XXXVIII. Notes on the seat of the electromotive forces in a voltaic cell

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might be merely to form silver sulphide by direct combination with the silver, I constructed a cell as follows:—A layer of copper sulphide was spread upon a plate of copper; a polished steel plate was laid upon the sulphide, and the whole was strongly compressed in a vice. The steel plate was then removed, and a thin layer of silver sulphide was spread upon the smooth surface of the copper sulphide. The cell was completed by pressing a silver plate upon the silver sulphide. This was found upon trial to give a current which, with an external circuit of low resistance, was many times stronger than that generated by any of the cells previously made. It seems to be exactly analogous in its action to a Daniell cell consisting of plates of zinc and copper in solutions of zinc sulphate and copper sulphate. The quantity of the copper sulphide would be gradually diminished, copper being deposited on the copper plate, while the quantity of silver sulphide would continually increase with consumption of the silver.

In conclusion, it seems probable that, by selecting such metals as experiment might prove to be better suited for the purpose than silver and copper, a cell might be constructed upon the principle of that described in the above paragraph which would be of practical and commercial value.

XXXVIII. Notes on the Seat of the Electromotive Forces in a Voltaic Cell. By J. Hopkinson, M.A., D.Sc., F.R.S.*

The following is an expansion of some short remarks I made when Dr. Lodge’s paper was read at the Society of Telegraph Engineers.

1. The controversy between those who hold that the difference of potential between zinc and copper in contact is what is deduced by electrostatic methods, and those who hold that it is measured by the Peltier effect, is one of the relative simplicity of certain hypotheses and definitions used to represent admitted facts.

Taking thermo-electric phenomena alone, we are not imperatively driven to the conclusion that the difference of potential between zinc and copper is the small quantity which the Peltier effect would indicate; but by assuming with Sir W. Thomson that there is an electric property which may be expressed as an electric convection of heat, or that electricity has specific heat, we may make the potential difference as great as we please without contradiction of any dynamical principle or known physical fact. Let us start with the physical facts, and introduce hypothesis as it is wanted.

* Communicated by the Author.
These are, as far as we want them:—(1) If a circuit consist of one metal only, the electromotive force around the circuit is nil however the temperature may vary in different parts; this of course neglecting the thermoelectric effects of stress and magnetism discovered by Sir W. Thomson. (2) If the circuit consist of two metals with the junctions at different temperatures $t_1$, $t_2$, then the electromotive force round the circuit is the difference of a function of $t_2$ and of the same function of $t_1$. According to Prof. Tait the function is

$$b(t_2 - t_1)\left(T - \frac{t_2 + t_1}{2}\right),$$

or, as we may write it, $A + Bt_3 - C\frac{t_2^2}{2}$

$$\left\{ A + Bt_1 - C\frac{t_1^2}{2} \right\};$$

the series may perhaps extend further, but, according to Tait's experiments, the first three terms are all that are needed.

Now, but for the second law of thermodynamics we should naturally assume that $A + Bt_3 - C\frac{t_3^2}{2}$ was the difference of potentials at the junction of temperature $t_3$, and $A + Bt_1 - C\frac{t_1^2}{2}$ at the junctions of temperature $t_1$; we should further assume that what the unit of electricity did was to take energy $A + Bt_3 - C\frac{t_3^2}{2}$ out of the region immediately around the hot junction with disappearance of that amount of heat, and to take energy $A + Bt_1 - C\frac{t_1^2}{2}$ into the region immediately surrounding the cold junction, with liberation of that amount of heat. Now apply the second law of thermodynamics in the form $\sum \frac{\Delta Q}{T} = 0$, and we have

$$A\left(\frac{1}{t_2} - \frac{1}{t_1}\right) - C\frac{t_2 - t_1}{2} = 0,$$

whence it follows that $A = 0$, which may be, and that $C = 0$, which is contrary to experiment. The current then must do something else than has been supposed, and the hypotheses differ in expression at least as to what that something else is. The fact to be expressed is simply this: when a current passes in an unequally heated metal, there is a reversible transference of heat from one part of the metal to another, whereby heat is withdrawn from or given to an element of the substance when a current passes through it between points differing in temperature, and is given to or withdrawn from that element if the current be reversed. Sir W.
Thomson proved that this follows from the fact of thermo-electric inversions and the second law of thermodynamics, and verified the inference by experiment, his reasoning being quite independent of any hypothesis.

Suppose wires of metals X and Y are joined at their extremities, and the junctions are kept at temperatures $t_2, t_1$. The observed electromotive force around the circuit is $f(t_2) - f(t_1)$ or within limits according to Tait, $B(t_2 - t_1) - \frac{1}{3} C(t_2^3 - t_1^3)$. The work done or dissipated by the current when unit of electricity has passed is $f(t_2) - f(t_1)$, and this is obtained by abstraction of heat from certain parts of the circuit and liberation of heat at other parts by a perfectly reversible process. Let $F(t_2)$ be the amount of heat which disappears from the region surrounding the junction $t_2$ when unit of electricity has passed from X to Y. Let an element of the wire X have its ends at temperatures $t$ and $t + dt$, and let the quantity of heat abstracted from this element when unit of electricity passes from $t$ to $t + dt$ be represented by $\phi(t) dt$, and let the same for Y be represented by $\psi(t) dt$. By the first law of thermodynamics we have

$$F(t_2) + \int_{t}^{t_2} \psi(t) dt - F(t_1) + \int_{t_1}^{t} \phi(t) dt = f(t_2) - f(t_1),$$

and by the second law, since the transference of heat from part to part is reversible,

$$F(t_2)/t_2 - F(t_1)/t_1 + \int_{t}^{t_2} \phi(t)/t . dt - \int_{t_1}^{t} \psi(t)/t . dt = 0.$$

Differentiating we have

$$\begin{cases} F'(t) + \phi(t) - \psi(t) = f'(t), \\ F'(t)/t - F(t)/t^2 + \phi(t)/t - \psi(t)/t = 0; \end{cases}$$

whence

$$\begin{cases} \frac{F(t)}{t} = tf''(t) = Bt - Ct^2, \\ \phi(t) - \psi(t) = tf''(t) = Ct. \end{cases}$$

This really contains the whole of thermoelectric theory without any reference to local differences of potential, but only to electromotive force round a complete circuit. But when we come to the question of difference of potential within the substance at different parts of the circuit, we find that according as we treat it in one or the other of the following ways we may leave the difference of potential at the junctions indeterminate and free to be settled in accordance with hypotheses which may be found convenient in electrostatics, or we find it determined for us, and must make our electrostatic hypotheses accord therewith.
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The first way is that of Thomson, as I understand it. Assume that there is no thermoelectric difference of potential between parts of the same metal at different temperatures, at all events till electrostatic experiments shall show that there is. It follows that we must assume that the passage of electricity between two points at different temperatures must cause a conveyance of energy to or from the region between those points by some other means than by passage from one potential to another. Such conveyance of energy may be very properly likened to the convection of heat by fluid in a tube, for although convection is in general dissipative, it is not necessarily so, e.g. a theoretically perfect regenerator. Suppose, then, that in metal $X$ unit of electricity carries with it $\int \phi(t)\,dt$ of heat, and in metal $Y$, $\int \psi(t)\,dt$; this will account for the proved transference of heat in the two metals. When a unit of electricity passes across a junction at temperature $t$ from $X$ to $Y$, it must liberate at that junction a quantity of heat $\int \phi(t)\,dt - \int \psi(t)\,dt$; but the actual effect at this junction is that heat $F(t)$ disappears; hence the excess of potential at the junction of $Y$ over $X$ must be

$$F(t) + \int \phi(t)\,dt - \int \psi(t)\,dt$$

$A$ being a constant introduced in integration. If, then, we assume a "specific heat of electricity," the actual difference of potential at a junction may contain a constant term of any value that electrostatic experiments indicate.

But the facts may be expressed without assuming that electricity conveys energy in any other way than by passing from a point of one potential to a point of different potential. This method must be adopted by those who maintain that the Peltier effect measures the difference of potential between two metals in contact. Define that if unit-electricity in passing from $A$ to $B$ points in a conductor homogeneous or heterogeneous does work, whether in heating the conductor, chemical changes, or otherwise, the excess of potential of $A$ over $B$ shall be measured by the work done by the electricity. This is no more than defining what we mean by the potential within a conductor, a thing we do not need to do in electrostatics. This definition accepted, all the rest follows. Between two points differing in temperature $dt$ the rise of potential is $\phi(t)\,dt$ in $X$, $\psi(t)\,dt$ in $Y$; at the junction the excess of potential of $Y$ over $X$ is $F(t) = Bt - \frac{1}{2}Ct^2$.

The second method of arranging one's ideas on this subject has the advantage that it dispenses with assuming a new property of that hypothetical something, electricity; but there is nothing confusing in the first method.
The thermodynamics of the voltaic circuit may be dealt with on either method of treatment; in the equations already used, instead of speaking only of the heat disappearing from any region, we have to consider the heat disappearing when the unit electricity passes plus the energy liberated by the chemical changes which occur. Consider a thermoelectric combination in which there is chemical action at the junctions when a current passes.

If \( G(t) \) be the function of the temperature which represents the energy of the chemical reaction which occurs when unit of electricity passes from \( X \) to \( Y \) across the junction, we have

\[
F(t_2) + G(t_2) - F(t_1) - G(t_1) + \int_{t_1}^{t_2} \psi(t) \, dt + \int_{t_1}^{t_2} \phi(t) \, dt = f(t_2) - f(t_1),
\]

\[
F'(t) + G'(t) + \phi(t) - \psi(t) = f'(t),
\]

\[
F'(t)/t - F(t)/t^2 + \phi(t)/t - \psi(t)/t = 0;
\]

whence

\[
F(t) = tf''(t) - tG'(t),
\]

\[
\phi(t) - \psi(t) = t \{ f'''(t) - G''(t) \}.\]
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passed is addition of copper to one plate, loss of copper from the other plate; what could be inferred? Imagine a region enclosing the anode, when a current has passed, what changes have occurred within the region? An equivalent of copper has disappeared from the anode, and that same quantity of copper has departed and gone outside the region. But by our supposition, nothing else has happened barring increase of volume for liquid by diminished volume of metallic copper; there is no more and no less CuSO₄ in the region, the same quantity therefore of SO₄. All the work done in the region is to tear off a little copper from the surface of the anode and to remove it elsewhere. If the fact were as assumed it would follow that the passage of the current did little work in the passage from copper to sulphate of copper, and consequently that the difference of potential between the two is small. But the fact is, other things happen in the cell than increase of the kathode and diminution of the anode. In contact with the anode there is an increase of CuSO₄, in contact with the kathode CuSO₄ disappears: this is a familiar observation to every one. Reconsider the region round the anode. Assume as another extreme hypothesis that after a current has passed we have in this region the same quantity as before of copper, but more CuSO₄; SO₄ has entered the region and has combined with the copper. A large amount of energy is therefore brought into the region, which can only be accounted for by supposing that the electricity has passed from a lower potential in the copper to a higher potential in the electrolyte. The legitimate conclusion is, then, that there is between Cu and CuSO₄ a difference of potential corresponding to the energy of combination; and the basis of the conclusion is the simple observation that the copper is dissolved off one plate but remains in its neighbourhood, whilst it is precipitated on the other plate, impoverishing the solution. In other words, it is the SO₄ that travels, not the Cu.

Now consider the ordinary Daniell's cell. Is there a substantial difference of potential at the junction of CuSO₄ and ZnSO₄? Is there, in fact, a difference apart from the Peltier difference? Imagine a region enclosing the junction in question; it might have been that the effect of a current passing was to increase the zinc and diminish the copper by an equivalent of the electricity which passed, from which we should have inferred that the seat of the electromotive force in a Daniell's cell was at the junction of the two solutions. But it is more nearly the fact that no change whatever occurs in the region in question when a current passes, and that all that
happens is that a certain quantity of $\text{SO}_4$ enters the region and an equal quantity departs from it, from which follows that there is no potential difference, other than a Peltier difference, at this junction.

Neither of the extreme suppositions we have made as to concentration or impoverishment of the solution is in fact true, but they serve to show that the position of the steps in potential depends entirely on the travelling of the ions. The fact is, that in general both ions travel in proportions dependent on the condition of the electrolytes; it is probable that the travelling of the $\text{SO}_4$ depends on some acidity of the solution. Given the proportion in which the ions travel and the energy of the reversible chemical reaction which occurs, and we can calculate the differences of potential at the junctions.

In the preceding reasoning an assumption has been made, but not stated. It has been assumed that the passage of a current in an electrolyte is accompanied by a movement of ions only, and not by a movement of molecules of the salt; that is, when unit of electricity passes through a solution of $\text{CuSO}_4$, $x\text{Cu}$ travels in one direction and $(1-x)\text{SO}_4$ in the opposite direction, but that $\text{CuSO}_4$ does not travel without exchanges of $\text{Cu}$ and of $\text{SO}_4$ between the molecules of $\text{CuSO}_4$. In the supposed case when there is no concentration around the anode, my assumption is that $\text{Cu}$ is dissolved off the anode, and that an equal quantity of $\text{Cu}$ leaves the region around the anode as $\text{Cu}$ by exchanges between the molecules of $\text{CuSO}_4$. But it is competent to some one else to assume that in this case $\text{SO}_4$ as $\text{SO}_4$ enters the region by exchanges between the molecules of $\text{CuSO}_4$, and that at the same time a molecule of $\text{CuSO}_4$ leaves the region without undergoing any change. Such a one would truly say that there was no inconsistency in his assumption; and that if it be admitted, it follows that the difference of potential at the junction $\text{CuSO}_4 \mid \text{Cu}$ is that represented by the energy of the reaction. I prefer the assumption I have made, because it adds nothing to the ordinary chemical theory of electrolysis; but it is easy to imagine that facts may be discovered more easily expressed by supposing that an electric current causes a migration of molecules of the salt, as well as a migration of the components of the salt.