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4. On a Mechanical Theory of Thermo-Electric Currents.

Professor William Thomson

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quantity of heat that must be supplied to it to augment its volume by $d\,v$ and its temperature by $d\,t$. The mechanical value of the work done upon it to produce this change is the excess of the mechanical value of the quantity of heat that has to be added above that of the work done by the fluid in expanding, and is therefore

$$J\,(M\,d\,v+N\,d\,t)-p\,d\,v.$$

It was shewn in the author's paper on the Dynamical Theory of Heat, that this expression is the differential of a function of v and t, so that, if this function be denoted by φ, we have,—

$$\varphi\,(v,\,t)=\int\{(JM-p)\,d\,v+N\,d\,t\}$$

This function would, if the constant of integration were properly assigned, express the *absolute quantity of mechanical energy contained in the fluid mass.* Failing an *absolute* determination of the constant, we may regard the function φ as expressing the mechanical value of the whole agency required to bring the fluid mass from a specified *zero* state to the state of occupying the volume v and being at the temperature t. In the present paper some formulæ are given, by means of which it is shewn that nearly all the physical properties of a fluid may be deduced from a table of the values of φ for all values of v and t; and experimental methods connected with the experimental researches proposed in the author's last paper, are suggested for determining values of φ for a gaseous fluid mass.

4. On a Mechanical Theory of Thermo-Electric Currents. By Professor William Thomson.

It was discovered by Peltier that heat is absorbed at a surface of contact of bismuth and antimony in a compound metallic conductor, when electricity traverses it from the bismuth to the antimony, and that heat is generated when electricity traverses it in the contrary direction. This fact, taken in connection with Joule's law of the electrical generation of heat in a homogeneous metallic conductor, suggests the following assumption, which is the foundation of the theory at present laid before the Royal Society.

When electricity passes in a current of uniform strength γ through a heterogeneous linear conductor, no part of which is permitted to *vary in temperature, the heat generated in a given time is expressible by the formula*

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

where A, *which may be either positive or negative, and* B, *which is essentially positive, denote quantities independent of* γ.

The fundamental equations of the theory are the following :—

$$F\ \gamma = J\ \left(\gamma\ \Sigma\ \alpha_t + B\ \gamma^2\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (a)$$

$$\Sigma\ \alpha_t = \Sigma\ \alpha_t \left(1 - \epsilon^{-\frac{1}{J}\int_T^t \mu\, d\, t}\right) \quad . \quad . \quad . \quad . \qquad (b)$$

where F denotes the electromotive force (considered as of the same sign with γ, when it acts in the direction of the current) which must act to produce or to permit the current γ to circulate uniformly through the conductor ; J the mechanical equivalent of the thermal unit ; $\alpha_t\ \gamma$ the quantity of heat evolved in the unit of time in all parts of the conductor which are at the temperature t when γ is infinitely small ; μ "Carnot's function"* of the temperature t ; T the temperature of the coldest part of the circuit ; and Σ a summation including all parts of the circuit.

The first of these equations is a mere expression of the equivalence, according to the principles established by Joule, of the work, F γ,† done in a unit of time by the electromotive force, to the heat developed, which, in the circumstances, is the sole effect produced. The second is a consequence of the first and of the following equation :—

$$\varphi .\ \gamma = \mu\ \Sigma\ \alpha_t\ \gamma .\ (t - T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (c)$$

where φ denotes the electromotive force when γ is infinitely small, and when the temperatures in all parts of the circuit are infinitely nearly equal. This latter equation is an expression, for the present circumstances, of the proposition‡ (first enunciated by Carnot, and first established in the dynamical theory by Clausius) that

* The values of this function, calculated from Regnault's observations, and the hypothesis that the density of saturated steam follows the "gaseous laws," for every degree of temperature from 0° to 230° cent., are shewn in Table I. of the author's "Account of Carnot's Theory," *Transactions*, vol. xvi., p. 541.

† See Philosophical Magazine, Dec. 1851, "On Applications of the Principle of Mechanical Effect," &c.

‡ "Dynamical Theory of Heat" (*Transactions*, vol. xx., part ii.) Prop. II., &c.

the obtaining of mechanical effect from heat, by means of a perfectly reversible arrangement, depends in a definite manner on the transmission of a certain quantity of heat from one body to another at a lower temperature. There is a degree of uncertainty in the present application of this principle, on account of the conduction of heat that must necessarily go on from the hotter to the colder parts of the circuit; an agency which is not reversed when the direction of the current is changed. As it cannot be shewn that the thermal effect of this agency is infinitely small, compared with that of the electric current, unless γ be so large that the term B γ^2, expressing the thermal effect of another irreversible agency, cannot be neglected, the conditions required for the application of Carnot and Clausius's principle, according to the demonstrations of it which have been already given, are not completely fulfilled: the author therefore considers that at present this part of the theory requires experimental verification.

1. A first application of the theory is to the case of antimony and bismuth; and it is shewn that the fact discovered by Seebeck is, according to equation (*c*), a consequence of the more recent discovery of Peltier referred to above,—a partial verification of the only doubtful part of the theory being thus afforded.

2. If $\Theta\,\gamma$ denote the quantity of heat evolved, [or $-\,\Theta\,\gamma$ the quantity absorbed] at the surface of separation of two metals in a compound circuit, by the passage of a current of electricity of strength γ across it, when the temperature t is kept constant; and if φ denote the electromotive force produced in the same circuit by keeping the two junctions at temperatures t and t', which differ from one another by an infinitely small amount, the magnitude of this force is given by the equation

$$\varphi = \Theta\,\mu\,(t'-t) \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

and its direction is such, that a current produced by it would cause the absorption of heat at the hotter junction, and the evolution of heat at the colder. A complete experimental verification of this conclusion would fully establish the theory.

3. If a current of electricity, passing from hot to cold, or from cold to hot, in the same metal produced the same thermal effects; that is, if no term of $\Sigma\,\alpha_t$ depended upon variation of temperature from point to point of the same metal; we should have, by equation (*a*)

$$\varphi = J\,\frac{d\,\Theta}{d\,t}(t'-t)\text{; and therefore, by }(d),\ \frac{d\Theta}{d\,t} = \frac{1}{J}\,\Theta\,\mu.$$

From this we deduce

$$\Theta = \Theta_0\ \epsilon^{\frac{1}{J}\int_0^t \mu\,d\,t}\text{; and }\varphi = (t'-t)\,\mu\,\Theta_0\,\epsilon^{\frac{1}{J}\int_0^t \mu\,d\,t}$$

A table of the values of $\frac{\varphi}{\Theta_0\ (t'-t)}$ for every tenth degree from 0 to 230 is given, according to the values of μ,* used in the author's previous papers; shewing, that if the hypothesis just mentioned were true, the thermal electromotive force corresponding to a given very small difference of temperatures, would, for the same two metals, increase very slowly, as the mean absolute temperature is raised. Or, if Mayer's hypothesis, which leads to the expression $\frac{JE}{1+E\,t}$ for μ, were true, the electromotive force of the same pair of metals would be the same, for the same difference of temperatures, whatever be the absolute temperatures. Whether the values of μ previously found were correct or not, it would follow, from the preceding expression for φ, that the electro-motive force of a thermo-electric pair is subject to the same law of variation, with the temperatures of the two junctions, whatever be the metals of which it is composed. This result being at variance with known facts, the hypothesis on which it is founded must be false; and the author arrives at the remarkable conclusion, that *an electric current produces different thermal effects, according as it passes from hot to cold, or from cold to hot, in the same metal.*

4. If $\vartheta\ (t'-t)$ be taken to denote the value of the part of $\Sigma\,\alpha_t$ which depends on this circumstance, and which corresponds to all parts of the circuit of which the temperatures lie within an infinitely small range t to t'; the equations to be substituted for the preceding are,

$$\varphi = J\,\frac{d\,\Theta}{d\,t}\,(t'-t) + J\,\vartheta\,(t'-t) \quad . \quad . \quad . \quad . \quad (e)$$

and therefore, by (d)

$$\frac{d\,\Theta}{d\,t} + \vartheta = \frac{1}{J}\,\Theta\,\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (f)$$

5. The following expressions for F, the electromotive force in a

* The unit of force adopted in magnetic and electro-magnetic researches, being that force which, acting on a unit of matter, generates a unit of velocity in the unit of time, the values of μ and J used in this paper are obtained by multiplying the values used in the author's former papers, by 32·2.

thermo-electric pair, with the two junctions at temperatures S and T differing by any finite amount, are then established in terms of the preceding notations, with the addition of suffixes to denote the particular values of Θ for the temperatures of the junctions.

$$\left.\begin{aligned} F &= \int_T^S \mu\,\Theta\, dt = J \left\{ \Theta_S - \Theta_T + \int_T^S \vartheta dt \right\} \\ &= J \left\{ \Theta_S \left(1 - \epsilon^{-\frac{1}{J}\int_T^S \mu\, dt}\right) + \int_T^S \vartheta \left(1 - \epsilon^{-\frac{1}{J}\int_T^t \mu\, dt}\right) dt \right\} \end{aligned}\right\} \quad (g)$$

6. It has been shewn by Magnus, that no sensible electromotive force is produced by keeping the different parts of a circuit of one homogeneous metal at different temperatures, however different their sections may be. It is concluded that for this case $\vartheta = 0$; and therefore that, for a thermo-electric element of two metals, we must have,—

$$\vartheta = \Psi_1 (t) - \Psi_2 (t)$$

where Ψ_1 and Ψ_2 denote functions depending solely on the qualities of the two metals, and expressing the thermal effects of a current passing through a conductor of either metal, kept at different uniform temperatures in different parts. Thus, with reference to the metal to which Ψ_1 corresponds, if a current of strength γ pass through a conductor consisting of it, the quantity of heat *absorbed* in any infinitely small part PP′ is $\Psi_1 (t)\,(t'-t)\,\gamma$, if t and t' be the temperatures at P and P′ respectively, and if the current be in the direction from P to P′. An application to the case of copper and iron is made, in which it is shewn that, if Ψ_1, and Ψ_2 refer to these metals respectively, if S be a certain temperature defined below (which, according to Regnault's observations, cannot differ much from 240° cent.), and if T be any lower temperature; we have

$$\int_T^S \{ \Psi_1 (t) - \Psi_2 (t) \} \, dt = \Theta_T + \frac{1}{J} F,$$

since the experiments made by Becquerel lead to the conclusion, that at a certain high temperature iron and copper change their places in the thermo-electric series (a conclusion which the author has experimentally verified), and if this temperature be denoted by S, we must consequently have $\Theta^S = 0$.

The quantities denoted by Θ_T and F in the preceding equation being both positive, it is concluded that, *when a thermo-electric current passes through a piece of iron from one end kept at about* 240° *cent., to the other end kept cold, in a circuit of which the remainder is copper, including a long resistance wire of uniform temperature throughout or an electro-magnetic engine raising weights, there is heat evolved at the cold junction of the copper and iron, and (no heat being either absorbed or evolved at the hot junction) there must be a quantity of heat absorbed on the whole in the rest of the circuit. When there is no engine raising weights, in the circuit, the sum of the quantities evolved, at the cold junction, and generated in the "resistance wire," is equal to the quantity absorbed on the whole in the other parts of the circuit. When there is an engine in the circuit, the sum of the heat evolved at the cold junction and the thermal equivalent of the weights raised, is equal to the quantity of heat absorbed on the whole in all the circuit except the cold junction.*

7. An application of the theory to the case of a circuit consisting of several different metals, shews that if

$$\varphi(A, B),\ \varphi(B, C),\ \varphi(C, D),\ \ldots\ \varphi(Z, A)$$

denote the electromotive forces in single elements, consisting respectively of different metals taken in order, with the same absolute temperatures of the junctions in each element, we have

$$\varphi(A, B) + \varphi(B, C) + \varphi(C, D)\ \ldots\ + \varphi(Z, A) = 0,$$

which expresses a proposition, the truth of which was first pointed out and experimentally verified by Becquerel. A curious experimental verification of this proposition (so far as regards the signs of the terms of the preceding equation) was made by the author, with reference to certain specimens of platinum wire, and iron and copper wires. He had observed that the platinum wire, with iron wires bent round its ends, constituted a less powerful thermo-electric element than an iron wire with copper wires bent round its ends, for temperatures within atmospheric limits. He tried, in consequence, the platinum wire with copper wires bent round its ends, and connected with the ends of a galvanometer coil; and he found that, with temperatures within atmospheric limits, a current passed from the copper to the platinum through the hot junction, and concluded that, in the thermo-electric series

$$\overset{+}{\text{Antimony}},\ \text{Iron},\ \left\{\begin{matrix}\text{Copper,}\\ \text{Platinum,}\end{matrix}\right\}\ \overset{-}{\text{Bismuth}},$$

this platinum wire must, at ordinary temperatures, be between iron and copper. He found that the platinum wire retained the same properties after having been heated to redness in a spirit-lamp and cooled again ; but with temperatures above some limit itself considerably below that of boiling water, he found that the iron and platinum constituted a more powerful thermo-electric element than the iron and copper; and he verified that for such temperatures, in the platinum and copper element the current was from the platinum to the copper through the hot junction, and therefore that the copper now lay between the iron and the platinum of the series, or in the position in which other observers have generally found copper to lie with reference to platinum. A second somewhat thinner platinum wire was found to lie invariably on the negative side of copper, for all temperatures above the freezing point; but a third, still thinner, possessed the same property as the first, although in a less marked degree, as the superior limit of the range of temperatures for which it was positive towards copper was lower than in the case of the first wire. By making an element of the first and third platinum wire, it was found that the former was positive towards the latter, as was to be expected.

In conclusion, various objects of experimental research regarding thermo-electric forces and currents are pointed out, and methods of experimenting are suggested. It is pointed out that, failing direct data, the absolute value of the electromotive 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 determinations by Weber, and of 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 16300 as the electromotive 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 electromotive 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 electromotive force of a copper and bismuth element, with its two junctions at 0° and 1°, being found by Pouillet to be about $\frac{1}{100}$ of the electromotive force when the junctions are at 0° and 100°, must be about 163. The value of Θ_0 for copper and bismuth, according to these results (and to the value 160·16 of μ at 0°), or the quantity of heat absorbed in a second of time by a current of unit strength in passing from bismuth to copper, when the temperature is kept at 0°, is $\frac{163}{160 \cdot 16}$, or very nearly equal to the quantity required to raise the temperature of a grain of water from 0° to 1° cent.

Monday, 5th January 1852.

RIGHT REVEREND BISHOP TERROT, Vice-President, in the Chair.

The following Communications were read :—

1. On the Absolute Intensity of Interfering Light. By Professor Stokes. Communicated by Professor Kelland.

In this communication Professor Stokes described a method which he had discovered, by which he could express, mathematically, the absolute intensity of interfering light, as in the case of the images found in the focus of a telescope pointed to a star, and having a grating over the object-glass. The result was the same as that previously aimed at by Professor Kelland, but the mode of getting at it was shorter.