CRYSTAL RECTIFIERS FOR ELECTRIC CURRENTS AND ELECTRIC OSCILLATIONS.

Part I. Carborundum.

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Introductian. — General H. H. C. Dunwoody of the United States Army has discovered[1] that a crystalline mass of carborundum when supplied with electrodes acts as a receiver for electric waves. In his patents pecification General Dunwoody shows several ways of attaching the electrodes to the crystal. One method is to wind the wires around the two ends of the specimen. Another method is to hold the crystal in a clamp of which the two jaws, insulated from each other, serve as electrodes. The crystal with its electrodes is put into a receiving circuit of a wireless telegraph system with a telephone and battery about the carborundum. The sounds heard in the telephone when a message is being re-

[1] U. S. Patent, No. 837,616, issued December 4, 1906; application filed March 23, 1906.

ceived are like those heard with the electrolytic detector. General Dunwoody also found that the battery could be omitted and the leads of the telephone connected directly about the terminals of the carborundum, and with this arrangement, without the battery, he says that he has read messages from a sending station several hundred miles away.

The present investigation was undertaken in the effort to obtain further knowledge of this interesting property of carborundum. The experiments were extended to include many other crystalline substances, but the present discussion is chiefly confined to carborundum.

Apparatus for Current-voltage Measurements. — Fig. 1 shows a sketch of a form of circuit employed in studying the conductivity of carborundum under various conditions. The crystal of carbo-

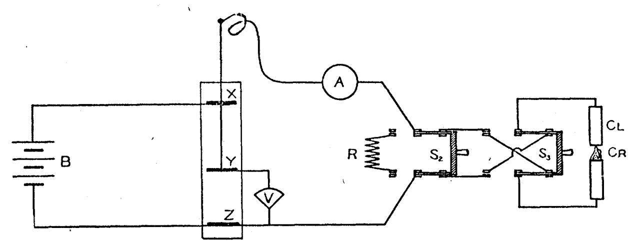

Fig. 1.

rundum, held in a clamp, is shown at *Cr*; *B* is a storage battery; *XYZ* is a potentiometer consisting of two fixed plates of zinc *X* and *Z*, and one movable plate *Y*, immersed in a zinc sulphate solution. By means of the voltmeter *V* the difference of potential between the plates *Y* and *Z* could be read, and the resulting current through the carborundum was given by a galvanometer or milliammeter at *A*. The resistance of the galvanometer was so small in comparison with the resistance of the carborundum that the reading of the voltmeter was practically the drop of voltage in the carborundum.

The switch S_3 enables the observer to reverse the current in the crystal under examination without reversing the galvanometer. A known resistance at *R*, could be thrown into circuit with the galvanometer for the purpose of calibrating it.

This method of experimenting has previously been employed by Eccles,[1] Guthe and Trowbridge[2] and others in the study of the coherer; by Rothmund and Lessing[3] and by Austin[4] and Armagnat[5] in the study of the electrolytic detector.

Current-voltage Curve for Carborundum. — A curve obtained by plotting the current against voltage in an experiment with carborundum is shown in Fig. 2. It is seen that the current through the carborundum is not a linear function of the voltage about it; the apparent resistance of the substance diminishes with increasing current. Curves of approximately this form were obtained by Greenleaf W. Picard[6] in a study of carborundum. This curve also resembles closely the curves obtained by Rothmund and Lessing, by Austin and by Armagnat for the relation of current to voltage in the electrolytic receiver. It resembles also the building up portion of the current-voltage curve in the coherer as obtained by Eccles.

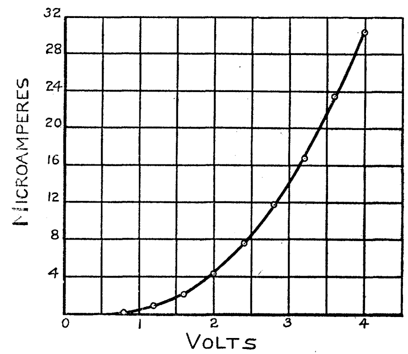

Fig. 2.

Experiments were made by the writer on a great many specimens of carborundum, and curves of approximately the shape shown in Fig. 2 were obtained in all the cases. The value of the current for a given voltage was found to depend on the temperature, and pressure, and on the method of leading the current to the crystal, and was different for different specimens. Before discussing these effects of temperature, pressure, etc., attention is called to a more interesting property of carborundum, the property of unilateral conductivity.

Unilateral Conductivity of Carborundum.— The current through the crystal in one direction under a given electromotive force was

[1] Electrician, 47, pp. 682 and 715, 1901.
[2] Phys. Rev., 11, p. 22, 1900.
[3] Ann. d. Phys., 15, p. 193, 1904.
[4] Bureau of Standards, 2, p. 261, 1906.
[5] Bull. soc. francaise, Session of Apl., 1906, p. 205.
[6] El. World, 48, p. 994, 1906.

found to be different from the current in the opposite direction under the same electromotive force; that is to say, carborundum is unilaterally conductive. This effect may be seen by a reference to

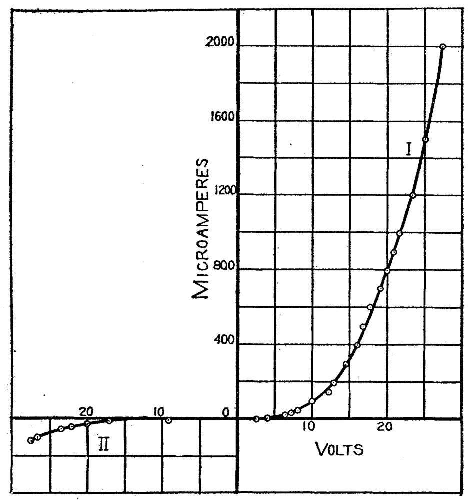

Fig. 3.

Fig. 3. The branch *I* of the curve shows the current, plotted against voltage, when the current is in one direction; branch *II* the corresponding values of the current obtained when the voltage is reversed. The accompanying table, Table I., contains the numerical values from which these curves were plotted. This property of unilateral conductivity of carborundum has been overlooked by previous experimenters on this substance. The property of unilateral conductivity has, however, been previously found in some of the crystalline metallic oxides and sulphides, by Ferdinand Braun. Reference to Braun's work is given in the historical note on page 58. None of the substances investigated by Braun showed such striking asymmetry as that obtained in the present experiments with carborundum.

In the experiment whose result is shown in Fig. 3 and Table I., the specimen of carborundum was held in a clamp under a pressure of about 500 grams, and it is seen that the current in one direction is 100 times as great as the current in the opposite direction when an electromotive force of 10 volts is applied in the two cases. With increase of current through the specimen, the ratio of the current in the two opposite directions diminishes. At 27.5 volts C_1 is only 17 times C_2.

TABLE I.

Relation of Current to Voltage, Showing unilateral Conductivity of Carborundum.

Volts.	Current in Microamperes.		C_1/C_2.
	C_1, Commutator Left.	C_2, Commutator Right.	
2.2	1		
2.8	2		
4.0	5		
4.7	10		
5.9	20		
6.5	30		
7.3	40		
8.0	50		
10.0	100	1	100
12.1	150		
12.8	200		
14.5	300	5	60
16.0	400		
16.8	500	10	50
17.7	600		
19.4	700		
20.0	800	20	40
21.0	900		
21.9	1,000	30	33
23.2	1,200	50	24
25.0	1,500		
27.5	2,000	120	17

In this particular experiment the piece of carborundum was submerged in an oil bath designed to keep the temperature of the specimen constant. The piece of carborundum was held in a clamp, the jaws of which served to lead the current to the specimen. The oil of which the temperature was 64°C., came freely into contact with the crystal.

Similar effects were obtained at various temperatures between − 10°C. and 100°C., both with and without the use of oil as a bath. A like result was had with different specimens and under different pressures. The relative values of the positive and negative currents, however, varied from piece to piece, and also was different under different conditions of temperature and pressure. The effects of temperature and pressure are investigated below.

An interesting property of some of the specimens is presented in Fig. 4. The curve of current against voltage obtained when the

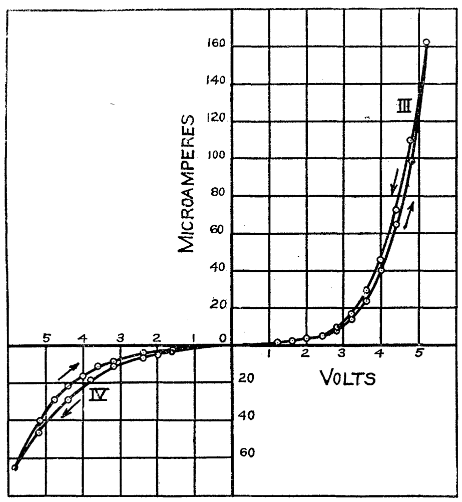

Fig. 4.

voltage was *increased* step by step did not exactly agree with the values of the current obtained with the same voltage when the voltage was decreasing step by step. The difference is indicated by the non-coincidence of the two curves marked *III* in Fig. 4. The arrows indicate the order of succession of the observations. Curve *IV* shows the corresponding effects when the current is in the opposite direction. This effect was apparently due to a slow building up of the current, and after several reversals of the current usually disappeared. The specimen that gave the curves of Fig. 4 was under a pressure of 2 kilograms.

Effects of Pressure. — Current-voltage curves were taken with the same specimen under various pressures. A series of results are shown in the curves of Fig. 5. In taking these observations the specimen was held in a clamp with jaws insulated from one another. One of the jaws was capable of being moved forward without rotation under the action of a screw and spring. The spring was calibrated, so that the pressure on the carborundum could be read off on a scale. Care was taken that the specimen was subjected to a steady compression without twisting. The pressure was in the direction of the current.

In taking the set of observations shown in Fig. 5 the pressure was first made three kilograms, giving the top curve of the series. The pressure was then reduced successively to two kilograms and one kilogram. From the first quadrant of the figure it is seen that

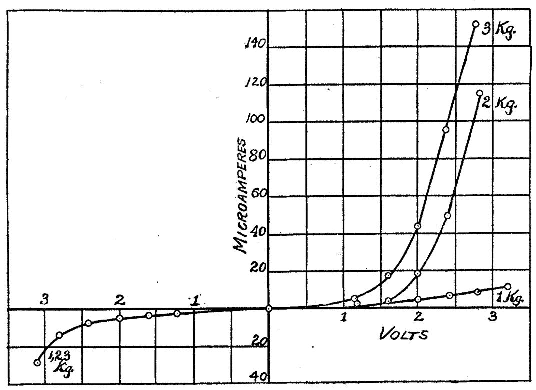

Fig. 5.

the conductivity of the specimen diminishes with diminishing pressure. This is the case when the current is in one direction. With the current in the opposite direction the current-voltage curves for the three different pressures coincide, and for the case of the pressure equal to one kilogram the prevailing conductivity is actually reversed with respect to its direction in the case of the higher pressure.

Several experiments were made with other specimens of carborundum with considerable disparity in the results, and the curves of Fig. 5 cannot be taken to represent a general occurrence.

Many of the results of the experiments here described are apparently confused by difficulties arising at the contact of the metallic electrodes with the crystal. On account of the irregularities of the surfaces of the specimens actual contact with the electrodes in general occurs at small areas. Although this contact is apparently not loose when the pressure on the clamp is several kilograms, it is evident that the carborundum, which is an exceedingly hard substance, will imbed itself in the electrodes to a depth depending on the pressure, and one cannot be certain that a specimen will return to its original condition when the pressure is put on and taken off or when the specimen is removed from the clamp and again replaced in it. On this account the experiments are sometimes incapable of repetition unless the clamp is left undisturbed.

Experiments with Platinized Specimens of Carborundum. — In the effort to avoid these difficulties and in the effort to ascertain what part the form of contact plays in the phenomenon of unilateral conductivity in crystals, a number of specimens of carborundum were selected with opposite faces plane and very approximately parallel. The faces thus found were parallel to the natural hexagonal base of the crystal, and were in several cases apparently the natural crystal faces.

Some of the parallel-faced crystals were platinized on one or both of their smooth surfaces by the cathode discharge so as to make firm contact with the electrodes. The metallic surfaces thus obtained were in many cases optically plane, as evidenced by the fact that when used as mirrors they did not appreciably distort the image. The platinized faces were put in contact with the electrodes. The current in these cases was perpendicular to the crystal base.

Platinized on One Face Only. — Some of the specimens, platinized on one face only, gave very remarkable unilateral conductivity. A specimen, called Carborundum 11, was platinized and broken into two parts. Table II. and Table III. show results obtained with one of these parts designated 11_b. This specimen was .6 mm. thick, with area of about 1 sq. mm. One of the faces, which was optically true, was heavily platinized. The other face was somewhat rough and was without platinum. The specimen was held in a clamp with silver jaws. Careful examination showed that the rough, unplatinized face of the crystal made contact at only a few points with the electrode on that side. Four different pressures were used, 350 grams, 1 kg., 2 kg., and 3 kg. With a given voltage the current *toward* the platinized face was in each case *greater* than the current in the opposite direction.

For a pressure 350 grams, recorded in Table II., and for voltages below 20 volts, the current from the platinized face gave no appreciable deflection of the milliammeter, of which one division was 3.92 microamperes, while the current toward the platinum was 172 microamperes at 20 volts. At 22 volts the current from the platinum was .39 microamperes, while the current in the opposite direction was 910 times as great. At 34.5 volts the current toward the platinum was 527 times the current from the platinum.

TABLE II.

Crystal 11_b. *Thickness* .6 *mm.*; *Area* 1 *sq. mm.* *Platinized on one side.*
Pressure 350 *Grams.*

Volts.	C_1, Current toward Platinum in Microamperes.	C_2, Current from Platinum in Microamperes.	C_1/C_2.
10.5	3.92		
14	11.8		
15	25.5		
17	55		
20	172		
22	355	.39	910
23	520	.60	850
25	850	1.06	800
30	1,920	3.05	630
34.5	3,100	5.90	527

Pressure 1 *Kg.*

Volts.	C_1.	C_2.	C_1/C_2.
4.5	3.92		
6	7.84		
7	19.6		
9	39.2		
10	64.0		
11	98.0		
13	168		
15	282		
16	350		
18	600		
21	1,000		
26	2,000		
30	3,000	.75	4,000
34.5	4,200	3.92	1,070

TABLE III.

Same Specimen as Table II. Pressure 2 Kg.

Volts.	C_1, Current toward Platinum in Microamperes.	C_2, Current from Platinum in Microamperes.	C_1/C_2.
4.2	3.92	.00	
5.8	7.84	3.92	2.0
7.0	19.6	4.70	4.2
8.1	39.2	9.4	4.2
9.2	78.4	19.6	4.0
10	118	39.2	3.0
11	210	71.0	2.96
12	255	121	2.10
13	380	175	2.18
14	440	260	1.72
15.8	700	350	2.0
17	1,000	420	2.38
21.2	2,000	770	2.6
23	2,500	1,000	2.5
24.5	3,000	1,500	2.65
26.2	3,500	1,360	2.58
28	4,000	1,500	2.66
31.5	5,500	1,900	2.90
34.5	6,700	2,600	2.68

Pressure 3 Kg.

Volts.	C_1.	C_2.	C_1/C_2.
3.5	3.92	.39	10
5	12.6	2.62	4.8
6	23.5	7	3.36
6.8	39.2		
8	78.5	21.5	3.55
9	118	33.2	3.55
10.2	196	78.4	3.52
12.0	314	158	2.00
13	392	240	1.60
14.2	500	392	1.30
15	600	420	1.43
17.5	1,000	700	1.43
20	1,500	1,100	1.36
21.7	2,000	1,400	1.43
24.5	3,000	1,950	1.54
30	4,500	3,300	1.37
34.5	6,700	4,400	1.56

With the pressure 1 kg., also recorded in Table II., the conductive asymmetry of the crystal was still greater, and at 30 volts the current toward the platinized face was 4,000 times the current in the opposite direction. These results for 350 grams and 1 kg. pressure are plotted in the curves of Fig. 6. The current toward

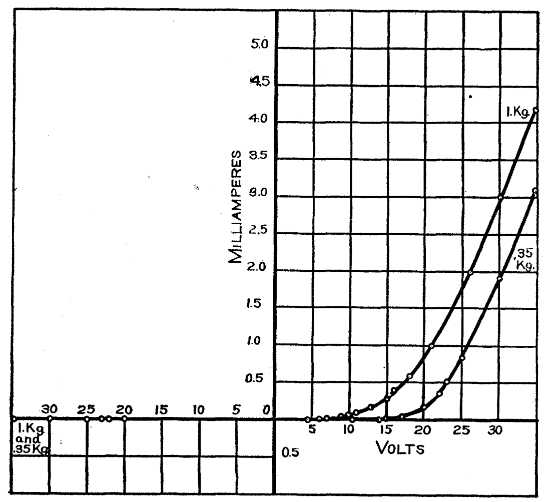

Fig. 6.

the platinized face is given in the right hand quadrant. The current in the opposite direction does not appreciably depart from the axis.

When the pressure was increased to 2 kg., and then to 3 kg. (Table III., Fig. 7) the currents in both directions were increased and the ratio of C_1/C_2 was reduced, so that the current toward the platinum was only two or three times as great as the current in the opposite direction for a given voltage.

The ratio of the current in one direction to the current in the opposite direction is reduced by increasing the pressure on the specimen from 1 kg. to 2 kg. On the other hand, if we examine these two currents with respect to their difference for a given electromotive force, it is seen that the *excess* of one of the currents over the opposite current is increased with increase of pressure.

Another small specimen also broken from crystal 11 platinized on one side gave analogous results. This small piece called 11_a had a very sharp point at one end and a wider base at the other end. This specimen was only a fine sliver in the form of a pyramid perhaps .5 mm. long, and .2 mm. wide at the base. The platinized side constituted the base. The pressure on it was very great for so slender a specimen, perhaps 3 kilograms, so that the sharp end was

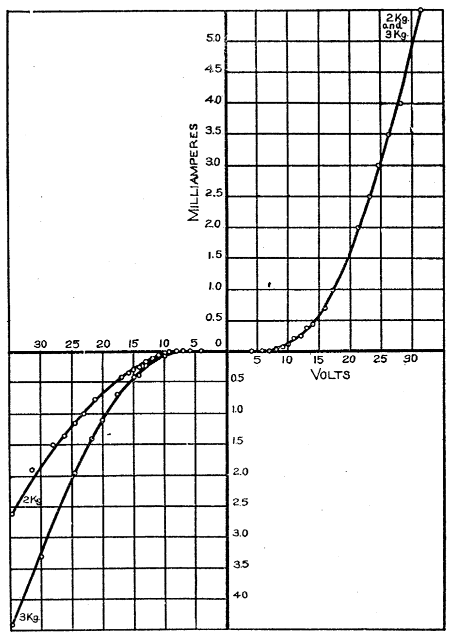

Fig. 7.

driven well into the electrode. The current toward the platinum (base) was again greater than the current in the opposite direction. The ratio of the current C_1 to C_2 in this case was 524 at 18 volts, and 271 and 32 volts.

Carborundum Platinized on Both Sides. — Specimen No. 19 gave the current-voltage values recorded in Table IV. This specimen was .82 mm. thick, had practically parallel plane faces, which were both heavily platinized by the cathode discharge. These flat faces were put into contact with the silver electrodes. The platinum of the edges, which would otherwise short-circuit the crystal, was removed by breaking away the edge of the crystal all around. This left an electrode area to the crystal of about 5 sq. mm. A pressure of 2.5 kg. was applied to the electrodes, but the amount of this pressure so long as the contact was not evidently loose or so large as to crush the carborundum seemed to have very little effect on the resistance of the specimen.

TABLE IV.

Specimen No. 19, platinized on both sides.

Volts.	Current in 10^{-4} Amperes.		C_1/C_2.	Resistance in Ohms.	
	C_2.	C_1.		R_1.	R_2.
1	1.5	2.0	1.36	6,660	5,000
1.5	6.0	10.0	1.66	2,500	1,500
2	9.5	15	1.59	2,100	1,330
3	20	30	1.50	1,500	1,000
4	37.9	54.2	1.42	1,060	740
5	68	95	1.40	735	530
6	109	150	1.37	550	400
7	152	210	1.38	455	332
8	217	288	1.33	370	280
9	278	370	1.33	323	243
10	380	485	1.28	263	207
11	460	620	1.35	240	178
12	580	780	1.35	207	154
13	760	970	1.28	171	134
14	920	1,110	1.22	152	125
15	1,100	1,450	1.32	136	103
16	1,350	1,700	1.26	119	94
17	1,650	2,000	1.21	102	85
18	2,000	2,450	1.23	90	73
19	2,500	2,830	1.13	76	67
20	2,940	3,600	1.23	68	55
21	4,200	4,820	1.13	50	43

The ratio of C_1 to C_2 in this table in only about 1.1–1.6, but on account of the low resistance of the specimen, the *difference* between the two currents for a given voltage is large. It should be noted that the current values in Table IV. are given in 10^{-4} amperes, while in the previous Tables the microampere (10^{-6} amperes) was the unit employed. This specimen shows unilateral conductivity with currents up to one half ampere. Up to this value the current through the specimen was also remarkably steady in comparison with the unplatinized specimens. At one half ampere the crystal was considerably heated, so that the massive electrodes in contact with the specimen became uncomfortably warm to the touch. Under this current the crystal glowed over a small area on both surfaces. Whether this glow was incandescence or a luminescence I am not able to say at present. The glow was examined with a spectroscope, but was so faint that the spectrum has not as yet been clearly made out. All of the specimens of carborundum thus far studied showed this glow at the electrodes when the current was pushed to a high value. Some specimens, apparently inhomogeneous, showed a glow also at a small region in the interior of the crystal. When the glow appeared the measurements were usually discontinued on account of the irregularity of the current readings.

Rectification of Alternating Currents by Carborundum.— In the previous experiments it has been shown that carborundum is unilaterally conductive, giving a greater current in one direction than in the opposite direction when the same electromotive force is applied in the two cases. If this property is manifested for rapid reversals of voltage, an alternating voltage ought to give more current in one direction than in the other. Experiments show this to be the case.

The form of circuit shown in Fig. 8 was designed to permit the employment of either direct or alternating voltage of the same

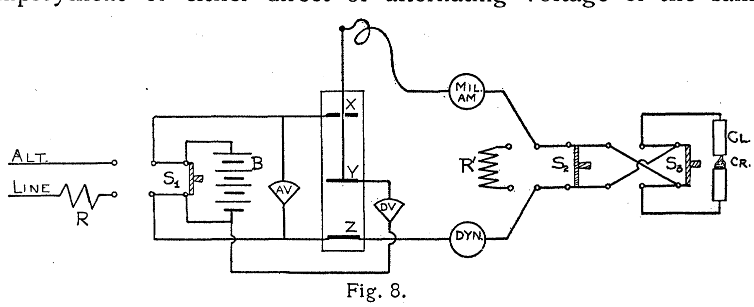

Fig. 8.

value, and to permit the ready measurement of the direct, alternating, and rectified current through the specimen.

The resistance R in the alternating line was adjusted so that the alternating current voltage between X and Z read on the Thomson alternating voltmeter AV with switch S_1 to the left was the same as the direct voltage between these plates when the switch S_1 was thrown to the right so as to put in the battery B instead of the alternating line.

Since the resistance *XYZ* was non-inductive it was assumed that the drop in potential between *Y* and *Z* was the same for either direct or alternating voltage. This drop between *Y* and *Z* was read, with the direct current source, on the Weston direct current voltmeter *DV*.

The resulting current through the crystal *Cr* was read on both the milliammeter and electrodynamometer in series with the crystal. With the alternating current source the former gave the rectified current and the latter gave a reading depending on the total alternating current through the specimen.

The specimen used in the experiment was taken almost at random from a beaker full of crystals of carborundum, and though this

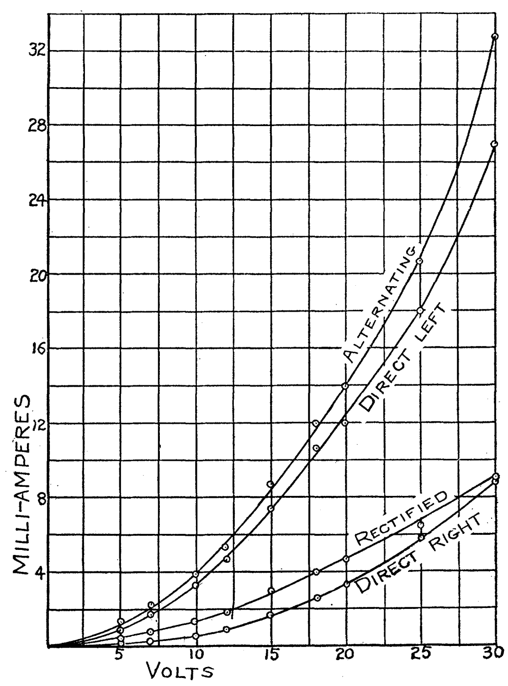

Fig. 9.

specimen does not possess polarity to the remarkable degree exhibited by specimens 11_a and 11_b, it yet shows the possibility of rectifying alternating currents by the use of carborundum. Table V. shows a series of observations which are plotted in Fig. 9. The table contains the voltage, the direct current in the two opposite directions obtained with the battery as source, the total alternating current as read on the dynamometer, and the rectified current with the alternating source. The alternating current made 60 cycles per second.

In Table VI. one half the difference between the two opposite values of the direct current is put in for comparison with the rectified current. This quantity $\frac{1}{2}(c_1 - c_2)$ is the reading we should have for the rectified current if a steady voltage of which the direction was reversed at a uniform rate were applied to the circuit. We should not expect agreement of the current obtained in this way with the rectified current under alternating voltage, but the fact that the two

Table V.

Direct, Reversed, Alternating and Rectified Current for Different Voltages.

Volts.	Current in Milliamperes.			
	Direct Left, C_1.	Direct Right, C_2.	A, Alternating.	R, Rectified.
5	.9	.07	1.3	.57
7	1.7	.2	2.21	.98
10	3.22	.52	3.9	1.61
12	4.53	.89	5.22	2.08
15	7.5	1.16	8.8	3.35
18	10.7	2.53	11.7	4.13
20	12.0	3.25	14.0	4.7
25	18.0	5.6	20.7	6.25
30	26.8	8.9	32.7	9.0

Table VI.

Efficiency.

Volts.	Rectified.	$(C_1 - C_2)/2$.	R/A.	$\pi R/2A$.
5	.57	.41	.44	.69
7	.98	.75	.44	.69
10	1.61	1.35	.42	.65
12	2.08	1.82	.40	.63
15	3.35	3.17	.38	.60
18	4.13	4.09	.36	.56
20	4.7	4.37	.34	.52
25	6.25	6.2	.30	.47
30	9.0	8.9	.28	.44

sets of values are of the same order of magnitude gives a rough method of predicting the rectified current from the reversed direct currents.

Efficiency of Rectification. — Table VI. contains also data in regard to the efficiency of rectification by carborundum. In the fourth column is the ratio of the rectified current, read on the Weston ammeter, to the total current read on the electrodynamometer. This, however, does not give the true efficiency because the current is no longer sinusoidal, and therefore the reading of the dynamometer, which is a deflection instrument calibrated with a direct current, does not give, even approximately, the proper value of the alternating current for the comparison. If the rectification were perfect the reading of the dynamometer would have to be multiplied by $2/\pi$ to give the same reading as the direct current ammeter. The fifth column of the table contains the ratio of the rectified current to $2/\pi$ times the dynamometer reading. This also is not the true efficiency, which is, however, perhaps somewhere between the ratios of column four and those of column five.

Since the efficiency is different for different specimens it is perhaps not important to enter into a more accurate discussion in this place.

The results of Tables V. and VI. show that direct reading instruments in series with a rectifying crystal are capable when properly

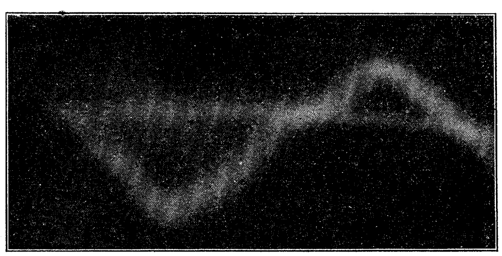

Fig. 10.

calibrated of reading on alternating current voltage, and are, therefore, capable of being used in the measurement of alternating currents. There is given below a description of an alternating current voltmeter constructed in this way.

The Modification of Wave Form by a Crystal of Carborundum. — In order to find out by a direct method the effect of a unilaterally conductive crystal on the wave form, when the crystal was used in a circuit with approximately a sinusoidal impressed voltage, photographs were taken with a Braun's cathode tube. The resulting cycle is shown in Fig. 10. For the experiment Professor Trowbridge kindly placed at my disposal his high-voltage storage battery, for use in producing the cathode beam in the tube. It was found that 20,000 volts in series with a water resistance with running water gave a brilliant and steady spot on the fluorescent screen.

Details of the apparatus are shown in Fig. 11. The coils *cc*

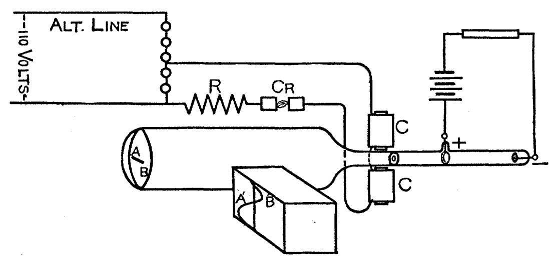

Fig. 11.

for deflecting the beam had together a resistance of about 500 ohms. These coils were provided with cores of soft iron, since it was found impossible to dispense with the iron and have sufficient deflection to show the wave form. The deflecting coils and an additional resistance of 3,720 ohms were in series with the crystal *Cr*. The alternating voltage applied to the circuit containing the crystal was 44 volts, obtained as the drop around two lamps of a lamp-resistance in circuit with the 110-volt line. The crystal was submerged in oil.

The current through the crystal *Cr* and the coils *cc* deflected the cathode beam so that the luminescent spot was spread out in a horizontal line *AB* on the fluorescent screen of the Braun tube. The deflection in one direction was greater than in the opposite direction. Viewed in a mirror revolving with axis horizontal, the fluorescent line was spread out vertically into the wavey line $A'B'$. This curve moved stroboscopically with the mirror. In order to take a photograph the speed of revolution was adjusted to synchronism with the cycle to be photographed. This was done by the adjustment of a conical bearing connecting the motor with the mirror. The motor was run at approximately constant speed, so that when the coupling was properly adjusted, the image in the mirror could be held stationary for sufficient time to make the exposure (15 seconds.)

The cycle shown in the photograph of Fig. 10 is in form what one might expect from the current-voltage curve previously given. The horizontal line was traced by the spot when the current was shut off, and is therefore the line of zero current. This is the proper axis of the cycle. The mirror was moving at uniform speed so that distances along the axis of the cycle are proportional to the time. The approach of the curve to a horizontal where it crosses the axis is due to the fact that the apparent resistance of the crystal for low voltages is more than the resistance for high voltages. The fact that this effect is shown with the alternating voltage reversing 120 times per second indicates that the change of apparent resistance with the change of current is extremely rapid. If the effect is due to heat, the photograph shows that a marked minimum of temperature coincides in time very closely with the minimum of current. We should perhaps hardly expect the crystal in contact with massive electrodes and submerged in oil to show decided fluctuations of temperature with each fluctuation of the rapidly reversing current.

Another matter for examination in the photograph is the comparative time interval between successive minima of current; that is the comparative time intervals between the zero values of the current on the oscillogram. These intervals are apparently unequal. We cannot, however, be quite sure of this inequality, because on account of the breadth of the band, the positions of these points are somewhat uncertain in the photograph, and if we place the first and second as near together as possible and the second and third as far apart as possible consistent with the picture, the two distances become about equal. If these distances on further experiment should prove to be unequal, we should have evidence of a *persistent* electromotive force in one direction acting to displace the cycle with respect to the axis. This would mean that the rectifying effect was in part an integral effect.

Such an integral effect exists, for example, in the case of a thermoelectromotive force produced by an electric current, which does not disappear as soon as the current is removed. Also an integral effect arises in galvanic polarization, which does not disappear as soon as the current producing it is removed. So we might expect in the case of the crystal an integral electromotive force persisting in one direction from cycle to cycle. From the picture we cannot say for certain that such a persistent electromotive force exists. If such a persistent electromotive force does exist, it does not necessarily follow that the cause is thermoelectric or galvanic in character.

Experiments on Question of Thermoelectric Origin of Electric Polarity in Carborundum. — Evidence that the action is not thermoelectric is given by the fact that submerging the crystal in oil does not appreciably change its behavior. Also, blowing air over the crystal when it is rectifying an alternating current does not change the current. When used on an alternating voltage, a lighted match held under the piece so as to heat it chiefly at one electrode does not much change the rectified current. These facts seem to be inconsistent with the assumption that the direct electromotive force obtained with an alternating voltage is thermoelectric in origin.

A direct experiment in search of an electromotive force persisting after current was removed was performed as follows. By means of a relay making 60 complete vibrations per second, a direct current from a battery of 35 volts was sent through the crystal of carborundum for intervals of about 1/120 second, disconnected and a capillary electrometer put about the crystal for alternate intervals of about 1/120 second. The capillary electrometer gave indications of a persistent electromotive force of less than .002 volt. This is entirely inadequate to account for the unilateral conductivity of the substance, which would require in some cases a back voltage as high as 10 or 15 volts to explain the phenomenon.

After a presentation of the data for other crystals now under investigation, it is proposed to return to a discussion of possible explanations of the phenomenon.

Crystal Rectifiers Employed in the Construction of Alternating Current Measuring Instruments.— On account of the unilateral conductivity of carborundum and certain other crystals to be later referred to, it is possible by the use of such crystals to adapt an ordinary direct current measuring instrument to the measurement of alternating currents. The utility of these crystals for this purpose will depend upon their permanence and constancy when submitted to long continued use. For this purpose long runs are at present being made.

An alternating current voltmeter making use of carborundum as the rectifying substance has stood satisfactory tests for several weeks. The crystal is put in a metallic clamp enclosed in a tube containing oil, and is used with a delicate Weston milliammeter, with a scale of 100 divisions, each division being 3.92×10^{-6} amperes. Shunt and series resistances as shown in Fig. 12 are used. When these resistances are properly chosen, the scale of the instrument used as an alternating current voltmeter will be nearly uniform over a wide range, or if desired the readings for the small voltages may be spread out instead of being compressed as in the ordinary alternating voltmeters. By dispensing with some of the series resistance, or by changing the shunts it is possible to give the instrument a multiple scale.

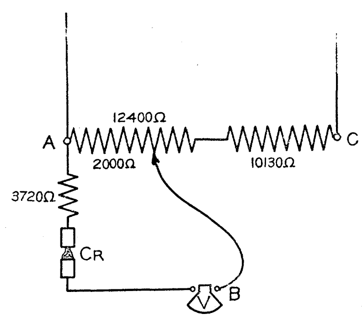

Fig. 12.

Calibration curves for the instrument are shown in Fig. 13 and Fig. 14. Curve *I*, Fig. 13, shows the reading of the direct current Weston instrument for different alternating voltages, the instruments being provided with the shunt and series resistances shown in Fig. 12. Curve *II*, Fig. 13, is the corresponding calibration curve without the 10,130 ohms series resistance. The curves are both nearly straight above 20 volts.

When the large series resistances and shunt resistances are omitted and the current sent directly through the 3,720-ohm resistance, the crystal, and the direct current millivoltmeter (resistance 638 ohms), curve *III*, Fig. 14, is obtained. The corresponding direct current curves *IV* and *V* are given in the same figure. With this arrangement the instrument may be read with accuracy from 2 to 10 volts. The deflection at 5 volts alternating is 36 one-hundredths as great as the larger *direct current* with the same voltage, and 7 times as large as the corresponding direct current in the opposite direction. That is to say the loss in sensitiveness of the

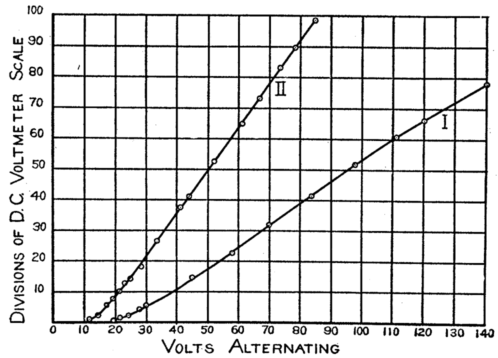

Fig. 13.

direct instrument used on the alternating voltage is not large. Of course, difficulty may in some cases arise in the use of these crystals on account of their high resistance. However, by the use of

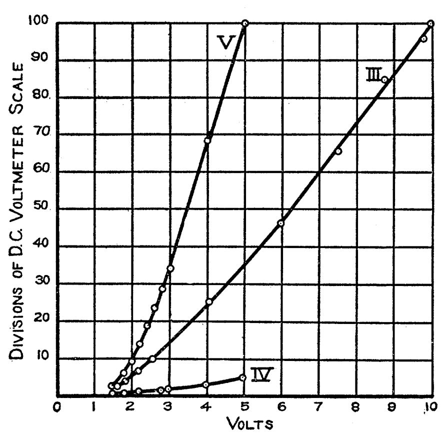

Fig. 14.

a transformer the voltage of an alternating current may be stepped up, and this difficulty avoided. Also by platinizing the specimens, the resistance of the crystal may be greatly reduced.

The alternating voltage used in this experiment made 60 complete cycles per second. Similar measurements with 175 cycles gave substantially the same curves. When used as an alternating current voltmeter, the instrument may be left permanently in circuit without heating or deterioration. The temperature coefficient of conductivity is considered on page 54 below.

The Unilateral Conductivity of Carborundum Used in the Measurement of Telephone Currents. — When it is desired to measure smaller voltages than those given above, a step-up transformer may be used to raise the voltage of the alternating circuit. On account of the high resistance of the carborundum the factor of transformation may be very great, so that the primary of the transformer may be of such small resistance that its introduction into a circuit will not materially modify the conditions of the circuit. In a telephone line a transformer of this kind might quite accurately replace one of the transformers between the talking and listening circuits of the line.

Very feeble currents may be measured in this way, and many experiments on resonance in telephone circuits may be performed. The following experiment serves as an example.

An apparatus similar to that devised by M. Wien, consisting of a rotating wheel carrying iron plugs between the poles of a small permanent magnet, was used to produce a feeble alternating current of 1,440 cycles per second. This alternating current was sent through the primary coil of a telephone transformer. The secondary of this transformer was connected with a delicate ammeter through the crystal of carborundum No. 19, platinized on both sides. A deflection of 16 divisions was shown by the milliammeter. Now the primary circuit was broken and a condenser of variable capacity was inserted in series in the primary circuit. The deflections obtained with various values of the capacity are plotted in Fig. 15. The dotted line shows the deflection without the condenser ($C =$ infinity). The curve shows clearly a resonant value of the capacity at .45 microfarad.

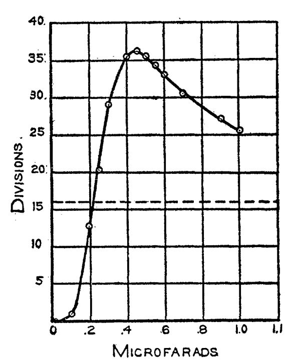

Fig. 15.

The rectifying action of carborundum is applicable in a similar manner to the study of many important problems in telephony.

I have found some other crystals that show greater sensitiveness than carborundum, when used as rectifiers of weak alternating currents. Experiments with these substances will be communicated in a subsequent paper.

Temperature Coefficient of Conductivity of Carborundum. — One of the greatest difficulties in the way of the use of carborundum in standard measuring instruments for alternating currents is the high temperature coefficient of this material. The platinized specimen No. 19 heated in an air bath gave the results shown in Fig. 16.

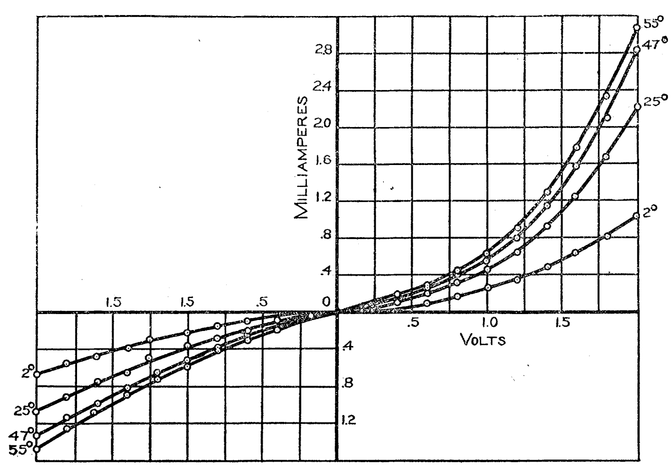

Fig. 16

Direct current was used and current-voltage curves were taken at various temperatures; namely at 2°, 25°, 47°, 55° C. By a reference to the figure it is seen that the conductivity of the substance increases with increase of temperature.

More accurate observations are shown in Fig. 17. In this case the crystal was heated in an oil bath. The electromotive force was constantly 2 volts. The curve C_1 was obtained with the current in one direction, the curve C_2, with the current in the opposite direction. The observations were carried down below 0° C., so that any moisture present on the crystal would be frozen, and would hence be evidenced by a sudden change in the inclination of the curve.

No such change was found, indicating that the presence of free water on the crystal could not account for the unilateral conductivity. It is proposed to carry the measurements to a still lower temperature at a subsequent time in the effort to see if a temperature can be found at which the conductivity of the crystal ceases to be unilateral.

At 20° the conductivity along the curve C_1 increases 2.06 per cent. per degree, while the corresponding coefficient along C_2 is 1.52 per cent. per degree. It is interesting to note that the temperature coefficient of conductivity of neutral salts in very dilute

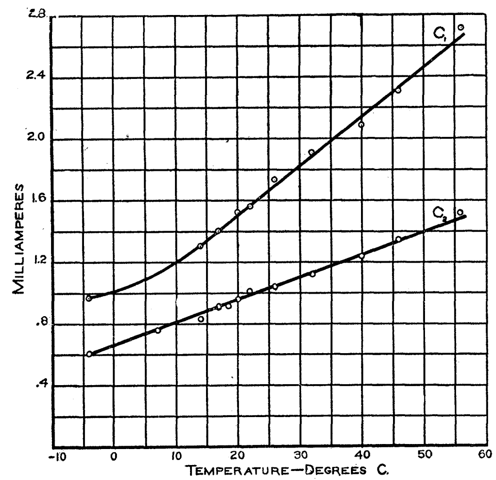

Fig. 17.

solutions is between 2.2 and 2.4 per cent. per degree, and is likewise an increase of conductivity with increase of temperature. The corresponding coefficient for copper and other pure metals is negative instead of positive and has a value in the neighborhood of .38 per cent. per degree C. It thus appears that in the matter of temperature coefficient carborundum resembles an electrolyte rather than a metallic conductor.

On the Action of Carborundum as a Detector for Electric Waves. — The facts obtained in the above experiments contribute to an explanation of the action of carborundum as a detector for electric waves. The current-voltage curve of carborundum is not linear ;

the apparent resistance of the substance drops when the current is increased, so that we might anticipate that electric oscillations through the carborundum, constituting an increase of the current, would cause a decrease of resistance and consequently a sound in the telephone, provided a local battery is used in series with the detector and telephone.

Even if the carborundum were not unilaterally conductive, this drop in resistance with increase of current would characterize the substance as a detector for electric waves as may be seen by reference to Fig. 2. For example, let us suppose that the local battery has a voltage of 2 volts, and suppose that the oscillating voltage impressed by the incident waves is ½ volt. When this impressed E.M.F. is in the same direction as the local voltage the total voltage is 2.5, and the resulting current from the curve is 8.4 microamperes. When the impressed voltage is opposite to the local voltage, the total voltage is 1.5 volts, and the resulting current 1.8 microamperes. The average of these two current values 8.4 and 1.8 is 5.1, which is an increase of 1 microampere over the local current under 2 volts. That is to say, the average effect of a train of waves produces an increase of current in the telephone or other current operated device in series with the specimen and a local battery.

This is, however, evidently not a complete explanation of the action of the carborundum; for as General Dunwoody points out in his patent application carborundum may be used as a detector for electric waves *without a local battery in circuit.*

When employed without the local battery, the action of the carborundum as a detector is undoubtedly due to its unilateral conductivity. My experiments show that under the action of an alternating voltage more current passes in one direction than in the opposite direction. In using the detector without local battery the carborundum is shunted with a telephone, and in the case of the simplest form of receiving circuit the carborundum is in series with the antenna and ground. Electric oscillations with the voltage in one direction give a large current through the carborundum, charging the antenna. When the voltage reverses the current from the antenna to ground through the carborundum is smaller, thus leaving the antenna charged with a small quantity of electricity. The effect of the whole train of waves is additive, so that this charge on the antenna is cumulative. The accumulated charge on the antenna escapes through the telephone shunted about the carborundum, causing the diaphragm to move. Each subsequent train of waves causes a similar motion of the diaphragm, which is evidenced as a note in the telephone with the train frequency of the waves.

This explanation of the action of carborundum when used as a detector for electric waves brings it into agreement in essential characteristics with a number of other detectors for electric waves, which have been comparatively studied by H. Brandes.[1] This author found that "in general, conductors or combinations of conductors which do not follow Ohm's Law are capable of acting as detectors of electric oscillations, owing to their rectifying effect. A verdict as to whether such an arrangement is more or less suitable for this purpose can be derived from the continuous-current characteristic (voltage current curve). If this characteristic be symmetrical in the first and third quadrants, such an arrangement can be used as a detector, the oscillations being superposed on a suitable continuous current. If the characteristic be asymmetric, the arrangement can be used as a detector without an external electromotive force, although a suitable auxiliary electromotive force, on which the oscillations are superposed, often increases the effect. These conclusions are arrived at as a result of considering the action of Braun's pyrolusite, Holtz's valve cell, the electrolytic detector, the Wehnelt oxycathode tube, the vacuum tube, the conductivity of flames, and Ferrie's so-called electrolytic detector without polarizing E.M.F." Among the detectors here enumerated by Brandes, pyrolusite is a crystalline solid substance of the formula MnO_2.

The question whether or not the action of carborundum when used as a detector for electric waves is a heat effect goes back to the question whether the unilateral conductivity of the substance is of thermal origin. I am at present of the opinion that heat is practically a negligible factor in the process.

The following historical sketch of previous experiments on the

[1] Elektrotechn. Zeitschr., 27, pp. 1015–1017, November 1, 1906. Quotation from Science Abstracts, 2078, December 28, 1906.

conductivity of crystals and allied substances is interesting in this connection.

Historical Sketch. — In 1874 Ferdinand Braun[1] in a research on the conductivity of metallic sulphides found that the current was different in different directions, and that the resistance depended on the intensity of the current. In some cases the current in one direction was as much as twice as great as the current in the opposite direction. The substances investigated were copper pyrites, iron pyrites, galena, and copper antimony sulphide. Contact was made by the use of a clamp. He says that he found no thermoelectric effect or polarization that was even remotely explicable of the phenomenon. In discussion of his results Braun puts forth a possible explanation, based on hypotheses as to the nature of the structure of the crystals.

In 1877[2] and 1878[3] Braun returned to the subject and reported the results of further experiments, including a study of the conductivity of Psilomelan, which is a "combination of a base with manganese superoxide and water." In these experiments he showed that the pressure of the surrounding atmosphere had no effect on the phenomenon. To ascertain whether the cause of the variation of the resistance with the strength of current was due to chemical processes, he connected a copper voltameter in series with a piece of copper pyrites between silver electrodes and a piece of Psilomelan between gold electrodes. After the current from eight Grove cells had been running for nine hours, he found that the current had separated out 1.404 grams of metallic copper in the voltameter while the silver electrodes in contact with the pyrites showed no trace of silver sulphide. Also the pyrites and Psilomelan showed no appreciable decrease in weight. As further evidence that there was no electrolysis of the substances, Braun found that two electrodes of different metals at the same temperature when placed in contact with the mineral gave no current.

Another important result obtained by Braun is the fact that when a constant current is sent through the body simultaneously with an induced current from an induction coil, the resistance is lowered, not only for the former but also for the latter.

[1] Pogg. Ann., 153, p. 556, 1874.
[2] W. A., 1, p. 95, 1877.
[3] W. A., 4, p. 476, 1878.

This work of Braun was considerably discussed at the time by writers who were unable to obtain the phenomenon or who advanced the opinion that the effects were of thermoelectric or electrolytic origin. In his papers of 1877 and 1878 and in 1883[1] Braun replied to these objections, and maintained that thermoelectric processes and electrolytic polarization could not account for the phenomenon.

In 1900 and 1902 in the course of a research on the electric conductivity of compressed powders, F. Streintz[2] investigated among other things a great many oxides and sulphides of metals. None of the substances examined (in the form of finely divided powder) "showed electrolytic conductivity." Streintz also determined the temperature coefficients of conductivity, and found that compounds that at ordinary temperature conduct well have positive temperature coefficients of resistance, less, however, than the coefficients of pure metals. Compounds, on the other hand, whose conductivity at ordinary temperature is relatively small were greatly influenced by temperature, their conductivity increasing with increase of temperature. In this lattes class belong PbS, HgS, Ag_2S, and MnO_2. A very remarkable change of conductivity with temperature was obtained with Ag_2S, as has been previously noticed by Faraday[3] and Hittorf.[4]

On the question of the thermoelectromotive force of metallic couples a very interesting series of results have been obtained by A. Abt[5] in a research entitled "Thermoelectromotive Force of Some Metal Oxides and Metal Sulphides in Combination with One Another and with Simple Metals with 100° Difference of Temperature of the Contact Points." According to these experiments oxides and sulphides of metals arrange themselves in the following thermoelectric series :

Chalcopyrites	Copper	Iron
Pyrolusite	Cadmium	Pyrrhotite
Bismuth	"Nickelerz"	Antimony
Zinc	Arc Light Carbon	Pyrite
Nickel.		

Relative to the couple bismuth-antimony considered as unity the chalcopyrite-pyrite couple has a thermoelectromotive force of 10.8.

[1] Wied. Ann., 19, p. 340, 1883.
[2] Ann. d. Phys., 3, p. 1, 1900; also 9, p. 854, 1902.
[3] Faraday, Pogg. Ann., 31, p. 241, 1834.
[4] Hittorf, Pogg. Ann., 84, p. 20, 1851.
[5] Abt, Ann. d. Phys., 2, p. 266, 1900.

From this work it is evident that the thermoelectric effects with crystals may be large in comparison with metallic couples, and this fact must be taken into account in dealing with the unilateral conductivity of crystalline substances.

SUMMARY OF RESULTS.

1. Current voltage curves for carborundum are shown.

2. Carborundum is unilaterally conductive. With one specimen under 10 volts the current in one direction is 100 times the current in the opposite direction. With another specimen platinized on one side the current at 34.5 volts is 527 times as great as the current in the opposite direction under the same voltage. In another case at 30 volts the current in one direction is 4,000 times the current in the opposite direction under the same voltage.

3. As the current increases the efficiency of rectification decreases.

4. A specimen platinized on both sides has a smaller efficiency of rectification and a much lower resistance than a piece not platinized. Though the efficiency of rectification is less with the platinized specimen, the *excess* of one current over the other for a given voltage is much greater with the platinized specimen on account of its low resistance.

5. An oscillogram is given showing the distortion of an alternating current wave by carborundum.

6. A method is shown of employing crystal rectifiers in the construction of alternating current measuring instruments.

7. These instruments are applicable to the measurement of telephonic currents, and may be used in experiments on resonance in telephone circuits.

8. A determination of the temperature coefficient of conductivity of carborundum is given. This coefficient is in the neighborhood of the temperature coefficient of weak electrolytes.

9. A discussion is given of the action of carborundum in General Dunwoody's detector for electric waves.

10. No theory is given as to the cause of the unilateral conductivity of carborundum. A number of other crystals have the same property, and it is proposed to accumulate data in regard to these other substances before attempting an explanation.

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HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
May 6, 1907.

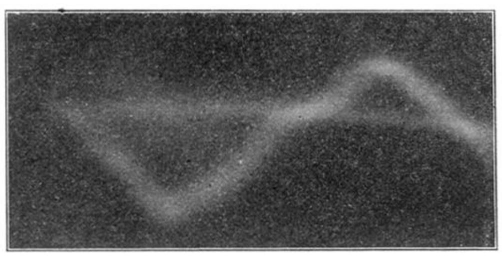

Fig. 10.