

## SOME ELECTRICAL PROPERTIES OF SILICON.

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## I. THERMO-ELECTRIC BEHAVIOR OF METALLIC SILICON.

THE physical properties of metallic silicon, in so far as they have been investigated, show this substance to be of peculiar interest. The position of the element in the periodic system between the metals and non-metals may explain some of the deviations of its properties from those of the stronger metals. It resembles carbon, which stands next above it in the same group, in that it is a poor conductor of electricity and has a negative temperature coefficient of resistance.

The work here given upon the thermal electromotive force of silicon is the first of a series of observations upon the properties of this element which have been undertaken by the writer at the suggestion of Professors Nichols and Merritt. The silicon used is the most recent product of The Carborundum Company. It was cast in rods about 30 cm. long and 3 mm. in diameter by H. E. Heath,<sup>1</sup> of The General Electric Company, of whose kindness the author wishes to express her appreciation. The Carborundum Company state that their commercial product is at least 95 per cent. pure, the chief impurities being iron and aluminum.<sup>2</sup>

The extreme hardness and brittleness of silicon made the manipulation of it very difficult, the greatest problem encountered being that of making good electrical contact. An attempt was made to solder terminals to it, but this was impossible. The best connections were made by copper-plating the silicon. Even this method was not entirely satisfactory, since the copper plate pulls off easily.

<sup>1</sup> Mr. Heath, recognizing the large thermal effect of silicon in combination with different metals, has patented a thermo-couple, one member of which is to be silicon. Patent No. 824,015. June 19, 1906.

<sup>2</sup> Tone, Trans. Am. Electro. Chem. Soc., Vol. VII., 1905.

The method of determining the E.M.F. generated by a thermoelectric couple made of copper and silicon was as follows: The ends of a silicon rod were copper plated. Upon each end of this rod were placed two wires, one of copper and one of constantan. The electro-plating process was then continued until these wires were firmly fastened to the silicon rod by a bridge of copper. Pipe stems were used for insulation. Copper wires were soldered to the ends of these wires as shown in Fig. 1, making in all three sets of thermo-junctions, one of copper-silicon, and firmly plated to each end of the silicon rod, one of copper-constantan. The copper-

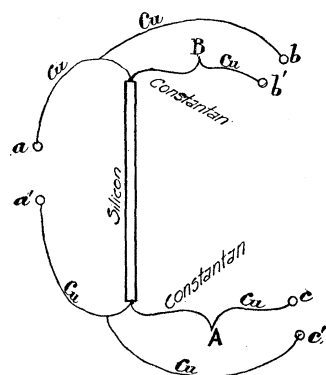


Fig. 1.

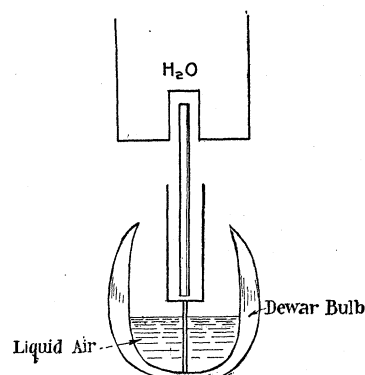


Fig. 2.

constantan couples were used for the determination of the temperature of the ends of the rod, the junctions not attached to the rod, *A* and *B* (Fig. 1), being kept at  $0^{\circ}$ .

The terminals of these thermo-elements *aa'*, *bb'*, *cc'* were dipped into mercury cups separated only by a thin layer of mica to avoid differences of temperature. Connections were thus easily made with potentiometer leads.

Measurements of thermal E.M.F. were made at temperatures ranging from about  $350^{\circ}$  to  $-190^{\circ}$  C., one end of the rod being kept as near  $0^{\circ}$  as possible. Since the silicon rod is a good conductor of heat it was difficult to maintain the ends at a great temperature difference. For high temperatures the upper end of the rod was placed in a heating coil made of iron wire wrapped around a porcelain tube covered with asbestos. The lower end of the rod was

placed in a metal tube and this in a Dewar bulb containing a freezing mixture. For low temperature ranges the lower end of the rod was placed in a metal tube from which heavy copper wires projected into liquid air in a Dewar bulb, as shown in Fig. 2. By raising and lowering this tube temperatures varying from  $0^{\circ}$  to liquid air temperatures could be maintained. The upper end of the rod was kept at approximately  $0^{\circ}$  by means of a heating coil or by projecting upward into a tube surrounded by water of the required temperature.

It was often impossible to get steady conditions with one end of the rod exactly at  $0^{\circ}$  when the temperature of the other end was extremely high or low, hence a number of tests were carefully made covering the range of temperature through which the end of the rod varied from  $0^{\circ}$ . A curve was drawn showing the relation between the E.M.F. of the copper-silicon junction and a copper-constantan junction, one end of each being kept at  $0^{\circ}$ . By means of this curve the E.M.F. obtained was corrected to give that which would be obtained with one end of the rod at  $0^{\circ}$ .

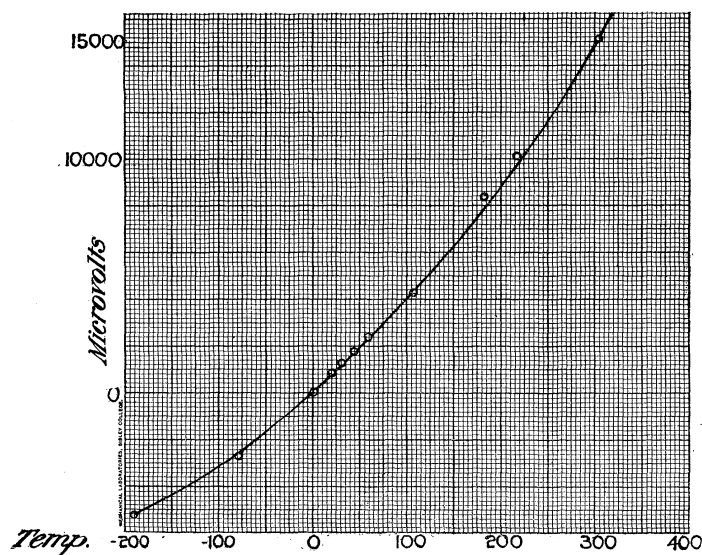


Fig. 3. Calibration curve of a copper constantan thermo-couple, one junction being kept at  $0^{\circ}$ .

The copper-constantan thermo-junctions on the ends of the rod were all made from the same spools of copper and constantan wire. A junction from these same spools had been made by Professor J. S. Shearer and calibrated from liquid air temperatures to the temperature of boiling benzophenone, the intermediate points being CO<sub>2</sub> and ether, water at temperatures from 0° to 100°, aniline and naphthalene. A similar junction made and calibrated through the same temperature range from -190° to +100° showed such agreement that the two calibration curves were identical.

TABLE I.

Rod No. 1. Length = 24.1 cm. Average Diameter = 3.24 mm. E.M.F. in Microvolts.

Copper-Constantan.		CuSi between (1) and (2).	CuSi between o and (2). From Calibration Curve.	CuSi between o and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
541	100	-4,421	-950	-5,371	13.5°
842.5	247	-6,119	-2,367	-8,486	22.5
865	240	-6,187	-2,300	-8,487	22.5
840.5	254	-6,095.5	-2,450	-8,545.5	22.8
1,605.5	180	-14,135.5	-1,720	-15,855.5	40.5
1,611	174	-14,170	-1,670	-15,840	40.6
2,282.5	277	-19,531	-2,600	-22,131	56.4
2,283.5	275	-19,583.5	-2,550	-22,133.5	56.6
2,446	307	-20,874.5	-3,000	-23,874.5	59.8
2,456	311	-20,931	-3,050	-23,981	60.4
2,460	308	-20,949.5	-3,000	-23,949.5	60.5
2,466	317	-20,960	-3,100	-24,060	60.8
2,889	260	-25,217.5	-2,500	-27,717.5	70.3
5,713	528	-47,061	-5,170	-52,231	129.8
10,374.5	727	-80,105.5	-7,200	-87,305.5	215
12,020	738	-90,890	-7,320	-98,210	252
12,113.5	670	-92,381	-6,620	-99,001	255
16,666.5	693	-118,732.5	-6,850	-125,582.5	339
16,207	681	-119,145	-6,750	-125,895	340
16,846.5	648	-120,351	-6,400	-126,751	342
			CuSi between o and (1).	Computed CuSi between o and (2).	
617.5	-1,437	+19,218.5	-6,100	13,118.5	-36°
483.57	-2,408.55	+27,419.3	-4,740	22,679.3	-69
604.5	-2,590.25	+30,005.5	-6,350	23,655.5	-72
519.3	-3,694.8	+41,812.6	-4,980	36,832.6	-110.5
161.25	-4,814.5	+51,324.3	-1,500	49,824.3	-159
63.3	-5,340	+58,819.7	-570	58,249.7	-187

This calibration curve is given in Fig. 3. The high temperature points are those taken from the observations of Professor Shearer, the low temperature points being those taken by the author. After the tests on thermal E.M.F. of silicon were completed the silicon rod with its two attached copper-constantan junctions together with the previously calibrated copper-constantan junction was completely immersed in liquid air. Comparison of these three junctions showed no variation among them.

## RESULTS.

The thermal E.M.F. between Cu and Si was thus obtained for three different rods. Tables I., II. and III. give the results. Table IV. gives the data used in drawing one of the calibration curves referred to above, from which the thermal E.M.F. which will be generated with one end of the rod at the given temperature and the other at  $0^{\circ}$  was computed. These curves are not reproduced here.

TABLE II.

Rod No. 3. Length = 21.2 cm. Average Diameter = 3.168 mm. E.M.F. in Microvolts.

Copper-Constantan.		CuSi between (1) and (2).	CuSi between o and (2).	Computed CuSi between o and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
140	0	-2,055	0	-2,055	4°
687.5	0	-7,721	0	-7,721	20.4
3,290	199	-31,005	-2,400	-33,405	79.2
4,753	318	-42,307	-3,550	-45,857	111
4,956	336	-43,865	-3,750	-47,615	114
4,965	331	-43,926	-3,670	-47,596	116
4,970	333	-43,910.5	-3,700	-47,610.5	116
7,988.5	557	-65,848	-6,220	-72,068	176
11,895	736	-91,835	-8,250	-100,085.5	250
14,247.5	877	-105,422.5	-9,780	-115,202.5	289
			CuSi between o and (1).	Computed CuSi between o and (2).	
439.7	-2,148.3	25,733	-4,700	21,033	-58°
262.36	-2,681.8	34,470	-2,920	31,550	-78.5
153.5	-3,732	41,076	-1,700	39,376	-113.5
1,543	-5,181	78,589	-15,000	63,589	-178.5
1,541	-5,181	78,537.5	-15,000	63,537.5	-178.5
300.4	-5,202	67,411	-2,950	64,461	-182.5

TABLE III.

Rod No. 4. Length = 30 cm. Average Diameter = 3.34 mm. E.M.F. in Microvolts.

Copper-Constantan.		CuSi between (1) and (2).	CuSi between o and (2).	Computed Cu Si between o and (1).	Temperature.
(1) Hot End.	(2) Cold End.				
104	0	-1,106	0	-1,106	3.3
560.5	0	-5,675.5	0	-5,675.5	15
768.5	0	-7,870	0	-7,870	18.5
754	0	-7,568	0	-7,568	19.3
1,395	0	-14,358.5	0	-14,358.5	35.5
1,632.5	60	-16,106.5	-600	-16,706.5	41
3,277.5	136	-31,635	-1,400	-33,035	79
4,403.5	0	-43,182	0	-43,182	103
8,780.5	60	-78,420	-600	-79,020	190
			CuSi between o and (1).	Computed CuSi between o and (2).	
205	-2,681	31,671	-2,100	29,571	-78.4
0	-5,204	60,442.5	0	60,442.5	-179

TABLE IV.

Calibration of Copper-Silicon Junction Against Copper-Constantan—one end of each being kept at 0°. E.M.F. in Microvolts.

Copper-Constantan.	Copper-Silicon.
560	-5,532.5
210	-1,996.5
190	-1,870
830	-7,950
81	-720

The direction of the current was found to be from Si to Cu through the hot junction. Silicon is therefore thermo-electrically negative with respect to Cu. Since Pb is also negative with respect to Cu the E.M.F. which would be generated between Pb and Si must be the difference between that generated by Cu-Si and Cu-Pb junctions at the given temperature.

This difference was computed by a table given by Dewar and Fleming.<sup>1</sup> The resulting curves for rods no. 1 and no. 2 are given in Fig. 4. The bismuth line from Dewar and Fleming's table has been put in for comparison. The original curve for thermal E.M.F. between Cu and Si at low temperatures is given in Fig. 5.

<sup>1</sup> Dewar & Fleming, Phil. Mag., Vol. 40, p. 95, 1895.

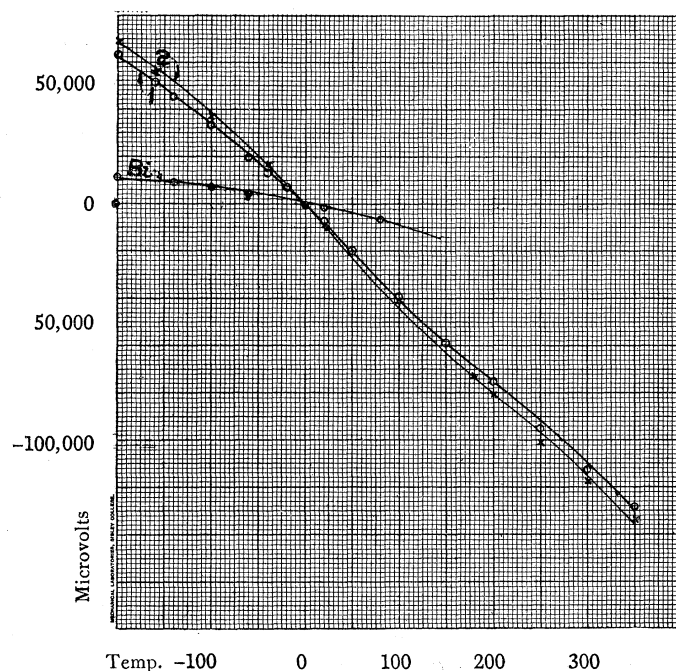


Fig. 4. Thermal E.M.F.

(1) Lead-silicon junction. Rod No. 1.

(2) Lead-silicon junction. Rod No. 2.

(B) Lead-bismuth junction.

Curves 1 and 2 were computed from Tables I. and II. and from copper-lead curve given by Dewar and Fleming.

It will be noticed that the thermal E.M.F. generated by a lead-silicon junction is very large. Another peculiarity about it is that the curve is not parabolic, being at least of the third degree. This double curvature may possibly be due to a large Thomson effect.

From curves drawn from the data given in Tables I. and II. the thermo-electric power of a silicon-copper junction was computed. This was done by finding the slope of these curves at intervals of  $20^\circ$ . The thermo-electric power line so found, given in Fig. 6, is not straight but has a maximum ordinate (negative) between  $0^\circ$  and  $100^\circ$  which diminishes as the temperature is raised or lowered.

The extremely large value of this thermal E.M.F. becomes evident by comparison with that produced by other metals in com-

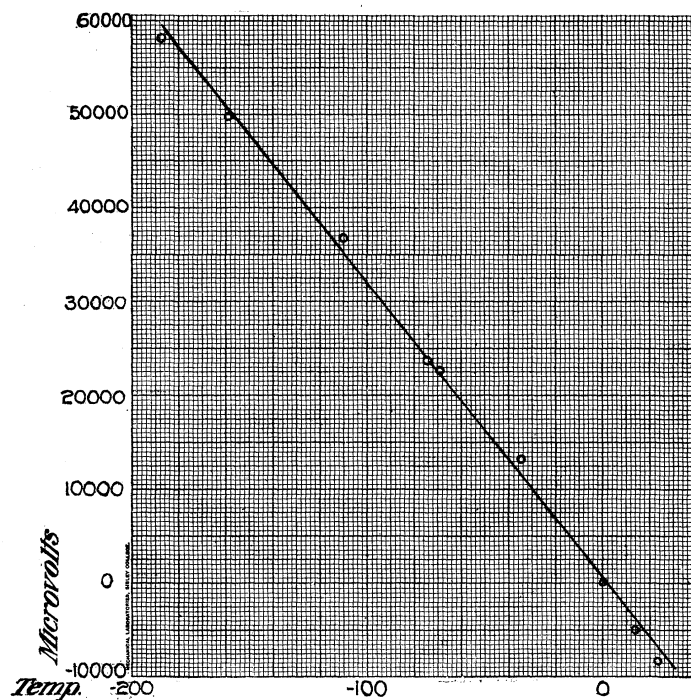


Fig. 5. Thermal E.M.F. between copper and silicon at low temperatures, one junction being kept at 0°.

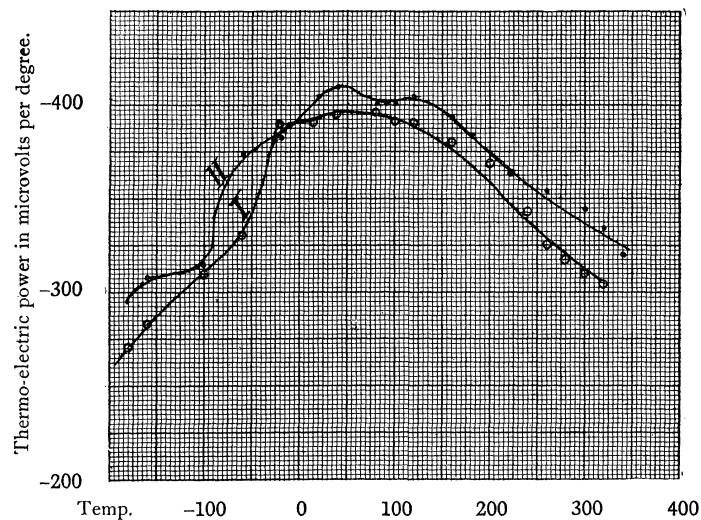


Fig. 6. Thermo-electric power of copper-silicon junctions in microvolts<sub>1</sub> per degree centigrade.

Curve I. computed from measurements upon Rod No. 1.

Curve II. computed from measurements upon Rod No. 2.

bination with lead measured in microvolts per degree centigrade at a mean temperature of  $20^{\circ}\text{C}$ . At this temperature a lead-silicon junction gives a thermo-electric power of about  $-400$ . The value for bismuth is  $-89$ , for antimony  $+26$ . Tellurium and selenium are comparable with silicon but of opposite sign, being  $+502$  and  $+807$  respectively.

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