly up to the highest point reached; then as slowly lowered again. Frequent readings of the thermometers in the hot and cold baths were taken. Simultaneously were noted the positions of the movable sliders on the graduated wire, for which no deflection was shown by the galvanometer on depressing the key in the secondary circuit.

When a temperature reading was intended to be taken, the temperature was kept as steady as possible for $\frac{1}{4}$ to $\frac{1}{2}$ a minute, accompanied with constant stirring of the hot bath. In this way a series of corresponding readings of temperature and of distances on the graduated wire were obtained. The results were plotted out, taking centimetres of the graduated wire as ordinates, and temperatures of the hot bath as abscissæ. A regular curve was then drawn amongst the points thus obtained, so as to give as nearly as could be judged the mean of the observations. The curves A, B, C (Plate II.) were obtained in this way. The scales for these curves are not quite the same. Details are given below. The curves A and B were obtained on successive days.

The want of regularity in the individual readings, after all the precautions taken, I considered could only be due to the properties of the carbon. Partly to satisfy myself that no essential precaution had been overlooked, however, and partly to test an idea I formed as to the cause of the irregularities, the apparatus was set up again about a month later. Curve C gives the results of the observations. The heating of the hot joint gave the curve to the left hand; the subsequent cooling gave the right-hand curve. These curves have not a point of intersection at their upper ends shown in the diagram (Plate II.), because the temperature was intentionally raised to a point higher than that for which a reading on the graduated wire could be obtained, before cooling down was begun.

Now, as $4\frac{1}{2}$ hours were given to the observations, the heating and cooling took place very slowly indeed. And as a stirrer was kept almost continuously in operation in the hot bath, the lagging of the thermometer behind the thermo-

joint must have been very small. I believe that the difference between the curves obtained by heating and by cooling is partly due to change taking place in the properties of the carbon as the temperature changes. Bearing on this there is an observation I made. Having calculated the neutral point of a carbon-iron couple as about $+208^{\circ}\text{C.}$, a glycerine bath was used to verify this result. Having raised the temperature to about 290°C. and cooled again to 220°C. several times, I found the E.M.F. of the carbon-iron couple rose gradually, until at the time of stopping the experiment the maximum E.M.F. had increased by more than 50 per cent. As is well known, a thermo-couple reaches a maximum E.M.F. when the temperature of one joint is that of the "neutral point." It was this maximum that was found to increase with the time during which heat was applied.

The conclusion is, that the thermoelectric properties of carbon alter with temperature. Principally for this reason I did not deem it of utility to begin a new series of observations, and by "loading" the hot joint with metal try to decrease the irregularities in the readings like those in curves A and B. Moreover, the results calculated from these curves agree as well as could be expected. Here are the details:—

Curve A.

Assuming the equation to the curve as

$$y = K(x - a) \left(T - \frac{x + a}{2} \right),$$

I find that $T = -147^{\circ}\text{C.}$, $K = 0.00470$

satisfy best the observations as represented by the curve A.

x = temperature of hot bath,

a = „ cold bath,

T = neutral point.

The agreement of calculated and observed values of y is exhibited by Table I.; these values, it will be recollected, represent centimetres of the bridge-wire. To calculate the E.M.F. of a carbon-platinum thermo-couple as given by curve A, we have the following data:—

Resistance of primary circuit = 303.6 ohms.

Observed E.M.F. of Daniell used = 1.03 volt.

Resistance of 1 centim. of the graduated wire = .00246 ohm.

Denoting the E.M.F. required by E_A , we get

$$E_A = 0.00470 \times 1.03 \times 10^8 \frac{0.00246}{303.6} (x-a) \left(147 + \frac{x+a}{2}\right),$$

$$\therefore E_A = 3.92(x-a) \left(147 + \frac{x+a}{2}\right) \text{ C.G.S. units.}$$

Hence the thermoelectric power of the couple is

$$e_A = +577 + 3.92 \times t \text{ C.G.S. units,}$$

t denoting the mean temperature of the joints. The direction of the current would be from Pt to C across the hot joint.

Curve B.

Taking an equation to the curve of the same form as that just used, $T = -140^\circ \text{ C.}$ and $K = 0.00406$ best satisfy observation.

TABLE I.

$x.$	$a.$	$y.$	
		Calculated.	Observed.
30°	9.75	15.9	15.8
40	9.82	24.4	24.2
50	9.85	33.4	33.4
60	"	42.9	43.1
70	"	52.9	53.0
80	9.9	63.2	63.4
90	"	74.2	74.1
100	"	85.5	85.1
110	"	97.4	97.7

TABLE II.

$x.$	$a.$	$y.$	
		Calculated.	Observed.
30°	9.6	13.5	13.2
40	9.65	20.3	20.3
50	9.70	27.8	27.8
60	9.75	35.7	35.7
70	"	43.8	44.0
80	"	52.6	52.7
90	9.80	61.9	61.9
100	"	71.7	71.4
110	9.85	81.8	82.4
120	"	92.6	91.6

Table II. exhibits the agreement of the calculated and observed values of y when these constants are inserted in the

equation to the curve. To calculate E.M.F. (E_B), the data are the same as were used in the calculation of E_A , except that the resistance in the primary circuit was 259.6 ohms.

$$\therefore E_B = .00406 \times 1.03 \times 10^8 \times \frac{.00246}{259.6} (x-a) \left(140 + \frac{x+a}{2} \right) \\ = 3.96(x-a) \left(140 + \frac{x+a}{2} \right) \text{ C.G.S. units.}$$

Hence for the thermoelectric power (e_B) at the mean temperature t , we get

$$e_B = +555 + 3.96t \text{ C.G.S. units.}$$

The mean of e_A and e_B being denoted by e_{pt-c} , we get

$$e_{pt-c} = +566 + 3.94t \text{ C.G.S. units,}$$

the result quoted in equation (2) above.

Thermoelectric Power of Carbon.

In order to find the position of carbon on the thermoelectric diagram, I determined the line on this diagram of the platinum employed in the above experiments.

A strip of commercial lead, about 80 centims. long, had the platinum wires soldered to the ends. The general arrangement of the apparatus and the precautions used were similar to what have already been described above. Curve D shows the results of the observations; the ordinates and abscissæ being the same as in the curves A, B, C. It will be noticed that the observations lie well on the mean curve, thus showing that the arrangements were not defective in any essential point.

Assuming

$$y = K(x-a) \left(T - \frac{x+a}{2} \right)$$

as the equation to the curve, as above, I find that $T = -85^\circ \text{ C.}$ and $K = .004815$ give results agreeing best with observation. (See Table III.)

TABLE III.

$x.$	$a.$	$y.$	
		Calculated.	Observed.
30°	13.1	8.67	9.05
50	"	20.7	20.6
70	"	34.6	34.7
90	"	50.5	50.8
110	"	68.3	68.2
130	"	88.1	88.0

The data for calculation are :—

Resistance of primary circuit = 1001 ohms.

Mean observed E.M.F. of the Grove cell } = 1.75 volt.
employed }

Hence the E.M.F. of the lead-platinum couple and the thermoelectric power of platinum are, respectively,

$$E = 0.004815 \times 1.75 \times 10^8 \frac{0.00246}{1001} (x-a) \left(85 + \frac{x+a}{2} \right);$$

$$\therefore E = 2.07(x-a) \left(85 + \frac{x+a}{2} \right) \text{ C.G.S. units,}$$

$$\therefore e_{pt} = +176 + 2.07t \text{ C.G.S. units.}$$

The current would be from Pt to Pb across the hot junction.

Using this value for e_{pt} , we find for the thermoelectric power of carbon

$$e_c = -390 - 1.87t \text{ C.G.S. units.}$$

This is the result quoted in equation (1) above.

In the table of thermoelectric powers given by Everett ('Units and Physical Constants,' § 186) there are given

$$\text{for Zn, } e_{zn} = -234 - 2.40t,$$

$$,, \text{ Ag, } e_{ag} = -214 - 1.50t.$$

The value for e_c shows that the place of carbon in the table is between zinc and silver. In the thermoelectric diagram it is easy to see that for temperatures below 50°C. , the line for carbon lies below that for cadmium, taking the value for e_{cd} from Everett's table (*loc. cit.*).

Concluding Remarks.

The disintegration preceding complete destruction of the carbon filament in an incandescent lamp, described by Mr. W. H. Preece, F.R.S., in a paper read before the Royal Society on March 26, 1885, is doubtless the result of molecular changes in the structure of the filament produced by the continued maintaining of the filament at an extremely high temperature. In my experiments, keeping carbon at a moderately high temperature altered the molecular condition of this material, the alteration being manifested as a change in the thermoelectric power of the carbon.

Physical Laboratory, University College,
London, June 1885.