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William Thomson

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IX.—*On the Dynamical Theory of Heat.* Part V. *Thermo-electric Currents.* By William Thomson, M.A., Professor of Natural Philosophy in the University of Glasgow.

(Read 1st May 1854.)

Preliminary §§ 97–101. *Fundamental Principles of General Thermo-dynamics recapitulated.*

97. Mechanical action may be derived from heat, and heat may be generated by mechanical action, by means of forces either acting between contiguous parts of bodies, or due to electric excitation; but in no other way known, or even conceivable, in the present state of science. Hence Thermo-dynamics falls naturally into two Divisions, of which the subjects are respectively, *the relation of heat to the forces acting between contiguous parts of bodies*, and *the relation of heat to electrical agency.* The investigations of the conditions under which thermodynamic effects are produced, in operations of any fluid or fluids, whether gaseous or liquid, or passing from one state to the other, or to or from the solid state, and the establishment of universal relations between the physical properties of all substances in these different states, which have been given in Parts I.–V. of the present series of papers, belong to that first great Division of Thermo-dynamics—to be completed (as is intended for future communications to the Royal Society) by the extension of similar researches to the thermoelastic properties of solids. The second Division, or Thermo-electricity, which may include many kinds of action as yet undiscovered, has hitherto been investigated only as far as regards the agency of heat in producing electrical effects in non-crystalline metals. In a mechanical Theory of electric currents, communicated to the Royal Society, Dec. 15, 1851,* the application of the General Laws of the Dynamical Theory of Heat to this kind of agency was made, and certain universal relations precisely analogous to the thermo-elastic properties of fluids established in the previous treatment of the First Division of the subject, were established between the thermo-electric properties of non-crystalline metals. The object of the present communication is to extend the theory to the phenomena of thermo-electricity in crystalline metals; but as recent experimental researches on air have pointed out an absolute thermometric scale,† the use of which in express-

* See "Proceedings" of that date, or Philosophical Magazine, 1852, where a sufficiently complete account of the investigations and principal results is given.

† That is a scale defined without reference to effects experienced by any particular kind of matter. Such a scale, founded on general thermo-dynamic relations of heat and matter, and requiring reference to a particular thermometric substance only for defining the unit or degree, was, so far as I know,

ing the general laws of the dynamical theory of heat, both leads to a very concise mode of stating the principles, and shows the most convenient forms of the expressions brought forward in my former communication, the whole subject of thermo-electricity in metals will be included in the theoretical investigations now communicated. I shall take the opportunity of introducing developments and illustrations, which, although communicated at the meeting of the Royal Society along with the original treatment of the subject, did not appear in the printed abstract; and I shall add some experimental conclusions which have since been arrived at, in answer to questions proposed in the former theoretical investigation.

98. Before entering on the treatment of the special subject, it is convenient to recal the fundamental Laws of the Dynamical Theory of Heat, and necessary to explain the thermometric assumption by which temperature is now to be measured.

The conditions under which heat and mechanical work are mutually convertible by means of any material system, subjected to either a continuous uniform action, or a cycle of operations at the end of which the physical conditions of all its parts are the same as at the beginning, are subject to the following laws:—

LAW I. The material system must give out exactly as much energy as it takes in, either in heat or mechanical work.

LAW II. If every part of the action, and all its effects, be perfectly reversible,

first proposed in a communication to the Cambridge Philosophical Society (Proceedings, May 1848, or Philosophical Magazine, October 1848). The particular thermometric assumption there suggested, was that a thermo-dynamic engine working to perfection, according to CARNOT's criterion, would give the same work from the same quantity of heat, with its source and refrigerator differing by one degree of temperature in any part of the scale; the fixed points being taken the same as the 0° and 100° of the centigrade scale. A comparison of temperature, according to this assumption, with temperature by the air thermometer, effected by the only data at that time afforded by experiment, namely, REGNAULT's observations on the pressure and latent heat of saturated steam at temperatures of from 0° to 230° of the air thermometer, showed, as the nature of the assumption required, very wide discrepance, even inconveniently wide between the fixed points of agreement. A more convenient assumption has since been pointed to by Mr JOULE's conjecture, that CARNOT's function is equal to the mechanical equivalent of the thermal unit divided by the temperature by the air thermometer from its zero of expansion; an assumption which experiments on the thermal effects of air escaping through a porous plug, undertaken by him in conjunction with myself, for the purpose of testing it, (Philosophical Magazine, Oct. 1852,) have shown to be not rigorously but very approximately true. More extensive and accurate experiments have given us data for a closer test (Phil. Trans., June 1853), and in a joint communication by Mr JOULE and myself to the Royal Society of London, to be made during the present session, we propose that the numerical measure of temperature shall be not founded on the expansion of air at a particular pressure, but shall be simply the mechanical equivalent of the thermal unit divided by CARNOT's function. We deduce from our experimental results, a comparison between *differences on the new scale from the temperature of freezing water*, and *temperatures centigrade of* REGNAULT's *standard air thermometer*, which shows no greater discrepance than a few hundredths of a degree, at temperatures between the freezing and boiling points, and, through a range of 300° above the freezing point, so close an agreement that it may be considered as perfect for most practical purposes. The form of assumption given below in the text as the foundation of the new thermometric system, without explicit reference to CARNOT's function, is equivalent to that just stated, inasmuch as the formula for the action of a perfect thermo-dynamic engine, investigated in § 25, expresses (§ 42) that the heat used is to the heat rejected in the proportion of the temperature of the source to the temperature of the refrigerator, if CARNOT's function have the form there given as a conjecture, and now adopted as the definition of temperature.

and if all the localities of the system by which heat is either emitted or taken in be at one or other of two temperatures the aggregate amount of heat taken in or emitted at the higher temperature, must exceed the amount emitted or taken in at the lower temperature always in the same ratio when these temperatures are the same, whatever be the particular substance or arrangement of the material system, and whatever be the particular nature of the operations to which it is subject.

99. *Definition of Temperature*, and *General Thermometric Assumption.*—If two bodies be put in contact, and neither gives heat to the other, their temperatures are said to be the same; but if one gives heat to the other, its temperature is said to be higher.

The temperatures of two bodies are proportional to the quantities of heat respectively taken in and given out in localities at one temperature and at the other, respectively, by a material system subjected to a complete cycle of perfectly reversible thermo-dynamic operations, and not allowed to part with or take in heat at any other temperature: or, the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermo-dynamic engine working with a source and refrigerator at the higher and lower of the temperatures respectively.

100. *Convention for thermometric unit, and determination of absolute temperatures of fixed points in terms of it.*

Two fixed points of temperature being chosen according to Sir Isaac Newton's suggestion, by particular effects on a particular substance or substances, the difference of these temperatures is to be called unity, or any number of units or degrees, as may be found convenient. The particular convention is, that the difference of temperatures between the freezing and boiling points of water under standard atmospheric pressure shall be called 100 degrees. The determination of the absolute temperatures of the fixed points is then to be effected by means of observations indicating the economy of a perfect thermo-dynamic engine, with the higher and the lower respectively as the temperatures of its source and refrigerator. The kind of observation best adapted for this object was originated by Mr Joule, whose work in 1844* laid the foundation of the theory, and opened the experimental investigation; and it has been carried out by him, in conjunction with myself, within the last two years, in accordance with the plan proposed in Part IV.† of the present series. The best results, as regards this determination, which we have yet been able to obtain is, that the temperature of freezing water is 273·7 on the absolute scale; that of the boiling point being consequently 373·7. Farther details regarding the new thermometric system will be found in

* On the Changes of Temperature occasioned by the Rarefaction and Condensation of Air. See Proceedings of the Royal Society, June 1844; or, for the paper in full, Phil. Mag., May 1845.

† On a Method of discovering experimentally the Relation between the Heat Produced and the Work Spent in the Compression of a Gas. Trans. R.S.E., April 1851.

a joint communication to be made by Mr JOULE and myself to the Royal Society of London before the close of the present session.

101. A corollary from the second General Law of the Dynamical Theory stated above in § 98, equivalent to the law itself in generality, is, that if a material system experience a continuous action, or a complete cycle of operations, of a perfectly reversible kind, the quantities of heat which it takes in at different temperatures are subject to a linear equation, of which the coefficients are the corresponding values of an absolute function of the temperature. The thermometric assumption which has been adopted is equivalent to assuming that this absolute function is the reciprocal of the temperature; and the equation consequently takes the form

$$\frac{H_t}{t} + \frac{H_{t'}}{t'} + \frac{H_{t''}}{t''} + \text{\&c.} = 0,$$

if t, t', &c., denote the temperatures of the different localities where there is either emission or absorption of heat, and $\pm H_t$, $\pm H_{t'}$, $\pm H_{t''}$, &c., the quantities of heat taken in or given out in those localities respectively. To prove this, conceive an engine emitting a quantity H_t of heat at the temperature t, and taking in the corresponding quantity $\frac{t'}{t} H_t$ at the temperature t'; then an engine emitting the quantity $\frac{t'}{t} H_t + H_{t'}$ at t', and taking in the corresponding quantity $t''\left(\frac{H_t}{t} + \frac{H_{t'}}{t'}\right)$ at the temperature t''; another emitting $t''\left(\frac{H_t}{t} + \frac{H_{t'}}{t'}\right) + H_t$ at t'', and taking in the corresponding quantity $t'''\left(\frac{H_t}{t} + \frac{H_{t'}}{t'} + \frac{H_{t''}}{t''}\right)$ at t'''; and so on. Considering $n-2$ such engines as forming one system, we have a material system causing, by reversible operations, an emission of heat amounting to H_t at the temperature t, $H_{t'}$ at the temperature t',....and $H_{t(n-2)}$ at $t^{(n-2)}$; and taking in $t^{(n-1)}\left(\frac{H_t}{t} + \frac{H_{t'}}{t'} + \ldots + \frac{H_{t(n-2)}}{t^{(n-2)}}\right)$ at the temperature $t^{(n-1)}$. Now this system, along with the given one, constitutes a complex system, causing on the whole neither absorption nor emission of heat at the temperatures t, t', &c., or at any other temperatures than $t^{(n-1)}$, $t^{(n)}$; but giving rise to an absorption or emission equal to $\pm\left[t^{(n-1)}\left(\frac{H_t}{t} + \frac{H_{t'}}{t'} + \ldots + \frac{H_{t(n-2)}}{t^{(n-2)}}\right) + H_{t(n-1)}\right]$ at $t^{(n-1)}$, and an emission or absorption equal to $\pm H_{t(n)}$ at $t^{(n)}$. This complete system fulfils the criterion of reversibility, and, having only two temperatures at localities where heat is taken in or given out, is therefore subject to Law II.; that is, we must have

$$H_{t(n)} = \frac{t^{(n)}}{t^{(n-1)}} - \left[t^{(n-1)}\left(\frac{H_t}{t} + \frac{H_{t'}}{t'} + \ldots + \frac{H_{t(n-2)}}{t^{(n-2)}}\right) + H_{t(n-1)}\right]$$

which is the same as

$$\frac{H_t}{t} + \frac{H_{t'}}{t'} + \ldots + \frac{H_{t(n-1)}}{t^{(n-1)}} + \frac{H_{t(n)}}{t^{(n)}} = 0 \quad . \quad . \quad . \quad . \quad . \quad (1).$$

This equation may be considered as the mathematical expression of the Second fundamental Law of the Dynamical Theory of Heat. The corresponding expression of the First Law is

$$W + J\,(H_t + H_{t'} + \ldots + H_{t(n-1)} + H_{t(n)}) = 0 \quad . \quad . \quad . \quad . \quad . \quad (2),$$

where W denotes the aggregate amount of work spent in producing the operations, and J the mechanical equivalent of the thermal unit.

§§ 102–106. *Initial examination of Thermo-dynamic circumstances regarding Electric Currents in Linear Conductors.*

102. PELTIER's admirable discovery that an electric current in a metallic circuit of antimony and bismuth produces cold where it passes from bismuth to antimony, and heat where it passes from antimony to bismuth, shows how an evolution of mechanical effect, by means of thermo-electric currents, involves transference of heat from a body at a higher temperature to a body at a lower temperature, and how a reverse thermal effect may be produced, by thermo-electric means, from the expenditure of work. For if a galvanic engine be kept in motion doing work, by a thermo-electric battery of bismuth and antimony; the current by means of which this is effected passing, as it does, from bismuth to antimony through the hot junctions, and from antimony to bismuth through the cold junctions, must cause absorption of heat in each of the former, and evolution of heat in each of the latter; and to sustain the difference of temperature required for the excitation of the electro-motive force, even were there no propagation of heat by conduction through the battery, it would be necessary continually, during the existence of the current, to supply heat from a source to the hot junctions, and to draw off heat from the cold junctions by a refrigerator:—Or, if work be spent to turn the engine faster than the rate at which its inductive reaction balances the electro-motive force of the battery, there will be a reverse current sent through the circuit, producing absorption of heat at the cold junctions, and evolution of heat at the hot junctions, and consequently effecting the transference of some heat from the refrigerator to the source.

103. We see then, that in PELTIER's phenomenon we have a reversible thermal agency of exactly the kind supposed in the second Law of the Dynamical Theory of Heat. Before, however, we can apply either this or the first Law, we must consider other thermal actions which are involved in the circumstances of a thermo-electric current; and with reference to the second Law we shall have to examine whether there are any such of an essentially irreversible kind.

104. It is to be remarked, in the first place, that a current cannot pass through a homogeneous conductor without generating heat in overcoming resistance. This effect, which we shall call the *frictional generation of heat,* has been discovered by JOULE to be produced at a rate proportional to the square of the

strength of the current; and taking place equally with the current in one direction or in the contrary, is obviously of an irreversible kind. Any other thermal action that can take place must depend on the heterogeneousness of the circuit, and must be of a kind reversible with the current.

105. Now if in an unbroken circuit with an engine driven by a thermo-electric current, the strength of the current be infinitely small compared with what it would be were the engine held at rest, or, which is the same, if the engine be kept at some such speed that its inductive electro-motive force may fall short of, or may exceed, by only an infinitely small fraction of itself, the amount required to balance the thermal electro-motive force of the battery, there will only an infinitely small fraction of the work done by the current in the former case, or of the work done in turning the engine in the latter, be wasted on the frictional generation of heat through the electric circuit. In these circumstances, it is clear, that whatever mechanical effect would be produced in any time by the engine from a direct current of a certain strength, an equal amount of work would have to be spent in forcing it to move faster and keeping up an equal reverse current for the same length of time; and as the direct and reverse currents would certainly produce equal and opposite thermal effects at the junctions, and elsewhere in all actions depending on heterogeneousness of the circuit, it appears that, were there no propagation of heat through the battery by ordinary conduction, CARNOT's criterion of a perfect thermo-dynamic engine would be completely fulfilled, and a definite relation, the same as that which has been investigated (§ 25) already by considering expansive engines fulfilling the same criterion, would hold between the operative thermal agency and the mechanical effect produced. It appears extremely probable that this relation does actually subsist between the *part of the thermal agency which is reversed with the current* and the mechanical effect produced by the engine, and that the ordinary conduction of heat through the battery takes place independently of the electrical circumstances. The following proposition is therefore assumed as a fundamental hypothesis in the Theory at present laid before the Royal Society.

106. *The electro-motive forces produced by inequalities of temperature in a circuit of different metals, and the thermal effects of electric currents circulating in it, are subject to the laws which would follow from the general principles of the dynamical theory of heat if there were no conduction of heat from one part of the circuit to another.*

In adopting this hypothesis, it must be distinctly understood that it is only a hypothesis, and that, however probable it may appear, experimental evidence in the special phenomena of thermo-electricity is quite necessary to prove it. Not only are the conditions prescribed in the second Law of the Dynamical Theory not completely fulfilled, but the part of the agency which does fulfil them is in all known circumstances of thermo-electric currents excessively small in proportion to agency inseparably accompanying it and essentially violating those conditions. Thus, if the current be of the full strength which the thermal electromotor alone can sustain against the resistance in its circuit, the whole mechanical energy of the thermo-electric action is at once spent in generating heat in the conductor;—an essentially irreversible process. The whole thermal agency immediately concerned in the current, even in this case when the current is at the strongest, is (from all we know of the magnitude of the thermo-electric force and absorptions and evolutions of heat,) probably very small in comparison with the transference of heat from hot to cold by ordinary conduction through the metal of the circuit. It might be imagined, that by choosing, for the circuit, materials which are good conductors of electricity and bad conductors of heat, we might diminish indefinitely the effect of conduction in comparison with the thermal effects of the current; but unfortunately we have no such substance as a *non-conductor* of heat. The metals which are the worst conductors of heat, are nearly in the same proportion the worst conductors of electricity; and all other substances appear to be comparatively very much worse conductors of electricity than of heat; stones, glass, dry wood, and so on, being, as compared with metals, nearly perfect non-conductors of electricity, and yet possessing very considerable conducting powers for heat. It is true, we may, as has been shown above, diminish without limit the waste of energy by frictional generation of heat in the circuit, by using an engine to do work and react against the thermal electro-motive force; but, as we have also seen, this can only be done by keeping the strength of the current very small compared with what it would be if allowed to waste all the energy of the electro-motive force on the frictional generation of heat; and it therefore requires a very slow use of the thermo-electric action. At the same time, it does not in any degree restrain the dissipation of energy by conduction, which is always going on, and which will therefore bear an even much greater proportion to the thermal agency electrically spent than in the case in which the latter was supposed to be unrestrained by the operation of the engine. By far the greater part of the heat taken in at all, then, in any thermo-electric arrangement, is essentially dissipated, and there would be no violation of the great natural law expressed in CARNOT's principle, if the small part of the whole action, which is reversible, gave a different, even an enormously different, and either a greater or a less, proportion of heat converted into work to heat taken in, than that law requires in all completely reversible processes. Still, the reversible part of the agency, in the thermo-electric circumstances we have supposed, is in itself so *perfect*, that it appears in the highest degree probable it may be found to fulfil independently the same conditions as the general law would impose on it if it took place unaccompanied by any other thermal or thermo-dynamic process.

§§ 107–111. *Mathematical expression of the Thermo-dynamic circumstances of Currents in Linear Conductors.*

107. In a heterogeneous metallic conductor the whole heat developed in a given time, will consist of a quantity generated *frictionally*, increased or diminished by the quantities produced or absorbed in the different parts by action depending on heterogeneousness of the circuit. The former, according to the law discovered by JOULE, may be represented by a term $B\gamma^2$, in which B denotes a constant depending only on the resistance of the circuit. The latter, being reversible with the current, may be assumed, at least for infinitely feeble currents, to be, in a given conductor, proportional simply to the strength of the current; and hence, the whole quantity of heat evolved in a given time, must be expressible by a term of the form $-A\gamma$, where A, whether it varies with γ or not, has a finite, positive, or negative value, when γ is infinitely small. Hence, the whole heat developed in any portion of a heterogeneous metallic conductor in a unit of time, must be expressible by the formula

$$-A\gamma+B\gamma^2;$$

where B is essentially positive, but A may be positive, negative, or zero, according to the nature of the different parts of the conducting arc. It may be assumed, with great probability, that the quantities A and B are absolutely constant for a given conductor with its different parts at given constant temperatures, and that when the temperatures of the different parts of a conductor are kept as nearly constant as possible with currents of different strengths passing through it, the quantities A and B can only depend on γ, inasmuch as it may be impossible to prevent the interior parts of the conductor from varying in temperature, and so changing in their resistance to conduction of electricity, or in their thermo-electric properties. In the present paper, accordingly, A and B are assumed to depend solely on the nature and thermal circumstances of the conductor, and to be independent of γ; but the investigations and conclusions would be applicable to cases of action with sufficiently feeble currents, probably to all currents due solely to the thermal electromotive force, even if A and B were in reality variable, provided the limiting values of these quantities for infinitely small values of γ be used.

108. Let us consider a conductor of any length and form, but of comparatively small transverse dimensions, composed of various metals, at different temperatures, but having portions at its two extremities homogeneous, and at the same temperature. These terminal portions will be denoted by E and E′, and will be called the *principal electrodes*, or *the electrodes of the principal conductor;* the conductor itself being called the *principal conductor* to distinguish it from others, either joining its extremities or otherwise circumstanced, which we may have to consider again.

Let an electro-motive force be made to act continuously and uniformly between these electrodes; as may be done for instance by means of a metallic disc included in the circuit touched by electrodes at its centre and a point of its circumference, and made to rotate between the poles of a powerful magnet, an arrangement equivalent to the "engine" spoken of above. Let the amount of this electromotive force be denoted by P, to be regarded as positive, when it tends to produce a current from E through the principal conductor, to E′. Let the absolute strength of the current, which, in these circumstances, passes through the principal conductor, be denoted by γ, to be considered as positive, if in the direction of P when positive.

109. Then, $P\gamma$ will be the amount of work done by the electro-motive force in the unit of time. As this work is spent wholly in keeping up a uniform electric current in the principal conductor, it must be equal to the mechanical equivalent of the heat generated, since no other effect is produced by the current. Hence, if $-A\gamma+B\gamma^2$ be, in accordance with the preceding explanations, the expression for the heat developed in the conductor in the unit of time by the current γ, and if J, as formerly, denote the mechanical equivalent of the thermal unit, we have

$$P\gamma=J\,(-A\gamma+B\gamma^2) \quad . \quad . \quad . \quad . \quad (3),$$

which is the expression for the particular circumstances of the first Fundamental Law of the Dynamical Theory of Heat.

Hence, by dividing by γ, we have

$$P=J\,(-A+B\gamma) \quad . \quad . \quad . \quad . \quad . \quad (4),$$

from which we deduce

$$\gamma=\frac{P+J\,A}{J\,B} \quad . \quad . \quad . \quad . \quad . \quad (5).$$

110. These equations show that, according as P is greater than, equal to, or less than $-J\,A$, the value of γ is positive, zero, or negative; and that, in any of the circumstances, the strength of the actual current is just the same as that of the current which an electro-motive force equal to $P+J\,A$ would excite in a homogeneous metallic conductor having J B for the absolute numerical measure of its galvanic resistance. Hence we conclude:—

(1.) That in all cases in which the value of A is finite, there must be an intrinsic electro-motive force in the principal conductor, which would itself produce a current if the electrodes E, E′, were put in contact with one another, and which must be balanced by an equal and opposite force, J A, applied either by means of a perfect non-conductor, or some electromotor, placed between E and E′, in order that there may be electrical equilibrium in the principal conductor;

And (2.) That J B, which cannot vanish in any case, is the absolute numerical measure of the galvanic resistance of the principal conductor itself.

It appears, therefore, that the whole theory of thermo-electric force in linear conductors is reduced to a knowledge of all the circumstances on which the value of the coefficient A, in the expression $-A\gamma+B\gamma^2$ for the heat developed throughout any given conductor, depends.

110. To express the Second General Law, we must take into account the temperatures of the different localities of the circuit in which heat is evolved or absorbed, when the current is kept so feeble (by the action of the electro-motive force P, against the thermo-electric force of the system), as to render the frictional generation of heat insensible. Denoting then by $a_t\gamma$ the heat absorbed in all parts of the circuit which are at the temperature t, by the action of a current of infinitely small strength γ: so that the term $-A\gamma$, expressing the whole heat generated not frictionally throughout the principal conductor in any case, will be the sum of all such terms with their signs changed, or

$$A\gamma=\Sigma a_t\gamma,$$

which gives

$$\Sigma a_t=A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6);$$

and, if F denote the value of the electro-motive force required to balance the thermo-electric tendency, we have

$$F=J\Sigma a_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

The Second General Law, as expressed above in equation (1), applied to the present circumstances, gives immediately,

$$\Sigma\frac{a_t\gamma}{t}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

or, since γ is the same for all terms of the sum,

$$\Sigma\frac{a_t}{t}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

111. Of these equations, (7), and (3) from which it is derived, involve no hypothesis whatever, but merely express the application of a great natural law,—discovered by JOULE for every case of thermal action whether chemical electrical or mechanical,—to the electrical circumstances of a solid linear conductor, having in any way the property of experiencing reverse thermal effects from infinitely feeble currents in the two directions through it. Equation (9) expresses the hypothetical application of the Second General Law discussed above in § 106. The two equations, (7) and (9), express all the information that can be derived from the General Dynamical Theory of Heat, regarding the special thermal and electrical energies brought into action by inequalities of temperature, or by the independent excitation of a current, in a solid linear conductor whether crystalline or not. The condition that the circuit is to be linear, being merely one of convenience in the initial treatment of the subject, may of course be removed by supposing linear conductors to be put together, so as to represent the circumstances of a solid conductor of electricity, with any distribution of electric currents whatever through it; and we may therefore regard these two equations as the Fundamental Equations of the Mechanical Theory of Thermo-electric Currents. To work out the theory for crystalline or non-crystalline conductors, it is necessary

to consider all the conditions which determine the generation or absorption of heat in different parts of the circuit, whatever be the properties of the metals of which it is formed. This we may now proceed to do; first for non-crystalline, and after that for crystalline metals.

§§ 112–124. *General Equations of Thermo-electric Currents, in non-crystalline Linear Conductors.*

112. The only reversible thermal effect of electric currents, which experiment has yet demonstrated, is that which PELTIER has discovered in the passage of electricity from one metal to another. Besides this, we may conceive that in one homogeneous metal formed into a conductor of varying section, different thermal effects may be produced by a current in any part, according as it passes in the direction in which the section increases, or in the contrary direction; and, with greater probability, we may suppose that a current in a conductor of one metal unequally heated, may produce different thermal effects according as it passes from hot to cold, or from cold to hot. But MAGNUS has shown, by careful experiments, that no application of heat can sustain a current in a circuit of one homogeneous metal, however varying in section; and from this it is easy to conclude, by equations (7) and (9), that there can be no reversible thermal effect due to the passage of a current between parts of a homogeneous metallic conductor having different sections. Now, it is clear that no circumstances, except those which have just been mentioned, can possibly give rise to different thermal effects in any part of a linear conductor of the same or of different metals, uniformly or non-uniformly heated, provided none of them be crystalline; and we have, therefore, at present nothing in the sum Σa_t, besides the terms depending on the passage of electricity from one metal to another, which certainly exist, and terms which may possibly be discovered, depending on its passage from hot to cold, or from cold to hot in the same metal.

113. Let the principal conductor consist of n different metals; in all $n+1$ parts, of which the first and last are of the same metal, and have their terminal portions (which we have called the electrodes E and E′) at the same temperature T_0, Let T_1, T_2, T_3, &c., denote the temperatures of the different junctions in order, and let Π_1, Π_2, Π_3, &c., denote the amounts (positive or negative) of heat absorbed at them respectively by a positive current of unit strength during the unit of time. Let $\gamma\,\sigma_1\,d\,t$, $\gamma\,\sigma_2\,d\,t$, $\gamma\,\sigma_3\,d\,t$, &c., denote the quantities of heat evolved in each of the different metals in the unit of time by a current of infinitely small strength, γ, passing from a locality at temperature $t+d\,t$ to a locality at temperature t. Without hypothesis, but by an obvious analogy, we may call the elements σ_1, σ_2, &c., the *specific heats of electricity in the different metals*, since they express the quantities of heat absorbed or evolved by the unit of current electricity in passing from cold to hot, or from hot to cold, between localities differing by a degree of temperature

in each metal respectively. It is easily shown (as will be seen by the treatment of the subject to follow immediately) that if the values of σ_1, σ_2, &c., depend either on the *section* of the conductor, or on the rate of variation of temperature along it, or on any other variable differing in different parts of the conductor, except the temperature, a current might be maintained by the application of heat to a homogeneous metallic conductor. We may, therefore, at once assume them to be, if not invariable, absolute functions of the temperature. From this it follows, that if $\phi\, t$ denote any function of t, the value of the sum, $\int \phi\, t\, \sigma\, d\, t$, for any conducting arc of homogeneous metal, depends only on the temperatures of its extremities; and therefore the parts of the sums $\Sigma\, a_t$ and $\frac{\Sigma\, a_t}{t}$, corresponding to the successive metals in the principal conductor, are respectively

$$-\int_{T_1}^{T_0} \sigma_1\, d\, t, \quad -\int_{T_2}^{T_1} \sigma_2\, d\, t, \cdots\cdots\cdots -\int_{T_n}^{T_{n-1}} \sigma_n\, d\, t, \quad -\int_{T_0}^{T_n} \sigma_1\, d\, t,$$

and $$-\int_{T_1}^{T_0} \frac{\sigma_1}{t}\, d\, t, \quad -\int_{T_2}^{T_1} \frac{\sigma_2}{t}\, d\, t \cdots\cdots\cdots -\int_{T_n}^{T_{n-1}} \frac{\sigma_n}{t}\, d\, t, \quad -\int_{T_0}^{T_n} \frac{\sigma_1}{t}\, d\, t.$$

Hence the general equations (7) and (9) become

$$F = J\left\{\Pi_1 + \Pi_2 + \cdots\cdots + \Pi_n - \int_{T_1}^{T_0} \sigma_1\, d\, t - \int_{T_2}^{T_1} \sigma_2\, d\, t - \cdots - \int_{T_n}^{T_{n-1}} \sigma_n\, d\, t - \int_{T_0}^{T_n} \sigma_1\, d\, t\right\} \quad . \quad . \quad (10)$$

$$\frac{\Pi_1}{T_1} + \frac{\Pi_2}{T_2} + \cdots\cdots + \frac{\Pi_n}{T_n} - \int_{T_1}^{T_0} \frac{\sigma_1}{t}\, d\, t - \int_{T_2}^{T_1} \frac{\sigma}{t}\, d\, t - \cdots\cdots - \int_{T_n}^{T_{n-1}} \frac{\sigma_n}{t}\, d\, t - \int_{T_0}^{T_n} \frac{\sigma_1}{t}\, d\, t = 0 \quad . \quad (11)$$

which are the fundamental equations of thermo-electricity in non-crystalline conductors. In these, along with the equation

$$\gamma = \frac{P+F}{J\,B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which shows the strength of the current actually sustained in the conductor when an independent electro-motive force, P, is applied between the principal electrodes E, E′, we have a full expression of the most general circumstances of thermo-electric currents in linear conductors of non-crystalline metals.

114. The special qualities of the metals of a thermo-electric circuit must be investigated experimentally before we can fix the values of Π_1, Π_2, &c., and σ_1, σ_2, &c., for any particular case. The relation between these quantities expressed in the general equation (11), having, as we have seen, a very high degree of probability, not merely as an approximate law, but as an essential truth, may be used as a guide, but must be held provisionally until we have sufficient experimental evidence in its favour. The first fundamental equation (10) admits of no doubt whatever in its universal application, and we shall see (§ 123 below) that it leads to most remarkable conclusions from known experimental facts.

The general principles are most conveniently applied by restricting the number of metals referred to in the general equations to two; a case which we accordingly proceed to consider.

115. Let the principal conductor consist of two metals, one constituting the middle, and the other the two terminal portions. Let the junctions of these portions next the terminals E, E′ be denoted by A, A′ respectively, and let their temperatures be T, T′. Let also $\Pi(T), -\Pi(T')$ be the quantities of heat absorbed at them per second by a current of unit strength. We should have

$$\Pi(T)=\Pi(T'),$$

if the temperatures were equal, since the PELTIER phenomenon consists, as we have seen, of equal quantities of heat evolved or absorbed, according to the direction of a current crossing the junction of two different metals; and if these quantities be not actually equal, we may consider them as particular values of a function Π of the temperature, which depends on the particular relative thermo-electric quality of the two metals. Accordingly, the preceding notation is reduced to $n=2$, $T_1=T$, $T_2=T'$, $\Pi_1=\Pi(T)$, $\Pi_2=-\Pi(T')$; and we have

$$\int_{T_1}^{T_0}\sigma_1\,dt+\int_{T_2}^{T_1}\sigma_2\,dt+\int_{T_0}^{T_2}\sigma_1\,dt=\int_{T}^{T'}(\sigma_1-\sigma_2)\,dt,$$

and similarly for the integral involving $\frac{1}{t}$. Hence the general equations become

$$F=J\left\{\Pi(T)-\Pi(T')+\int_{T'}^{T}(\sigma_1-\sigma_2)dt\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13.)$$

$$\frac{\Pi(T)}{T}-\frac{\Pi(T')}{T'}+\int_{T'}^{T}\frac{\sigma_1-\sigma_2}{t}\,dt=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If in the latter equation we substitute t for T, and differentiate with reference to this variable, we have, as an equivalent equation,

$$\frac{d\left(\frac{\Pi}{t}\right)}{dt}+\frac{\sigma_1-\sigma_2}{t}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or

$$\sigma_1-\sigma_2=\frac{\Pi}{t}-\frac{d\Pi}{dt} \quad . \quad . \quad . \quad . \quad (16)$$

This last equation leads to a remarkably simple expression for the electro-motive force of a thermo-electric pair, solely in the terms of the PELTIER evolution of heat at any temperature intermediate between the temperatures of its junctions; for we have only to eliminate by means of it $(\sigma_1-\sigma_2)$ from (13), to find

$$F=J\int_{T'}^{T}\frac{\Pi}{t}\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

116. Let us first apply these equations to the case of a thermo-electric pair,

with the two junctions kept at temperatures differing by an infinitely small amount τ. In this case we have

$$\Pi(\mathrm{T}) - \Pi(\mathrm{T}') = \frac{d\,\Pi}{d\,t}\,\tau,$$

$$\int_{\mathrm{T}'}^{\mathrm{T}} (\sigma_1 - \sigma_2)\,d\,t = (\sigma_1 - \sigma_2)\,\tau\,;$$

and equation (13) becomes

$$\mathrm{F} = \mathrm{J}\left\{\frac{d\,\Pi}{d\,t} + \sigma_1 - \sigma_2\right\}\tau \qquad (18).$$

If we make use of (16) in this, we have

$$\mathrm{F} = \mathrm{J}\,\frac{\Pi}{t}\,\tau \qquad (19).$$

The first of these expressions for the electro-motive force involves no hypothesis, but only the general principle of equivalence of heat and work. Its agreement with any experimental results is only to be looked on as a verification of the accuracy of the experiments, and can add nothing to the certainty of the part of the theory from which it is deduced. On the other hand, it would be extremely important to test the second expression (18) by direct experiment, and so confirm or correct the only doubtful part of the theory. The way to do so would be to determine, in absolute measure, the electro-motive force, F, due to a small difference of temperature, τ, in any thermo-electric pair, and to determine, in known thermal units, the amount of the PELTIER effect at a junction of the two metals, with a current of strength measured in electro-dynamic units, as we should then, by these determinations, be able to evaluate from direct experiments the values of the two members separately which appear equated in (18). As yet no observations have been made which lead, directly or indirectly, to the evaluation of the second member of (18) in any case; but I hope before long to succeed in carrying out a plan I have formed for this object. Neither have any observations been made yet, which give in any case a determination of the first member; but they may easily be accomplished by any person who possesses a conductor of which the resistance has been determined in absolute measure. Mr JOULE having kindly put me in possession of the silver wire on which his observations of the electrical generation of heat, in 1845, were made with currents measured by a tangent galvanometer used by him about the same time in experimenting on the electrolysis of sulphate of copper and sulphate of zinc, I hope to be able to complete the test of the theoretical result without difficulty, in any case in which I may succeed in determining the amount of the PELTIER thermal effect.

117. In the mean time, it is interesting to form an estimate, however rough, of the absolute values of the thermo-electric elements, in any case in which observations that have been made afford, directly or indirectly, the requisite data. This I have done for copper and bismuth, and copper and iron, in the manner

shown in the following explanation; which was communicated in full to the Royal Society, when the theory was first brought forward in 1851, although only the part inclosed in double quotation marks was printed in the Proceedings.

Example 1. *Copper and Bismuth.*—" ' Failing direct data, the absolute value of the electro-motive force in an element of copper and bismuth, with its two junctions kept at the temperatures 0° and 100° Cent., may be estimated indirectly from POUILLET'S comparison of the strength of the current it sends through a copper wire 20 metres long and 1 millimetre in diameter, with the strength of a current decomposing water at an observed rate; by means of the determinations by WEBER, and others, of the specific resistance of copper and the electro-chemical equivalent of water, in absolute units. The specific resistances of different specimens of copper having been found to differ considerably from one another, it is impossible, without experiments on the individual wire used by M. POUILLET, to determine with much accuracy the absolute resistance of his circuit; but the author has estimated it on the hypothesis that the specific resistance of its substance is $2\frac{1}{4}$ British units. Taking ·02 as the electro-chemical equivalent of water in British absolute units, the author has thus found 16,300 as the electro-motive force of an element of copper and bismuth, with the two junctions at 0° and 100° respectively. About 154 of such elements would be required to produce the same electro-motive force as a single cell of DANIELL'S—if, in DANIELL'S battery, the whole chemical action were electrically efficient.* A battery of 1000 copper and bismuth elements, with the two sets of junctions at 0° and 100° Cent., employed to work a galvanic engine, if the resistance in the whole circuit be equivalent to that of a copper wire of about 100 feet long and about one-eighth of an inch in diameter, and if the engine be allowed to move at such a rate as by inductive reaction to diminish the strength of the current to the half of what it is when the engine is at rest, would produce mechanical effect at the rate of about one-fifth of a horse-power. The electro-motive force of a copper and bismuth element, with its two junctions at 0° and 1°, being found by POUILLET to be about $\frac{1}{100}$th of the electro-motive force when the junctions are at 0° and 100, must be about 163. The value of Θ_0' " [*i. e.*, in terms of the notation now used, Π (273·7), or the value of Π (t), for the freezing point] " ' for copper and bismuth, or the quantity of heat absorbed in a second of time by a current of unit strength in

* M. JULES REGNAULD has since found experimentally, that 165 copper-bismuth elements balance the electro-motive force of a single cell of DANIELL'S (See Comptes Rendus, Jan. 9, 1854, or Bibliothéque Univ. de Genève, March 1854), a result agreeing with the estimate quoted in the text, more closely than the uncertainty and indirectness of the data on which that estimate was founded would have justified us in expecting. The comparison of course affords no test of the thermo-electric theory; and only shows that, as far as the observations of WEBER, and others alluded to, render POUILLET'S available for determining the absolute electro-motive force of a copper-bismuth element, the absolute electro-motive force of a single cell of DANIELL'S, obtained by multiplying it by the number found by M. REGNAULD, agrees with that which I first gave on the hypothesis of all the chemical action being electrically efficient (Phil. Mag., Dec. 1851), and so confirms this hypothesis.

passing from bismuth to copper, when the temperature is kept at 0° Cent. must therefore be $\frac{163}{160 \cdot 16}$, or very nearly equal to the quantity required to raise the temperature of a grain of water from 0° to 1° Cent.'"

119. Example 2. *Copper and Iron.*—"By directing the electro-motive force of one copper and bismuth element against that of a thermo-electric battery of a variable number of copper and iron wire elements in one circuit, I have found, by a galvanometer included in the same circuit, that when the range of temperature in all the thermo-electric elements is the same, and not very far at either limit from the freezing point of water, the current passes in the direction of the copper-bismuth agency when only three, and in the contrary direction when four or more, of the copper-iron elements are opposed to it. Hence the electro-motive force of a copper-bismuth element is between three and four times that of a copper-iron element with the same range of temperature, a little above the freezing point of water. The electro-motive force of a copper-iron element, with its two junctions at 0° and 1° Cent. respectively, must therefore be something greater than one-fourth of the number found above for copper-bismuth with the same range of temperature, that is, something more than 40 British absolute units, and we may consequently represent it by $m \times 40$, where $m > 1$. We have then by the equation expressing the application of CARNOT's principle, [equation (19) of § 116.],

$$\Theta_0 \mu = \Theta_0 \frac{J}{273 \cdot 7} = m \times 40,$$

whence*

$$\Theta_0 = \tfrac{1}{4} m \text{ nearly} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a).$$

"Now, by the principle of mechanical effect, we have

$$F_0^{280} = J \left(\int_0^{280} \vartheta \, d\, t - \Theta_0 \right);$$

if F_0^{280} denote the electro-motive force of a copper-iron element, of which the two junctions are respectively 0° and 280° Cent., and $\vartheta\, d\, t$, the quantity of heat absorbed per second by a current of unit strength, in passing in copper from a locality at temperature t to a locality at $t + d\, t$, and in iron from a locality at $t + d\, t$ to a locality at t:† since the PELTIER generation of heat between copper and iron at their neutral point, 280°, vanishes;‡ and therefore the only absorption of heat is that due to the electric convection expressed by $\int \vartheta\, d\, t$; while there is evolution of

* The value of J now used being $32 \cdot 2 \times 1390 = 44{,}758$, which is the equivalent of the unit of heat in "absolute units" of work. The "absolute unit of force" on which this unit of work is founded, and which is generally used in magnetic and electro-magnetic expressions, is the force which acting on the unit of matter (one grain) during the unit of time (one second), generates a unit of velocity (one foot per second). The "absolute unit of work" is the work done by the absolute unit of force in acting through the unit of space (one foot).

† That is, if ϑ denote the algebraic excess of the specific heat of electricity in copper, above the specific heat of electricity in iron, according to the terms more recently introduced.

‡ See § 123. below. Instead of 240°, conjectured from REGNAULT's observation when these details were first published, 280° is now taken as a closer approximation to the neutral point of copper and iron.

heat amounting to Θ_0 at the cold junction, and of mechanical effect by the current amounting to F units of work. If we estimate the value of F_0^{280} as half what it would be were the electro-motive force the same for all equal differences of temperature as for small differences near the freezing point,* that is, if we take $F_0^{280} = \frac{1}{2} \times 40m \times 280$, the preceding equation becomes

$$140 \times m \times 40 = J\left(\int_0^{280} \vartheta\, dt - \Theta_0\right).$$

But we found $$m \times 40 = \mu\, \Theta_0 .$$

Hence $$\int_0^{280} \vartheta\, dt = \Theta_0 \left(1 + \frac{140\,\mu}{J}\right) = \Theta_0 \left(1 + \frac{140}{272{\cdot}7}\right) = \Theta_0 \times \frac{3}{2} \text{ nearly} \quad . \quad . \quad . (b);$$

or, according to (a),

$$\int_0^{280} \vartheta\, dt = m \times \frac{3}{8} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c);$$

results, of which (b) shows how the difference of the aggregate amount of the theoretically indicated convective effect in the two metals is related to the PELTIER effect at the cold junction; and (c) shows that its absolute value is rather more than one-third of a thermal unit per second per unit strength of current.

120. If the specific heats of current electricity either vanished or were equal in the different metals, we should have, by (15) and (16),

$$\frac{\Pi}{t} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20),$$

and $$F = J\,\frac{\Pi}{t}(T - T') \quad . \quad . \quad . \quad . \quad . \quad . \quad (21),$$

or, the PELTIER thermal effect at a junction of two metals would be proportional to the absolute temperature at which it takes place, and the electro-motive force in a circuit of any two metals would vary in the simple ratio of the difference of temperature on the new absolute scale between their junctions.† Whatever thermometric system be followed, the second of these conclusions would require the same law of variation of electro-motive force with the temperatures of the junctions, in every pair of metals used as a thermo-electric element.

121. Before the existence of a convective effect of electricity in an unequally heated metal had even been conjectured, I arrived at the preceding conclusions by a theory in which the PELTIER effect was taken as the only thermal effect reversible with the current in a thermo-electric circuit, and found them at variance with

* See § 122, below.

† When the Theory was first communicated to the Royal Society, I stated these conclusions with reference to temperature by the air thermometer, and therefore in terms of CARNOT's absolute function of the temperature, not simply as now in terms of absolute temperature. At the same time, I gave as consequences of MAYER's hypothesis, the same statement in terms of air thermometer temperatures, as is now made absolutely. See Proceedings, Dec. 15, 1851; or Philosophical Magazine, June 1852, p. 532.

known facts which show remarkably different laws of electro-motive force in thermo-electric pairs of different metals. I therefore inferred, that besides the PELTIER effect there must be other reversible thermal effects; and I showed that these can be due to no other cause than the inequalities of temperature in single metals in the circuit. A convective effect of electricity in an unequally heated conductor of one metal was thus first demonstrated by theoretical reasoning; but only the difference of the amount of this effect produced by currents of equal strength in different metals, not its quality or its absolute value in any one metal, could be inferred from the data of thermo-electric force alone. The case of a thermo-electric circuit of copper and iron, being that which first forced on me the conclusion that an electric current must produce different effects according as it passes from hot to cold, or from cold to hot, in an unequally heated metal, was taken as an example in my first communication of the Theory to this Society;* and the two metals, copper and iron, were made the subjects of a consequent experimental investigation, to ascertain the quality of the anticipated property in each of them separately. The application of the general reasoning to this particular case, and the answers which I have derived by experiment to the question which it raises, are described in the following extract of a Report communicated to the Royal Society of London, March 31, and published in the Proceedings, May, of the present year :—

122. " BECQUEREL discovered that if one junction of copper and iron, in a circuit of the two metals, be kept at an ordinary atmospheric temperature, while the other is raised gradually, a current first sets from copper to iron through the hot junction, increasing in strength only as long as the temperature is below about 300° Cent.; and becoming feebler with farther elevation of temperature until it ceases, and a current actually sets in the contrary direction when a high red heat is attained.† Many experimenters have professed themselves unable to verify this extraordinary discovery; but the description which M. BECQUEREL gives of his experiments leaves no room for the doubts which some have thrown upon his conclusion, and establishes the thermo-electric inversion between iron and copper, not as a singular case (extraordinary and unexpected as it appeared), but as a phenomenon to be looked for between any two metals, when tried through a sufficient range of temperatures. M. REGNAULT has verified M. BECQUEREL'S conclusion so far, in finding that the strength of a current in a circuit of copper and iron wire did not increase sensibly for elevations of temperature above 240° Cent., and began to diminish when the temperature considerably exceeded this limit;

* See Proceedings, R. S. E., Dec. 15, 1851.

† Since this was written, I have found that thermo-electric inversions between copper and an alloy of antimony and bismuth, and between silver and the same alloy, precisely analogous to that between copper and iron more recently discovered by M. BECQUEREL, were discovered as early as 1823, by Professor CUMMING of Cambridge, shortly after the thermo-electricity of metals was first brought to light by SEEBECK. These, with other experiments, leading to important results, especially as to the order of metals and metallic compounds in the thermo-electric series, are described in the Cambridge Transactions for 1823, and in Professor CUMMING'S Treatise on Electro-dynamics.

but the actual inversion observed by M. BECQUEREL is required to show that the diminution of strength in the current is due to a real falling off in the electromotive force, and not to the increased resistance known to be produced by an elevation of temperature.

123. "From BECQUEREL'S discovery it follows that, for temperatures below a certain limit, which, for particular specimens of copper and iron wire, I have ascertained, by a mode of experimenting described below, to be 280° Cent., copper is on the negative side of iron in the thermo-electric series; on the positive side for higher temperatures; and at the limiting temperature these two metals are thermo-electrically neutral to one another. It follows, according to the general mechanical theory* of thermo-electric currents, referred to above, that electricity passing from copper to iron causes the absorption or the evolution of heat according as the temperature of the metals is below or above the neutral point: but neither absorption nor evolution of heat, if the temperature be precisely that of neutrality; (a conclusion which I have already partially verified by experiment). Hence, if in a circuit of copper and iron, one junction be kept about 280°, that is, at the neutral temperature, and the other at any lower temperature, a thermo-electric current will set from copper to iron through the hot, and from iron to copper through the cold, junction; causing the evolution of heat in the latter, and the raising of weights, too, if it be employed to work an electro-magnetic engine, but not causing the absorption of any heat at the hot junction. Hence there must be an absorption of heat at some part or parts of the circuit consisting solely of one metal or of the other, to an amount equivalent to the heat evolved at the cold junction, together with the thermal value of any mechanical effects produced on other parts of the circuit. The locality of this absorption can only be where the temperatures of the single metals are non-uniform, since the thermal effect of a current in any homogeneous uniformly-heated conductor is always an evolution of

* This is the only part of the theoretical reasoning as first given, which depended on the application of CARNOT'S principle, and consequently, is the only part capable of being objected to as uncertain. All doubt would be removed by an experimental verification of the stated PELTIER effects for copper and iron, at the different temperatures, such as I hope very soon to have completed. In the meantime, instead of the theoretical reasoning, we may, if it is preferred, use an ample foundation of analogy to conclude that heat is absorbed at the hotter junction, and evolved at the colder, by the actual thermo-electric current in every case of a circuit of two metals, with their junctions differing but little in temperature. For it was found by PELTIER himself, that currents from bismuth to copper, from copper to antimony, from zinc to iron, from copper to iron, and from platinum to iron, cause absorption, and the reverse current in each case, evolution of heat; experimental conclusions, with which I was not acquainted when I first published the Theory. Very soon after I found, myself, by experiment, that copper and iron at ordinary atmospheric temperatures, exhibit the anticipated thermal phenomenon; and corresponding experimental results have been obtained still more recently in the cases of bismuth and copper, copper and antimony, copper and iron, German silver and iron, by FRANKENHEIM. (POGGENDORFF'S *Annalen*, Feb. 1854); in every case, the current which would be produced by heating one junction a little, being that which in the same junction causes an absorption of heat. If we consider the induction sufficient to establish this as a universal law in thermo-electricity, the reasoning in the text becomes independent of any hypothesis to which objections can possibly be raised.

heat. Hence there must be on the whole absorption of heat caused by the current passing from cold to hot in copper, and from hot to cold in iron. When a current is forced through the circuit against the thermo-electric force, the same reasoning establishes an evolution of heat to an amount equivalent to the sum of the heat that would be then taken in at the cold junction, and the value in heat of the energy spent by the agency (chemical, or of any other kind) by which the electromotive force is applied. The aggregate reversible thermal effect, thus demonstrated to exist in the unequally-heated portions of the two metals, might be produced in one of the metals alone, or (as appears more natural to suppose) it may be the sum or difference of effects experienced by each. Adopting, as a matter of form, the latter supposition, without excluding the former possibility, we may assert that either there is absorption of heat by the current passing from hot to cold in the copper, and evolution to a less extent, in the iron of the same circuit; or there is absorption of heat produced by the current from hot to cold in the iron, and evolution of heat to a less amount in the copper; or there must be absorption of heat in each metal: with the reverse effect in each case, when the current is reversed. The reversible effect in a single metal of non-uniform temperature may be called a convection of heat; and, to avoid circumlocution, I shall express it, that the vitreous electricity carries heat with it, or that the specific heat of vitreous electricity is positive, when this convection is in the nominal 'direction of the current;' and I shall apply the same expressions to 'resinous electricity,' when the convection is against the nominal direction of the current. It is established, then, that one or other of the following three hypotheses must be true:—

124. "Vitreous electricity carries heat with it in an unequally heated conductor, whether of copper or iron; but more in copper than in iron:

"Or, resinous electricity carries heat with it in an unequally heated conductor, whether of copper or iron; but more in iron than in copper:

"Or, vitreous electricity carries heat with it in an unequally heated conductor of copper, and resinous electricity carries heat with it in an unequally heated conductor of iron.

125. "Immediately after communicating this theory to the Royal Society of Edinburgh, I commenced trying to ascertain by experiment which of the three hypotheses is the truth, as Theory, with only thermo-electric data, could not decide between them. I had a slight bias in favour of the first rather than the second, in consequence of the positiveness which, after FRANKLIN, we habitually attribute to the vitreous electricity, and a very strong feeling of the improbability of the third. With the able and persevering exertions of my assistant, Mr M'FARLANE, applied to the construction of various forms of apparatus, and to assist me in conducting experiments, the research has been carried on with little intermission for more than two years. Mr ROBERT DAVIDSON, Mr CHARLES A. SMITH, and

other friends, have also given much valuable assistance during a great part of this time, in the different experimental investigations, of which the results are now laid before the Royal Society.

126. "Only nugatory results were obtained until recently, from multiplied and varied experiments both on copper and iron conductors; but the theoretical anticipation was of such a nature, that no want of experimental evidence could influence my conviction of its truth. About four months ago, by means of a new form of apparatus, I ascertained that *resinous electricity carries heat with it in an unequally heated iron conductor*. A similar equally sensitive arrangement showed no result for copper. The second hypothesis might then have been expected to hold; but to ascertain the truth with certainty, I have continued ever since getting an experiment on copper nearly every week, with more and more sensitive arrangements; and at last, in two experiments, I have made out with certainty, that *vitreous electricity carries heat with it in an unequally heated copper conductor*.

"The third hypothesis is thus established; a most unexpected conclusion, I am willing to confess.

"I intend to continue the research; and hope not only to ascertain the nature of the thermal effects in other metals, but to determine its amount in absolute measure in the most important cases, and to find how it varies, if at all, with the temperature; that is, to determine the character (positive or negative) and the value of the specific heat, (varying or not with the temperature,) of the unit of current electricity in various metals."

127. The relations

$$\sigma_1 - \sigma_2 = \frac{\Pi}{t} - \frac{d\Pi}{dt} \quad . \quad . \quad . \quad (16) \qquad \text{and } F = J\int_{T'}^{T} \frac{\Pi}{t} dt \quad . \quad . \quad . \quad . \quad . \quad (17)$$

established above, "show how important it is towards the special object of determining the specific heats of electricity in metals, to investigate the law of electro-motive force in various cases, and to determine the thermal effect of electricity in passing from one metal to another at various temperatures. Both of these objects of research are therefore included in the general investigation of the subject.

128. "The only progress I have as yet made in the last-mentioned branch of the inquiry, has been to demonstrate experimentally, that there is a cooling or heating effect produced by a current between copper and iron, at an ordinary atmospheric temperature, according as it passes from copper to iron, or from iron to copper, in verification of a theoretical conclusion mentioned above; but I intend shortly to extend the verification of theory to a demonstration, that reverse effects take place between those metals, at any temperature above their neutral point of about 280° Cent.; and I hope also to be able to make determinations in absolute

measure of the amount of the PELTIER effect for a given strength of current between various pairs of metals.

129. "With reference to laws of electro-motive force in various cases, I have commenced by determining the order of several specimens of metals in the thermo-electric series, and have ascertained some very curious facts regarding varieties in this series, which exist at different temperatures. In this I have only followed BECQUEREL's remarkable discovery, from which I had been led to the reasoning and experimental investigation regarding copper and iron described above. My way of experimenting has been, to raise the temperature first of one junction as far as the circumstances admit, keeping the other cold, and then to raise the temperature of the other gradually, and watch the indications of a galvanometer during the whole process. When an inversion of the current is noticed, the changing temperature is brought back till the galvanometer shows no current; and then (by a process quite analogous to that followed by Mr JOULE, and Dr LYON PLAYFAIR, in ascertaining the temperature at which water is of maximum density), the temperatures of the two junctions are approximated, the galvanometer always being kept as near zero as possible. When the difference between any two temperatures on each side of the neutral point which give no current is not very great, their arithmetical mean will be the neutral temperature. A regular deviation of the mean temperature from the true neutral temperature is to be looked for with wide ranges, and a determination of it would show the law according to which the difference of the specific heat of electricity in the two metals varies with the temperatures; but I have not even as yet ascertained with certainty the existence of such a deviation in any particular case. The following is a summary of the principal results I have already obtained in this department of the subject.

130. "The metals tried being—three platinum wires (P_1 the thickest, P_2 the thinnest, and P_3 of intermediate thickness), brass wires (B), a lead wire (L′), slips of sheet-lead (L), copper wires (C), and iron-wire (I); I find that the specimens experimented on stand thermo-electrically, at different temperatures, in the orders shown in the following table, and explained in the heading by reference to bismuth and antimony, or to the terms "negative" and "positive," as often used:—

Temperature Centigrade.	Bismuth "Negative." ... Antimony "Positive."
$-20°$	. . . P_3 . . . *c* . . . . P_2 . . . . P_1 . . . . I . . . . . .
0	. . . P_3 . . . *l′* . . . . P_2 . . . C . . . P_1 . . , ... I . . . . . .
37	. . . P_3 . . . . . *b* . {$L'P_2$}. . . . . . C . P_1 . . . . I . . . . . .
64	. . . P_3 . . . . P_2 . . . *b* . *l′*. . {CP_1} . . . . I . . . . . .
130	. . . P_3 . . . . P_2 . . . . {BP_1} . L . . C . . I . . . . . .
140	. . . P_3 . . . . P_2 . . . . P_1 . . {BL} . C . I . . . . . .
280	. . . P_3 . . . . P_2 . . . . P_1 . . . . *b* . . {CI} . . . . .
300	. . . P_3 . . . . P_2 . . . . P_1 . . . . . *b* . I . . . C . .

It must be added, by way of explanation, that the bracket enclosing the symbols of any two of the metallic specimens indicates that they are neutral to one another at the corresponding temperature; and the arrow-head below one of them shows the direction in which it is changing its place with reference to the other, in the series, as the temperature is raised. When there is any doubt as to a position as shown in the table, the symbol of the metal is a small letter instead of a capital.

131. "The rapidity with which copper changes its place among some of the metals (the platinums and iron) is very remarkable. Brass also changes its place in the same direction, possibly no less rapidly than copper; and lead changes its place also in the same direction, but certainly less rapidly than brass, which, after passing the thick platinum wire P_1 at 130° Cent., passes the lead at 140°, the lead itself having probably passed the thick platinum at some temperature a little below 130° [at 121, as I afterwards found]. The conclusion, as regards specific heats of electricity in the different metals, from the equation expressing thermo-electric force given above, is,—that the specific heat of vitreous electricity is greater in each metal passing another from left to right in the series, as the temperature rises, than in the metal it passes; thus in particular—

132. "*The specific heat of vitreous electricity is greater in copper than in platinum or in iron; greater in brass than in platinum or in lead; and greater in lead than in platinum.*

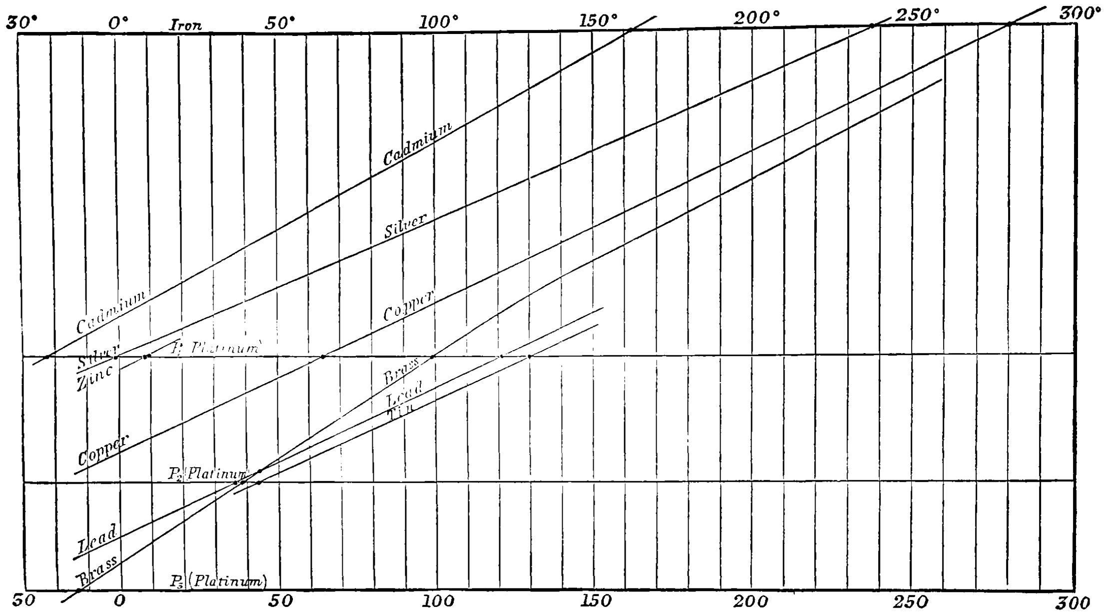
133. "It is probable enough, from the results regarding iron and copper mentioned above, that the specific heat of vitreous electricity is positive in brass; and very small positive or else negative in platinum, perhaps about the same as in iron. It will not be difficult to test these speculations either by direct experiments on the convective effects of electric currents in the different metals, or by comparative measurements of thermo-electric forces for various temperatures in circuits of the metals, and I trust to be able to do so before long."

§§ 134, 135. *Inserted September* 15, 1854.

134. A continuation of the experiments has shown many remarkable variations of order in the thermo-electric series. The following table exhibits the results of observations to determine neutral points for different pairs of metals: the number at the head of each column being the temperature centigrade at which the two metals written below it are thermo-electrically neutral to one another; and the lower metal in each column being that which *passes the other from bismuth towards antimony*, as the temperature rises.

−14° Cent.	−12·°2	−1·°5	8·°2	36°	38°	44°	44°	64°	99°	121°	130°	162·°5	237°	280°
P_3 Brass.	P_1 Cadmium.	P_1 Silver.	P_1 Zinc.	P_2 Lead.	P_2 Brass.	P_2 Tin.	Lead Brass.	P_1 Copper	P_1 Brass.	P_1 Lead.	P_1 Tin.	Iron Cadmium.	Iron Silver.	Iron Copper

I also found that brass becomes neutral to copper, and copper becomes neutral to silver, at some high temperatures, estimated at from 800° to 1400° Cent., in the former case, and from 700° to 1000° in the latter, being a little below the melting point of silver. The following diagram exhibits the results graphically, constructed on the principle of drawing a line through the letters corresponding to any one of the metallic specimens in a table such as that of § 130, and arranging the spaces so that each line shall be as nearly straight as possible, if not exactly so.



Explanation of Thermo-electric Diagram.

The orders of the metals in the thermo-electric series, at different temperatures, are shown by the points in which the vertical lines through the numbers expressed by the temperatures centigrade are cut by the horizontal and oblique lines named for the different metallic specimens.

The object to be aimed at in perfecting a thermo-electric diagram, and perhaps approximately attained to (conjecturally) in the preceding, is to make the ordinates of the lines (which will, in general, be curves) corresponding to the different metallic specimens, be exactly proportional to their *thermo-electric powers*,* with reference to a standard metal (P_3 in the actual diagram).

135. Judging by the eye from the diagram, as regards the convective agency of electricity in unequally heated conductors, I infer that the different metals are probably to be ranked as follows, in order of the values of the specific heat of electricity in them.

Specific Heat of Vitreous Electricity:—

In	Cadmium,	Positive.
„	Brass,	...
„	Copper,	...
„	Lead, Tin, Silver,	Positive, zero, or negative.
„	Platinum,	Probably negative.
„	Iron.	Negative.

Zinc probably stands high, certainly above platinum.

* See § 140, below.

136. A very close analogy subsists between the thermo-dynamical circumstances of an electrical current in a circuit of two metals, and those of a fluid circulating in a closed rectangular tube, consisting of two vertical branches connected by two horizontal branches. Thus if, by the application of electro-motive force in one case, or by the action of pistons in the other, a current be instituted, and if, at the same time, the temperature be kept uniform throughout the circuit, heat will be evolved and absorbed at the two junctions respectively in the former case, and heat will be evolved in one and absorbed in the other of vertical branches of the tube in the latter case, in consequence of the variations of pressure experienced by the fluid in moving through those parts of the circuit. If the temperature of one junction of the electrical circuit be raised above that of the other, and if the temperature of one vertical branch of the tube containing fluid be raised above that of the other, a current will in each case be occasioned, without any other motive appliance. If the current be directed to do work with all its energy, by means of an engine in each case, there will be a conversion of heat into mechanical effect, with perfectly analogous relations as to absorption and evolution of heat in different parts of the circuit, provided the engine worked by the fluid current be arranged to pass the fluid through it without variation of temperature from or to either of the vertical branches of the tube. If σ_1 and σ_2 denote the specific heat of unity of mass of the fluid, under the constant pressures at which it exists in the lower and upper horizontal branches of the tube in the second case; $\Pi(\mathrm{T})$, $\Pi(\mathrm{T}')$ the quantities of heat evolved and absorbed respectively by the passage of a unit mass of fluid through the two vertical branches kept at the respective temperatures T, T′; and if F denote the work done by a unit mass of the fluid in passing through the engine; the fundamental equations obtained above, with reference to the thermo-electric circumstances, may be at once written down for the case of the ordinary fluid, as the expression of the two fundamental laws of the Dynamical Theory of Heat, both of which are applicable to this case, without any uncertainty such as that shown to be conceivable as regards the application of the second law to the case of a thermo-electric current. The two equations thus obtained are equivalent to the two general equations given, in §§ 20 and 21 of the First Part of this series of papers, as the expressions of the fundamental laws of the Dynamical Theory of Heat applied to the elasticity and expansive properties of fluids. In fact, when we suppose the ranges of both temperature and pressure in the circulating fluid to be infinitely small, the equation $\mathrm{F}=\mathrm{J}\int_{\mathrm{T}'}^{\mathrm{T}} \frac{\Pi}{t}\,dt$, reduced to the notation formerly used, and modified by changing the independent variables from (t, p) to (t, v), becomes

$$\mathrm{M}=\frac{t}{\mathrm{J}}\frac{dp}{dt},$$

which is the same as (3) of § 21; and a combination of this with $\frac{d}{dt}\left(\frac{\Pi}{t}\right)=\frac{\sigma_2-\sigma_1}{t}$, gives

$$\frac{dM}{dt}-\frac{dN}{dv}=\frac{1}{J}\frac{dp}{dt},$$

which is identical with (2) of § 20. It appears, then, that the consideration of the case of fluid motion here brought forward as analogous to thermo-electric currents in non-crystalline linear conductors, is sufficient for establishing the general thermo-dynamical equations of fluids, and consequently the universal relations among specific heats, elasticities, and thermal effects of condensation or rarefaction, derived from them in Part III., are all included in the investigation at present indicated. Not going into the details of this investigation, because the former investigation, which is on the whole more convenient, is fully given in Parts I. and III., I shall merely point out a special application of it to the case of a liquid which has a temperature of maximum density, as for instance water.

137. In the first place, it is to be remarked, that if the two vertical branches be kept at temperatures a little above and below the point of maximum density, no current will be produced; and therefore if T_0 denote this temperature, the equation $F=\int\frac{\Pi}{t}\,dt$ gives $\Pi(T_0)=0$. Again, if one of the vertical branches be kept at T_0, and the other be kept at a temperature either higher or lower, a current will set, and always in the same direction. Hence $\int_{T_0}^{T}\frac{\Pi}{t}\,dt$ has the same sign, whether T be greater or less than T_0, and consequently $\Pi(t)$ must have contrary signs for values of t above and below T_0: which, by attending to the signs in the general formulæ, we see must be such as to express evolution of heat by the actual current in the second vertical branch, when its temperature is below, and absorption when above, T_0. As the current in each case ascends in this vertical branch, we conclude that a slight diminution of pressure causes evolution or absorption of heat, in water, according as its temperature is below or above that of maximum density; or conversely,—That when water is suddenly compressed, it becomes colder if initially below, or warmer if initially above, its temperature of maximum density. This conclusion from general thermo-dynamic principles was first, so far as I know, mentioned along with the description of an experiment to prove the lowering of the freezing point of water by pressure, communicated to the Royal Society in January, 1850.* The quantitative expression for the effect, which was given in § 50 of Part III., may be derived with ease from the considerations now brought forward. The other thermo-dynamic equation $\frac{\sigma_2-\sigma_1}{t}=\frac{d\left(\frac{\Pi}{t}\right)}{dt}$ shows that the specific heat of the water must be greater in the upper horizontal branch

* See Proceedings of that date, or Philosophical Magazine, 1850.

than in the lower; or that the specific heat of water under constant pressure is increased by a diminution of the pressure. The same conclusion, and the amount of the effect, are also implied in equations (18) and (19) of Part III. We may arrive at it without referring to any of the mathematical formulæ, merely by an application of the general principle of mechanical effect, when once the conclusion regarding the thermal effects of condensation or rarefaction is established; exactly as the conclusion regarding the specific heats of electricity in copper and in iron was first arrived at.* For if we suppose one vertical branch to be kept at the temperature of maximum density (corresponding to the neutral point of the metals in the corresponding thermo-electric case), and the other at some lower temperature, a current will set downwards through the former branch, and upwards through the latter. This current will cause evolution of heat, in consequence of the expansion of the fluid, in the branch through which it rises, but will cause neither absorption nor evolution in the other vertical branch, since in it the temperature is that of the maximum density. There will also be heat generated in various parts by fluid friction. There must then be, on the whole, absorption of heat in the horizontal branches; because otherwise there would be no source of energy for the heat constantly evolved to be drawn from. But heat will be evolved by the fluid in passing in the lower horizontal branch from hot to cold; and therefore, exactly to the extent of the heat otherwise evolved, this must be over-compensated by the heat absorbed in the upper horizontal branch by the fluid passing from cold to hot. On the other hand, if one of the vertical branches be kept above the temperature of maximum density, and the other at this point, the fluid will sink in the latter, causing neither absorption nor evolution of heat, and rise in the former, causing absorption; and therefore more heat must be evolved by the fluid passing from hot to cold in the upper horizontal branch than is absorbed by it in passing from cold to hot in the lower. From either case, we infer that the specific heat of the water is greater in the upper than in the lower branch. The analogy with the thermo-electric circumstances of two metals which have a neutral point, is perfect algebraically in all particulars. The proposition just enunciated corresponds exactly to the conclusion arrived at formerly, that if one metal passes another in the direction from bismuth towards antimony in the thermo-electric scale, the specific heat of electricity is greater in the former metal than in the latter; this statement holding algebraically, even in such a case as that of copper and iron, where the specific heats are of contrary origin in the two metals, although the existence of such contrary effects is enough to show how difficult it is to conceive the physical circumstances of an electric current as physically analogous to those of a current of fluid in one direction.

* Proceedings R. S. E., Dec. 15, 1851, or extract of Proceedings R. S., May 1854, quoted above, § 124.

§§ 138–140. *General Lemma, regarding relative thermo-electric properties of Metals, and multiple combinations in a Linear Circuit.*

138. The general equation (11), investigated above, shows that *the aggregate amount of all the thermal effects produced by a current, or by any system of currents, in any solid conductor or combination of solid conductors must be zero, if all the localities in which they are produced are kept at the same temperature.*

COR. 1. If in any circuit of solid conductors the temperature be uniform from a point P through all the conducting matter to a point Q, both the aggregate thermal actions, and the electro-motive force are totally independent of this intermediate matter, whether it be homogeneous or heterogeneous, crystalline or non-crystalline, linear or solid, and is the same as if P and Q were put in contact. [The importance of this simple and elementary truth in thermo-electric experiments of various kinds is very obvious. It appears to have been overlooked by many experimenters who have scrupulously avoided introducing extraneous matter (as solder) in making thermo-electric junctions, and who have attempted to explain away CUMMING'S and BECQUEREL'S remarkable discovery of thermo-electric inversions, by referring the phenomena observed to coatings of oxide formed on the metals at their surfaces of contact.]

COR. 2. If Π (A, B), Π (B, C), Π (C, D), ... Π (Z, A) denote the amounts of the PELTIER absorption of heat per unit strength of current per unit of time, at the successive junctions of a circuit of metals A, B, C, ... Z, A, we must have,

$$\Pi\,(A, B) + \Pi\,(B, C) + \ldots\ldots\ldots + \Pi\,(Z, A) = 0\,.$$

Thus if the circuit consist of three metals,

$$\Pi\,(A, B) + \Pi\,(B, C) + \Pi\,(C, A) = 0\,;$$

from which, since $\Pi\,(C, A) = -\,\Pi\,(A, C)$, we derive

$$\Pi\,(B, C) = \Pi\,(A, C) - \Pi\,(A, B).$$

139. Now, by (19) above, the electro-motive force in an element of the two metals (A, B), tending from B to A through the hot junction, for an infinitely small difference of temperature τ, and a mean absolute temperature t, is $\frac{J\,\Pi\,(A, B)}{t}\,\tau$, and so for every other pair of metals. Hence, if ϕ (A, B), ϕ (B, C), &c., denote the quantities by which the infinitely small range τ must be multiplied to get the electro-motive forces of elements composed of successive pairs of the metals in the same thermal circumstances, we have

$$\phi\,(A, B) + \phi\,(B, C) + \ldots\ldots + \phi\,(Z, A) = 0\,;$$

and, for the case of three metals,

$$\phi\,(B, C) = \phi\,(A, C) - \phi\,(A, B).$$

Since the thermo-electric force for any range of temperature is the sum of the thermo-electric forces for all the infinitely small ranges into which we may divide the whole range (being, as proved above, equal to $\int_{T}^{T'} \phi\, dt$), in the case of each element, the theorem expressed by these equations is true of the thermo-electric forces in the single elements for *all ranges* of temperature, provided the absolute temperatures of the hot and cold junctions be the same in the different elements. The second equation, by successive applications of which the first may be derived, is the simplest expression of a theorem which was, I believe, first pointed out and experimentally verified by BECQUEREL in researches described in the second volume of his Traité d'Electricité.

140. For brevity, we shall call what has been denoted by ϕ (B, C) *the thermo-electric relation* of the metal B to the metal C; we shall call a certain metal (perhaps copper or silver) the standard metal; and if A be the standard metal, we shall call ϕ (A, B) the *thermo-electric power of the metal B.* The theorem expressed by the last equation may now be stated thus: *The thermo-electric relation between two metals is equal to the difference of their thermo-electric powers;* which is nearly identical with BECQUEREL'S own statement of his theorem.

§§ 141–146. *Elementary Explanations in Electro-cinematics and Electro-mechanics.*

141. When we confined our attention to electric currents flowing along linear conductors, it was only necessary to consider in each case, the *whole strength of the current*, and the longitudinal electro-motive force in any part of the circuit, without taking into account any of the transverse dimensions of the conducting channel. In what follows, it will be frequently necessary to consider distributions of currents in various directions through solid conductors, and it is therefore convenient at present to notice some elementary properties, and to define various terms, adapted for specifications of systems of electric currents and electro-motive forces, distributed in any manner whatever throughout a solid.

142. It is to be remarked, in the first place, that any portion of a solid traversed by current electricity may be divided, by tubular surfaces coinciding with lines of electric motion, into an infinite number of channels or conducting arcs, each containing an independent linear current. The *strength* of a linear current being, as before, defined to denote the quantity of electricity flowing across any section in the unit of time, we may now define the *intensity of the current*, at any point of a conductor, as the strength of a linear current of infinitely small transverse dimensions through this point, divided by the area of a normal section of its channel. The elementary proposition of the composition of motions, common to the cinematics of ordinary fluids and of electricity, shows that the superposition of two systems of currents in a body gives a resultant system, of which the intensity and direction at any point are represented by the diagonal of a parallelogram described upon lines representing the intensity and direction of the component systems

respectively. Hence we may define the components, along three lines at right angles to one another, of the intensity of electric current through any point of a body, as the products of the intensity of the current at that point into the cosines of the inclination of its direction to those three lines respectively; and we may regard the specification of a distribution of currents through a body as complete, when the components, parallel to three fixed rectangular axes of reference, of the intensity of the current at every point are specified.

143. The term electro-motive force has been applied, in what precedes, consistently with the ordinary usage, to the whole force urging electricity through a linear conducting arc. When a current is sustained through a conducting arc, by energy proceeding from sources belonging entirely to the remainder of the circuit, the electro-motive force may be considered as applied from without to its extremities; and in all such cases it may be measured—electro-statically, by determining in any way the difference of potential between two conducting bodies, insulated from one another and put in metallic communication with the extremities of the conducting arc;—or electro-dynamically, by applying to these points the extremities of another linear conductor, of infinitely greater resistance (practically, for instance, a long fine wire used as a galvanometer coil), and determining the strength of the current which it conveys when so applied. These tests may, of course, be regarded as giving either the amount of the electro-motive force with which the remainder of the circuit acts on, or the whole of the electro-motive force efficient in, the passive conducting arc first considered. On the other hand, the electro-motive force acting in the portion from which the energy proceeds is not itself determined by such tests, but is equal to the whole electro-motive force of the sources contained in it, diminished by the reaction of the force which is measured in the manner just explained. The same tests applied to any two points whatever of a complete conducting circuit, however the sources of energy are distributed through it, show simply the electro-motive force acting and reacting between the two parts into which the circuit might be separated by breaking it at these points. In some cases, for instance some of thermo-electric action which we shall have to consider, these tests would give a zero indication to whatever two points of a circuit through which a current is actually passing they are applied, and would therefore show that there is no electric action and reaction between different parts of the circuit, but that each part contains intrinsically the electro-motive force required to sustain the current through it at the existing rate. An actual test of the electro-motive force of sources contained in any part of a linear conductor is defined, with especial reference to the circumstances of thermo-electricity, in the following statement:—

144. Def. The actual intrinsic electro-motive force of any part of a linear conducting circuit is the difference of potential which it produces in two insulated conductors of a standard metal at one temperature, when its extremities are

connected with them by conducting arcs of the same metal, and insulated from the remainder of the circuit.

The electro-motive force so defined may be determined either by determining, by some electro-statical method, the difference of potentials in the two conductors of standard metal mentioned in the definition; or by measuring the strength of the current produced in a conducting arc of the standard metal of infinitely greater resistance than the given conducting arc, applied to connect its extremities, when insulated from the remainder of its own circuit.

145. With reference to the distribution of electro-motive force through a solid, the following definitions are laid down:—

DEF. 1. The intrinsic electro-motive force of a linear conductor at any point is the actual intrinsic electro-motive force in an infinitely small arc through this point, divided by its length.

DEF. 2. The efficient electro-motive force at any point of a linear conducting circuit is the sum of the actual intrinsic electro-motive force in an infinitely small arc, and the electro-motive force produced by the remainder of the circuit on its extremities, divided by its length.

DEF. 3. The intrinsic electro-motive force at any point in a solid, in any direction, is the electro-motive force that would be experienced by an infinitely thin conducting arc of standard metal, applied with its extremities to two points in a line with this direction, in an infinitely small portion insulated all round from the rest of the solid, divided by the distance between these points.

DEF. 4. The electro-motive force efficient at any point of a solid, in any direction, is the difference of the electro-motive forces that would be experienced by an infinitely thin conducting arc of standard metal, with its extremities applied to two points infinitely near one another in this direction, divided by the distance between the points, in the two cases separately of the solid being left unchanged, and of an infinitely small portion of it containing these points being insulated from the remainder.

146. Principle of the superposition of thermo-electric action. It may be assumed as an axiom, that each of any number of co-existing systems of electric currents produces the same reversible thermal effect in any locality as if it existed alone.

§§ 147–155. *On Thermo-electric Currents in Linear Conductors of Crystalline Substance.*

147. The general characteristic of crystalline matter is that physical agencies, having particular directions in the space through which they act, and depending on particular qualities of the substance occupying that space, take place with different intensities in different directions, if the substance be crystalline. Substances not naturally crystalline may have the crystalline characteristic induced in them by the action of some directional agency, such as mechanical strain or

magnetization; and may be said to be inductively crystalline. Or again, minute fragments of non-crystalline substances may be put together, so as to constitute solids, which, on a large scale, possess the general characteristic of homogeneous crystalline substances; and such bodies may be said to possess the crystalline characteristic by structure, or to be structurally crystalline.

148. As regards thermo-electric currents, the characteristic of crystalline substance must be, that bars cut from it in different directions would, when treated thermo-electrically as linear conductors, be found in different positions in the thermo-electric series; or that two bars cut from different directions in the substance would be thermo-electrically related to one another like different metals. This property has been experimentally demonstrated by SVANBERG, for crystals of bismuth and antimony; and there can be no doubt but that other natural metallic crystals will be found to possess it. I have myself observed, that the thermo-electric properties of copper and iron wires are affected by alternate tension and relaxation in such a manner, as to leave no doubt but that a mass of either metal, when compressed or extended in one direction, possesses different thermo-electric relations in different directions. Fragments of different metals may be put together so as to form solids, possessing by structure the thermo-electric characteristic of a crystal, in an infinite variety of ways. Thus, a structure consisting of thin layers alternately of two different metals, possesses obviously the thermo-electric qualities of a crystal with an axis of symmetry. I have investigated the thermo-electric properties in all directions of such a structure, in terms of the conducting powers for heat and electricity, and the thermo-electric powers, of the two metals of which it is composed; and bars made up of alternate layers of copper and iron, one with the layers perpendicular, another with the layers oblique, and a third with the layers parallel, to the length, illustrating the theoretical results, which were communicated along with this paper, were exhibited to the Royal Society. The principal advantage of considering metallic structures with reference to the theory of thermo-electricity is, as will be seen below, that we are so enabled to demonstrate the possibility of crystalline thermo-electric qualities of the most general conceivable type, and are shown how to construct solids (whether or not natural crystals may be ever found) actually possessing them.

149. The following two propositions with reference to thermo-electric effects in a particular case of crystalline matter are premised to the unrestricted treatment of the subject, because they will serve to guide us as to the nature of the agencies for which the general mathematical expressions are to be investigated.

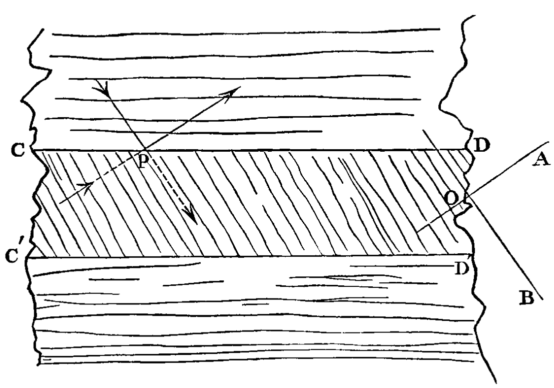
PROP. I. If a bar of crystalline substance, possessing an axis of thermo-electric symmetry, has its length oblique to this axis, a current of electricity sustained in it longitudinally will cause evolution of heat at one side, and absorption of heat at the opposite side, all along the bar, when the whole substance is kept at the same temperature.

PROP. II. If the two sides of such a bar be kept at different temperatures, and a homogeneous conducting arc be applied to points of the ends which are at the same temperature, a current will be produced along the bar, and through the arc completing the circuit.

150. For proving these propositions, it will be convenient to investigate fully the thermo-electric agency experienced by a bar cut obliquely from a crystalline substance possessing an axis of symmetry, when placed longitudinally in a circuit of which the remainder is composed of the standard metal, and kept with either its sides or its ends unequally heated. Let θ and ϕ denote the thermo-electric powers of two bars cut from the given substance in directions parallel and perpendicular to its axis of symmetry respectively. Let us suppose the actual bar to be of rectangular section with two of its opposite sides perpendicular to the plane of its length, and the axis of symmetry of its substance. Let a longitudinal section in this plane be represented by the accompanying diagram; let O A or any line parallel to it be the direction of the axis of symmetry through any point; and let ω denote the inclination of this line to the length of the bar. Let the breadth of the two opposite sides of the bar perpendicular to the plane of the diagram be denoted by a, and in the plane of the diagram, b. The area of the transverse section of the bar will be $a\,b$; and therefore if γ denote the strength, and i the intensity of the current in it, we have,—

$$i = \frac{\gamma}{a\,b}\,.$$

151. We may suppose the current, itself parallel to the length of the bar and in the direction from left to right of the diagram, to be resolved, at any point P at the side of the bar, into two components in directions parallel and perpendicular to O A, of which the intensities will be $i \cos \omega$, and $i \sin \omega$, respectively. The former of these components may be supposed to belong to a system of currents crossing the bar in lines parallel to O A and passing out of it, across the side C D, into a conductor of the standard metal: and the latter, to a system of currents entering the bar across C D, from the same conductor of standard metal, and crossing it in lines perpendicular to O A. The resultant current in the supposed standard metal beside the bar will clearly be parallel to the length, and can therefore (this metal being non-crystalline) produce no effect influencing the thermal agency at the side of the bar or within it. The inclinations of the currents to a perpendicular to the separating plane of the two metals being respectively $90° - \omega$ and ω, their strength per unit of area of this



plane, obtained by multiplying their intensities by the cosine of those angles respectively, will be each equal to

$$i \cos \omega \sin \omega .$$

Hence the absorptions of heat which they will produce at the surface of separation of the metals per unit of area per second will be,

$$-\frac{1}{J} i \cos \omega \sin \omega \, t \, \theta, \quad \text{and} \quad \frac{1}{J} i \cos \omega \sin \omega \, t \, \phi,$$

respectively. According to the general principle of the superposition of thermo-electric actions stated above, the sum of these is the rate of absorption of heat per unit of surface, when the two systems of currents coexist. But the resultant of these systems is simply the given longitudinal current in the bar, with no flow, either out of it or into it, across any of its sides. Hence, a simple current of intensity i, parallel to the sides of the bar, causes absorption of heat at the side C D, amounting to

$$\frac{1}{J} i \cos \omega \sin \omega \, t \, (\phi - \theta),$$

per unit of area per second; and the same demonstration shows that an equal amount of evolution must be produced at the opposite side C′ D′. These effects take place quite independently of the matter round the bar, since the metal carrying electric currents which we supposed to exist at the sides of the bar in the course of the demonstration, can exercise no influence on the phenomena.

152. If l denotes the length of the bar, the area of each of the sides perpendicular to the plane of the diagram will be $l\,a$; and therefore, the absorption over the whole of the side C D, and the evolution over the whole of the other side C′ D′, per second will be

$$\frac{1}{J} i \, l \, a \cos \omega \sin \omega \, t \, (\phi - \theta),$$

or

$$\frac{1}{J} \gamma \frac{l}{b} \cos \omega \sin \omega \, t \, (\phi - \theta).$$

It is obvious, that there can be neither evolution nor absorption of heat at the two other sides.

153. An investigation, similar to that which has just been completed, shows that if the actual current enter from a conductor of the standard metal at one end of the bar, and leave it by a conductor of the same metal at its other end, the absorption and evolution of heat at these ends respectively will amount to

$$\frac{1}{J} \gamma \, (t \, \theta \cos^2 \omega + t \phi \sin^2 \omega)$$

per second.

154. Let us now suppose the two sides C D, C′ D′ to be kept at uniform temperatures, T, T′, and the two ends to be kept with equal and similar distributions of temperatures, whether a current is crossing them or not. Then if a current of strength γ be sent through the bar from left to right of the diagram, in a circuit

of which the remainder is the standard metal, there will be reversible thermal action, consisting of the following parts, each stated per unit of time.

(1.) Absorption amounting to $\Omega(\mathrm{T})\frac{l}{b}\gamma$, in a locality at the temperature T.

(2.) Evolution amounting to $\Omega(\mathrm{T}')\frac{l}{b}\gamma$, in a locality at the temperature T′,

(3.) Absorption amounting to $\Pi\gamma$ at one end, (that beyond C C′,)

and (4.) Evolution amounting to $\Pi\gamma$ at the other end;

where, for brevity, $\Omega(\mathrm{T})$ and $\Omega(\mathrm{T}')$ are assumed to denote the values of $\frac{t}{\mathrm{J}}(\phi-\theta)\sin\omega\cos\omega$, at the temperatures T and T′; and Π the mean value of $\frac{t}{\mathrm{J}}(\theta\cos^2\omega+\phi\sin^2\omega)$ for either end of the bar. The contributions towards the sums appearing in the general thermo-dynamic equations which are due to these items of thermal agency, are as follows:—

$$\left[\Omega(\mathrm{T})-\Omega(\mathrm{T}')\right]\frac{l}{b}\gamma \qquad \text{towards } \Sigma\,\mathrm{H}_t,$$

and

$$\left[\frac{\Omega(\mathrm{T})}{\mathrm{T}}-\frac{\Omega(\mathrm{T}')}{\mathrm{T}'}\right]\frac{l}{b}\gamma \qquad \text{towards } \Sigma\,\frac{\mathrm{H}_t}{t};$$

the thermal agencies at the ends disappearing from each sum, in consequence of their being mutually equal and opposite, and being similarly distributed through localities equally heated. Now when every reversible thermal effect is included, the value of $\Sigma\frac{\mathrm{H}_t}{t}$ must be zero, according to the second general law. Hence either $\frac{\Omega(\mathrm{T})}{\mathrm{T}}-\frac{\Omega(\mathrm{T}')}{\mathrm{T}'}$ must vanish, or there must be a reversible thermal agency not yet taken into account. But probably $\frac{\Omega(\mathrm{T})}{\mathrm{T}}-\frac{\Omega(\mathrm{T}')}{\mathrm{T}'}$ may not vanish, that is, $\frac{\Omega}{t}$ may vary with the temperature, for natural crystals, and it certainly does vary with the temperature for metallic combinations structurally crystalline: (for a bar cut obliquely from a solid consisting of alternate layers of copper and iron, for instance, the value of Ω decreases to zero, as the temperature is raised from an ordinary atmospheric temperature up to about 280°, and has a contrary sign for higher temperatures.) Hence, in general, there must be another reversible thermal agency, besides the agencies at the ends and at the sides of the bar which we have investigated. This agency must be in the interior; and since the substance is homogeneous, and uniformly affected by the current, the new agency must be uniformly distributed through the length, as different points of the same cross section can only differ in virtue of their different circumstances as to temperature. If there were no variation of temperature, there could be no such effect anywhere in the interior of the bar; and therefore, if $d\,t$ denote the variation of temperature in an infinitely small space dx across the bar in the plane of the diagram, and χ an unknown element, constant or a function of the temperature, depending on the nature of the substance, we may assume

$$i\,\chi\,\frac{dt}{dx}$$

as the amount of absorption, per unit of the volume of the bar, due to a current of intensity i, by means of the new agency. The whole amount in a lamina of thickness $d\,x$, length l, and breadth a perpendicular to the plane of the diagram, is therefore

$$i\chi\,\frac{dt}{dx}\,a\,l\,dx,$$

or

$$\gamma\,\frac{l}{b}\,\chi\,dt.$$

As there cannot possibly be any other reversible thermal agency to be taken into account, we may now assume

$$\Sigma\,\mathrm{H}_t = \gamma\,\frac{l}{b}\left\{\Big[\Omega(\mathrm{T}) - \Omega(\mathrm{T}')\Big] + \int_{\mathrm{T}'}^{\mathrm{T}} \chi\,dt\right\} \quad . \quad . \quad . \quad (22),$$

$$\Sigma\,\frac{\mathrm{H}_t}{t} = \gamma\,\frac{l}{b}\left\{\frac{\Omega(\mathrm{T})}{\mathrm{T}} - \frac{\Omega(\mathrm{T}')}{\mathrm{T}'} + \int_{\mathrm{T}'}^{\mathrm{T}} \frac{\chi}{t}\,dt\right\} \quad . \quad . \quad . \quad . \quad (23).$$

The second General Law showing that $\Sigma\,\frac{\mathrm{H}_t}{t}$ must vanish, gives, by the second of these equations,

$$\frac{\Omega(\mathrm{T})}{\mathrm{T}} - \frac{\Omega(\mathrm{T}')}{\mathrm{T}'} + \int_{\mathrm{T}'}^{\mathrm{T}} \frac{\chi}{t}\,dt = 0 \quad . \quad . \quad . \quad . \quad (24).$$

Substituting, in place of T, t, and differentiating with reference to this variable, we have, as an equivalent equation,

$$\frac{\chi}{t} = -\,\frac{d\,\frac{\Omega}{t}}{dt} - \frac{d\,\frac{\Omega}{t}}{dt} \quad . \quad . \quad . \quad . \quad . \quad (25);$$

and using this in (22), we have

$$\Sigma\,\mathrm{H}_t = \gamma\,\frac{l}{b}\int_{\mathrm{T}'}^{\mathrm{T}} \frac{\Omega}{t}\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (26).$$

This expresses the full amount of heat taken in through the agency of the current γ; of which the mechanical equivalent is therefore the work done by the current. Hence (according to principles fully explained above) the thermal circumstances actually cause an electro-motive force F, of which the amount is given by the equation

$$\mathrm{F} = \mathrm{J}\,\frac{l}{b}\int_{\mathrm{T}'}^{\mathrm{T}} \frac{\Omega}{t}\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (27),$$

to act along the bar from left to right of the diagram; which will produce a current, unless balanced by an equal and contrary reaction. This result both establishes Proposition II., enunciated above in § 149, and shows the amount of the electro-motive force producing the stated effect, in terms of T and T′, the temperatures of the two sides of the bar, the obliquity of the bar to the crystalline axis of symmetry, and the thermo-electric properties of the substance; since, if θ and ϕ denote its thermo-electric powers, along the axis of symmetry, and along lines perpendicular to this axis, at the temperature t, and ω the inclination of this axis to the length of the bar when the substance is at the temperature t, we have

$$\Omega = \frac{t}{\mathrm{J}}(\phi - \theta)\sin\omega\cos\omega \quad . \quad . \quad . \quad . \quad (28).$$

155. By an investigation exactly similar to that of § 115 which had reference to non-crystalline linear conductors, we deduce the following expression for the electro-motive force, when the ends of the bar are kept at temperatures T, T′, from the terminal thermal agency Π, of a current investigated in § 153.

$$\mathrm{F} = \mathrm{J}\int_{\mathrm{T}'}^{\mathrm{T}} \frac{\Pi}{t}\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (29),$$

where

$$\Pi = \frac{t}{\mathrm{J}}(\theta\cos^2\omega + \phi\sin^2\omega) \quad . \quad . \quad . \quad . \quad . \quad (30).$$

§§ 156–170. *On the Thermal Effects and the Thermo-electric Excitation of Electrical Currents in Homogeneous Crystalline Solids.*

156. The Propositions I. and II., investigated above, suggest the kind of assumptions to be made regarding the reversible thermal effects of currents in uniformly heated crystalline solids, and the electro-motive forces induced by any thermal circumstances which cause inequalities of temperature in different parts. The formulæ expressing these agencies in the particular case which we have now investigated, guide us to the precise forms required to express those assumptions in the most general possible manner.

157. Let us first suppose a rectangular parallelepiped (a, b, c) of homogeneous crystalline conducting matter, completely surrounded by continuous metal of the standard thermo-electric quality touching it on all sides, to be traversed in any direction by a uniform electric current, of which the intensity components parallel to the three edges of the parallelepiped are h, i, j, and to be kept in all points at a uniform temperature t. Then taking ϕ, θ, ψ, to denote the thermo-electric powers of bars of the substance cut from directions parallel to the edges of the parallelepiped, quantities which would be equal to one another in whatever directions those edges are if the substance were non-crystalline; and θ' θ'', ϕ', ϕ'', ψ', ψ'', other elements depending on the nature of the substance with reference to the directions of the sides of the parallelepiped, to which the name of thermo-electric obliquities may be given, and which must vanish for every system of rectangular

planes through the substance, if it be non-crystalline; we may assume the following expression for the reversible thermal effects of the current:—

$$\left.\begin{aligned} Q_{(b\,c)} &= b\,c\,\frac{t}{J}\,(h\,\theta + i\,\phi'' + j\,\psi') \\ Q_{(c\,a)} &= c\,a\,\frac{t}{J}\,(h\,\theta' + i\,\phi + j\,\psi'') \\ Q_{(a\,b)} &= a\,b\,\frac{t}{J}\,(h\,\theta'' + i\,\phi' + j\,\psi) \end{aligned}\right\} \quad . \quad . \quad (31),$$

where $Q_{(b\,c)}$, $Q_{(c\,a)}$, $Q_{(a\,b)}$, denote quantities of heat absorbed per second at the sides by which positive current components enter, and quantities evolved in the same time at the opposite sides. Hence, if the opposite sides be kept at different temperatures, currents will pass, unless prevented by the resistance of surrounding matter; and the electro-motive forces by which these currents are urged, in directions parallel to the three edges of the parallelepiped, have the following expressions, in which $u\,a$, $v\,b$, and $w\,c$ denote the difference of temperature between corresponding points in the pairs of sides $b\,c$, $c\,a$, and $a\,b$, respectively reckoned positive, when the temperature increases in the direction of positive components of current;

$$\left.\begin{aligned} E &= -a\,(u\,\theta + v\,\theta' + w\,\theta'') \\ F &= -b\,(u\,\phi'' + v\,\phi + w\,\phi') \\ G &= -c\,(u\,\psi' + v\,\psi'' + w\,\psi) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (32).$$

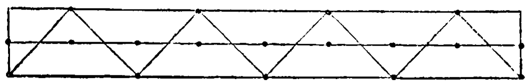
The negative signs are prefixed, in order that positive values of the electro-motive components may correspond to forces in the direction assumed for positive components of current.

158. The most general conceivable elementary type of crystalline thermo-electric properties is expressed in the last equations, along with the equations (31) by which we arrived at them, and we shall see that every possible case of thermo-electric action in solids of whatever kind may be investigated by using them with values, and variations it may be, of the coefficients ϕ, θ, &c., suitable to the circumstances. It might be doubted, indeed, whether these nine coefficients can be perfectly independent of one another; and indeed it might appear very probable that they are essentially reducible to six independent coefficients, from the extraordinary nature of certain conclusions which we shall show can only be obviated by supposing

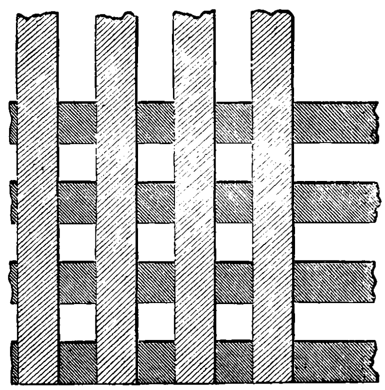
$$\theta' = \phi'', \quad \theta'' = \psi', \quad \text{and} \quad \phi' = \psi''.$$

Before going on to investigate any consequences from the unrestricted fundamental equations, I shall prove that it is worth while to do so, by demonstrating that a metallic structure may be actually made, which, when treated on a large scale as a continuous solid, according to the electric and thermal conditions specified for the substance with reference to which the equations (31) and (32) have been applied, shall exhibit the precise electric and thermal properties respectively expressed by those sets of equations with nine arbitrarily prescribed values for the coefficients θ, ϕ, &c.

159. Let two zigzag linear conductors of equal dimensions, each consisting of infinitely short equal lengths of infinitely fine straight wire alternately of two different metals, forming right angles at the successive junctions, be placed in perpendicular planes, and touching one another at any point, but with a common straight line joining the points of bisection of the small straight parts of each



conductor. Let an insulating substance be moulded round them, so as to form a solid bar of square section, just containing the two zigzags imbedded in it in planes parallel to its sides. Although this substance is a non-conductor of electricity, we may suppose it to have enough of conducting power for heat, or the wires of the electric conductors to be fine enough, that the conduction of heat through the bar when it is unequally heated may be sensibly the same as if its substance were homogeneous throughout, and, consequently, that the electric conductors take at every point the temperatures which the bar would have at the same point if they were removed. Let an infinite number of such bars, equal and similar, and of the same substance, be constructed; and let a second system of equal and similar bars be constructed with zigzag conductors of different metals from the former; and a third with other different metals: the sole condition imposed on the different zigzag conductors being that the two in each bar, and those in the bars of different systems, exercise the same resistance against electric conduction. Let an infinite number of bars of the first set be laid on a plane, parallel to one another, with intervals between every two in order, equal to the breadth of each. Lay perpendicularly across them



an infinite number of bars of the second system similarly disposed relatively to one another; place on these again bars of the first system, constituting another layer similar and parallel to the first; on this, again, a layer similar and parallel to the second; and so on, till the thickness of the superimposed layers is equal to the length of each bar. Then let an infinite number of the bars of the third system be taken and pushed into the square prismatic apertures perpendicular to the plane of the layers; the cubical hollows which are left (not visible in the diagram) being previously filled up with insulating matter, such as that used in the composition of the bars. Let the complex solid cube thus formed be coated round its sides with infinitely thin connected sheets of the standard metal, so thin that the resistance to the conduction of electricity along them is infinitely great, compared to the resistance to conduction experienced by a current traversing the interior of the cube by the zigzag linear conductors imbedded in it. (For instance, we may suppose the resistance of four parallel sides of the cube to be as great as, or greater than, the resistance of each one of the zigzag linear conductors.) Let an infinite number of such cubes be built together, with their structural directions preserved parallel, so as to form a solid, which, taken on a large scale, shall be homogeneous. A rectangular parallelepiped, $a\,b\,c$, of such a solid, with its sides parallel to the sides of the elementary cubes, will present exactly the thermo-electric phenomena expressed above by the equations (31) and (32) provided the thermo-electric powers ϖ_1, ϖ_1', ϖ_1'', ϖ_1''', ϖ_2, ϖ_2', ϖ_2'', ϖ_2''', and ϖ_3, ϖ_3', ϖ_3'', ϖ_3''', of the metals used in the three systems, fulfil the following conditions:—

$$\left.\begin{array}{ll}\tfrac{1}{4}(\varpi_1 + \varpi'_1 + \varpi_1'' + \varpi_1''') = \theta, & \\ \tfrac{1}{4}(\varpi_1 - \varpi_1') = \theta', & \tfrac{1}{4}(\varpi_1'' - \varpi_1''') = \theta'', \\ \tfrac{1}{4}(\varpi_2 + \varpi_2' + \varpi_2'' + \varpi_2''') = \phi, & \\ \tfrac{1}{4}(\varpi_2 - \varpi_2') = \phi', & \tfrac{1}{4}(\varpi_2'' - \varpi_2''') = \phi'', \\ \tfrac{1}{4}(\varpi_3 + \varpi_3' + \varpi_3'' + \varpi_3''') = \psi, & \\ \tfrac{1}{4}(\varpi_3 - \varpi_3') = \psi', & \tfrac{1}{4}(\varpi_3'' - \varpi_3''') = \psi''.\end{array}\right\} \quad . \quad . \quad . \quad (33).$$

160. To prove this, let us first consider the condition of a bar of any of the three systems, taken alone, and put in the same thermal circumstances as those in which each bar of the same system exists in the compound mass. If, for instance, we take a bar of the first system, we must suppose the temperature to vary at the rate u per unit of space along its length; at the rate v across it, perpendicularly to two of its sides; and at the rate w across it, perpendicular to its other two sides. If l be its length, and e the breadth of each side, its ends will differ in temperature by $u\,l$; corresponding points in one pair of its sides by $v\,e$, and corresponding points in the other pair of sides, by $w\,e$. Now, it is easily proved that the longitudinal electro-motive force (that is, according to the definition, the electro-motive force between conductors of the standard metal) would, with no difference of temperatures between its sides, and the actual difference $u\,l$ between its ends, be equal to $\frac{1}{2}(\varpi_1 + \varpi_1')\,u\,l$, if only the first of the zigzag conductors existed imbedded in the bar, or equal to $\frac{1}{2}(\varpi_1'' + \varpi_1''')\,u\,l$, if only the second; and, since the two have equal resistances to conduction, and are connected by a little square disc of the standard metal, it follows that the longitudinal electro-motive force of the actual bar, with only the longitudinal variation of temperature, is

$$\tfrac{1}{4}(\varpi_1 + \varpi_1' + \varpi_1'' + \varpi_1''')\,u\,l.$$

Again, with only the lateral variation $v\,e$, we have in one of the zigzags a little thermo-electric battery, of a number of elements amounting to the greatest integer in $\frac{l}{2\,e}$, which is sensibly equal to $\frac{l}{2\,e}$, since the value of this is infinitely great; the electro-motive force of each element is $(\varpi_1 - \varpi_1{}')\,v\,e$; and, therefore, the whole electro-motive force of the zigzag is $\frac{l}{2\,e} \times (\varpi - \varpi_1{}')\,v\,e$, or $\frac{1}{2}\,l \times (\varpi_1 - \varpi_1{}')\,v$. This battery is part of a complete circuit with the little terminal squares and the other zigzag, and therefore its electro-motive force will sustain a current in one direction through itself, and in the contrary through the second zigzag; but since the resistances are equal in the two zigzags, and those of the terminal connections may be neglected, just half the electro-motive force of the first zigzag, being equal to the action and reaction between the two parts of the circuit, must remain ready to act between conductors applied to the terminal discs of the standard metal. In the circumstances now supposed, the second zigzag is throughout at one temperature, and therefore has no intrinsic electro-motive force; and the resultant intrinsic electro-motive force of the bar is therefore

$$\tfrac{1}{4}\,l\,(\varpi_1 - \varpi_1{}')\,v\,.$$

Similarly, if there were only the lateral variation $w\,e$ of temperature in the bar, we should find a resultant longitudinal electro-motive force equal to

$$\tfrac{1}{4}\,l\,(\varpi_1{}'' - \varpi_1{}''')\,w\,.$$

If all the three variations of temperature are maintained simultaneously, each will produce its own electro-motive force, as if the others did not exist, and the resultant electro-motive force due to them all will therefore be,—

$$\frac{l}{4}\left\{(\varpi_1 + \varpi_1{}' + \varpi_1{}'' + \varpi_1{}''')\,u + (\varpi_1 - \varpi_1{}')\,v + (\varpi_1{}'' - \varpi_1{}''')\,w\right\}.$$

This being the electro-motive force of each bar of the first system in any of the cubes composing the actual solid, must be the component electro-motive force of each cube in the direction to which they are parallel; and, therefore,

$$a\,\tfrac{1}{4}\left\{(\varpi_1 + \varpi_1{}' + \varpi_1{}'' + \varpi_1{}''')\,u + (\varpi_1 - \varpi_1{}')\,v + (\varpi_1{}'' - \varpi_1{}''')\,w\right\}$$

must be the component electro-motive force of the entire parallelepiped in the same direction. Similar expressions give the component electro-motive forces parallel to the edges b and c of the solid, which are similarly produced by the bars of the second and third systems, and we infer the proposition which was to be proved.

161. Cor. By choosing metals of which the thermo-electric relations, both to the standard metal and to one another, vary, we may not only make the nine coefficients have any arbitrarily given values for a particular temperature, but we may make them each vary to any extent with a given change of temperature.

162. For the sake of convenience in comparing the actual phenomena of thermo-electric force in different directions presented by an unequally heated crystal-

line solid; let us now, instead of a parallelepiped imbedded in the standard metal, consider an insulated sphere of the crystalline substance, with sources of heat and cold applied at its surface, so as to maintain a uniform variation of temperature in all lines perpendicular to the parallel isothermal planes. Let the rate of variation of temperature per unit of length, perpendicular to the isothermal surfaces, be q, and let the cosines of the inclinations of this direction to the three rectangular directions in the substance to which the edges of the parallelepiped first considered were parallel, and which we shall now call the lines of reference, be l, m, n, respectively. Then if we take

$$q\,l = u, \quad q\,m = v, \quad q\,n = w,$$

the substance of the sphere will be in exactly the same thermal condition as an equal spherical portion of the parallelepiped; and it is clear that the preceding expressions for the component electro-motive forces of the parallelepiped will give the electro-motive forces of the sphere between the pairs of points at the extremities of diameters coinciding with the rectangular lines of reference, if we take each of the three quantities, a, b, c, equal to the diameter of the sphere. Calling this unity, then we have

$$\left.\begin{aligned} -\mathrm{E} &= u\,\theta + v\,\theta' + w\,\theta'' \\ -\mathrm{F} &= u\phi'' + v\,\phi + w\,\phi' \\ -\mathrm{G} &= u\,\psi' + v\,\psi'' + w\,\psi \end{aligned}\right\} \quad . \quad . \quad . \quad (34).$$

According to the definition given above (§ 144, Def. 3), it appears that these quantities, E, F, G, are the three components of *the intrinsic electro-motive force at any point in the substance*, whether the portion of it we are considering be limited and spherical, or rectangular, or of any other shape, or be continued to any indefinite extent by homogeneous or heterogeneous solid conducting matter with any distribution of temperature through it. The component electro-motive force P along a diameter of the sphere inclined to the rectangular lines of reference at angles whose cosines are l, m, n, is of course given by the equation

$$\mathrm{P} = \mathrm{E}\,l + \mathrm{F}\,m + \mathrm{G}\,n \quad . \quad . \quad . \quad . \quad . \quad (35),$$

which may also be employed to transform the general expressions for the components of the electro-motive force to any other lines of reference.

163. A question now naturally presents itself, Are there three principal axes at right angles to one another in the substance possessing properties of symmetry, with reference to the thermo-electric qualities, analogous to those which have been established for the dynamical phenomena of a solid rotating about a fixed point, and for electro-statical and for magnetic forces, in natural crystals or in substances structurally crystalline as regards electric or magnetic induction? The following transformation, suggested by Mr STOKES' paper on the Conduction of Heat in Crystals,* in which a perfectly analogous transformation is applied to the

* Cambridge and Dublin Mathematical Journal.

most general conceivable equations expressing flux of heat in terms of variations of temperature along rectangular lines of reference in a solid, will show the nature of the answer.

164. The direction cosines of the line of greatest thermal variation, or the perpendicular to the isothermal planes, are $\frac{u}{q}, \frac{v}{q}, \frac{w}{q}$, where q, denoting the rate of variation of temperature in the direction of that line, is given by the equation

$$q = (u^2 + v^2 + w^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (36).$$

Taking these values for l, m, n, in the preceding general expression for the electro-motive force in any direction, we find

$$P = \frac{1}{q}\left\{ \theta\, u^2 + \phi\, v^2 + \psi\, w^2 + (\phi' + \psi'')\, v\, w + (\psi' + \theta'')\, w\, u + (\theta' + \phi'')\, u\, v \right\}$$

the negative sign being omitted on the understanding that P shall be considered positive when the electro-motive force is from hot to cold in the substance. This formula suggests the following changes in the notation expressing the general thermo-electric coefficients:—

$$\left.\begin{array}{l} \phi' + \psi'' = 2\,\theta_1, \quad \psi' + \theta'' = 2\,\phi_1, \quad \theta' + \phi'' = 2\,\psi_1 \\ -\phi' + \psi'' = 2\,\zeta, -\psi' + \theta'' = 2\,\eta, \quad -\theta' + \phi'' = 2\,\vartheta \end{array}\right\} \quad . \quad . \quad . \quad . \quad (37),$$

which reduce the general equations, and the formula itself which suggests them, to—

$$\left.\begin{array}{l} -\mathrm{E} = \theta\, u + \psi_1\, v + \phi_1\, w + (\eta\, w - \vartheta\, v) \\ -\mathrm{F} = \psi_1\, u + \phi\, v + \theta_1\, w + (\vartheta\, u - \zeta\, w) \\ -\mathrm{G} = \phi_1\, u + \theta_1\, v + \psi\, w + (\zeta\, v - \eta\, u) \end{array}\right\} \quad . \quad . \quad . \quad (38),$$

$$P = \frac{1}{q}\left(\theta\, u^2 + \phi\, v^2 + \psi\, w^2 + 2\,\theta_1\, v\, w + 2\,\phi_1\, w\, u + 2\,\psi_1\, u\, v\right) \quad . \quad . \quad . \quad (39).$$

165. The well-known process of the reduction of the general equation of the second degree shows that three rectangular axes may be determined for which the coefficients θ_1, ϕ_1, ψ_1, in these expressions vanish, and for which, consequently, the equations become

$$\left.\begin{array}{l} -\mathrm{E} = \theta\, u + (\eta\, w - \vartheta\, v) \\ -\mathrm{F} = \phi\, v + (\vartheta\, u - \zeta\, w) \\ -\mathrm{G} = \psi\, w + (\zeta\, v - \eta\, u) \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (40),$$

$$P = \frac{1}{q}\left(\theta\, u^2 + \phi\, v^2 + \psi\, w^2\right) \quad . \quad . \quad . \quad . \quad (41).$$

166. The law of transformation of the binomial terms $(\eta\, w - \vartheta\, v)$, &c., in these expressions is clearly, that if ρ denote a quantity independent of the lines of reference, and expressing a specific thermo-electric quality of the substance, which I shall call its thermo-electric rotatory power, and if λ, μ, ν denote the inclinations of a cer-

tain axis fixed in the substance, which I shall call its axis of thermo-electric rotation to any three rectangular lines of reference, then the values of ζ, η, ϑ for these lines of reference are as follows:—

$$\zeta = \varrho \cos \lambda\,, \quad \eta = \varrho \cos \mu\,, \quad \vartheta = \varrho \cos \nu.$$

If i denote the inclination of the direction $\left(\frac{u}{q}, \frac{v}{q}, \frac{w}{q}\right)$, in which the temperature varies most rapidly, to the axis of thermo-electric rotation, and if α, β, γ denote the angles at which a line perpendicular to the plane of this angle i is inclined to the axes of reference, we have

$$\left.\begin{aligned} \eta w - \vartheta v &= \varrho\, q \sin i \cos \alpha \\ \vartheta u - \zeta w &= \varrho\, q \sin i \cos \beta \\ \zeta v - \eta u &= \varrho\, q \sin i \cos \gamma \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (42).$$

Hence we see that the last terms of the general formula for the component electro-motive forces along the lines of reference express the components of an electro-motive force acting along a line perpendicular both to the axis of thermo-electric rotation, and to the direct line from hot to cold in the substance, and equal in magnitude to the greatest rate of variation of temperature perpendicular to that axis, multiplied by the coefficient ϱ.

167. Or again, if we consider a uniform circular ring, of rectangular section, cut from any plane of the substance inclined at an angle λ to a plane perpendicular to the axis of thermo-electric rotation, and if the temperature of the outer and inner cylindrical surfaces of this ring be kept each uniform, but different from one another, so that there may be a constant rate of variation, q, of temperature in the radial direction, but no variation either tangentially or in the transverse direction perpendicular to the plane of the ring, we find immediately, from (42), that the last terms of the general expressions indicate a tangential electro-motive force, equal in value to $\varrho\, q \cos \lambda$, acting uniformly all round the ring. This tangential force vanishes if the plane of the ring contain the axis of thermo-electric rotation, and is greatest when the ring is in a plane perpendicular to the same axis.

168. The peculiar quality of a solid expressed by these terms would be destroyed by cutting it into an infinite number of plates of equal infinitely small thickness, inverting every second plate, and putting them all together again into a continuous solid; a process which would clearly not in any way affect the thermo-electric relations expressed by the first term of the general expressions for the components of electro-motive force: and it is therefore of a type, to which also belongs the rotatory property with reference to light discovered by FARADAY as induced by magnetization in transparent solids, which I shall call dipolar, to distinguish it from such a rotatory property with reference to light as that which is naturally possessed by many transparent liquids and solids, and which may be called an

isotropic rotatory property. The axis of thermo-electric rotation, since the agency distinguishing it as a line, also distinguishes between the two directions in it, may be called a dipolar axis; so may the axis of rotation of a rotating rigid body,* or the direction of magnetization of a magnetized element of matter; and its general type is obviously different from that of a principal axis of inertia of a rigid body, or a principal axis of magnetic inductive capacity in a crystal, or a line of mechanical tension in a solid; any of which may be called an isotropic axis.

169. The general directional properties expressed by the first terms of the second members of (40) are perfectly symmetrical regarding the three rectangular lines of reference, and are of a type so familiar that they require no explanation here. We conclude that every substance has three principal isotropic axes of maximum and minimum properties regarding thermo-electric power, which are at right angles to one another; but that it is only for a particular class of conceivable substances that the thermo-electric properties are entirely symmetrical with reference to these axes; all substances from which the rotatory power, ϱ, does not vanish, having besides a dipolar axis of thermo-electric rotation which may be inclined in any way to them.

170. These principal isotropic axes lose distinction from all other directions in the solid, when the thermo-electric powers along them (the values of the coefficients θ, ϕ, ψ) are equal; but a rotatory property, distinguishing a certain line as a dipolar axis, may still exist. By § 159, we see how metallic structures possessing any of these properties (for instance having equal thermo-electric power in all directions, and possessing a given rotatory power, ϱ, in a given direction about a given system of parallel lines), may be actually made.

171. [*Added, July* 1854.] It is far from improbable that a piece of iron in a state of magnetization, which I have, since § 147 was written, ascertained to possess different thermo-electric properties in different directions, may also possess rotatory thermo-electric power,† distinguishing its axis of magnetization, which is essentially, in its magnetic character, dipolar, as thermo-electrically dipolar also.

§§ 172–181.—*On the general equations of Thermo-Electric Action in any homogeneous or heterogeneous crystallized or non-crystallized solid.*

172. Let t denote the absolute temperature at any point, x, y, z, of a solid. Let θ, ϕ, ψ, θ', ϕ', ψ', θ'', ϕ'', ψ'', be the values of the nine thermo-electric coefficients,

* [*Added, Liverpool, Sept.*, 27, 1854.]—As is perfectly illustrated by M. Foucault's beautiful experiment of a rotating solid, placing its axis parallel to that of the earth's, and so turned that it may itself be rotating in the same direction as the earth; which the meeting of the British Association just concluded has given me an opportunity of witnessing.

† [*Added, Sept.* 13, 1854.]—By an experiment made to test its existence, which has given only negative results, I have ascertained that this "rotatory power" if it exists in inductively magnetized iron at all, must be very small in comparison with the amount by which the thermo-electric power, in the direction of magnetization, differs from the thermo-electric power of the same metal not magnetized.

for the substance at this point, quantities which may vary from point to point, either by heterogeneousness of the solid, or in virtue of non-uniformity of its temperature. Let h, i, j be the components of the intensity of electric current through the same point (x, y, z).

173. Then, applying equations (31) of § 157 to infinitely small contiguous rectangular parallelepipeds in the neighbourhood of the point (x, y, z), and denoting by $\mathrm{H}\,dx\,dy\,dz$ the resultant reversible absorption of heat occasioned by the electric current across the infinitely small element $dx\,dy\,dz$, we find

$$\mathrm{H}=\frac{t}{\mathrm{J}}\left\{\frac{d}{dx}(h\,\theta+i\,\phi''+j\,\psi')+\frac{d}{dy}(h\,\theta'+i\,\phi+j\,\psi'')+\frac{d}{dz}(h\,\theta''+i\,\phi'+j\psi)\right\} \quad . \quad . \quad (43).$$

174. By the analysis of discontinuous functions this expression may be applied not only to homogeneous or to continuously varying heterogeneous substances, but to abrupt transitions from one kind of substance to another. Still it may be convenient to have formulæ immediately applicable to such cases, and therefore I add the following expression for the reversible thermal effect in any part of the bounding surface separating the given solid from a solid of the standard metal in contact with it.

$$\mathrm{Q}=\frac{t}{\mathrm{J}}\left\{p\,(h\,\theta+i\,\phi''+j\,\psi')+q\,(h\,\theta'+i\,\phi+j\,\psi'')+r\,(h\,\theta''+i\,\phi'+j\,\psi)\right\} \quad . \quad . \quad (44),$$

where Q denotes the quantity of heat absorbed per second per unit of surface at a point of the bounding surface, and (p, q, r) the direction cosines of a normal at the point.

175. Equations (34) give explicitly the intrinsic electro-motive force at any point of the solid, when the distribution of temperature is given; but we must take into account also the reaction proceeding from the surrounding matter, to get the efficient electro-motive force determining the current through any part of the body. This reaction will be the electro-statical resultant force due to accumulations of electricity at the bounding surface and in the interior of the conducting mass throughout which the electrical circuits are completed. Hence if V denote the electrical potential at (x, y, z) due to these accumulations, the components of the reactional electro-motive force are—

$$-\frac{d\mathrm{V}}{dx}, \quad -\frac{d\mathrm{V}}{dy}, \quad -\frac{d\mathrm{V}}{dz};$$

and the components of the efficient electro-motive force in the solid, are therefore—

$$\mathrm{E}-\frac{d\mathrm{V}}{dx}, \quad \mathrm{F}-\frac{d\mathrm{V}}{dy}, \quad \mathrm{G}-\frac{d\mathrm{V}}{dz},$$

where E, F, G are given by the following equations, derived from (34) by substituting for u, v, w, their values $\frac{dt}{dx}, \frac{dt}{dy}, \frac{dt}{dz}$, in terms of the notation now introduced:—

$$\left.\begin{aligned} -\mathrm{E} &= \frac{dt}{dx}\theta + \frac{dt}{dy}\theta' + \frac{dt}{dz}\theta'' \\ -\mathrm{F} &= \frac{dt}{dx}\phi'' + \frac{dt}{dy}\phi + \frac{dt}{dz}\phi' \\ -\mathrm{G} &= \frac{dt}{dx}\psi' + \frac{dt}{dy}\psi'' + \frac{dt}{dz}\psi \end{aligned}\right\} \quad . \quad . \quad . \quad (45).$$

176. The body, being crystalline, probably possesses different electrical conductivities in different directions, and the relation between current and electro-motive force cannot, without hypothesis, be expressed with less than nine coefficients. These, which we shall call the coefficients of electric conductivity, we shall denote by κ, λ, &c.; and we have the following equations, expressing by means of them the components of the intensity of electric current in terms of the efficient electro-motive force at any point of the solid:—

$$\left.\begin{aligned} h &= \kappa\left(\mathrm{E} - \frac{d\mathrm{V}}{dx}\right) + \kappa'\left(\mathrm{F} - \frac{d\mathrm{V}}{dy}\right) + \kappa''\left(\mathrm{G} - \frac{d\mathrm{V}}{dz}\right) \\ i &= \lambda''\left(\mathrm{E} - \frac{d\mathrm{V}}{dx}\right) + \lambda\left(\mathrm{F} - \frac{d\mathrm{V}}{dy}\right) + \lambda'\left(\mathrm{G} - \frac{d\mathrm{V}}{dz}\right) \\ j &= \mu'\left(\mathrm{E} - \frac{d\mathrm{V}}{dx}\right) + \mu''\left(\mathrm{F} - \frac{d\mathrm{V}}{dy}\right) + \mu\left(\mathrm{G} - \frac{d\mathrm{V}}{dz}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (46).$$

These equations (45) and (46), with

$$\frac{dh}{dx} + \frac{di}{dy} + \frac{dj}{dz} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47),$$

which expresses that as much electricity flows out of any portion of the solid as into it, in any time, (in all seven equations,) are sufficient to determine the seven functions E, F, G, V, h, i, j, for every point of the solid, subject to whatever conditions may be prescribed for the bounding surface, and so to complete the problem of finding the motion of electricity across the body in its actual circumstances; provided the values of $\frac{dt}{dx}$, $\frac{dt}{dy}$, $\frac{dt}{dz}$ are known, as they will be when the distribution of temperature is given. We may certainly, in an electrical problem such as this, suppose the temperature actually given at every point of the solid considered, since we may conceive thermal sources distributed through its interior to make the temperature have an arbitrary value at every point.

177. Yet practically the temperature will, in all ordinary cases, follow by conduction from given thermal circumstances at the surface. The equations of motion of heat, by which, along with those of thermo-electric force, such problems may be solved, are as follows:—(1) Three equations,

$$\left.\begin{aligned} \zeta &= -\left(k\,\frac{dt}{dx} + k'\,\frac{dt}{dy} + k''\frac{dt}{dz}\right) \\ \eta &= -\left(l''\,\frac{dt}{dx} + l\,\frac{dt}{dy} + l'\,\frac{dt}{dz}\right) \\ \vartheta &= -\left(m'\,\frac{dt}{dx} + m''\,\frac{dt}{dy} + m\,\frac{dt}{dz}\right) \end{aligned}\right\} \quad \ldots \ldots \quad (48).$$

to express the components ζ, η, ϑ of the "flux of heat" at any point of the solid, in terms of the variations of temperature $\left(\frac{dt}{dx}, \frac{dt}{dy}, \frac{dt}{dz}\right)$ multiplied by coefficients k, l, m, k', &c., which may be called the nine coefficients of thermal conductivity of the substance;—and (2) the single equation,

$$\frac{d\zeta}{dx}+\frac{d\eta}{dy}+\frac{d\vartheta}{dz} = -\frac{t}{\mathrm{J}}\left\{\frac{d}{dx}\,(h\,\theta+i\,\phi''+j\,\psi')+\frac{d}{dy}\,(h\,\theta'+i\,\phi+j\,\psi'')+\frac{d}{dz}\,(h\,\theta''+i\,\phi'+j\,\psi)\right\}$$
$$+\frac{1}{\mathrm{J}}\left\{h\left(\mathrm{E}-\frac{d\mathrm{V}}{dx}\right)+i\left(\mathrm{F}-\frac{d\mathrm{V}}{dy}\right)+j\left(\mathrm{G}-\frac{d\mathrm{V}}{dz}\right)\right\} \quad \ldots \quad (49)$$

of which the first member expresses the rate at which heat flows out of any part of the solid per unit of volume, and the second member, to which it is equated, the resultant thermal agency (positive when there is on the whole evolution at $x\,y\,z$ produced by the electric currents.

178. The general treatment of these eleven equations (45), (46), (47), (48), (49), leads to two non-linear partial differential equations of the second order and degree for the determination of the functions t and V.

179. It may be remarked, however, that the second term of the second member of (49), when the prefixed negative sign is removed, expresses the frictional generation of heat by currents through the solid, and will, therefore, when the electro-motive forces in action are solely thermo-electric, be very small, even in comparison with the reversible generation and absorption of heat in various parts of the circuit, provided the differences of temperature between these different localities are small fractions of the temperature, on the absolute scale from its zero. Excepting then cases in which there are wide ranges (for instance, of 50° Cent. or more) of temperature, the second principal term of the second member of (49) may be neglected, and the partial differential equations to which t and V are subject will become linear; so that one of the unknown functions may be readily eliminated, and a linear equation of the fourth order obtained for the determination of the other.

180. Farther, it may be remarked that probably in most, if not in all known cases, the reversible as well as the frictional thermal action of the currents, when excited by thermo-electric force alone, is very small in comparison with that of conduction, perhaps quite insensible. [See above, § 106.] Hence, except when more powerful electro-motive forces than the thermo-electric forces of the solid itself and of its relation to the conductors touching it at any part of its surface,

act to drive currents through it, we may, possibly in all, certainly in many cases, neglect the entire second member of (49) without sensible loss of accuracy; and we then have a differential equation of the second order for the determination of the temperature in the interior of the body, simply from ordinary conduction, according to the conditions imposed on its surface. To express these last conditions generally, a superficial application of the three equations (48) with their nine independent coefficients is required.

181. When t is either given or determined in any way, the solution of the purely electrical problem is, as was remarked above, to be had from the seven equations (45), (46), and (47). These lead to a single partial differential equation of the second order for the determination of V through the interior, subject to conditions as to electro-motive force and electrical currents across the surface, for the expression of which superficial applications of (45) and (46) will be required. When V is determined, the solution of the problem is given (45) and (46) expressing respectively the electro-motive force and the motion of electricity through the solid.

[*Additional Note Regarding the Discovery of Thermo-electric Inversions.*]

In a foot-note on the passage quoted above from the Proceedings of the Royal Society of London I referred to phenomena observed in the use of certain alloys of bismuth and antimony in thermo-electric circuits completed by copper and by silver, as constituting the first discovery of thermo-electric inversions, having been described by Professor CUMMING, in a paper published as early as 1823 in the Transactions of the Cambridge Philosophical Society. On becoming farther acquainted with the experimental results contained in that important paper, I find that they include inversions, not only, in cases like those first mentioned, which might be regarded as anomalies dependent on singular properties of strange alloys, but between pure metals, in various cases; and that the actual phenomenon in the case of copper and iron, the observation of which several years later by M. BECQUEREL had been very generally regarded as the first discovery of thermo-electric inversion, is there described; as the following extracts show:—

"If silver and iron wires be heated in connection, the deviation attains a maximum; diminishes on increasing the heat, and again attains the former maximum on cooling."—Camb. Phil. Trans., 1823; Note on p. 61.

"Addition to p. 61" [occurring in a page of additions at the end of the paper]. "If gold, silver, copper, brass, or zinc wires be heated in connection with iron, the deviation, which is at first positive, becomes negative at a red heat."