ART. XL.—*An Elementary Expression in Thermo-electrics*;
by CARL BARUS.

1. THE thermo-electric equation due respectively to Avenarius* and to Tait,† does not reproduce the observations satisfactorily when long temperature ranges ($>1000^{\circ}$ C.) are dealt with.‡ Within an interval of a few hundred degrees, however, the equation is usually in good accord with the experimental results. It is desirable, therefore, to endeavor to find a more general relation, from which the Tait equation may be derived as an approximation. This is my object in the present paper. I have tried to throw some light on the subject without explicit reference either to the Peltier or to the Thomson effect, and in a deductively experimental way, as follows:

2. In an investigation of the relation between the thermo-electric power and the specific resistance of steel varying with hardness, Dr. Stronhal and I found a linear relation§ to obtain. Some 90 states of hardness were examined, all tempered with scrupulous care. I have since endeavored to test this relation further, by making as many different platinum alloys as I could (54 in all), but found|| that marked changes of specific resistance (10–65 microhms) were as common, as marked changes of thermoelectric power were rare, and no law was apparent. Nevertheless I am unwilling to concede that the results for steel in their bearing on the subject in hand are devoid of suggestion; at least I believe that the relation which holds for temper will also hold for temperature because in the latter case the structure of the metal is to a less extent interfered with.

3. When long ranges of temperature are considered the relation of metallic resistance¶ to temperature is not such that its nature can be closely enough inferred, experimentally. Electrolytic resistance, however, presents a promising case. The thermal variation of the resistance of an electrolyte, as I found both in the case of aqueous solutions (zinc sulphate)

* Avenarius: Pogg. Ann., cxix, p. 406, 1863.

† Tait: Trans. R. S. Edinbgh., xxvii, p. 125, 1872–73.

‡ Prof. Tait does not claim that the formula will do so.

§ Wied. Ann., xi, p. 969 et seq., 1880. It will be remembered that the resistance of hard steel is 3 to 4 times as large as that of soft steel. Cf. Phil. Mag., (5), viii, p. 341, 1879.

|| Barus: this Journal, xxxvi, p. 427, 1888: Bull. U. S. G. S., No. 54, pp. 143, 146, 1889.

¶ The striking results of Dewar and Fleming (Phil. Mag., xxxvi, p. 271, 1893), from which an absence of metallic resistance at the absolute zero of temperature may be inferred, are rather of the nature of an initial tangent to the curve above in question.

under pressure,* and in connection with the examination of rock magmas† made by Prof. J. P. Iddings and myself, can be reproduced by an elementary equation, $dr/d\theta = a - br$, where r denotes the resistance, θ the temperature, a and b are constants, and where a is probably introduced by observational errors.

4. Following out the suggestions of §§2, 3, I tested the elementary expression

$$de/d\theta = -Ae \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e may be called the thermoelectric *condition* of an element of length of either wire of the couple, at the temperature θ . A is a specific constant for the metal, and may be either positive or negative.

Let θ , θ_0 be the temperatures of the hot and the cold junction, and θ_n the neutral temperature of the two given wires. Let e_n be the thermoelectric condition of one of the wires at the neutral temperature θ_n . Then (1) leads to the integral

$$\frac{e}{e_n} = \varepsilon^{A(\theta_n - \theta)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ε is the base of Napier's logarithms. Hence if the two wires of the couple be distinguished by accents, the parts which the hot junction contributes to the total electromotive force E , will be

$$\frac{e}{e_n} = \varepsilon^{A(\theta - \theta_n)}, \text{ and } \frac{e'}{e'_n} = \varepsilon^{A'(\theta_n - \theta)};$$

and the cold function contributes,

$$\frac{e_0}{e_n} = \varepsilon^{A(\theta_n - \theta_0)}, \text{ and } \frac{e'_0}{e'_n} = \varepsilon^{A'(\theta - \theta_0)}.$$

Hence since the observed or total electromotive force is $E = e \pm e' - (e_0 \pm e'_0)$ in the most general case; and since $e_n = e'_n$ by definition, therefore

$$(3) \quad E = e_n \left\{ \varepsilon^{A(\theta_n - \theta)} \pm \varepsilon^{A'(\theta_n - \theta)} - \left(\varepsilon^{A(\theta_n - \theta_0)} \pm \varepsilon^{A'(\theta_n - \theta_0)} \right) \right\},$$

which is the equation required. With reference to (3) it is to be noted that A , A' , θ_n , may be either positive or negative; hence the exponents may represent either a sum or a difference. Again if θ_m be the temperature at which E is a maximum or minimum, then

$$A\varepsilon^{A(\theta_n - \theta_m)} \pm A'\varepsilon^{A'(\theta_n - \theta_m)} = 0, \quad . \quad . \quad . \quad . \quad (4)$$

whence
$$\theta_m = \theta_n + \frac{\log A \pm \log A'}{A \pm A'}.$$

* This Journal, xlii, p. 134, 1891.

† This Journal, xlii, pp. 242, 255, 1892.

5. Now to show that equation (3) contains Tait's equation as one of its approximate forms, suppose that in an expansion of the exponentials in (3), terms involving higher powers than the second can be rejected. Then (3) leads to

$$(5) \quad E = (\theta - \theta_u) (A^2 \pm A'^2) e_n \left\{ - \left(\frac{A \pm A'}{A^2 \pm A'^2} + \theta_n \right) + \frac{\theta + \theta_u}{2} \right\}$$

But for $dE/d\theta = 0$, $\theta = \theta_m$, and θ_m may therefore be found either by differentiating (5) or by expanding (4). Its value is

$$\theta_m = \theta_n + \frac{A \pm A'}{A^2 \pm A'^2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Substituting (6) in (5),

$$(7) \quad . \quad . \quad . \quad E = (\theta - \theta_u) (A^2 \pm A'^2) e_n \left\{ - \theta_m + \frac{\theta + \theta_u}{2} \right\}.$$

Since $(A^2 \pm A'^2) e_n$ is constant for the given couple, and since θ_m for reasons already given, § 4, may be either positive or negative, equation (7) is identical with Tait's equation.

6. Now it is desirable to look somewhat more in detail at the physical meaning of the elementary equation (1). In my work* on the thermal variation of the viscosity, η , of a very viscous body like marine glue I found that the elementary equation $d\eta/d\theta = -B\eta$, where θ denotes temperature, very fully reproduced the results. But since by Maxwell's theory of viscosity, η is immediately dependent on the configurational stability of a body, the same is true of the rate $d\eta/d\theta$ at which viscosity varies with temperature. Again the result, mentioned in §3, put in the form $dr/d\theta = -br$ shows that like the resistance r , so also the rate $dr/d\theta$ at which resistance decreases with temperature is immediately dependent on the molecular stability of the electrolyte. An interesting research of Auerbach's† on the resistance and bulk density of a given metallic powder (silver) is particularly suggestive here. He finds $dr/d\delta = -nr$, where δ is the bulk density and n constant. Comparing this with the preceding equation, it is clear at once that the internal contacts are similarly increased in the two cases. I therefore infer finally that equation (1) is open to an analogous interpretation, viz: that the thermoelectric condition e of an element of length of the thermocouple is directly related to the molecular stability of the element. In other words two metals are thermoelectrically identical, when the sign and the number of *available* molecular paths which the current (or better the elementary charge) is free to take, is the

* Proceedings Am. Acad., xxvii, p. 13, 1892; this Journal, xlv, p. 87, 1893.

† Auerbach: Wied. Ann., xxviii, p. 609, 1886.

same in both metals; and they differ thermoelectrically when this is not the case. If the transfer of charges is brought about in essentially similar ways both in metals and in electrolytes,* it follows that the available paths of a charge must be in its immediate neighborhood.

Long ago Wild† pointed out that bad metallic conductors were apt to occupy extreme positions in the thermoelectric scale, relative to good conductors. An analogous but much more definite result was brought out strikingly in the investigations on tempered steel‡ already cited, §2. Indeed we found it expedient to refer all our thermoelectric data to an imaginary steel rod whose specific resistance is zero, and an independent consideration§ then showed that this rod would be nearly given by steel (better perhaps by iron) cooled down to the absolute zero of temperature.

7. A somewhat pictorial yet nevertheless interesting development of the preceding paragraphs is obtained as follows: From its mode of derivation, the thermoelectric condition, e , depends on the state of electric dissociation at the given point of the couple, for the given temperature. Hence it is conceivable that a current in the wire, and e , will at all points be reciprocally related. Indeed a serviceable mechanism for Peltier and the Thomson effects is apparently near at hand. To begin with the former: if the two wires of the couple are thermoelectrically active, then they cannot be at the same state of dissociation. If therefore a current crosses the junction, it passes suddenly from a wire in a lower state of dissociation (say) to one in a higher state; or in other words from a metal having relatively fewer available paths to one having relatively more available paths. The case is thus closely analogous to that of a fluid passing from a state of compression suddenly into a state of dilatation, whereby heat is absorbed because internal work is done. Conversely if the current pass from a metal in a more advanced state of dissociation to one in a lower state, the case is that of a liquid passing from greater to smaller bulk and heat is evolved. Here therefore is a tangible mechanism for the Peltier effect: for if it be admitted that electricity travels in definite charges, its condition in a given space must be quite as atomic|| as the matter which transports it, and heat is therefore absorbed or given off in marked degree at the thermoelectric junction for much the same reasons that

* Cf. J. J. Thomson: Application of dynamics, etc., p. 296, and others.

† Wild: cf. Mousson Physik, III, 2d ed., p. 387.

‡ Barus and Strouhal: l. c., p. 62 et seq.

§ l. c., pp. 65, 92.

|| v. Helmholtz commenting on Faraday's law: "... gerade so, als wäre die Elektrizität selbst in Atome getheilt." Berliner Sitzungsberichte, 1883. p. 651.

may be brought forward in accounting for the thermal effects of the expansion of the metals themselves.

Again since in virtue of the character of e the same state of things must supervene at any section between parts of the same wire at different temperatures, a mechanism for the Thomson effect is also apparent and differs from that of the Peltier effect only in degree.

If the current passing through a thermoelectric junction be spoken of as having a certain sectional density or intensity in each of the wires, it is clear that this quantity need not vary from the first wire to the second. What has varied is the number and the internal or molecular distribution of the component paths. The postulated expansion is a configurational change within the fixed bulk of the wires. An example might be given of charges traveling bivalently in one metal and univalently in the other, though I do not wish to limit myself to such a case.

8. In the further pursuit of the subject it is advisable to proceed from a different point of view, by taking advantage of vant'Hoff's* conception of a solid solution. Seeing moreover that in a large and important class of thermo-couples (iridio-platinum and other platinum alloys, iron and steel, etc.) the metals consist of what may be regarded as two different states of concentration of the same alloy, Helmholtz's† results for "Concentrationsströme" are available, particularly in the form given in a remarkable paper by Nernst.‡ Eliminating the osmotic pressures in the usual way, an equation results in which the electromotive force of the couple is expressed in terms of the concentrations and of the velocities of the ions at the temperatures of the junctions together with those temperatures. The problem then consists in finding the conditions or approximations under which the equation reduces to Tait's form. I have carried this out obtaining results of a certain degree of interest but not enough so to make it worth while to reproduce the long computation here.

9. In closing the present paper I had hoped to make a test of equation (3) above, by the aid of data obtained in a direct comparison§ of the platinum-iridioplatinum couple with the air thermometer. Moreover as the corresponding electromotive forces of this couple and of platinum-rhodioplatinum, in

* vant'Hoff: *Zeits. Phys. Chem.*, v, p. 322, 1890. Ideas of this kind seem to have originated with Matthiessen, cf. *Rep. Br. Assoc.* 1866, p. 15, and *Bulletin U. S. G. S.*, No. 14, 1885.

† Helmholtz: *Zur Thermodynamik chem. Vorgänge*, *Verh. d. Berliner Ak.*, July, 1882, p. 489.

‡ Nernst: *Zeits. Phys. Chem.*, iv, p. 129, 1889.

§ Barus: *Bull. U. S. Geolog. Survey*, No. 54, p. 216 et seq., 1889; cf. *Phil. Mag.*, July, 1892, p. 1.

their variations with temperature throughout an interval of nearly 2000° centigrade remain strictly linear functions* of each other, both may be reasonably looked upon as evidencing a clearly pronounced thermoelectric law. However, in the absence of a set of tables similar to Kulik's† for the catenary, the labor of computation becomes so great as to be almost prohibitory. In the mean time I have therefore contented myself by suitably stretching a chain across the chart of observed results (electromotive force in terms of temperature) for iridio-platinum, and noting the essential similarity of the two curves in question.

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