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XVIII.—*The Laws of Variation of Resistance with Voltage at a Rectifying Contact of Two Solid Conductors, with Applications to the Electric Wave Detector.* By D. OWEN, B.A., B.Sc., Birkbeck College, London.

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VARIOUS theories have been put forward to account for the rectifying action at a contact such, for example, as that between zincite and chalcopyrite, to which an alternating voltage is applied. It is not necessary to refer to more than two, which alone have up to the present claimed serious consideration. Both before and since Dunwoody's application of the mineral detector to wireless telegraphy, it was recognised that certain minerals possess extraordinarily large thermoelectric powers, exceeding in some instances by ten times or more that between bismuth and antimony. A natural explanation in terms of thermoelectric action thus lay to hand, which appeared all the more probable from the fact that these minerals also possess a large negative temperature coefficient of resistance.

In 1907, however, appeared a Paper by Prof. G. W. Pierce, containing an account of experiments which were regarded as precluding such an explanation, the main ground for this conclusion being the undoubted fact that the direction of flow of the rectified current across a junction is generally (in the case of mineral contacts) contrary to that of the current set up on heating the same junction.

A theory—since known as the electronic valve theory—was thrown out in that Paper, according to which we have in certain minerals a new phenomenon, namely, the easy passage of free electrons in one direction across the contact, but not in the contrary direction. This is the second view which has held the field.

The thermoelectric explanation has been developed by Dr. W. Eccles, who in 1913 expressed it in mathematical form, and showed the concordance of this theory with many of the observed phenomena.

On the other hand, despite the attraction which the free electronic view has possessed for many writers, little, if anything, has been done to establish definite laws answering to that view; and this tempting hypothesis has not advanced beyond the stage of mere speculation.

Most workers on this subject have directed their attention

to the determination of the current characteristic, both current and voltage being directly measured. This method has several defects: it involves the application of the voltage for a comparatively long interval of time; again it is least accurate where the results are of the greatest interest, namely, at very small voltages. Current characteristics are usually taken with applied voltages up to or beyond 1 volt, and some workers have extended the range up to 20 volts. The minimum voltage which is necessary to produce a signal in the receiving circuit of a wireless station is probably only of the order of a hundredth of a volt.

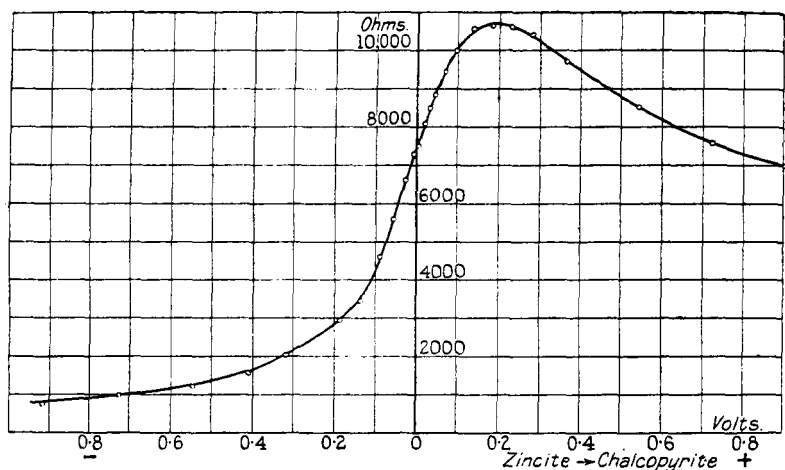


FIG. 1.—RESISTANCE CHARACTERISTIC OF A ZINCITE-CHALCOPYRITE CONTACT.

The present Paper deals with measurements of the resistance of the contact. The primary aim was to examine to what extent the resistance-characteristic expresses the nature of the physical actions occurring, and to obtain data leading to a discrimination between the hypotheses referred to.

Preliminary measurements showed that with care to avoid mechanical disturbance, and provided time was allowed for the contact to "settle down"—a process sometimes occupying minutes, sometimes hours—the resistance was sufficiently definite and reliable to permit of the application of the Wheatstone bridge, with all the power and flexibility of this method of attack.

The characteristic obtained with a zincite-chalcopyrite contact is shown in Fig. 1.

This type was followed by all the mineral combinations tried. The main points of interest are as follows: When a small voltage is applied the resistance rises, falling at the same rate when the voltage is reversed; a maximum occurs on the side of initial increase; at the higher voltages the characteristic is a falling one, the gradient diminishes on either side, positive or negative. Let

v = voltage applied across the contact.

R_0 = resistance when v is zero.

R_m = maximum value of resistance, occurring at voltage v_m .

Investigation of a great number of contacts has led to the following quantitative results:—

1. At $v=0$ the gradient of the resistance characteristic is proportional to the limiting resistance R_0 , that is, $\left(\frac{1}{R} \frac{dR}{dv}\right)_0$ is a constant for a given pair of materials. This quantity, which is analogous to the temperature coefficient of resistance, may be termed the voltage coefficient of the contact;

2. v_m is independent of R_0 ;

3. The ratio R_m/R_0 is independent of R_0 . When a series of characteristics are obtained from contacts of widely varying resistance or area of contact, and the ordinates of each reduced in the ratio $1 : R_0$, the resulting curves are found to coincide, yielding what may be called the *specific characteristic* of the given pair of substances (Figs. 2 and 10).

The above results are found to conform to an expression connecting R and v derived on the basis that the phenomena are thermoelectric.

A series of experiments was carried out on a number of contacts both elements of which were metallic, and for which the thermoelectric and other relevant constants are known. These confirm the same view.

The facts as to the sign of the rectified current will be shown on close examination to be, not in opposition, but in simple accordance with the thermoelectric explanation.

The experimental results above outlined form the basis of a calculation of the conditions of best sensibility in a wireless receiving circuit, with or without a polarising voltage. Similar considerations determine the sensitiveness to be expected in a combination of rectifying contact and direct-current galvanometer, as applied to the detection of small alternating voltages in bridge or other null methods of measurement.

I. *Experimental Details.*

The contacts tested were found to range in resistance from fractions of an ohm in the case of metallic combinations to millions of ohms in the case of zincite or carborundum contacts. The Wheatstone bridge was employed throughout. The applied voltage was varied from a millivolt or less up to 1 or 2 volts, the value being read on a multiple-range millivoltmeter in shunt with the bridge. If P and Q denote the ratio arm resistances, S that of the variable arm, V the voltage across the bridge, then the voltage v applied to the contact, and its apparent resistance R are calculated from the formulæ,

$$v = \frac{P}{P+Q} \cdot V, \text{ and } R = \frac{P}{Q} \cdot S.$$

The current through the contact is, of course, given by the expression v/R .

The two elements of the contact were—in the case of minerals—soldered by means of Wood's fusible metal into copper cups hard-soldered on to copper plates. In order to damp mechanical vibration the contact was mounted on a thick pad of cotton wool. A simple lever arrangement permitted of continuous adjustment of the mechanical pressure at the contact. Non-rigid electrical connection was obtained by the use of mercury cups wherever necessary.

The effect of time of application of the voltage was found to be considerable at the higher voltages. By limiting the duration of the testing current the measured resistance becomes quite determinate. Small periods of contact were obtained by aid of a metallic ball or ring suspended by a fine wire which also served as battery lead. On pulling out by a fine thread, then letting go, the ball was made to strike a heavy metal plate, thus making the circuit for the period of collision, which was determined in a separate experiment. Many of the measurements recorded were taken with a contact lasting 0.003 second. In order to secure the requisite sensibility under these conditions a Broca galvanometer of 1,000 ohms resistance was used.

In all the measurements the galvanometer key was kept closed, the resistance in the variable arm of the bridge being adjusted to give balance on closing the battery circuit.

The sign of the thermo E.M.F. was found for each contact *in situ*, the small rise of temperature required being obtained without any disturbance of the contact by applying a flame

momentarily to a thick copper wire attached to the plate which supported the contact.

II. *The Experiments on Minerals.*

The mineral contacts tested were the following :—

Zincite-platinum.	Galena-platinum.
Zincite-chalcopyrite.	Chalcopyrite-platinum.
Carborundum-platinum.	Bornite-platinum.
Chalcopyrite-bornite.	

It was considered desirable from the point of view of simplicity and reproducibility to use a metal as an element of the contact. Platinum was chosen on account of its unoxidisability and high melting point.

Zincite.—Early observations showed that remarkably steady resistances were obtainable with the zincite-chalcopyrite combination. Thus, tests were conducted on the same contact at intervals extending over a week without any variation of the limiting resistance greater than 5 per cent. After a series of measurements over a range up to 1 volt, lasting about an hour and a half, the initial resistance was reproduced often to within a few parts in a thousand. To secure such constancy it is necessary to avoid excessive voltages—say, more than 1.5 volt—or at all events to apply them for only a small fraction of a second.

The following example of readings refers to the test from which the resistance characteristic of Fig. 1 was drawn.

TABLE I.—*Zincite-Chalcopyrite.*

$P=1,000$, $Q=100$.

v	R	Direction of current.	v	R	Direction of current.
0.0045	7,490	Zinc—>Chalc	0.0045	7,300	Chalc—>Zincite
0.0236	8,170	"	0.091	4,620	"
0.0463	8,910	"	0.136	3,520	"
0.0682	9,530	"	0.182	3,000	"
0.091	10,030	"	0.227	2,600	"
0.136	10,650	"	0.318	2,100	"
0.186	10,750	"	0.409	1,640	"
0.232	10,680	"	0.545	1,300	"
0.0045	7,500	"	0.727	1,040	"
0.282	10,500	"	0.910	830	"
0.364	9,800	"	0.0045	7,350	"
0.545	8,650	"
0.727	7,700	"
0.91	7,100	"
0.0045	7,600	"

Ten different contact points were taken in succession between the same pair of mounted minerals, and sets of readings taken from which the resistance characteristics were plotted. The limiting resistances were found to vary from a few thousands to a few millions of ohms. The contacts were chosen so as to give values of resistance approximately equispaced over the whole range, otherwise no selection was exercised. Variation of the mechanical pressure serves conveniently to secure the above adjustment. The highest value used was 540,000 ohms, since for higher values the diminishing sensibility of the bridge becomes unfavourable to accuracy at the lowest voltages. The following table summarises the results of the series :—

TABLE II.—*Series of Contacts Between Zincite and Chalcopyrite.*

No.	R_0	R_m	R_m/R_0	v_m	$(dR/dv)_0$	$\left(\frac{1}{R} \frac{dR}{dv}\right)_0$
1	6,480	10,100	1.59	0.17	27,700	6.70
2	7,360	10,800	1.47	0.18	32,800	4.40
3	20,340	30,600	1.47	0.17	113,800	5.07
[4	24,000	28,100	1.17	0.30	39,500	1.64]
5	57,200	83,000	1.45	0.15	296,000	5.17
6	77,200	104,200	1.35	0.12	405,000	5.24
7	80,800	132,000	1.63	0.16	591,000	7.32
8	123,000	202,500	1.62	0.14	925,000	7.40
9	251,500	445,000	1.77	0.18	2.18×10^6	8.70
10	540,000	855,000	1.58	0.11	4.1×10^6	7.6
		Mean	Mean	Mean		Mean
		=1.54		=0.15		=6.40

$(dR/dv)_0$ is in every case found to be positive for current from zincite to chalcopyrite across the contact. With the exception of No. 4 (which was excluded in calculating mean values), it will be seen that the variations in the three quantities v_m , R_m/R_0 and $\left(\frac{1}{R} \frac{dR}{dv}\right)_0$ are insignificant compared with the range of resistance covered by the series. When the *a priori* probability of lack of homogeneity in the material is considered, the variation of individual results from the mean for the nine contacts is surprisingly small. It seems safe to conclude that the essential action at the contact is expressed in the statement that $\left(\frac{1}{R} \frac{dR}{dv}\right)_0$, R_m/R_0 , and v_m are dependent only on the materials constituting the contact, and not on the area or resistance of the contact itself.

An examination of the curves indicates that at every point (unless v is large) the ratio R/R_0 is independent of the value of R_0 . The graphs were reduced in scale so as to make R_0 unity in each case. The specific characteristics thus obtained for the zincite-chalcopyrite and other mineral contacts are shown in Fig. 2.

Galena.—A similar series of measurements was undertaken on contacts between platinum and galena. The specific resistance of the latter is much smaller than that of zincite, so that very small mechanical pressure at the contact must be used in

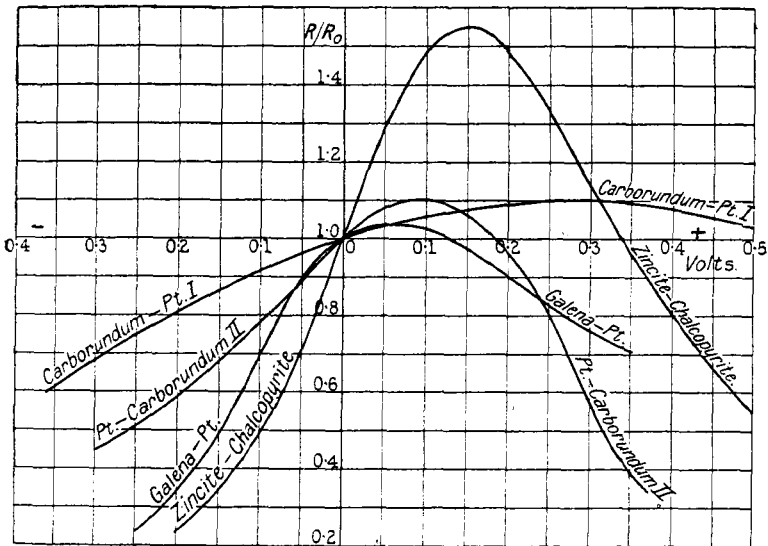


FIG. 2.—SPECIFIC RESISTANCE-CHARACTERISTICS OF SOME MINERAL CONTACTS.

order to secure even moderately high values of the resistance. A platinum wire of No. 24 S.W.G. was found suitable. The pressure was supplied by the spring action of this wire, or rather of a copper wire which terminated in a short length of the platinum wire. It is not easy to work with these light contacts, and much time and care were necessary to secure a satisfactory set of readings. Ten contacts were examined, the lowest being 34.1 ohms and the highest 1,400 ohms. Attempts at measurement on still higher values, a finer platinum wire being substituted, were abandoned as hopeless.

One specimen curve is given in Fig. 3. The summarised results are contained in Table III.

$(dR/dv)_0$ is in every case positive when the current crosses the contact from galena to platinum. The conclusion to be

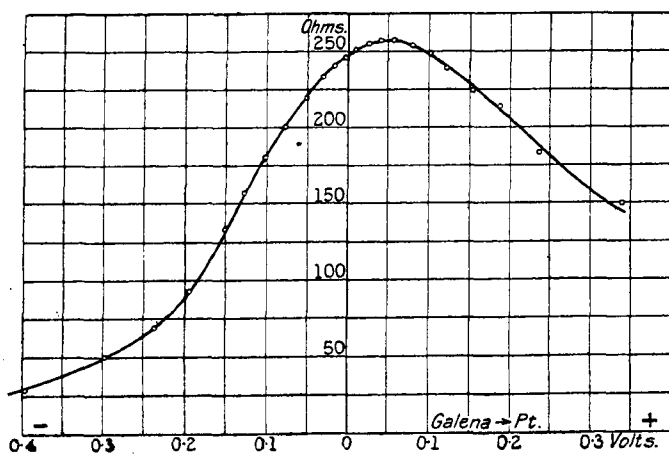


FIG. 3.—A GALENA-PLATINUM RESISTANCE CHARACTERISTIC.

TABLE III.—Series of Contacts between Galena and Platinum.

No.	R_0	R_m	R_m/R_0	v_m	$(dR/dv)_0$	$\left(\frac{1}{R} \frac{dR}{dv}\right)_0$
1	34.1	34.5	1.012	0.061	15.5	0.45
2	116.7	140.0	1.05	0.077	140.0	1.20
3	132.8	139.2	1.048	0.066	172.5	1.30
4	247.4	258.0	1.047	0.055	411.0	1.66
5	299.0	308.0	1.027	0.060	365.0	1.22
6	440.0	454.0	1.032	0.067	322.0	0.73
7	570.0	593.0	1.04	0.068	503.0	0.88
8	750.0	781.0	1.04	0.072	1,200.0	1.60
9	1,305.0	1,390.0	1.065	0.067	2,320.0	1.78
10	1,368.0	1,436.0	1.056	0.070	1,650.0	1.20
			Mean	Mean		Mean
			=1.042	=0.066		=1.20

drawn is again that the quantities $\left(\frac{1}{R} \frac{dR}{dv}\right)_0$, v_m , and R_m/R_0 are independent of the limiting resistance of the contact. The voltage coefficient is about one-fifth the value of the same quantity for zincite-chalcopyrite.

Carborundum.—A contact of this material exhibits the same

general behaviour, as is shown in the specimen curve of Fig. 4. Seven contacts were investigated, five on one specimen, which consisted of a conglomerate of small crystals (Series C), and

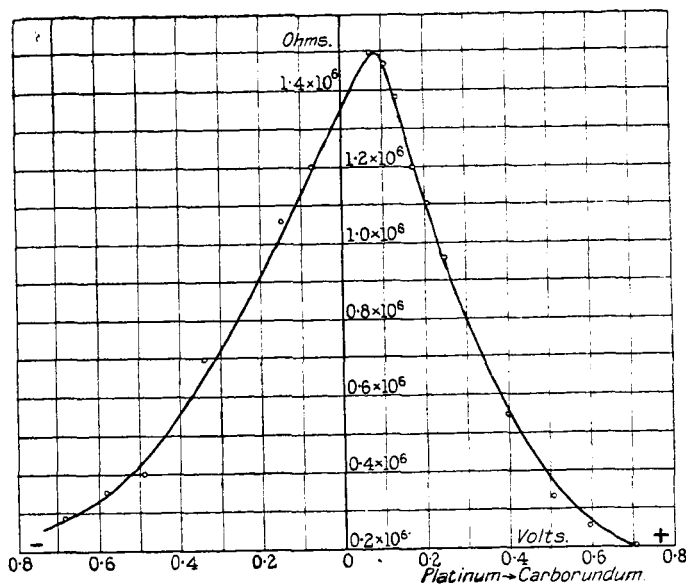


FIG. 4.—A HIGH-RESISTANCE PLATINUM-CARBORUNDUM CHARACTERISTIC.

two on another specimen, bounded by a large facet of crystal (Series C'). The resistances of contacts over the latter were never less than two million ohms, even under mechanical pressure as great as a kilogram weight.

TABLE IV.—Carborundum-Platinum Contacts.
Series C :—

No.	R_0	R_m	R_m/R_0	v_m	$(dR/dv)_0$	$\left(\frac{1}{R} \frac{dR}{dv}\right)_0$	Direction of current for $\left(\frac{dR}{dv}\right)_0$ positive.
1	460	510.5	1.11	0.28	370	0.86	Carb. to plat.
2	525	590.0	1.12	0.26	550	1.05	" "
3	612	680.0	1.11	0.30	401	0.65	" "
4	923	953.0	1.04	0.30	206	0.22	" "
5	198,000	225,000	1.14	0.16	562,500	2.81	Plat. to carb.

Series C' :—

1	1.34×10^6	1.5×10^6	1.12	0.075	2.0×10^6	1.49	Plat. to carb.
2	2.05×10^6	2.6×10^6	1.04	0.04	3.6×10^6	1.44	" "

Omitting No. 5 of Series C, the following mean values may be assigned :—

Series.	$\left(\frac{1}{R} \frac{dR}{dv}\right)_0$.	r_m .	R_m/R_0 .	Direction of current for $\left(\frac{dR}{dv}\right)_0$ positive.
C	0.67	0.285	1.10	Carb. to plat.
C'	1.46	0.057	1.08	Plat. to carb.

It will be seen that four of the contacts were of low resistance (under a thousand ohms), and the remaining three of high resistance. In the former the resistance *rises* for currents increasing from zero in the direction carborundum to platinum across the contact, whilst in the latter the resistance *falls* for currents in that same direction. Tests of the thermo-E.M.F.s obtained on heating the contacts showed that the thermoelectric power of the high resistance contacts was opposite in sign to that of the low resistance contacts. Apart from this striking evidence of heterogeneity of structure, the contacts of carborundum exhibit the same characteristic behaviour as galena and zincite, and thus fall within the same category of phenomena.

Other Minerals.—Experiments on the combinations of platinum-chalcopyrite and chalcopyrite-bornite show that the sensitiveness of these contacts is negligibly small compared with that of the preceding combinations. In the case of chalcopyrite-bornite three contacts were tested, the values of R_0 being respectively 1,952, 1,880 and 1,500 ohms. The corresponding voltage-coefficients at $v=0$ were 0.073, 0.05 and 0.00. Three contacts of platinum-chalcopyrite had resistances 160, 473 and 793 ohms respectively at $v=0$; the corresponding voltage-coefficients being 0.00, 0.00 and 0.026. A few contacts of platinum-zincite were also tested; they yielded values of $\left(\frac{1}{R} \frac{dR}{dv}\right)_0$, R_m/R_0 , and r_m , practically agreeing with those of chalcopyrite-zincite.

We may conclude that chalcopyrite, bornite and platinum are almost interchangeable elements of a combination whose other member belongs to minerals of the class zincite or carborundum. Bornite has the advantage of possessing a lower specific resistance than chalcopyrite.

The Thermo-electric Sign.—This was determined for all the above minerals in the manner indicated at the end of Section I. One element was platinum in each case.

TABLE V.—*Thermo-electric Sign of Minerals against Platinum.*

Material.	Direction of current across heated junction.
Zincite.....	Zincite to <i>Pt.</i>
Chalcopyrite.....	Chalcopyrite to <i>Pt.</i>
Bornite.....	<i>Pt</i> to bornite.
Galena.....	Galena to <i>Pt.</i>
Carborundum (low resistance)	Carborundum to <i>Pt.</i>
Carborundum (high resistance)	<i>Pt</i> to carborundum.

The characteristics shown in the Paper are drawn in accordance with the above results, the applied voltage being treated as positive when producing current across a junction in the same direction as that caused by a slight rise of temperature at that junction.

III. *The Thermo-electric Theory of the Phenomena.*

The contacts under investigation are such that on the one side the current passes across an area which may be of the order of a square centimetre, whilst on the other side it crosses an area many thousands of times smaller. Regarding the combination as a thermo-electric element, there will be a disengagement of heat on two accounts: Joulean heat, proportional to the square of the current and irreversible in sign; and Peltier heat, proportional to the current, and, therefore, reversed in sign when the current is reversed. The changes of temperature will be negligibly small at the junction of large area in comparison with that at the minute contact. We may, therefore, confine our attention to the latter only.

When the applied voltage is large—say, half a volt or higher—the heat at the contact is sufficiently great to cause appreciable softening, with consequent increase of contact area and drop of resistance. This effect supervenes earlier for current in one direction across the contact than when reversed.

The effects are simple provided the applied voltage is restricted to a sufficiently small value. In the account that follows this limitation is assumed.

Consider in the first place the case of a contact having zero temperature coefficient of resistance. If the Joulean heat could be neglected a rise of temperature would occur on applying a voltage in one direction, and an equal fall with voltage reversed. Equal and opposite thermo-E.M.F.s will be generated, the direction being such as in each case to

oppose the applied voltage. The apparent resistance of the contact will be greater than the true resistance, the excess being independent of the direction of the current. Its value will be constant, since for small voltages the back thermo-E.M.F. will be proportional to the applied voltage. Now let us correct this result by taking the Joulean heat into account. For one direction of current this will be added to the Peltier heat, thereby increasing the rise of temperature and the back E.M.F., and consequently the apparent resistance. For current in the opposite direction the Joulean heat will partially neutralise the Peltier cooling; and the fall of temperature, the back thermo-E.M.F. and the apparent resistance will all be reduced. The resultant effect will be to give a straight line law connecting apparent resistance and applied voltage, the line being now inclined to the axis of voltage.

Another elementary thermodynamic principle of importance here is that when current across the junction causes Peltier *absorption* of heat, an external supply of heat must cause an E.M.F., and, therefore, a current, in the *same* direction across that junction. It follows that at a junction of materials possessing zero temperature-coefficients of resistance the apparent resistance *falls* when the current is of the same sign as that caused by heating the junction. Such a case is found in the combination manganin-constantan, observations on which are described below.

Let us next proceed to the case in which the specific resistances of the elements forming the contact vary appreciably with temperature. If the temperature coefficient is positive the effect will be to augment both the fall of resistance for one direction of current, and the rise for current in the reverse direction. The slope of the resistance characteristic in the immediate neighbourhood of zero voltage will be of the same sign as before, but increased in value.

When the temperature coefficient is negative, on the other hand, the slope of the characteristic at zero voltage is reduced, and changes sign when the coefficient is sufficiently large numerically, in which case we have a *rise* of apparent resistance when the current is in the same direction as that caused by applying heat to the junction. It will be shown that the large negative coefficients occurring in minerals like zincite and galena are amply sufficient to produce this rise. Thus is explained the apparent anomaly of a reduction in resistance despite the fact of a back thermo-E.M.F., and, vice versa, of a

rise in resistance although the thermo-E.M.F. is in the direction to assist the applied E.M.F.

Attention may be further directed to the importance of the part played by a large negative temperature coefficient of resistance. Neglect of this consideration has given rise to fantastic views of the rises of temperature which must be invoked to account for actual resistance variations. Take, for example, the case of a zincite-chalcopyrite contact, at which was observed a fall of resistance from 20,000 ohms at zero voltage to 500 ohms under 1 volt. If temperature variation of resistance is neglected we are faced with the necessity of supposing a thermo-E.M.F. e in the direction of the applied voltage, such that $(1+e)$ volts across 20,000 ohms would produce the same current as 1 volt across 500 ohms—that is, e must be 39 volts. Assuming the thermo-electric power to be 1,000 microvolts per degree Centigrade, and independent of temperature, the required rise of temperature is $39,000^{\circ}\text{C}$. But if we suppose, on the other hand, zero thermo-electric power and a temperature variation of resistance at the rate of -1.5 per cent. per 1°C ., then assuming a compound interest law we have $20,000 (1-0.015)^t = 500$, whence the rise of temperature is 243°C .; and we are back in the region of probability as well as possibility.

In working out an exact treatment of the actions which are assumed to take place at a contact the author is indebted to the Papers of Dr. W. Eccles* on this subject. Nevertheless the conclusions of the present Paper will be found to differ from those of the Paper quoted in several material respects.

Thus, whereas much importance is attached in the latter to the part played by the Thomson effect, in the present treatment the experimental results find their explanation in terms of the Peltier effect and the temperature coefficient resistance.

Again, the softening effect already referred to produces a considerable variation of resistance at the higher voltages, and this fact limits the range of voltage within which calculations can be made. This limitation renders unnecessary the supposition of a "dead resistance"; the elimination of the coefficient representing this allows of still further simplification and increased definitions in the final expressions obtained.

* Eccles, "Proc." Phys. Soc., Lond., XXV., p. 273, 1913.

Let—

- T = Absolute temperature at the contact.
 T_0 = Absolute temperature of the surroundings.
 $t = T - T_0$ = rise of temperature.
 a = Thermo-electric power.
 e = Thermo-E.M.F.
 P = Peltier effect = aT .
 i = Current.
 v = Voltage.
 $R = v/i$ = apparent resistance.
 R' = True resistance.
 b = Temperature coefficient of true resistance.
 H = Total rate of heat developed at contact.
 K = Cooling coefficient.

Both v and i will be considered to be positive when in the direction of the current due to a slight heating of the contact.

Assuming the thermo-E.M.F. to be a linear function of temperature change,

$$e = at. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Taking the rate of removal of heat from the contact to be proportional to temperature rise, then in the steady state,

$$H = Kt. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

R and R' are related as follows :—

$$\frac{v}{R} = \frac{v+e}{R'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Assuming a linear variation of R' with temperature—

$$R' = R'_0(1+bt). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The total heat developed at the contact by a current i is the sum of the Joule and Peltier effects. Observing the convention above defined for the positive direction of current, we have

$$\frac{1}{2} H = i^2 R' - Pi. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

On eliminating t , T , e , i , H , and P by aid of these relations we obtain the following expression for the apparent resistance of the contact in terms of the applied voltage :—

$$KR^2 - R(KR'_0 + a^2 T_0) = v^2 b R'_0 - av(R + bT_0 R'_0). \quad . \quad . \quad (6)$$

This is the equation of the resistance-characteristic. Three

main types of characteristic are derivable, which are represented diagrammatically in Fig. 5.

Type I. is the limiting case where $b=0$, when equation (7) simplifies to a straight line, denoting a resistance which falls for voltage applied in the positive direction. It is practically realised in the contact constantan-manganin.

Type II. includes all cases where b is positive, and thus covers all combinations of pure metals. With voltage in the positive direction the resistance at first falls, reaches a minimum, and afterwards rises.

Type III. represents cases for which b is negative and large. It includes all the mineral contacts possessing marked recti-

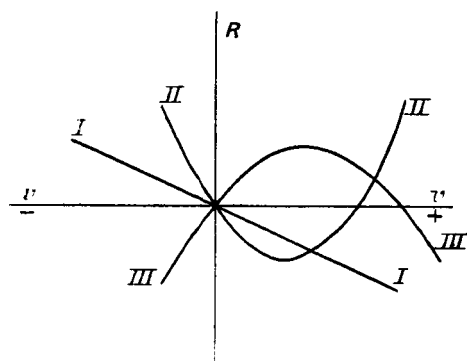


FIG. 5.—THREE THEORETICAL TYPES OF RESISTANCE CHARACTERISTIC.

Type I, $b=0$. Type II, b positive. Type III, b negative and large.

fying properties. The resistance *rises* at first with a positive voltage, reaches a maximum, and then falls continuously.

We now proceed to an examination of the values of $\left(\frac{1}{R} \frac{dR}{dv}\right)_0$, R_m/R_0 , and v_m which, it has been concluded from experimental observation, are constant quantities for any contact between the same pair of materials. It will now be shown that this constancy results from the theory, *provided* that the product KR_0 is a constant for the given pair of materials.

Putting $v=0$, equation (6), reduces to

$$R_0 = R_0' + \frac{\alpha^2 T_0^2}{K} = R_0' \left(1 + \frac{\alpha^2 T_0^2}{K R_0'}\right). \quad (7)$$

The apparent resistance is greater than the true resistance by an amount proportional to the square of the thermo-electric

power. Calculation shows that in the case of metals the term $\frac{a^2 T_0}{KR_0}$ is negligible compared with unity, and it is probable that in the case of minerals also its value is less than unity. Approximate results may, therefore, be obtained by neglecting the term in a^2 in equation (6).

Differentiating (6), we have

$$\frac{dR}{dv} = \frac{2bR_0'v - a(R + bT_0R_0')}{2KR - KR_0' - a^2T_0 + av} \quad (8)$$

There are two important special cases. First, let $v=0$. Then

$$\left(\frac{dR}{dv}\right)_0 = \frac{-a(R_0 + bT_0R_0')}{KR_0} \quad (9)$$

or
$$\left(\frac{1}{R} \frac{dR}{dv}\right)_0 = \frac{-a(1 + bT_0R_0'/R_0)}{KR_0} \quad (10)$$

The expression in (10) represents the value of the voltage-coefficient of resistance of the contact. Its value is independent of R_0 provided that KR_0 is a constant.

In the next place let us consider the point at which dR/dv is equal to zero, that is, R a maximum or minimum. The applied voltage at which this occurs is given by

$$v_m = \frac{a(R_m + bT_0R_0')}{2bR_0'} = \frac{a(R_m/R_0' + bT_0)}{2b} \quad (11)$$

Substituting this expression for v in the general equation, we obtain a function of the form $f(R_m/R_0, KR_0)=0$, which means that provided KR_0 is independent of R_0 , so also is R_m/R_0 .

Returning to equation (11), and putting R_m/R_0' equal to a constant, we see that v_m necessarily becomes independent of R_0 .

It follows, therefore, that on the thermo-electric theory of the effect the three quantities $\left(\frac{1}{R} \frac{dR}{dv}\right)_0$, v_m , and R_m/R_0 are independent of R_0 , provided KR_0 is independent of R_0 .

The Value of KR_0 .—In seeking for a theoretical basis yielding the requirement that KR_0 should be a constant, or approximately a constant, for any given pair of materials, two views of the nature of the contact have been taken. From either of these the required condition can be deduced.

(a) We may assume that the contact resistance is given by the end-correction formula applied to, say, a uniform column of mercury in a capillary tube terminating within a considerable bulk of mercury. Applying Lord Rayleigh's formula to a

contact supposed circular, of radius r , and denoting the specific resistance of the badly conducting component of the contact by ρ , we have

$$R_0' = \frac{0.8r}{\pi r^2} \rho = \frac{0.252\rho}{r}. \quad \dots \dots \dots (12)$$

In the next place let us assume the heat to be developed symmetrically within a spherical volume whose linear dimensions are of the order of r of (12), and that the amount set free per unit volume at a point distant r from the centre of the sphere is proportional to r^n , where n is some constant. Then total heat developed per second within the sphere of radius r_0

$$= H = \alpha \int_0^{r_0} 4\pi r^2 \cdot r^n dr = \frac{4\pi \alpha r_0^{n+3}}{n+3} \quad \dots \dots \dots (13)$$

where α is a constant.

In the steady state the heat crossing any isothermal surface is equal to the heat liberated within it. Denoting the thermal conductivity by k ,

$$-4\pi r^2 k \frac{dt}{dr} = \frac{4\pi \alpha r^{n+3}}{n+3},$$

whence

$$\frac{dt}{dr} = \frac{-\alpha r^{n+1}}{k(n+3)}.$$

Hence for the excess of temperature t' of the centre over the boundary of the sphere we have

$$t' = \frac{\alpha}{k(n+3)} \int_0^{r_0} r^{n+1} dr = \frac{\alpha r_0^{n+2}}{k(n+2)(n+3)} \quad \dots \dots (14)$$

Similarly the excess temperature t'' of the boundary of the sphere of radius r_0 over that of the surroundings is found to be given by

$$t'' = \frac{\alpha r_0^{n+2}}{k(n+3)} \quad \dots \dots \dots (15)$$

Adding t' and t'' the excess temperature t_0 of the centre of the sphere over that of the surroundings has the value

$$t_0 = \frac{\alpha r_0^{n+2}}{k(n+2)} \quad \dots \dots \dots (16)$$

Since $H = Kt_0$, we find from (13) and (16)

$$K = H/t_0 = 4\pi k r_0 (n+2)/(n+3) \quad \dots \dots \dots (17)$$

Now, according to (18) $K \propto r_0$; whilst by (12) $R_0' \propto \frac{1}{r_0}$.
Combining (12) and (17),

$$KR_0' = 0.8k\rho(n+2)/(n+3) \quad . \quad . \quad . \quad (18)$$

The value of this expression depends upon the ratio of the thermal and electrical conductivities, and is independent of the dimensions of the contact.

This same conclusion may also be reached if we assume

(b) That the resistance R_0 is located mainly—let us suppose entirely—in a thin film of molecular dimensions whose area is that over which the two elements of the contact intimately meet. There is an *a priori* improbability that the resistance of a mere contact such as is here under consideration can be calculated exactly as though the materials were welded in perfect molecular union across the minute area of the contact—which is really what is assumed in the view (a). According to the second view, to the resistance calculated on the lines of (a) should be added a resistance inversely proportional to the area of contact.

Assuming this latter contribution to be the main part of the total resistance, it follows that the Joulean heat, as well as the Peltier heat, is located in a thin film of molecular dimensions at the interface of the two materials. The stream lines of heat and of electricity will be similar in form. We shall have K proportional to the area of contact, and R_0 inversely proportional to the area of contact. KR_0 will thus be independent of the contact area, and proportional to the ratio of the thermal and electrical conductivities.

*The Slope of the Resistance-Characteristic when $v=0$.—*Equations (9) and (10) indicate how the gradient at zero voltage depends on the value of the temperature coefficient of resistance.

When b is positive, $(dR/dv)_0$ must be negative. The resistance assumes a minimum at the positive voltage v_m . This case, as well as the limiting case when $b=0$, is the subject of the experiments described in section IV.

When b is negative, the gradient becomes positive if $(1+bT_0R_0'/R_0)$ is negative, or since R_0'/R_0 differs little from unity, when $-b > \frac{1}{T_0}$. Now, in the case of minerals b is negative and often much larger numerically than for a pure metal. Thus, Pierce, in a careful determination, obtained the value

-0.0153 for molybdenite at 0°C. There is thus an ample margin for concluding from thermo-electric theory that $(dR/dv)_0$ should be positive at mineral contacts, so that theory and observation are in agreement as to the direction of the rectified current under an alternating voltage.

IV. *Experiments with Metallic Contacts.*

Experiments on metallic combinations are of interest, since they supply the case where b is positive or zero. Moreover, the values of a and b are definitely known. The following were selected as test cases:—

Bismuth-Antimony.— a large, $b+$.

Iron-Nickel.— a fairly large, $b+$.

Constantan-Manganin.— a fairly large, $b=0$.

Copper-Manganin.— a very small, $b=0$.

Bismuth-Bismuth.— a zero, $b+$.

Attention was specially directed to the junctions bismuth-antimony and constantan-manganin. A series of contacts was examined in each of these cases, the results being to show (1) that the voltage-coefficient at zero voltage is independent of the resistance; (2) that the sign of the above coefficient is negative; (3) that a minimum occurs on the side of positive voltage.

We may conclude that the phenomena occurring at metallic contacts are thermo-electric in nature, and are essentially identical with those of mineral contacts.

The voltage coefficient is largest in the case antimony-bismuth, though even here it has only one-fifth the value found at a galena-platinum contact, and about one twenty-fifth that of a zincite contact. The specific characteristics of the above two contacts are shown in Fig. 10, which is drawn to the same scale as Fig. 2.

Softening of the Contact due to Rise of Temperature.—All the resistance-characteristics of this class exhibit a droop on both the positive and the negative side when the voltage rises to a certain value dependent on the duration of the current. It occurs most readily in contacts containing bismuth as one element, the melting point of which is 269°C. The effect is evidently due to softening and plastic yielding at the contact, which results in rapid increase of area. There is little doubt that this effect is present to an important extent in the case

of mineral contacts also, though not so obvious since it then occurs on a falling characteristic.

Bismuth-Antimony.—An example of a characteristic is shown in Fig. 6. In order to obviate or diminish the softening

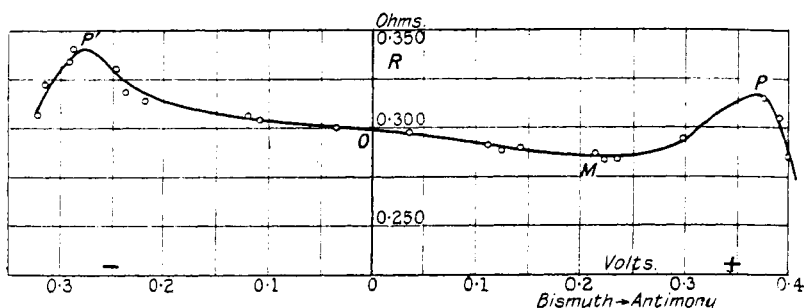


FIG. 6.—AN ANTIMONY-BISMUTH RESISTANCE CHARACTERISTIC.

effect the voltage was applied for only 0.003 second. The droop then occurs when v is between 0.3 and 0.4 volt. Four contacts were examined. The results of Table VI. show the constancy of the voltage-coefficient.

TABLE VI.—*Bismuth-Antimony Contacts.*

No.	1.	2.	3.	4.	—
R	0.092	0.50	10.5	145.4	
$(dR/dv)_0$	-0.019	-0.13	-2.75	-42.5	
$\left(\frac{1}{R} \frac{dR}{dv}\right)_0$	-0.206	-0.256	-0.26	-0.29	Mean = -0.254

At the lower range of voltage the characteristic is evidently of the type II. of Fig. 5.

Iron-Nickel.—The characteristic is of the same type as the last. The voltage-coefficient found was -0.16 , and a minimum of resistance occurred at $v_m = 0.016$ volt. The droops occur later than in the preceding case, and no difficulty was found in obtaining the point of minimum.

Constantan-Manganin.—This constitutes the case $b=0$. The characteristic equation (7) reduces to $R = R_0' - \frac{a}{K} v$, which represents a straight line. This linear type of characteristic was found as expected. An example is shown in Fig. 10; the duration of the applied voltage was 0.1 second.

The values of the voltage-coefficient for five different contacts are as follows :—

TABLE VII.—*Constantan-Manganin Contacts.*

No.	1.	2.	3.	4.	5.	—
R_0	0.0735	0.108	0.112	0.171	1.30	
$(dR/dv)_0$	-0.0083	-0.0095	-0.012	-0.0195	-0.133	
$\left(\frac{1}{R} \frac{dR}{dv}\right)_0$	-0.113	-0.088	-0.107	-0.114	-0.103	Mean = -0.105

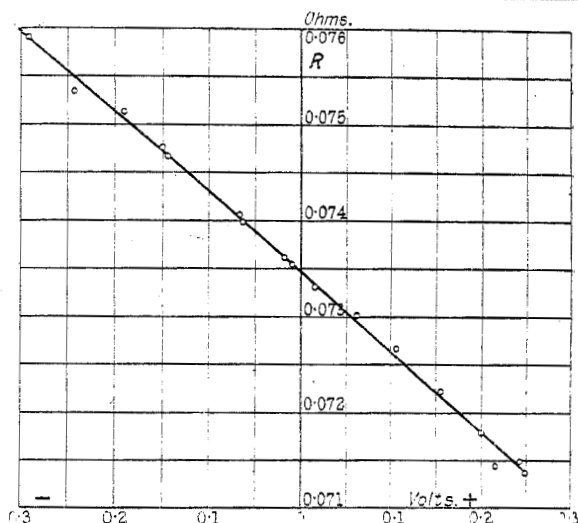


FIG. 7.—A CONSTANTAN-MANGANIN RESISTANCE CHARACTERISTIC.

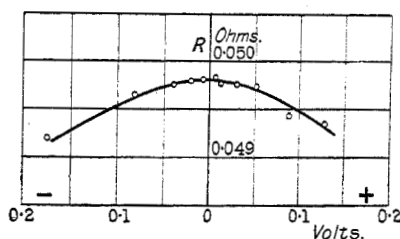


FIG. 8.—A COPPER-MANGANIN RESISTANCE CHARACTERISTIC.

Copper-Manganin.—Here $a \neq 0$, $b \neq 0$, so that on the theory R should be independent of v . Fig. 8 represents a specimen set of observations. The curve is symmetrical about the

vertical axis. The slight fall is attributed to the softening effect.

A similar curve, though still flatter, was found with carbon-manganin.

Bismuth-Bismuth.—The object of this test was to examine the view of a softening due to rise of temperature. The characteristic, shown in Fig. 9, possesses a slight asymmetry due possibly to a slight difference in chemical quality of the two components of the contact. The anticipated droops were found to occur very sharply. If the duration of the current is prolonged the resistance goes on falling, and past a certain point the original resistance cannot be reproduced. The effect is paralleled exactly in the case of mineral contacts at the higher voltages.

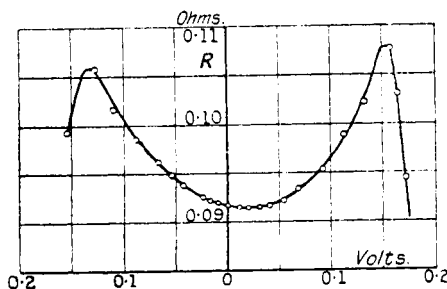


FIG. 9.—A BISMUTH-BISMUTH RESISTANCE CHARACTERISTIC.

V. Some Calculations.

The Value of KR_0 .—When the values of a and b are known this can be calculated from equation (10). For antimony-bismuth the value is 8.6×10^{-4} ; for iron-nickel 4.3×10^{-4} ; and for manganin-constantan 3.9×10^{-4} . These values are all of the same order, thus supporting the views of the nature of the contact proposed in Section IV., according to which the value of this quantity is determined by the ratio of the thermal and electrical conductivities, which is practically a constant in the case of metals.

The Ratio R/R' .—By equation (7) the ratio of the apparent and real resistance of a contact at zero voltage is given by the expression $(1 + a^2 T_0 / KR_0')$. Applying the calculation to the case manganin-constantan, we have $a = 40 \times 10^{-6}$, $KR_0 = 3.9 \times 10^{-4}$, whence $a^2 T_0 / KR_0' \doteq 0.0012$, which is very small compared

with unity. The same holds practically in the case bismuth-antimony.

The Rise of Temperature at the Contact.—Substituting for R the value $R_0'v(1+bt)/(v+at)$ derived from equations (1), (3) and (4), we obtain an expression for t in terms of v , which for small values of v reduces to

$$t = -v \cdot \frac{aT_0}{KR_0} \quad (19)$$

The temperature change is thus proportional to the applied voltage and to the thermo-electric power. In the case of constantan-manganin the equation becomes $t = -30.5v$, which denotes a fall of temperature for current in the direction constantan to manganin across the contact, at the rate of

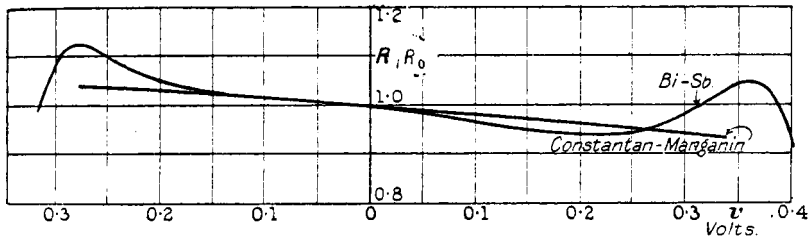


FIG. 10.—THE SPECIFIC RESISTANCE-CHARACTERISTICS OF TWO METALLIC CONTACTS.

30.5°C. per volt. For antimony-bismuth $t = -36v$. We may obtain an estimate in the case of mineral contacts by assuming values for (a) and (b). Thus, in the case of galena we may accept roughly $a = 500 \times 10^{-6}$, $b = -0.01$, whence $t = -177v$, i.e., a fall at the rate of 177°C. per volt for current crossing the contact from galena to platinum.

The Value of v_m .—The agreement between the observed values of v_m and those calculated by equation (11) are shown in the Table below :—

Contact.	$a \times 10^6$	b	R_m/R	v_m	
				Calculated.	Observed.
Iron-nickel	32	+0.004	0.998	0.008	0.016
Antimony-bismuth	100	+0.004	0.96	0.027	0.22
Galena-platinum ...	500	-0.01	1.04	0.05	0.066
Zincite-platinum ...	(assumed)	(assumed)	1.54	0.136	0.15
	1,000	-0.01			
	(assumed)	(assumed)			

VI. *The Reception of Electric Waves by the Contact Rectifying Detector. Conditions of Highest Sensibility.*

The law of constancy of the voltage coefficient can be applied to the receiving circuit in which a contact detector is employed in series with a magnetic telephone. It will be supposed, in the first place, that no polarising voltage is used. Since the oscillatory E.M.F. required to produce a signal is only a small fraction of a volt, the relation between R and v is practically a linear one. Let

$$v = v_0 \sin pt = \text{applied voltage.}$$

$$i = \text{instantaneous current.}$$

$$R = \text{apparent resistance of contact.}$$

$$R_t = \text{resistance of telephone.}$$

$$A = \left(\frac{1}{R} \frac{dR}{dv} \right)_0.$$

A simple treatment will be adopted, the induction of the telephone and leads being neglected and the resistance assumed to be independent of frequency. The conclusions thus reached may be corrected in the direction required by the practical conditions applying in any given case.

The current at any instant is given by

$$i = \frac{v_0 \sin pt}{R + R_t} \quad \dots \dots \dots (20)$$

Also $R = R_0(1 + Av) \quad \dots \dots \dots (21)$

Hence $i = \frac{v_0 \sin pt}{R_t + R_0 + R_0 A v_0 \sin pt} \quad \dots \dots \dots (22a)$

which, since v_0 is considered small compared with unity, may be written with sufficient accuracy

$$i = \frac{v_0 \sin pt \left(1 - \frac{AR_0}{R_t + R_0} \cdot v_0 \sin pt \right) \sin pt}{R_t + R_0} \quad \dots \dots (22)$$

The mean or rectified current is

$$\frac{1}{T} \int i dt = \frac{-AR_0 v_0^2}{2(R_t + R_0)^2} \quad \dots \dots \dots (23)$$

Its value is proportional to the square of the R.M.S. value of the applied voltage, a result first empirically deduced by L. W. Austin.*

* Austin, "Phys. Rev.," 1907.

The pull on the telephone diaphragm is determined by the number of ampere-turns. The best resistances of contact and telephone are those which make the ampere-turns a maximum for a given applied voltage. For maximum sensibility of receiving circuit, therefore, $\frac{nAR_0}{2(R_t+R_0)^2}$ must be a maximum, where n denotes turns on telephone.

Three cases will be discussed :—

i. The telephone supposed given, *i.e.*, n and R_t fixed. The ampere-turns are then proportional to $\frac{AR_0}{(R_t+R_0)^2}$, which is a maximum when $R_0=R_t$.

ii. The contact resistance supposed given. Assuming a constant weight of copper in the coil, and neglecting the correction for space occupied by insulation, we have $R=kn^2$. The required condition then reduces to $\frac{\sqrt{R_t}}{(R+R_0)^2}=\text{maximum}$. The solution is $R_t=\frac{1}{3}R_0$.

iii. The contact resistance and resistance of telephone variable at choice. The condition now is $\frac{R_0\sqrt{R_t}}{(R_t+R_0)^2}=\text{maximum}$.

As R_0 is varied it is necessary, as the preceding case shows, to follow suit by rewinding the telephone so that $R_t=\frac{1}{3}R_0$. The condition thus reduces to $R_0^{-\frac{1}{2}}=\text{maximum}$. The smaller the resistance of contact and telephone the better. In practice, however, a limit to this reduction is evidently imposed by the impedance in other parts of the receiving circuit, which has not been considered.

To sum up, we conclude that for high sensibility :—

(1) The contact should be of materials having as large a voltage-coefficient as possible ;

(2) The resistance of the contact should be low (the lowest value depending on the impedance in receiving antenna, &c.) ;

(3) The resistance of the telephone should be about one-third that of the contact.

Use of a Polarising Voltage.—By applying the above considerations, and paying due regard to the form of the resistance characteristic for any combination, the effect of a polarising voltage may be foreseen. It is evident that if the polarising voltage be such as to lead to the point of maximum resistance on the characteristic, then the rectifying power and the sensibility become zero.

Again, if the resistance of the contact is below that of the telephone, it is quite possible that a polarising voltage in either direction may be deleterious or at least ineffective.

It is when the resistance of the contact happens to be much larger than that of the telephone that the advantage of a polarising voltage will be decisively seen. Its sign must evidently be chosen in the direction of the initial fall in the characteristic, *e.g.*, for the perikon the polarising current must cross the contact from chalcopyrites to zincite.

An examination of the curves shows that with voltages increasing from zero in the direction just specified, the slope of the characteristic at first increases. As the polarising voltage is increased further the slope at the corresponding points of the characteristic falls off, and evidently a value of the polarising voltage will be reached at which a maximum effect occurs. This value will depend on the initial resistance of the contact; it is thus not possible to specify any definite figure for the optimum polarising voltage at a contact of given materials.

Theoretically it appears that, given the receiving telephone, the ideal contact is one to which is applied the small polarising voltage leading to the point of maximum slope on the characteristic; and of initial resistance such that under that polarising voltage the resistance falls to a value exactly equal to that of the telephone.

VII. *Use of Direct-Current Galvanometer in Series with a Rectifying Contact in Null Alternating-Current Bridge Methods.*

This problem is amenable to the treatment applied in the last section. If the galvanometer be regarded as given, then for highest sensibility the resistance of the contact should be equal to that of the galvanometer, but if a given contact be taken then the best galvanometer to choose is one of resistance one-third that of the contact at zero voltage.

Treated as a millivoltmeter, we see that the arrangement shares with hot-wire instruments and dynamometers the defect that the square law is involved; and it may be shown that the minimum voltage detectable cannot be reduced greatly below a millivolt. For currents within the range of useful frequency of the telephone and the vibration galvanometer the combination of contact and direct-current galvano-

meter thus falls much below those instruments in sensibility. This conclusion is in accordance with experimental results.

The following example of a test may be quoted. The agreement between the observed rectified current and that calculated by equation (23) is very satisfactory :

Contact of galena-platinum : $A=1.20$.

$R_0=95$ ohms.

Galvanometer resistance $=250$ ohms.

Sensibility $=186$ scale-divisions $(1/40$ in.) per microampere.

Applied voltage (R.M.S.) $=0.05$ volt, at 85° .

Observed steady deflection $=383$ scale-divisions ; whence rectified current $=2.06 \times 10^{-6}$ amperes.

Rectified current calculated by (23)

$$= \frac{1.2 \times 95 \times 0.05^2}{345^2} = 2.38 \times 10^{-6} \text{ amperes.}$$

Taking half a scale-division as the minimum observable deflection, the minimum alternating voltage detectable with the given galvanometer and contact $= \frac{0.05}{\sqrt{766}} = 1.81 \times 10^{-3}$ volt.

Summary.

1. Measurements by the Wheatstone bridge have been made of the electric resistance at various rectifying mineral contacts ; the results being expressed in the form of resistance characteristics. The thermo-electric sign of the current was found in each case.

A series of similar measurements are recorded on contacts both elements of which are metallic.

2. A formula for the resistance characteristic is derived on the view that the phenomena in question are due to thermo-electric action. The experimental results are shown to be fully explained on this view. The fact that the rectified current (when an alternating voltage is applied) is generally, in the case of mineral detectors, in the opposite direction to that produced by heating the contact, is shown to be in harmony with the thermo-electric view, and not, as has generally been supposed, in collision with it. The determining factor in respect of sign proves to be a large negative temperature coefficient of resistance.

3. In relation to the thermo-electric theory, two views as to the location of the resistance at a contact are proposed and discussed.

4. Some calculations, including that of the rise of temperature at a contact, are given.

5. The experimental results form the basis of calculation of the best values to choose for the resistances of the contact and telephone in a wireless receiving circuit.

6. The influence of a polarising voltage on the sensibility of the receiving circuit is discussed.

7. It is shown that the combination of direct-current galvanometer and sensitive contact cannot respond to an alternating voltage much below 1 millivolt.

8. Observed values of rectified current are found to be in close agreement with those calculated on the thermo-electric theory.

ABSTRACT.

The Paper contains an account of an investigation, the primary object of which was to determine the nature of the physical actions occurring at a rectifying contact. Resistance characteristics are given for various contacts, some including a mineral, some in which both elements are metals. It is shown that a *specific characteristic* may be drawn for any given pair of materials. The experimental results are in accordance with the view that the actions are thermo-electric, the main determining factors being the thermo-electric power and the temperature-coefficient of electric resistance.

Based on the law of constancy of the voltage-coefficient calculations are given showing the best value of the resistance of the telephone in a wireless receiving circuit in which the contact detector is employed. The influence of a polarising voltage is also traced.

The use of the combination of rectifier with a direct-current galvanometer as indicator of the balance point in an alternating-current bridge is examined, and it is shown that the minimum detectable alternating voltage cannot be reduced much below a millivolt.

DISCUSSION.

Mr. DUBDELL thought the Paper was a very important contribution. He had no definite opinion as to the true explanation of rectifying contacts. In practice very much depends on the exact part of the crystal at which contact is made. With regard to thermo-electric forces, he had examined a large number of crystals in the hope of obtaining contacts which were more stable than those ordinarily employed, and he had concluded that no mineral which did not show thermo-electric effects was of any use as a detector. There might be exceptions in the case of metals, but the rule applied to all sulphides. His experience with regard to the receiving telephone differed somewhat from the author's. In a telephone the resistance and impedance depend on the frequency. In practice it seemed desirable to keep the impedance of the telephone of the same order as the resistance of the detector, and adjust the latter until the desired sensitivity is attained. In receiving strong signals one may employ very tight contacts in which it appears to be impossible that there should be any air film. A satisfactory rectifying action is still, however, obtained.

Prof. G. W. O. HOWE thought that it was well to avoid flying off to new hypotheses in order to explain new phenomena if they could possibly be accounted for on well-known grounds. He was pleased to see that the author had been able to explain rectifying contacts without invoking any mysterious new properties. He was rather surprised to gather from the author's remarks that the thermo-electric theory was generally discredited. His impression had been that the work of Dr. Eccles had established it as the accepted explanation. Had any of the exponents of the electron theory attempted to give a detailed explanation of the observed phenomena on that basis? What was the origin of the "settling down" of contacts mentioned by the author? Was it a mechanical or thermal effect? He would like to hear just in what respect the results of Mr. Owen's work differed from those of Dr. Eccles.

Dr. W. ECCLES remarked that he was glad to find such agreement on the absurdity of rushing to special explanations of these phenomena. Certain workers had thought that electrostatic attraction altered the area of contact. Others assumed the opening of trapdoors to let electrons through, the mechanism of the process being considerably more difficult to explain than the original results themselves. Prof. Fleming had found that many of the substances used as detectors were photo-electric—*i.e.*, they give off electrons under the action of light—and he assumed that rectifying phenomena were caused by a similar action of the longer electro-magnetic waves. He (Dr. Eccles) had tried to put these points straight by explaining the phenomena in terms of well-known physical properties, such as the resistance coefficient, Peltier effect, &c., and had found it possible to account for all the effects. The theory proved unpopular because it had nothing occult about it. Mr. Owen had dropped the Thomson effect from his treatment. He thought this was not justifiable, as the Thomson effect was a physical fact which must enter into the result in practice. Leaving it out of consideration simplifies the treatment, but loses the explanation of several of the erratic properties of detectors. For instance, the theoretical resistance characteristic curves obtained by Mr. Owen are parabolic. It is obvious, however, that the experimental curves are of the fourth degree. The Thomson effect must be introduced to explain the way the curve bends off at the extremities. One important result of the author's was that for the same materials the value of R_m/R_o was constant for any contact, light or heavy. This appeared to him to be due to the fact that increasing the area of contact by increasing the pressure was equivalent to putting two or more similar contacts in parallel.

Mr. A. F. HALLMOND (communicated): I should like to congratulate the author on his reduction of the curves for each contact-pair to a specific resistance characteristic. If it is found that the same process can be employed in all cases a very useful and simple means of comparison will be established. The result seems the more remarkable in being based upon the resistance-curves, and I should like to ask whether the relation throws any light on the conditions obtaining at the contact when the pressure is varied. With reference to the heating of the contact, I believe that Prof. Pierce observed that at 80 cycles no lag occurred, such as might be due to heating. The author's arrangement by which the current may pass from 0.003 second would seem to be even more sensitive. Was any variation observed in the resistance with the time of passage of the current? With regard to the thermal effects, might I suggest the investigation of pyrite, a mineral in which adjoining areas may exhibit widely different thermal E.M.F.s?

Mr. P. R. COURSEY communicated the following remarks: The three main results arrived at will be of especial value, even if they do no more than form a basis of comparison for the work of different investigators, which up to the present has only been applicable (quantitatively) to the particular

contacts on which the experiments were made. I should, therefore, like to ask the author whether he has found the "specific resistance characteristics" that he has obtained to be applicable to results derived from measurements on different crystals of the same materials, or merely to contacts of various pressures and resistances between individual crystals. The two very different curves given for carborundum crystals would seem rather to support the latter view. As to the accuracy of this method of determining the characteristic, it would not seem to possess much ultimate advantage where very small voltages are concerned, as in any case the limit of accuracy depends on the galvanometer employed, whether for the direct measurement of the current passing through the crystal or for the indication of balance of the bridge. Moreover, the method of obtaining the resistance with very brief currents, although leading to consistent results from the "curve" point of view, scarcely corresponds to the use in practice of a steady polarising or boosting voltage (often of the order of 1 volt, as is usual, for instance, with most carborundum crystals) which may be impressed on the crystal for many hours at a time, and would, therefore, probably produce a maximum of softening effects at the contact. It would, therefore, be interesting if a series of curves could be obtained with different contact times in order that the magnitude of this effect might be gauged. On the other hand, it is just possible that if any appreciable temperature rise occurs at the contact this factor of itself may cause an increase in the sensitiveness of the detector, quite apart from the purely electrical effect of the applied voltage. These considerations, however, perhaps affect rather the practical applications of the detectors than the physical processes underlying their action with which the Paper is chiefly concerned.

The AUTHOR (in reply) said he was glad to learn that it was Mr. Duddell's uniform experience that high thermo-electric power and sensitiveness of a contact detector go together. In regard to the relation of impedance of telephone to the resistance of the contact he was quite prepared to find that the conclusions deduced from the simple treatment employed in the Paper required modification to conform to the actual conditions of practice. In reply to Prof. Howe's inquiry as to the cause of the "settling down," this was not due to thermal action; the small testing voltage was applied only at intervals, and was not itself the cause of the change described. The effect appeared to be of the nature of an adjustment of the molecules bounding the contact when their setting was changed; it was probably allied to the slow changes met with in the study of elastic strains. He did not go so far as to say that the thermo-electric theory had become generally discredited, but rather that it stood in need of confirmation. He would endeavour briefly to point out in what relation his own work appeared to stand to that of Dr. Eccles; this reply would cover some points of difference which Dr. Eccles had commented upon. Dr. Eccles employed coefficients representing the Peltier effect, the Thomson effect, and the temperature coefficient of resistance. The author finds that the existence of softening and consequent increase of area of contact due to rise of temperature becomes very important at the higher voltages. This effect is complicated and thus not amenable to mathematical treatment; the course adopted in the present Paper is, therefore, to restrict the application of the formulæ within small limits of voltage—say, a few tenths of a volt. Apart from this, the chief point of difference is in the emphasis laid on the relative value of the coefficients. The author finds that the experimental results in the case of all the mineral and metallic contacts tested may be explained without invoking the Thomson effect; the conclusion is, therefore, drawn that this term is of small importance in comparison with the Peltier effect, at all events at low voltages. It thus fortunately becomes possible to simplify the theory appreciably. Again, in the author's view not only does resistance admit of more precise measure-

ment, but the statement of results in the form of resistance characteristics brings out the essential features of the behaviour of these contacts more clearly than if current characteristics are employed. In reply to Mr. Hallimond, the determination of resistance of contact as a function of pressure is not specially considered in the Paper. The tests here recorded tend, however, to show that pressure only enters in so far as it alters the area of contact. In regard to the question of time-lag, this is the subject of experiments now in progress. In reference to pyrite, the author fully grants that heterogeneity may and does exist in this and other cases; for further instance, in the high and low-resistance specimens of carborundum referred to in the Paper, both possessing high thermo-electric power, but of opposite signs in the two cases.

In reply to Mr. Coursey's first question, it is a matter for experiment to discover to what extent various specimens of nominally the same mineral agree in behaviour. Reference may be made to the remarks immediately preceding. As to the matter of accuracy, the bridge method carries the advantage that a null method has over a deflectional one; and, further, that of permitting of practical elimination of the effects caused by prolongation of time of application of applied voltage. It is, of course, true that when a polarising voltage is applied the time effect must enter; but even here the all-important changes caused by the superposition of a rapidly oscillatory voltage are in themselves independent of softening action.