

L. *Note on a slight Error in the customary Specification of Thermo-electric Current-direction, and a Query with regard to a point in Thermodynamics.* By OLIVER J. LODGE, D.Sc., Professor of Physics in University College, Liverpool\*.

[Plate III.]

IN a paper written for the British Association at Montreal, "On the Seat of the Electromotive Forces in the Voltaic Cell," printed in the Philosophical Magazine for March, April, and May this year, there occurs the following footnote to section 23 (Phil. Mag. May 1885, vol. xix. p. 355):—

"It is always easy to tell from thermoelectric data which way the force acts at a junction; but it is not always the same way as the current flows, by any means. A current often flows against the E.M.F. even at a hot junction, and it may flow against the force at *both* junctions. This is the case, for instance, in a copper-iron circuit with one junction above 275°, and the other below that temperature by a greater amount. It is customary to say that the current flows across a hot junction from the metal of higher to the metal of lower thermoelectric value: this is not necessarily true. The safe statement is to say that the E.M.F. acts from high to low thermoelectric value at either junction."

A short statement like this is apt to be buried in a long paper on other matters, and though not of any high importance, it is always worth while to keep as clear as possible on all elementary matters, if only for the sake of one's students. The point is perhaps most easily illustrated by considering special cases; but I may first briefly explain my general point of view in case there may be some objection to it.

It is well known that the whole E.M.F. of a thermoelectric circuit is obtainable by integrating, all round, a certain function of the temperature and of the metals in circuit, which may be called the Peltier function,  $\Pi$ ,

$$E = \int \frac{\Pi d\theta}{\theta},$$

where the  $\theta$  stands for absolute temperature. On Tait's assumption that what Thomson called "the specific heat of electricity in a metal" is proportional to  $\theta$ —equal, say, to  $k_a\theta$  for metal A, and to  $k_b\theta$  for metal B—the value of  $\Pi$  is

$$\Pi = (k_a - k_b)\theta(\theta_0 - \theta),$$

where  $\theta_0$  is a constant to be determined by experiment, just as  $k_a$  and  $k_b$  are to be determined.

\* Communicated by the Author.

From these equations the value of the total E.M.F. of the simple circuit, with its two junctions at temperature  $\theta_1$  and  $\theta_2$ , is obviously

$$E = (k_a - k_b)(\theta_1 - \theta_2) \left\{ \theta_0 - \frac{1}{2}(\theta_1 + \theta_2) \right\};$$

a well-known formula, first established empirically by Avenarius as far as the variable part is concerned.

Now although  $\Pi$ , the Peltier coefficient, can thus be regarded as a function to be integrated all round the circuit, it is possible also to regard it as localized—part of it constituting an E.M.F. residing at the junctions, and part of it having its abode wherever a slope of temperature occurs in either metal. And, indeed, the generation and destruction of heat at the junctions, observable when a current flows round the circuit and known as the Peltier effect, together with the apparent convection of heat by electricity discovered by Sir William Thomson, and which in 1876\* I ventured to call the Thomson effect, compel us to picture to ourselves an E.M.F. at each junction, which may be called specifically *Peltier forces* and be denoted by  $\Pi_1$  and  $\Pi_2$ , and another E.M.F. in each metal wherever the temperature slopes; the total force in the metal A between the temperatures  $\theta_1$  and  $\theta_2$  being denoted by  $\Theta_a$ , that in the other metal by  $\Theta_b$ , and both being called *Thomson forces*.

The Peltier effect and the Thomson effect depend on a current passing; the existence of the *forces* is independent of such an accident. The Thomson force depends for its existence upon inequality of temperature; the Peltier force does not, it varies only with absolute temperature and nature of metals. Equality of temperature throughout the circuit abolishes the Thomson forces, but only renders equal the Peltier ones, their continued existence being provable by producing the Peltier effect. The resultant E.M.F. of the whole simple circuit, with junctions at  $\theta_1$  and  $\theta_2$ , is

$$E = \Pi_1 - \Pi_2 + \Theta_a - \Theta_b;$$

whence, from the preceding equations, we get

$$\Pi_1 = (k_a - k_b)\theta_1(\theta_0 - \theta_1),$$

$$\Pi_2 = (k_a - k_b)\theta_2(\theta_0 - \theta_2),$$

$$\Theta_a = k_a(\theta_1^2 - \theta_2^2),$$

$$\Theta_b = k_b(\theta_1^2 - \theta_2^2),$$

where the  $k$ 's may quite easily be negative in certain metals.

By these formulæ the tables of Peltier and Thomson contact series, given in section 23 of the paper† above referred to, were

\* Phil. Mag. [5] Dec. Suppl. vol. ii. p. 534.

† Phil. Mag. May 1885, pp. 354, 355.

reckoned from Tait's experimental data of thermoelectric powers : the term "thermoelectric power" being defined, for a circuit of two metals, A and B, thus:—

$$P_a - P_b = \frac{E}{\theta_1 - \theta_2}.$$

It is now easy to follow out the changes in magnitude and sign of the four forces  $\Pi_1$ ,  $\Pi_2$ ,  $\Theta_a$ , and  $\Theta_b$  for a circuit of any two metals as their junctions are varied in temperature ; and the diagrams (Plate III.), illustrative of twelve typical cases observable with an iron-copper circuit, are not without interest.

The Peltier force acts from copper to iron for all temperatures below the neutral point  $275^\circ \text{C.}$ ; at this point it vanishes, and above this point it is reversed : in other words, copper is the metal of higher thermoelectric power below  $275^\circ$ , but iron is, above. The Thomson force happens to act from hot to cold in iron, and from cold to hot in copper, always ; and it increases uniformly with the difference of the squares of the absolute end-temperatures.

The temperature of each junction is indicated on the figures in Centigrade degrees. The arrows indicate the direction of the electromotive forces at the different places, and numbers attached to the arrows show their magnitude. The central arrow represents the resultant E.M.F., or current, in magnitude and direction. The unit in which all the E.M.F.s are specified is the ten-thousandth of a volt.

It will be observed that in cases 4 and 7 the current flows against the force at the hot junction ; and that in cases 6 and 9 it flows with the force at the cold junction, being helped on thereby. The common statement that the current flows from a metal of higher to a metal of lower thermoelectric value across the hot junction is thus by no means necessarily true. Its truth depends upon circumstances. It is not even true to say that the self-generated current necessarily cools the hot junction and warms the cold one. It may warm both ; it may cool both. It may even, in some peculiar cases, cool the cold junction and warm the hot : see below.

These diagrams, though they express nothing but what is well known, the numbers being calculated from Tait's table of thermoelectric values as given in any textbook, yet are interesting from the point of view of the second law of thermodynamics, being some of them apparent exceptions to, or contradictions of, some statements of that law.

It will be observed that the current usually flows with the force at the hot junction, and therefore cools it ; but it may

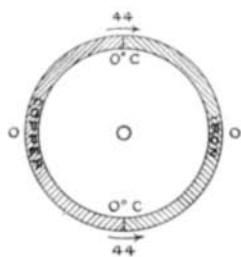


Fig. 1.

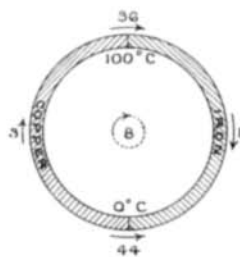


Fig. 2.

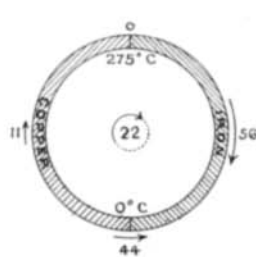


Fig. 3.

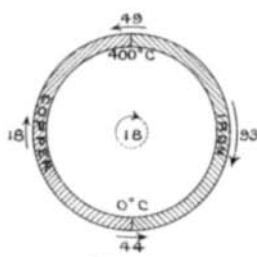


Fig. 4.

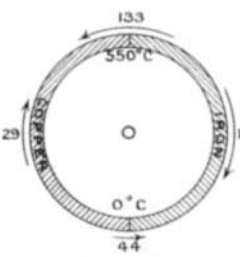


Fig. 5.

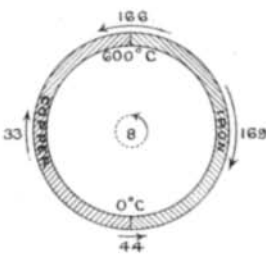


Fig. 6.

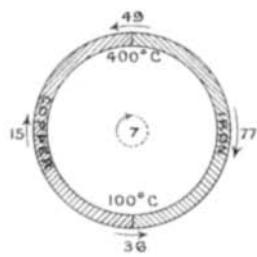


Fig. 7.

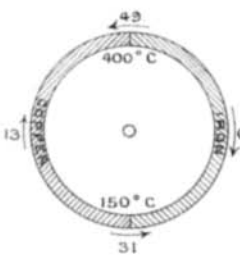


Fig. 8.

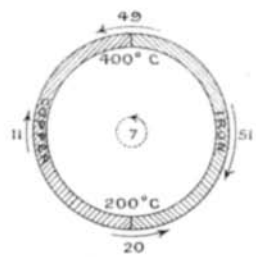


Fig. 9.

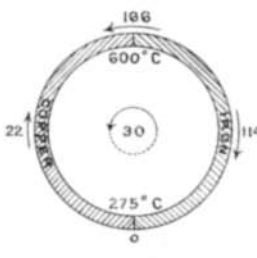


Fig. 10.

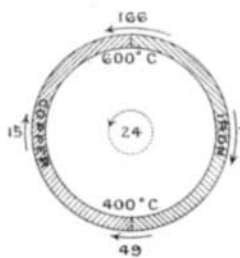


Fig. 11.

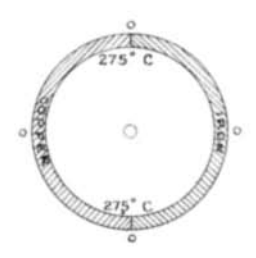


Fig. 12.

flow against this force, thus *increasing the temperature of the hottest part of the circuit*.

Again, the current usually flows against the force at the cold junction, and therefore warms it; but it may flow with this force, thus *lowering the temperature of the coolest portion of the circuit*.

It would be curious to obtain a case where the current flowed *with* the force at the cold junction and *against* that at the hot, thus carrying heat from the coldest to the hottest parts of the system. But, so long as the lines of a thermoelectric diagram are straight, this is not possible; as may be seen by proving the following criteria:—

Calling the temperature of the hot junction  $t_1$ ,  
                   "                  "                  cold junction  $t_2$ ,  
                   "                  "                  neutral point  $t_0$ ,  
 and denoting by  $t$  the average temperature  $\frac{1}{2}(t_1 + t_2)$ , we can say:—

The current flows against the force at the hot junction only when the neutral point lies between the highest and the average temperatures;

i. e. when

$$t_1 > t_0 > t.$$

The current flows with the force at the cold junction only when the neutral point lies between the lowest and average temperatures;

i. e. when

$$t > t_0 > t_2.$$

These conditions, though either of them is easily possible, are mutually incompatible; hence *both* cases cannot occur at once. In other words, if the current flow against the force at the hot junction, it must flow against the force at the cold one too.

The same thing is also evident by considering a thermoelectric diagram, though perhaps not quite so easily. It will then, however, be further perceived that the impossibility under consideration is not a fundamental one depending on thermodynamic laws, but is a mere consequence of the experimental straightness of the thermoelectric lines; and that if for any metal the line is really curved\*, as may well be the case, so that between it and another there are two neutral points, it is quite possible to arrange so that the current shall be assisted by the force at the cold junction, and opposed by the force

\* Prof. Tait says that the line is strongly curved for nickel; and that an iron-nickel junction may have three neutral points (Tait's 'Heat,' p. 178).

at the hot. In other words, it is possible for the hot junction to be heated and the cold junction cooled, or for the initial inequality of temperature to be *increased* by the current excited by reason of that very inequality; unless the electric convection of heat along the metals reduces the inequality of temperature to a greater extent. But for this act of reparation there is no necessity; for instance, in the special cases considered, the current opposes the flow of heat by conduction both in iron and in copper; carrying cold with it, so to speak, in both cases. Thus the electric convection of heat, on the whole, tends to accentuate the difference of temperature in these cases. *Conduction* may reduce it, but in Thomson's theory conduction is carefully regarded as a non-essential concomitant.

Now how is it possible for the hottest part of a system to be automatically warmed, and for the coldest portion to be automatically cooled? Or, again, how can an automatically generated current be assisted by heat derived from the coldest part of a system, and be opposed by having to generate heat at the hottest part?

According to some statements of the second law of thermodynamics, such a result would be paradoxical or impossible. And yet the result is deduced by help of the second law itself:

the form of the law being,  $\int \frac{dH}{\theta} = 0$  when taken round a circuit, or  $\frac{dH}{\theta}$  is a complete differential of a temperature-function; dependent therefore on end-temperatures only, not on nature of metal or distribution of intermediate temperatures.

If  $H$  is the heat converted into electrical energy at any part of the circuit, and  $E$  the resultant total E.M.F., then no doubt, as in any reversible heat-engine, the work done per cycle

$$E\gamma = J \int \frac{H d\theta}{\theta} \text{ taken round the circuit ;}$$

and the disappearance of heat exactly accounts for the electrical energy without having to fall back upon degradation by irreversible processes such as conduction. But the noteworthy thing is that, whereas usually heat is destroyed at the hotter parts and generated at the colder parts of a system, in this case heat may be generated at the hottest and destroyed at the coldest parts; the great bulk of the conversion of heat into electrical energy being carried on at intermediate temperatures.  $H$  is not a bit proportional to absolute temperature, as it is in a simple heat-engine; it may even be zero or negative, and may attain its maximum at any temperature, except indeed at the very lowest in the system.

I am sorry to say that I did not see this clearly at first, nor do I see it now as clearly as I should like, and I have accordingly wasted three days in an attempt to take account of conduction of heat, or at least of a certain minimum amount of it, as if it were an essential part of the process; the raising of heat-potential by the current in certain cases being only accountable, as it seemed to me, by reason of a definite and calculable amount of degradation by conduction; after the manner of a water-ram.

Liverpool, 8th May, 1885.

LI. *On Supersaturation of Salt-Solutions.* By W. W. J. NICOL, M.A., D.Sc., Lecturer on Chemistry, Mason College, Birmingham\*.

“Le sulfate de soude dissous dans l’eau à des températures quelconques est anhydre. Il n’y a de solution sursaturée.”†

**B**EFORE I proceed to give an account of my experiments on this subject and the conclusions based on them, it is necessary to point out that there are two distinct kinds of supersaturation.

Supersaturation, in general, may be defined as—

The existence in solution of a larger quantity of salt than the water is normally capable of holding in solution at the temperature of experiment.

Or as clearly expressed by Mulder‡—

“Oververzadiging is: meer in oplossing hebben bij eene zekere temperatuur dan bij die temperatuur in oplossing kan overgaan, wanneer men begint met het vaste zout en dat behandelt met water bij die temperatuur. . . Oververzadiging is dus: behoud van een toestand, aan het zout gegeven door eene hoogere temperatuur.”

“Supersaturation is the holding in solution at a given temperature more salt than can be dissolved at that temperature, starting with the solid salt and treating it with water at that temperature. It is thus the possession of a condition which is conferred on a salt by a higher temperature.”

Supersaturation as thus defined is common to all salts without exception. But it will be seen on reflection that, as I have said, there are two kinds:—

1st. That occurring in *presence* of undissolved salt.

\* Communicated by the Author, having been read before the Royal Society of Edinburgh, April 1885.

† Loewel, *Ann. d. Chim. et Phys.* [3] xlix. p. 51.

‡ *Bijdragen tot de Geschiedenis van het scheikundig gebonden Water* (Rotterdam, 1864).