Researches
on
Contact Electricity

A Thesis

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At the surface of separation of any two different substances in contact, there exists in general an electromotive force tending to maintain a certain difference of potential between them. This principle, established for metals by Volta in 1797, has been extended by later investigators to other substances, including liquids and gases. From these early researches of Volta, and the later more elaborate enquiries of Kohlrausch (1853), Hankel (1861-5), and Gerland (1868), there have been deduced certain fundamental laws, which have been fully corroborated by the recent work of Clifton and Ayrton and Perry. If, of a number of conductors set serially in contact, the difference of potential between each successive pair be quantitatively estimated and reckoned positive or negative according as the first member of the pair is at a higher or lower potential than its successor, then the difference of potential between the first and last members of the chain is equal to the algebraic sum of the potential-differences between the successive contiguous pairs.

Should the series be made up of simple conductors, the potential-difference between the extremities is quite independent of the nature, number, and order, of the intervening components, and is indeed equal to the difference obtained by direct contact of these extreme members. Hence

if a circuit be composed of such substances, metals for example, the sum of the differences of potential existing at the various surfaces of contact taken in order all round the circuit is zero, the resultant electromotive force is therefore zero, and no current can exist — provided the system be at a uniform temperature, a condition which is assumed unless otherwise stated.

This result of experiment is in full accordance with the recognised principle of the Conservation of Energy; for, were there a current, where were the source from which the current could derive its energy?

Should the contact-chain, however, consist partly of compound or chemically-decomposable conductors, the potential-difference between the extremities may and frequently does become a function of the intermediate structure, and is then no longer equal to the direct contact difference between the extreme members.

With a circuit formed of such materials the resultant total electromotive force does not in general vanish, so that the existence of a current is possible and necessary; and the energy of this current is derived from the energy of ^{the} chemical combination, which is the one aspect

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of the accompanying reaction, whose other aspect is the decomposition of the compound conductor. Except such chemical action were possible, no current could be generated; so that, probably, the possibility of chemical action conditions the non-vanishing character of the resultant total electromotive force in the circuit. Such, at present, seems to be the most complete theory of the ~~cell~~ voltaic cell.

Although no current is possible in a circuit of simple conductors maintained at a uniform temperature, because of the mutual balancing of the contact forces, it is possible to cause a current to flow by heating or cooling one of the junctions, thereby destroying the equilibrium of the contact forces.

The energy of the current so obtained is a part-transformation of the energy which was originally expended in unequalising the temperature of the system. Apparently, then, the contact difference of potential between two metals or other simple conductors depends upon temperature — a conclusion verified in a remarkable way by consideration of the so-called Peltier Effect, or reversible thermal effect produced by the passage of a current across the junction of two different-metals.

By an application of the dynamical theory of heat to the problem, Sir W. Thomson (1851) proved that this evolution or absorption of heat at the junction according as the current flowed in one or other direction indicated an electromotive con-

tact force, acting against the current when heat was evolved, with the current when heat was absorbed. In other words, because of the difference of potential at the junction, the current has to do work when passing in one direction and has work done upon it when passing in the other — giving rise respectively to an evolution and absorption of heat. From consideration of the principle of dissipation of energy, Professor Tait has developed a formula for this electromotive contact force, expressing it as a parabolic function of the temperature; and this theory has been indirectly verified by a long series of experiments upon the thermoelectric properties of metals (see Transactions Roy. Soc. Edin. 1870-71).

With a view of testing by direct contact experiments the variation with temperature of the contact difference of potential between dissimilar metals, I undertook the experiments whose results form the subject of this thesis. It must be premised, however, that any positive result cannot be regarded as due only to the metals; for, as pointed out by Professor Clerk Maxwell (Electricity and Magnetism Vol I, section 249), Volta's electromotive force of contact is in general greater than that indicated by the Peltier Effect and sometimes of opposite sign — a discrepancy to be accounted

for by the fact that in direct contact experiments there is always a film of condensed air or other gas between the metals when they are in so-called contact, and that possibly the chief effect "must be sought for, not at the junction of the two metals, but at one or both of the surfaces which separate the metals from the air or other medium which forms the third element of the circuit." After a few preliminary experiments I concluded that direct contact of the surfaces under investigation was a sufficiently accurate and constant method for indicating any appreciable change which might occur. It was found necessary, however, to keep the surfaces continually polished in a particular manner, since they gradually altered their condition when exposed to the action of the air — a fact formerly established by Hankel (1861, 65; see Wiedemann's Galvanismus ^{Vol.} ~~Band~~ I. page 27) Before discussing the results obtained it is advisable first to give a description of the apparatus used.

Of the two metallic surfaces which were ^{the} subject of experiment, the lower was the upper surface of a flat cylindrical flask-shaped vessel which rested on an insulated stand in electric connection with one pair of opposite quadrants of a Thomson Quadrant Electrometer. The

temperature of this surface was determined by the temperature of the water contained in the flask. Three such flasks were used, one of iron, one of zinc, and the third with the one surface copper and the other tin. The diameters of the plane faces, the thicknesses of the flasks and their ~~the~~ volume capacities are given as follows:

Material	Diameter (in mm.)	Thickness (in mm.)	Volume (in cub. mm.)
Iron	128	17	198,000
Zinc	131	16	168,000
Copper & Tin	129	16	196,000

The upper surface of the condenser was a disc of approximately the same area as the lower, on which it pressed during contact by its own weight. It could be readily adjusted by screws to a practically accurate parallelism with the lower surface, and had only one degree of freedom, an up-and-down motion directed by a pin and guiding slot. It depended from the brass top of a cylindrical glass case which surrounded the insulated stand and flask on all sides, if we except the small aperture through which the internal arrangement was put in connection with the electrometer. Great care was necessary during dry weather to avoid rubbing and thereby electrifying the glass case, which had to be repeatedly removed, so that the temperature inside might be observed and the surfaces repolished.

Not a few experiments during the severe frosts of last winter were rendered unreliable on account of this electrification & by friction of the case, which then acted inductively upon the enclosed conductors. The upper and movable surface of the condenser was connected with the other pair of electrometer quadrants, which were put to earth and kept constantly at zero potential.

In the first series of experiments, the surfaces of the condenser remained, for the most part, in contact, being separated only when a reading was to be taken, or when the surfaces had to be repolished and the temperature of the water in the flask observed. The upper disc was then virtually at the same temperature as the lower. Readings were taken in groups of five at a time, the interval between each reading being determined conditioned by the swing of the electrometer mirror, which, suspended by a bifilar, had of course to come to rest, or nearly so, before its indications could be of any value. After each group of readings, the surrounding glass case was removed, the temperature of the cooling water observed, the surfaces repolished, and the whole arrangement re-adjusted precisely as before. On the whole, the five consecutive readings of any group were very consistent, considering the difficulties besetting electrometer

measurements of contact forces, and were sufficiently
 so in all but a few very exceptional cases to
 warrant the belief that during the two or three
 minutes necessary to make the complete set of
 readings ~~little~~ comparatively little change took
 place on the surfaces. From theoretical
 considerations I was led to try Iron and
 Copper as likely metals to give positive results.
 In this I was not disappointed; but the dif-
 ficulty of drawing any sure conclusion from
 the indications so obtained, or of in any way de-
 ciding between the claims of the various possible
 explanations which might be given to account for
 the facts, induced me, after four months experi-
 menting, to conduct the enquiry on a different
 and what turned out to be an improved principle.
 In these earlier experiments, it is to be particu-
 larly observed that the two surfaces were both
 at the same temperature: in the later researches,
 the temperature of the lower surface only was
 made to vary. By the former method it
 was found that the difference of potential be-
 tween polished iron and polished copper fell off
 by at least $\frac{1}{130}$ th of its original value for a
 rise in temperature of 1° Centigrade. Many
 series of observations were made with these two
 metals, - and each day's results gave the same
 general indications; although, as might have
 been expected from the nature of the enquiry,

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it is hardly possible to deduce from them any definite quantitative law. The general results of eleven series of experiments are given in the following table. The first column represents the lowest temperature for which readings were taken; the second gives the deflection electrometer deflection for that temperature due to the electrification of the lower surface; the third indicates the deflection for the higher temperature; the fourth registers that higher temperature; and the fifth notes the percentage for decrease of the deflection for unit increase of temperature.

Temper ^{re} (lower)	Deflect ⁿ	Deflect ⁿ	Temper ^{re} (higher)	per centage Decrease
7°C.	70	50	30°C.	1.32
14	60	35	40	1.60
13	78	58	45	.83
10	77	56	45	.78
18	110	80	50	.85
20	93	76	41	.87
23	110	85	50	.84
16	110	60	48	1.42
16	110	85	35	1.22
20	112	91	38	1.04
16	112	90	36	.98

The first four experiments give much smaller readings than the last seven — a discrepancy easily accounted for by the change of cir-

circumstances occasioned by removal to another room and a refitting of the surfaces. Yet, that, in such altered circumstances, the average percentage temperature-variation of the deflection should be so consistent throughout, argues strongly in favour of the reality of such a variation. A like series of experiments was commenced with a zinc surface substituted for the copper or under surface; but, though there were indications of a somewhat similar variation, these were too vague to admit of any definite deductions being made. The same was true of the Aluminium-Zinc pair, which was experimented upon with the hope that their comparatively small difference of potential would more readily show any variation which might possibly exist. The large deflections given by the iron-zinc combination were undoubtedly a serious objection — an objection which put quite out of the question copper and zinc, perhaps the most frequently employed of all metals in contact investigations. Further, it was impossible to determine how much of the resultant variation of a given pair was due to the action of a particular component, or how far this variation depended directly

upon the change of temperature, or indirectly through consequent material alteration of the surfaces — through oxidation, for example.

These considerations led me to abandon my first method of experimenting; and in the modified method subsequently ~~and~~ adopted the temperature of the upper surface was kept constant, while the temperature of the lower was made to vary. This required the contact to be instantaneous, so that only one reading could be taken between each preparation of the surfaces, and observation of the variable. During this interval the upper surface was laid upon an iron slab and thus kept at the temperature of the room. Both surfaces were repeatedly polished with emery. The first experiments were made with two iron surfaces, which, after sufficient polishing at the ordinary temperature of the air, gave no deflection on separation after contact. The lower surface was heated up to 70° or 80° in the manner formerly described, and then allowed to cool, while at rapid intervals instantaneous contacts were made ~~at the~~ with the upper surface, each contact being made as soon after ~~contact~~ polishing as possible. In this way I found that iron hot was strongly negative to iron cold, and apparently more negative the higher its temperature — in other

temperature

words, the difference of potential between iron and iron increases with the difference of temperature, being zero when the temperature difference is zero. A glance at the representative curve (Fig. I) shows the nature of this change.

The six different symbols represent six different curves, five of which give the results of as many independent experiments, while the sixth (represented by the circle and dot) is the average curve formed by the combination of the others. Each point on any one of

the five primary curves is, as far as possible, the mean of five successive readings — any two contiguous mean points having four of their components in common. This method of reduction commended itself as giving the most probable values for the mean contact. Each point of the final mean curve is obtained by taking the average of all such points as lie in the same temperature decade. Subjoined are the tabulated results of these experiments; the upper row of which each of which gives the temperature, and the lower the corresponding deflection on the electrometer scale, 60 divisions of which represented a difference of equal potential equivalent to that between the poles of a Daniell cell composed of saturated cupric sulphate and semi-saturated zinc sulphate.

Experiment I (Feb. 27, 1879)
(curve-symbol .)

Temperature (in °Cent.)	53.8	49.4	45.4	31	23.1
Deflection	21.8	21	17.4	10.8	7.2

Experiment II (Feb. 28, 1879)
(curve-symbol +)

Temperature (in °Cent.)	61.9	40.7	31.6	22.4
Deflection	31.7	25.2	14.7	7.7

Experiment III (Mar. 5, 1879)
(curve-symbol $\times$)

Temperature (in $^{\circ}$ Cent.)	64.6	47.3	31	22.2
Deflection	37.7	26	15.2	12

Experiment IV. (Mar 6, 1879)
(curve-symbol $\vee$)

Temperature (in $^{\circ}$ Cent.)	66.5	36.7	34.2	25
Deflection	47.5	17	16	3

Experiment V. (Mar 13, 1879)
(curve-symbol $\wedge$)

Temperature (in $^{\circ}$ Cent.)	60.4	55.5	38	30	23.2
Deflection	37	36	20	9.3	6

The reduced means for curve VI (symbol $\odot$) are as follows:

Temp ^{re}	Deflect ^{re}
63 $^{\circ}$.1 C.	38.5
54 $^{\circ}$.6	28.9
45 $^{\circ}$.7	22.4
33 $^{\circ}$.4	14.9
23 $^{\circ}$.2	7.2

The temperature of the room, and therefore of the upper surface, was 12° C., at which point then the curve should meet the line of temperatures.

The mean curve is obviously best represented by a straight line, whose tangent of inclination to the temperature-line is $-.68$, expressed in dia-

gram units. In seeking for an explanation of the results of these experiments, the possible effects due to oxidation or to the change in density of the film of gas condensed upon the metallic surface must not be neglected. If the negative character of heated iron to cold iron disappeared on the cooling of the former, then the effect must be the result either of the difference of temperature ~~or~~ simply or of the driving-off of the condensed gases at the higher temperature, or of both causes combined. Experiments, however, clearly proved that the originally heated surface, when cooled to the temperature of colder surface, retained its strong negative characteristics with no appreciable diminution in the quantitative estimate: from which it would appear that the observed phenomena are to be attributed to a permanent change of surface condition depending upon temperature — probably to oxidation. It was also found by trial that ~~a~~ ~~com~~ no appreciable increase in the deflection corresponding to a given temperature resulted when the heated surface was left a considerable ~~time~~ interval of time was suffered to elapse between the polishing of the heated surface and the making of contact between it and the upper and colder surface. Whether the instantaneous contact ~~was~~ was made 15" (the usual interval), 40" or 60" after the polishing; the electrometric deflection was, as far as the method admitted of judging, the same. Probably, after a longer lapse of time than that here specified, a change might become

manifest — such a change as Hankel long ago established for iron and other metals at the ordinary temperature of the air. In order to compare this time-variation of surface condition with the temperature-variation established above, I made a series of observations, at sufficiently distant intervals of time, of the deflections produced by contact and separation of two iron surfaces, one of which was kept constant by polishing, while the other was permitted to vary by being simply left to itself. Both were initially polished so as to be the same electrically — a state of affairs evidenced by the absence of any deflection on the electrometer scale. Readings were first taken at intervals of five minutes, then at intervals of ten minutes, finally at half-hour intervals.

Time (in minutes)	Deflection (Iron against Iron)
0	0
5	- 11
10	- 14
15	- 15
20	- 16
30	- 18
45	- 19.4
75	- 20

The curve corresponding to these numbers is given in Fig II, *b*. In its main characteristics it is very similar to an ordinary curve of cooling, and is markedly dissimilar to the curve depicted above

as representative of the temperature-variation of surface condition. Curves a and c on the same diagram indicate the corresponding variations for copper and aluminium respectively. The copper was electrified by contact with iron, both surfaces being allowed to vary; and the real time-variation of the copper was obtained by properly introducing the known time-variation of the iron. The aluminium was electrified by contact with polished zinc, to which it was originally positive but in the course of half-an-hour became as strongly negative. The tabulated values for these metals are given below, the chemical symbol

for each metal being employed to represent the corresponding surface, and the suffix p signifying that the surface was kept polished and therefore constant.

Time (in minutes)	Cu Fe	Cu Fe _p	Cu Cu _p (21/5/79) (curve a)
0	-63	-63	0
2	-61	-67	-4
7	-58	-70	-7
17	-57	-73.7	-10.7
47	-55	-75.5	-12.5

Time	Al Zn _p	Al Al _p (9/5/79) (curve c)
0	+18	0
10	-7.4	-25.4
20	-14.6	-32.6
30	-16.2	-34.2
45	-24.2	-42.2
60	-24	-42
90	-36	-54

1350 (observed next mom.) -47 -65

Corresponding curves for zinc and tin are not represented on the diagram, because of their great proximity to the iron-curve. In the course of an hour, the change on the zinc was only 6 per cent. greater than the corresponding change on the iron; while in 40 minutes there was no appreciable difference between the tin and iron. The

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gradual character of the change here indicated is of special value in the present Enquiry, as I hope to bring out in the final conclusions to which I have been led. Meanwhile it is advisable to give the results of the experiments on the temperature-variation of the other metals which I investigated. Though not so full and satisfactory as the results for iron, these later researches all indicate the same general facts. The following are the readings for Copper hot against iron cold — both surfaces being polished immediately before contact.

Experiment I (March 24, '79)

Temperature	Deflection ($Cu_p Fe_p$)
62° C.	- 66.6
57	- 68.2
52	- 64.5
48	- 61.5
44	- 57.3
32	- 54
24	- 52
12	- 50

Experiment II (March 25, '79)

Temperature	Deflection ($Cu_p Fe_p$)
70° C.	- 69
55	- 65
43	- 62
30	- 52
23	- 47
12	- 47

The representative curve is shown in Fig III., all the points clustering approximately round a ~~line~~ straight line whose tangent of inclination to the temperature axis is $-.425$, measured in diagram units. The temperature-variation of copper is therefore smaller than that of iron; and hence, since iron is the more positive metal, the difference of potential between iron and copper falls off as the temperature of both is raised — a result which was already proved in the earlier experiments (see page 9).

Zinc was the next metal which came under investigation. At first it was electrified by contact with aluminium, kept polished at a constant temperature. This latter metal is not very suitable, on account of its proneness to rapid change in time as evidenced by its curve on Diagram II. The same negative-growth of the

heated metal was however indicated, and more self-consistent results were obtained by contact of zinc hot with zinc cold, both polished as usual. The numbers are as follows:

Experiment I (March 28 '79)	
Temperature	Deflection ($Zn_p Al_p$)
63°·8 C.	- 78
46·5	- 66
34	- 64
21·8	- 56·3
10	- 40

These are averaged from 16 independent observations.

Experiment II (April 4, '79)	
Temperature	Deflection ($Zn_h Zn_p$)
65° C.	- 42
45	- 22·5
42·7	- 19·2
40·6	- 17·7
38·8	- 18·5
28·6	- 8

In the diagram (Fig IV.), two lines are drawn, each representing one of above experiments. The dotted line is that which best agrees with the readings of Experiment ~~one~~ I, of which the points are represented on the diagram as "dots". The points of the second experiment are entered as

Fig. IV.

crosses, and they all lie very near the continuous line drawn on the diagram. The tangent of inclination of this line is -0.9 , expressed in diagram units. Apparently then zinc varies more rapidly with temperature than iron; and hence, since zinc is the more positive, the contact difference of potential between zinc and iron falls off as both are simultaneously raised in temperature — a result in complete accordance with the early experiments between zinc and iron where both were made to vary similarly in temperature. This suggested the possibility that the more positive metal might be subject to the greater temperature-variation. According to this hypothesis, tin, which occupies in the electromotive series a position intermediate to zinc and iron, should give a correspondingly intermediate

line for its temperature-variation. It was impossible, however, with the means I had at my disposal to arrive at anything like a quantitative result for tin. Not having at the time another tin surface, I was compelled to make use of either zinc or iron as the other condenser-plate; and, as both of these ~~gave~~ gave considerable deflections with tin, the readings proved wild and unsatisfactory. No experiment gave even self-consistent results; and no two of them had much in common — except the undoubted characteristic, ~~of~~ which indicated a similar "negative-growth" with temperature of the tin surface. In such investigations the most reliable results are given by a combination condenser-wise of plates of the same metal, the one of which is kept polished at a constant temperature, while the other is kept polished at different temperatures. The deflections are then comparatively small, and well within the range of a Thomson Quadrant Electrometer ~~which~~ measuring easily to the hundredth part of a Daniell Cell.

As already noticed, the permanency of this "negative-growth" with temperature after the surface ~~was~~ ^{is} cooled — a characteristic which was established by direct experiment in every case — proves conclusively that whatever

change in the electromotive contact force of any two of the metals, iron, zinc, copper, and tin, may be due directly to change of temperature, such a possible change is quite inappreciable by ordinary contact methods, and is altogether masked by changes due to other and secondary causes. In seeking for such causes, we can hardly regard the probable alteration with temperature in the density of the gaseous film condensed over the surface of ^{the} metal plate as having an appreciable effect, inasmuch as such an alteration is not permanent on restoration to the original temperature.

The only efficient cause seems to be chemical change produced on the surface by the action of the atmosphere at the given temperature: an hypothesis which is supported by the known phenomena of time-variation of metal surfaces in both their chemical and electrical relations.

The electrically negative character of unpolished iron, copper, zinc, tin, aluminium, etc., to polished iron, copper, zinc, tin, aluminium, etc., is generally believed to be due to surface oxidation; probably, then, the electrically negative character of polished-and-heated iron, copper, zinc, and tin, to polished-but-unheated iron, copper, zinc, and tin, is to be referred to a similar cause.

If so, then the above experiments lead to the interesting result that, for these metals at least, there is for every temperature a definite surface condition which no amount of polishing can alter — a surface condition

produced most probably by a film of oxide or other similar compound formed over the metallic surface by the action of atmospheric air; and that, further, this surface-change is a direct function of the temperature-change, being greater at the higher temperature. This surface-state or oxide-film forms within the first few seconds after polishing — perhaps instantaneously; and thereafter no appreciable change ensues till several minutes have elapsed, when the inevitable time-variation of surface as depicted in the curves of Fig II begins to show itself. There being no difference, save in degree, between the surface at the ordinary temperature of the air and the same surface at higher temperatures, it would appear that a chemically pure surface of these four metals in air is an impossibility; and that the same holds true for other metals, even for the so-called non-oxidisable, is a not improbable surmise. In this connection it should be remarked that to the eye there was no appreciable attestation of surface, no dimming of the bright-metallic polish, even after the lapse of a considerable interval of time. In conclusion I would refer to two brief but suggestive papers, published in the Philosophical Magazine (August 1878, and Feb. 1879) in which their author, J. Brown, Esq., gives reasons for believing that the relative positions of the metals in Volta's electromotive contact series are

greatly, if not mainly, dependent, upon the medium by which they are surrounded, the more positive metal being in general that which has the greatest chemical affinity for the medium. Thus he found that copper became strongly positive to iron in a sulphur atmosphere, whereas in the ordinary air it is strongly negative. If, then, the more positive metal have the greater affinity for the surrounding medium, we should expect its time-variation to be more marked; and a glance at Fig II shows that this really is the case for the metals aluminium, iron, and copper; and to these we should add zinc, whose curve, though very close to that of iron still lies below it, i.e., towards the aluminium curve. Beginning with the most positive, and arranging them in the order in which they occur in the Volta series, we have aluminium, zinc, iron, copper, exactly their arrangement if arranged according to the magnitude of their respective time-variations. As already pointed out, the order, zinc, iron, copper, is also the arrangement indicated by their temperature-variations; and that the metal with strongest chemical affinity for air should also be the one, whose affinity changes most rapidly with temperature is a plausible enough hypothesis. Apparently then, the above results support Mr. Brown's theory, which is also supported by the well known fact that the most negative metals are the very metals which are commonly regarded as unacted upon by air.

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However much this Volta contact effect may be due to chemical affinity between solids and gases, there can be no reasonable doubt that the Peltier and Thomson effects, together with the whole phenomena of thermoelectricity, imply a contact force at the surface of separation of different substances; but to measure such a difference of potential directly is still beyond even our most delicate methods of experiment.

The experiments which form the subject of this thesis were made in the Physical Laboratory of Edinburgh University during the summer session of 1878, and the winter session of 1878-79. The apparatus was, for the most part, lent me by Professor Gait, whom I take this opportunity of thanking for the kindly interest he has ~~been~~ evinced in my work, and the ever-ready advice with which he has aided me.

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