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THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

*A TENTATIVE THEORY OF THERMO-ELECTRIC ACTION.**

LET the lines (1)–(1) and (2)–(2) in Fig. 1 be the lines representative respectively, of two metals M_1 and M_2 in the ordinary thermo-electric diagram. We may, if we please, think of these metals as copper and iron, respectively. The lowest horizontal line is the temperature coordinate and begins at the absolute zero.

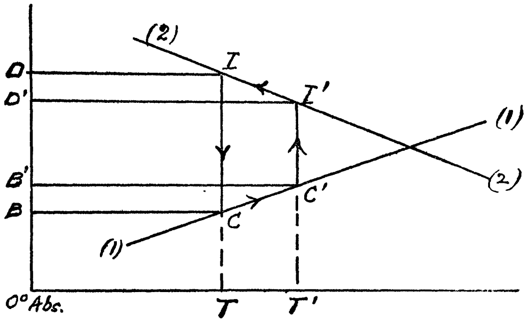

FIG. 1.

The diagram is so constructed that the area $CC'I'IC$ is equal to the net thermo-electromotive force, E, counterclockwise, in the circuit indicated by Fig. 2, in which the left-hand junction is kept at temperature T and the right-hand junction at temperature T'. We will suppose that E is expressed in mechanical units, as the

* Address of the vice-president and chairman of Section B—Physics, American Association for the Advancement of Science, Philadelphia, December, 1904. [The theory here given is certainly incomplete, and I fear that it is not entirely self-consistent. It is intended to be suggestive rather than conclusive or exhaustive.—E. H. H.]

amount of work done, at the expense of heat, on unit quantity of electricity while it goes once around the circuit. Evidently, then, the area $CC'I'IC$, which rep-

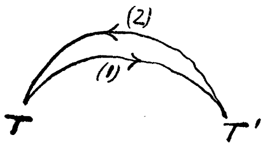

FIG. 2.

resents E, represents also the mechanical equivalent of the net amount of heat consumed by unit quantity of electricity in one cycle.

The arrow-points in Fig. 1 indicate merely the direction of the current resulting from the net E of the circuit.

It is consistent with what precedes to consider the area $BCC'B'B$ as representing that part of the total, or net, E which lies in the unequally heated M_1 between T and T', the area $B'C'I'D'B'$, as representing that part of E which lies in the junction M_1-M_2 at T', etc.; and this interpretation is sometimes given as a mere statement of fact. In the course of this paper it will, I hope, be shown that another view of the matter is consistent with the known facts of the case.

As this declaration puts me for the moment into a somewhat heretical attitude, let me hasten to say that I hold as strongly as any one to the proposition that the area $BCC'B'B$ represents the amount of heat absorbed by unit quantity of electricity in going through the metal M_1 from the temperature T to the temperature T', that the area $B'C'I'D'B'$ represents the heat absorbed by unit quantity of electricity in going from M_1 to M_2 at temperature T', etc. This proposition is familiar and needs no proof from me; but I wish to develop a little one aspect of it which is sometimes overlooked, an aspect which has a decided pedagogic value and which is at least suggestive of the line of thought I wish to follow later.

As we have in Fig. 1 a diagram in which areas represent heat absorbed, and in which one of the coordinate axes represents temperature, the other axis must represent entropy. Let us, therefore, in order to conform to the common practise in the use of the temperature-entropy diagram, make the T axis vertical, and the entropy, or S, axis horizontal, thus getting as the equivalent of Fig. 1 the Fig. 3.

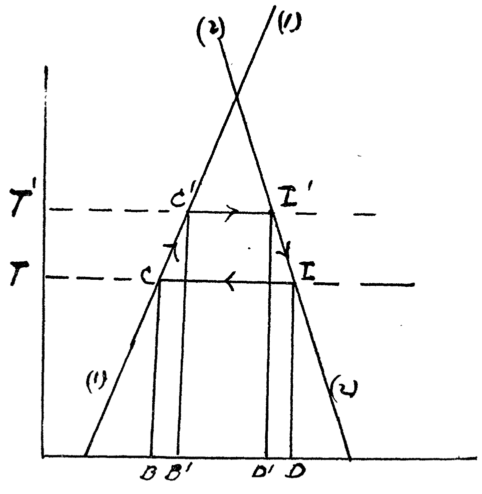

FIG. 3.

It is to be observed that Fig. 3 is the obverse of Fig. 1 so that the arrow points, without any relative change of position in going from one figure to the other, now lead clockwise around the area $CC'I'IC$.

Any one who is familiar with the temperature-entropy diagram of the steam-boiler-engine cycle, as given and discussed by Ewing, will see at once interesting points of resemblance between Fig. 3 and that diagram. For example, the sloping line CC', which indicates one phase of the Thomson effect, the absorption of heat by the electric current in passing through the metal M_1 from a point at temperature T to a point at the highest temperature, T', is analogous to the sloping line which in the steam-boiler-engine diagram indicates the absorption of heat by the feed water from the condenser in mixing with the hot water in the boiler. The slope of each line implies that the working agent, electricity in one case and water in the other, takes in the particular quantity of heat represented by the area under the line at a temperature below the highest of the cycle, and therefore, does not make the best possible thermodynamic use of the heat supplied and of the range of temperature available. Similarly the inclined line $I'I$, which indicates that heat is absorbed by the electric current in passing through the metal M_2, from temperature T' to the lower temperature T, is analogous to the line of the steam cycle which indicates the recovery of heat from the cylinder wall during expansion after cut-off.

Furthermore, the horizontal lines $C'I'$ and IC, indicating the absorption or emission of heat by the electric current in passing, without change of temperature, from one metal to the other, are analogous to those horizontal lines of the steam cycle which indicate absorption or emission of heat in the act of evaporation or of condensation. To this analogy we shall presently return.

Let us for the moment occupy ourselves with a reexamination of the prevailing opinion as to the relation between the heat absorption or emission at the junction of two metals and the difference of potential, or the electromotive force, at that junction, that is, between the thermal aspect and the electrical aspect of the Peltier effect. We shall find the situation not quite so clear as it is often supposed to be.

Maxwell* states that the amount of heat taken up or given out by unit quantity of electricity in going from one metal to another at any temperature is a measure of 'the electromotive contact force at the junction'; and he says that 'this application * * * of the dynamical theory of heat to the determination of a local electromotive force' is due to Sir Wm. Thomson.* He then goes on to declare that—"The electromotive force at the junction of two metals, as determined by this method, does not account for Volta's electromotive force. * * * The latter is in general far greater than that of this article, and is sometimes of opposite sign," etc.

* 'Electricity and Magnetism,' § 249.

* *Proc. Roy. Soc. Edin.*, Dec. 15, 1851; *Trans. Roy. Soc. Edin.*, 1854.

But it is a remarkable fact that Thomson, years after he had pointed out the method which Maxwell approves for determining contact electromotive force, came out (in 1862) with a letter giving a 'New Proof of Contact Electricity,' his famous 'divided ring' experiment, in which letter he says "For nearly two years I have felt quite sure that the proper explanation of voltaic action in the common voltaic arrangement is very nearly Volta's," etc.

I do not feel called upon to take up the cudgels for Thomson or for Volta. The point of immediate interest is that Thomson, after proposing the thermodynamic method of determining contact electromotive force, found it possible to hold a view contradictory to the soundness of this method. This fact may give the rest of us courage to question the finality even of Maxwell's opinion as to the relation between electromotive force and heat in the Peltier effect. I believe, too, that Poincaré, in article 292 of his 'Thermodynamique,' holds that the opinion supported by Maxwell may be wrong. Let us see what we can do with the question thus raised.

By *difference of potential*, $D_{2.1}$, between two points I shall mean the net amount of work which must be done because of the attractions and repulsions of electric charges (to use the convenient terms of action at a distance) in carrying unit quantity of positive electricity from point 1 to point 2.

By *electromotive force*, $E_{1.2}$, along a given path from the point 1 to the point 2, I shall mean

$$E_{1.2} = D_{2.1} + i_{1.2}R_{1.2},$$

where $i_{1.2}$ is the current from (1) to (2) and $R_{1.2}$ is the resistance of the chosen path from (1) to (2).

If either i or R is zero,

$$E_{1.2} = D_{2.1},$$

which is practically the case when we have a battery in open circuit, (1) being one terminal and (2) the other, or when we have under consideration two points on opposite sides of a junction of two metals, but exceedingly near together, even if a current is flowing from one to the other.

We have already, looking at Fig. 3, compared the passage of electricity from metal 1 to metal 2 to the evaporation of water in a boiler. Now in this evaporation work of two kinds is done upon the water, internal work and external work. The movement of electricity across a junction against a difference of potential corresponds to the external work of evaporation. Is there accompanying this movement anything corresponding to the internal work of evaporation? If so, the heat absorbed by the electricity in the movement may be as bad a measure for the difference of potential at the junction as the latent heat of evaporation would be for the external work of evaporation.

It is not absurd to imagine that there may be some change of state of electricity besides change of potential. It is possible that we should take account of something like an attraction between electricity and the metals with which it is associated. Helmholtz imagined such an attraction in order to explain the action of a galvanic cell. Indeed, we are familiar with the idea that attraction or repulsion exerted on the electric charge which ordinary matter may bear is communicated to the matter itself. When the charge on a pith ball is drawn this way or that, it carries the pith ball along with it. To be sure, this phenomenon and others like it may not indicate any fundamental attraction between ordinary matter and electricity. Perhaps they can all be explained by stresses in the dielectric surrounding or penetrating the ordinary matter; but whatever the true agencies may be, they at least simulate attraction or some physical tie between ordinary matter and electricity. We may, therefore, feel free to make speculative use of such attraction.

Our problem is to find, if we can, by use of any reasonable hypothesis, an explanation of the way in which heat drives an electric current around the circuit of dissimilar metals unequally heated.

There are two types of mechanical circuits or cycles operated by heat with which we are very familiar, the steam-boiler-engine cycle, in which the circulation may be practically in a horizontal plane, and various convection cycles, commonly used for heating and ventilation, which may be in vertical planes. In the horizontal cycle we must have valves. Circulation is secured by heating or cooling a fluid which is free to expand or to contract on one side, but not on the other side, the valves being so contrived as to give the necessary freedom and the necessary restriction. In the convection cycle we do not necessarily make use of valves. If the heating and cooling are effected at the right parts of the circuit, gravity supplies the differential force necessary to maintain circulation.

How can the metals of our thermo-electric circuit take the function of valves or the function of gravitation and so determine the flow of electricity at the expense of heat energy?

Let us consider first the case of a thermo-electric couple in which neither metal has any Thomson effect, but in which there is a tendency of positive electricity from (1) to (2) at each junction. The thermo-electric force of such a circuit can be accounted for by assuming that metal 2 attracts positive electricity more and negative electricity less than metal 1, and that both these differential attractions increase or decrease with change of temperature of the *electricity*.

At first glance one is likely to think that the differential forces here imagined must increase with rise of temperature, as it may at first seem that the forces at the hot junction must prevail over the opposing forces at the cold junction. But this need not be. The action must be such as to *take in heat at the hot junction* and to *give out heat at the cold junction;* but this condition is perfectly consistent with the prevailing of the attractive forces at the cold junction.

For, consider the analogous case of circulation of water in a pipe circuit made up of two verticals and two horizontals (see Fig. 5). If heat is applied at the proper part of one vertical and if heat is taken away from the proper part of the other vertical, the water will ascend against the force of gravity at the heated place and descend under the pull of gravity at the cooled place. That is, the attractive force, upon the differential action of which the circulation depends, prevails at the place where heat is taken out from the system.

Another analogous case is that of two galvanic cells of precisely the same kind, one cold and the other warm, set to work in opposition to each other. If the cells are such that each would grow warm (aside from the development of resistance heat within its parts) by its own direct action, the cooler cell will prevail, and *vice versa.*

So, if the spontaneous action at each junction of our two metals, if each junction could have its own way, would be such as to generate heat at the junction, the cooler junction will prevail when the two are opposed, and *vice versa.*

Now we have rather more reason for expecting, in a given untried case, that the free action of attractive forces will generate heat than we have for expecting that it will absorb heat. Consider, for example, the heat freed as the result of molecular attractions in the condensation of a vapor. Accordingly, if we are to account for a thermo-electric current, in such a combination of metals as we have imagined, by attraction of ordinary matter for electricity, this attraction varying with the temperature of the electricity, we are naturally led to the opinion that the colder junction prevails.

The assumption of such an attraction as we have here imagined, with its dependence on the temperature of the electricity and its independence of the temperature of the metal, except as the temperature of the metal determines that of the electricity within it, is much less violent than it at first appears. If there is such a phenomenon as the expansion of electricity, that is, a diminution of general volume density of electricity, with rise of temperature of the metal containing it, corresponding to the expansion of air or water in the heated part of a convection circuit, this is enough to give just the temperature relation required. For, the lessened volume density of the electricity at the hot junction of the two metals would imply a diminished tendency of the electricity to pass over to the more strongly attracting metal at that junction; but just as there is no tendency of water to flow by gravitation along an unequally heated pipe, if this pipe is horizontal, so there would be no tendency for electricity to flow along an unequally heated homogeneous metal bar, unless the hot parts of this bar attracted a given quantity of electricity more or less strongly than the cold parts. The two metals in which we have stipulated that there shall be no Thomson effect correspond in our thermo-electric circuit to the horizontal pipes of our imagined convection system; and for the comparison which we are here making it is well to go back to the usual disposition of the thermo-electric diagram, in which unequally heated metals having no Thomson effect are represented by horizontal lines.

Let us now consider a case in which the Thomson effect does play a part, such a case as that illustrated by Figs. 1 and 3. We can, apparently, account for the Thomson effect in any metal by assuming that this metal has a greater attraction for electricity of one sign than for electricity of the opposite sign, and that the difference of these attractions is a function of the temperature of the *metal*. With this condition the electricity of one sign at any part of a homogeneous but unequally heated metal bar will be subject to a net attraction, exerted by the metal, toward a place of higher temperature or toward one of lower temperature, according as the attraction between the metal and this kind of electricity increases or decreases with rise of temperature of the metal; and the other kind of electricity will be subject to a different, greater or less, net attraction from the metal; so that a difference of potential would be set up between the hot and cold part of the bar, if the bar were left to itself.

If we take the view that the electromotive forces which prevail are those at places where heat is given out, we shall in Fig. 3 have the local electromotive force, due to the attraction between metal and electricity, opposite at every place to the electromotive force commonly supposed to reside at that place; so that the unequally heated metals and the hot junction will still conspire against the cold junction; but, as the direction of the current is known by experiment to be that which is indicated by the arrow points in Fig. 3, we must in this case suppose that *the cold junction prevails over the opposing combination.*

Let us now consider the magnitude of the local electromotive forces. In any case the net electromotive force of the whole circuit is expressed, as we agreed at the beginning, by the area $CC'I'IC$ of Fig. 1 or Fig. 3. But knowledge of the net electromotive force of the circuit tells us little or nothing of the magnitude of the individual four electromotive forces of the circuit. Ordinary doctrine represents these by the areas, already mentioned, under the lines CC', $C'I'$, etc., in Fig. 3, down to the line of absolute zero of temperature, but as we now undertake to have the electromotive force at the cold junction prevail over the other three, it is evident that we must look for other areas on the thermo-electric diagram to represent these local forces. In this case we find such areas *above* the lines CC', $C'I'$, etc., in Fig. 3, or in Fig. 4, which we will now use in place

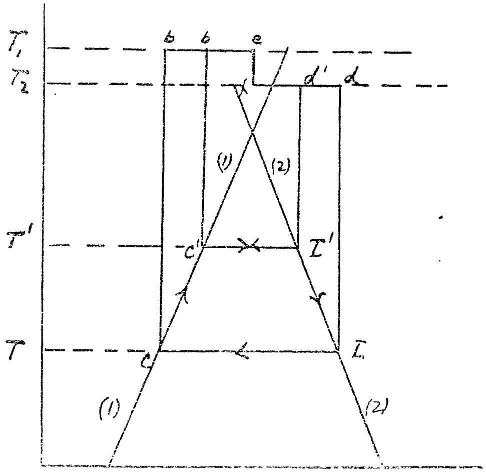

Fig. 4.

of Fig. 3. Thus the area $Cbb'C'C$, terminated above by the temperature line T_1, characteristic of metal 1, may represent the thermo-electromotive force directed from C' to C in the unequally heated (1).

Similarly the area $I'd'dII'$, terminated above by the temperature line T_2, characteristic of metal 2, may represent the thermo-electromotive force directed from I to I' in the unequally heated (2).* The area $C'b'efd'I'C'$, terminated above by the broken line $b'efd'$, depending on both T_1 and T_2, may represent the thermo-electromotive force directed from I' to C' at the hot junction. Finally the area $Cbb'efd'dIC$, terminated above the broken line $bb'efd'd$, depending on both T_1 and T_2, may represent the thermo-electromotive force directed from I to C at the cold junction. This last, larger than the sum of the others, which oppose it, would be the prevailing electromotive force. The net electromotive force of the circuit would be, as in Fig. 3, represented by the area $CC'I'IC$, and the current would run, as before, clockwise with respect to the boundary of this area.

We have apparently succeeded in accounting for the circulation of the electricity by means of differential attractions conditioned by differences of temperature and in showing that the local electromotive forces of the thermo-electric circuit may be opposite in direction to those which are commonly supposed to exist. But we have as yet given no conclusive reason why heat should go in at one part and out at the other, and we have not yet made any attempt to show how heat is used up in the circuit. Our explanation, so far as it has now gone, utilizes difference of temperature but does not utilize heat.

* T_1 is apparently the temperature at which the differential attraction of M_1 for the two kinds of electricity becomes zero. A like explanation holds for T_2. [The sloping lines might curve so as to strike the lines T_1 and T_2, respectively, at any angle.]

If we return to the consideration of our analogical convection system, we see that, if we were to put in heat at any point p only and take out heat at the point p' only, these two points being on the same level, there would be no continued circulation, as we should presently have the fluid at a uniform temperature all the way over from

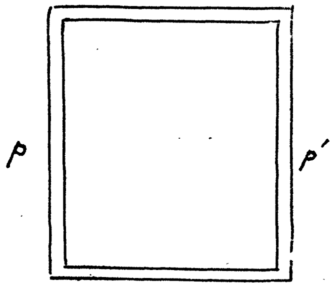

FIG. 5.

p to p' and at a uniform, though different, temperature all the way under from p' to p. To maintain circulation we must have the point p, at which heat enters, at a lower level, and therefore at a higher pressure, than the level and the pressure of the point p', at which heat comes out. The work and the absorption of heat at expansion under high pressure would be greater than the return work and the emission of heat at the lower pressure, and the difference between the inflow and the outflow of heat would be utilized in maintaining circulation against some resistance.

Do we naturally find anything in our thermo-electric circuit corresponding to this heat differential?

We have already assumed that the electricity within each metal acts like an expansible fluid, and it is natural to assume that the rise of temperature which causes the expansion of the electricity absorbs heat. That is, we naturally assume next that there is a real thermal capacity of electricity, or of the corpuscles moving with it, which would come to the same thing. Moreover, we can hardly avoid supposing that the attraction which we have assumed to exist between metal and electricity holds the electricity within the metal in a state of pressure; and accordingly we must recognize in the thermal capacity of the electricity a part accomplished against this pressure in the expansion which accompanies rise of temperature.

Returning, with these additional ideas, to the examination of a thermo-electric circuit showing no Thomson effect, we find that we must in such a case suppose that in each metal the heat absorbed by the current of electricity, positive or negative, which is flowing from cold to warm within that metal is balanced by the heat given out by the current of opposite sign, negative or positive, which is flowing in equal strength from hot to cold within the same metal.

But at the junctions the case is different. At the junction which is the prevailing one, across which each kind of electricity flows from the metal by which its kind is attracted less to the metal by which its kind is attracted more, that is, from a place where the pressure caused by the attraction is less to a place where the pressure caused by attraction is more, each kind of electricity will, without change of temperature, suffer contraction of volume in the transition, and evolution of heat will result. On the other hand, at the other junction, where each kind of electricity moves, without change of temperature, from a place of high attractive pressure to a place of low attractive pressure, each kind will expand in the transit, and absorption of heat will accompany this expansion.

Thermodynamic considerations show us that in such a case as that which we are considering, in which there is no Thomson effect, heat must be taken in at the hot junction and heat must be given out at the cold junction. Hence our theory, with its later assumptions, assumptions suggested, as others have been, by reflection on the manner and reason of the working of an ordinary convection cycle, has led us clearly to the conclusion that the cold junction should be, in the case considered, the prevailing junction. But thermodynamic considerations go further. They require that the amount of heat, Q', taken in at the hot junction at temperature T', must bear to the heat, Q, given out at the cold junction at temperature T, such a relation that

$$\frac{Q'}{T'} = \frac{Q}{T}.$$

Can we without a straining extension of our assumptions meet this condition? Apparently we can do so by supposing that electricity in its state of compression within each metal obeys the law of a perfect gas. At the hot junction we have the positive electricity going, at constant temperature T', from the attractive pressure p to the attractive pressure $p - dp$, with consequent expansion, work of expansion, W', and absorption of heat equivalent to this amount of work. At the cold junction we have the positive electricity going, at constant temperature T, from the attractive pressure $p - dp$ to the attractive pressure p, with consequent compression, work of compression, W, and evolution of heat equivalent to this amount of work. From the gas law, $pv = KT$, we have, when T is constant,

$$pdv = -vdp = -\frac{KT}{p}dp.$$

This gives us, since p and dp are the same at the hot junction as at the cold junction,

$$W' : W :: pdv' : pdv :: T' : T.$$

And so

$$Q' : Q :: T' : T.$$

The production of absorption of heat within a single unequally heated metal, the calorimetric aspect of the Thomson effect, is, apparently, easily accounted for without additional assumptions. Thus, according to the theory already stated, the line CC' in Fig. 4 represents a case in which the attractive pressure of the positive electricity is greater at the cold end than at the warm end, while the attractive pressure of the negative electricity is greater at the warm end than at the cold end, of metal 1. According, positive electricity moving from the cold end to the warm end of this metal will expand more, and therefore absorb more heat, than the mere rise of temperature requires, while the negative electricity in moving from hot to cold within the same metal will contract less, and therefore give out less heat, than the mere fall of temperature requires. That is, to use the conventional mode of expression, the current absorbs heat where it flows from cold to hot in metal 1. For the line II' and the metal 2 the case is *vice versa.*

The conception of electricity, each kind of electricity, as acting within a metal like a perfect gas seems very revolutionary to one who has been strongly impressed by Maxwell's discussion of the analogy which the behavior of electricity in Faraday's 'ice-pail' experiment presents to the behavior of an 'incompressible fluid,' though Maxwell in pointing out this analogy warns us against being too much influenced by it.

The ice-pail experiment, however, as I understand it, proves merely the difficulty in putting an appreciable excess of either kind of electricity into a given space, a difficulty which still exists after all the assumptions of this paper are made. Consider, for example, the difficulty of putting any considerable excess of positive or of negative ions into an electrolyte. Indeed, the idea of the electric current within a solid as consisting of two oppositely moving perfect gases is so like the familiar and commonly accepted idea of the current in an electrolyte, where we apparently have two oppositely moving bodies of ions, each body obeying the gas law in its osmotic pressure, that, instead of being troubled by the heretical character of this view of the current in a solid, I am somewhat concerned lest I am failing to give due credit to some one who has already proposed it. Of course, Drude in his electron theory does apply the gas laws in some particulars to the electrons within metals, and I can not be sure that he has not anticipated me in much that is given in this paper, though I did not, so far as I am aware, get from him any of the main features of the theory here proposed.

The question naturally arises, Why not determine the direction and magnitude of the local electromotive forces of the thermo-electric circuit, and so get a decisive trial of the case between the ordinary and the proposed view of thermo-electric action? The reply is that physicists have been trying for more than a hundred years to get a satisfactory determination of a single one of these local forces, the one measured by the true contact difference of potential between any two metals, and have, apparently, not yet succeeded in the attempt. It is the old question of the Volta effect. Some months ago I was of the opinion that Mr. John Brown, F.R.S., of Belfast, had found a way of getting rid of the disturbing effect of the medium surrounding the two metals, zinc and copper in his case, by heating them for several hours in a certain kind of oil. Considerable recent experience with various kinds of oil at the Harvard Physical Laboratory has led me quite unwillingly to the conclusion that the kind of treatment to which Mr. Brown subjects his metal plates may substitute for the disturbing surface condition acquired in air an equally baffling surface condition produced by the action of the oil.

An attempt to measure directly the difference of potential between the two ends of an isolated unequally heated bar of metal would, apparently, encounter obstacles quite as great as those which have thus far proven unsurmountable in the case of attempts to measure directly the contact difference of potential between metals. The outlook is, therefore, not bright for any immediate and final answer, on experimental grounds, to this question of the direction and magnitude of the local electromotive forces with which we have been dealing.

I wish to add one afterthought. If electricity flows like a perfect gas through a homogeneous solid conductor of uniform cross-section, its velocity at any given cross-section of the conductor must be, approximately at least, proportional to the absolute temperature of this cross-section. Now the ordinary law of resistance in the case of a fluid moving through small passages is this: Resistance is proportional to the velocity. Accordingly, we are led to the conclusion that the resistance encountered by our electric stream should be proportional to its velocity, that is, other things being equal, proportional to the absolute temperature at the part of the conductor considered. Now we know that in pure metals this is the general law of resistance, and the fact that this law finds an explanation in a conception of the electric current formed without any reference to electrical resistance adds considerable weight to the argument in favor of that conception.

Edwin H. Hall.

Harvard University.

THE ALAMOGORDO DESERT.*

The Alamogordo desert of southern New Mexico lies immediately west of the 106th meridian, west, and approximately between thirty-two and thirty-four, north. It is bounded on the north by the Oscuro range of mountains, on the east by the Sacramentos, on the south by the Jarillas and the Organ mountains, on the west by the San Andreas. As here defined, therefore, the desert is of comparatively limited area, one hundred or one hundred and twenty-five miles from north to south, and perhaps thirty-five to fifty from east to west; a very convenient little desert, easily manageable, one might suppose, for any naturalist, who, with inborn love of adventure, starts out in search of the wilderness to find scenes and pastures new.

A year ago in this presence, it may be recalled, the present speaker, by aid of photographic illustrations, attempted to sketch the relations obtaining, as would appear, between the geology of the desert and its flora; in the present paper it is intended briefly to resume the earlier argument with such added reflections as may be suggested by present conditions and by recent renewed acquaintance with the problem.

The desert of Alamogordo or Tularosa is a great plain, not unmarked, however, by singular topographic inequalities later on to be described. Only the most casual geologic examination is sufficient to show that the plain floor corresponds stratigraphically with the beds in some places exposed at or near the tops of the surrounding mountains, in any case far up their flanks. On the east especially limestones of carboniferous age rise sheer some 1,000 feet or more straight up from the desert floor, and are again capped by other strata only at length, perhaps 1,000 feet higher, surmounted by materials correspondent with those in the level of the plain.

On the west the same thing is true; but more emphasized still is the difference in

* Address by the vice-president and chairman of Section G for 1904. Philadelphia, Pa.