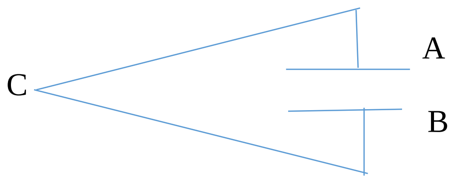
Contact Difference of Potential

Editor's Note: this article is based on hand-written notes in the archives of William McFadden-Orr FRS, Professor of Mathematics in the Royal College of Science. The time of drafting is unknown but was probably around 1900. Parts of the document were difficult to read due to fading but no part has been added or amended. Editorial changes are confined to general lay-out and paragraph structures.

Brian Patrick McArdle; The Library, Royal Irish Academy, Dublin.

The existence of such difference of potential or, to be precise, the fact that, if flexible wires of 2 metals (A and B) are connected at C and each terminates in a plate of its own metal the plates attract one another, shows that there is some modification of the law of electrical force in the neighbourhood of a surface separation or else that the charged electrons which carry the electricity are subject to forces not of electrical origin which must be taken into account. If we define electrical potential V as $\sum e/r$ (with usual notation), then electrical equilibrium between 2 metals A and B requires an equation:



$V_B - V_A = {}_AV^1_B$ (1)

where ${}_AV^1_B$ denotes the work by 2 forces of non-electrical type on a unit charge of electricity in its passage from A to B. Either side of equation (1) is thus the basis of B's potential over A's when in equilibrium. This difference depends on the temperature. The quantity ${}_AV^1_B$ may have the same value whether there is equilibrium or not but we cannot write it as a function of B and B's temperature or as a function of A and A's temperature. The forces from which it arises do not have a potential energy function.

If we have a charge e_A on a metal A, then the energy may be written as $[e_A(V_A+E^1_A) + E_A]$ with E_A being the same as if no charge and E^1_A depending only on A and its temperature. If we have another metal B at the same temperature, then E^1_A, E^1_B and $(E^1_B - E^1_A)$ depend only on A, B and θ. But $(E^1_B - E^1_A)$ may be expressed as the sum of two terms; one involving work and the other involving heat. Neither of these terms is a perfect differential though their sum is. Also the entropy may be written as $(e_A\xi^1_A + \xi_A)$ where ξ_A is the same as if no charge existed. The specific heat of electricity in A is:

$$\sigma_A = d(E^1_A)/d\theta. \quad (2)$$

For equilibrium between A and B we have the further expression:

heat taken in by unit quantity of electricity = $\theta(\xi^1_B - \xi^1_A)$. (3)

And as no work is done on the quantity by all forces; in other words as the electricity is in equilibrium this is equivalent to:

increase of energy = $\theta(\xi^1_B - \xi^1_A)$ (4)

or $(V_B + E^1_B) - (V_A + E^1_A) = \theta(\xi^1_B - \xi^1_A)$ (5)

also $\sigma_A = \theta\, d(\xi_A)/d\theta$. (6)

Differentiating (5) with respect to θ we have in equilibrium:

$$\begin{aligned} d(V_B - V_A)/d\theta &= d(E^1_A - E^1_B)/d\theta + d[\theta(\xi^1_B - \xi^1_A)]/d\theta \\ &= \sigma_A - \sigma_B + \xi^1_B - \xi^1_A + \theta\, d(\xi^1_B - \xi^1_A)/d\theta \\ &= \xi^1_B - \xi^1_A \end{aligned} \quad (7)$$

Thus in equilibrium:

$$\begin{aligned} \sigma_B - \sigma_A &= \theta\, d(\xi^1_B - \xi^1_A)/d\theta \\ &= \theta\, d^2(V_B - V_A)/d\theta^2 \end{aligned} \quad (8)$$

These equations give the laws of the thermoelectric circuit. If electricity passes from A to B at θ_1, is cooled to θ_2, passes across to A and is then heated to θ_1 the result is the same (except as regards heat conduction) as if it passed round the thermoelectric circuit.

The same results can be obtained by a Carnot Cycle passing the current reversibly across from A to B by moving the plates. Note that the attraction between the plates is the same as if the charges were fixed and depend only on the terms of type eV.