at the junction, and transforming heat into electrical energy or vice versa. If *R* is the whole resistance of the circuit, and *E* the E.M.F. of the couple, and if the flow of the current does not produce any other thermal effects in the circuit besides the Joule and Peltier effects, we should find by applying the principle of the conservation of energy, *i.e.* by equating the balance of the heat absorbed by the Peltier effects to the heat generated in the circuit by the Joule effect,

(P-P')C= Cl?=£C, whence E=P-P' . . (5) If we might also regard the couple as a reversible thermo­dynamic engine for converting heat into work, and might neglect irreversible effects, such as conduction, which are independent of the current, we should expect to find the ratio of the heat absorbed at the hot junction to the heat evolved at the cold junction, namely, *P∣P',* to be the same as the ratio Γ∕Γ' of the absolute temperatures of the junctions. 'Phis would lead to the conclusion given by R. J. E. Clausius (1853) that the Peltier effect varied directly as the absolute temperature, and that the E.M.F. of the couple should be directly proportional to the difference of temperature between the junctions.

10. *Thomson Effect.—*Thomson (Lord Kelvin) had already pointed out *(Proc. R.S. Edin.,* 1851) that this conclusion was in­consistent with the known facts of thermoelectric inversion.

(1) The E.M.F. was not a linear function of the temperature difference.

(2) If the Peltier effect was proportional to the thermoelectric {»wer and changed sign with it, as all experiments appeared to indicate, there would be no absorption of heat in the circuit due to the Peltier effect, and there­fore no thermal source to account for the energy of the current, in the case in which the hot junction was at or above the neutral temperature. He therefore predicted that there must be a reversible absorption of heat in some other part of the circuit

due to the flow of the current through the unequally heated conductors. He succeeded a few years afterwards in verifying this remarkable prediction by the experimental demonstration that a current of positive electricity flowing from hot to cold in iron produced an absorption of heat, as though it possessed *negative* specific heat in the metal iron. He also succeeded in showing that a current from hot to cold evolved heat in copper, but the effect was smaller and more difficult to observe than in iron.

The Thomson effect may be readily demonstrated as a lecture experiment by the following method (fig. 1). A piece of wire (No. 28) about 4 cm. long is soldered at either end A, B to thick wires (No. 12), and is heated 100° to 15o0 C. by a steady current from a storage cell adjusted by a suitable rheostat. The experi­mental wire AB is connected in parallel with about 2 metres of thicker wire (No. 22), which is not appreciably heated. A low- resistance galvanometer is connected by a very fine wire (2 to 3 mils) to the centre C of the experimental wire AB, and also to the middle point D of the parallel wire so as to form a Wheatstone bridge. The balance is adjusted by shunting either AD or BD with a box, S, containing 20 to ι<x> ohms. All the wires in the quadrilateral must be of the same metal as AB, to avoid accidental thermoelectric effects which would obscure the result. If the current flows from A to B there will be heat absorbed in AC and evolved in CB by the Thomson effect, if the specific heat of elec­tricity in AB is positive as in copper. When the current is reversed, the temperature of AC will be raised and that of CB lowered by the reversal of the effect. This will disturb the resist­ance balance by an amount which can be measured by the deflection of the galvanometer, or by the change of the.shunt-box, S, required to restore the balance. Owing to the small size of the experimental wire, the method is very quick and sensitive, and the apparatus can be set up in a few minutes when once the experimental quadri­laterals have been made. It works very well with platinum, iron and copper. It was applied with elaborate modifications by the writer in 1886 to determine the value of the Thomson effect in platinum in absolute measure, and has recently been applied with further improvements by R. O. King to measure the effect in copper.

it. *Thomson’s Theory.—*Taking account of the Thomson effect, the thermodynamical theory of the couple was satis­factorily completed by Thomson *(Trans. R. S. Edin.,* 1854). If the quantity of heat absorbed and converted into electrical energy, when unit quantity of electricity (one ampere-second) flows from cold to hot through a difference of temperature, *dt,* be represented by *sdt,* the coefficient s is called the specific heat of electricity in the metal, or simply the coefficient of the Thomson effect. Like the Peltier coefficient, it may be measured in joules or calories per ampere-second per degree, or more conveniently and simply in microvolts per'degree.

Consider an elementary couple of two metals A and B for which 5 has the values *s’* and s\* respectively, with junctions at the tempera­ture. T and *T-∖-dT* (absolute), at which the coefficients of the Peltier effect are *P* and *P+dP.* Equating the quantity of heat absorbed to the quantity of electrical energy generated, we have by the first law of thermodynamics the relation

*dE'dT≈dP∕dT+(s'-s") . .* . (6)

If we apply the second law, regarding the couple as a reversible engine, and considering only the reversible effects, we obtain

*(s'-s")∕T≈-d(P∕T)∣dT . .* . (7)

Eliminating *(s,-sr)* we find for the Peltier effect

*P=TdE∣dT=Tp . . . .* (8)

Whence we obtain for the difference of the specific heats

*(s’-s"'l = -T<Γ-EpiΓ-≈ -Tdp∣dT . .* (9)

From these relations w,e observe that the Peltier effect P, and the difference of the Thomson effects (s'—s\*), for any two metals are easily deduced from the tabulated values of *dE·dt* and *<PE./dP* respectively. The signs in the above equations are chosen on the assumption that positive electricity flows from cold to hot in the metal *s'.* The signs of the Peltier and Thomson effects will be the same as the signs of the coefficients given in Table I., if we suppose the metal *s'* to be lead, and assume that the value of s' may be taken as zero at all temperatures.

12. *Experimental Verification of Thomson's Theory.—*In order to justify the assumption involved in the application of the second law of thermodynamics to the theoYy of the thermocouple in the manner above specified, it would be necessary and sufficient, as Thomson pointed out *(Phil. Mag.,* December 1852), to make experi­ments to verify quantitatively the relation *P∣T\*=dE∣dT* between the Peltier effect and the thermoelectric power. A qualitative relation was known at that time to exist, but no absolute measure­ments of sufficient accuracy had been made. The most accurate measurements of the heat absorption due to the Peltier effect at present available are probably those of H. Μ. Jahn (H'⅛d. *Ann.,* 34, p. 7β5, 1888). lie enclosed various metallic junctions in a Bunsen ice calorimeter, and observed the evolution of heat per hour with a current of about 1 ·6 amperes in either direction. The Peltier effect was only a small fraction of the total effect, but could be separated from the Joule effect owing to the reversal of the current. The values of *dEdT* for *the same specimens* of metal at 0° C. were determined by experiments between -∣-200 C. and — 20° C. The results of his observations are contained in the following table, heat absorbed being reckoned positive as in Table I.:—

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table II. | | | | |
| Thermo­couple. | ***dE/dT*** Microvolts per deg. | ***P≈TdE∕dT*** Microvolts at oβ C. | Heat calc. Calories per hour. | Heat observed Calories per hour. |
| Cu-Ag | J-2-I2 | +579 | +o-495 | +o∙413 |
| Cu-Fe | + ll∙2β | +3079 | 4-2-640 | +3-163 |
| Cu-Pt | —1∙40 | -382 | -0∙327 | -0-320 |
| Cu-Zn | +l∙51 | +412 | +o∙353 | +0∙585 |
| Cu-Cd | +2∙64 | +721 | +0∙617 | +0∙616 |
| Cu-Ni | -20-03 | -5468 | -4-680 | -4∙362 |

The agreement between the observed and calculated values in the last two columns is as good as can be expected considering the great difficulty of measuring such small quantities of heat. The analogous reversible heat effects which occur at the junction of a metal and an electrolyte were also investigated by Jahn, but he did not succeed in obtaining so complete an agreement with theory in this case.