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THERMODYNAMICS OF THE VOLTAIC CELL.

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I. THEORETICAL.

THE theory, commonly known as Thomson's, that the electrical energy of a reversible Voltaic cell is the equivalent of the chemical energy transformed has been abandoned as an exact expression of the facts since the appearance of Helmholtz's paper on "Die Thermodynamik Chemischer Vorgänge,"¹ followed by the experimental corroboration of Jahn² and others. It is now well understood that the electrical energy output of a reversible cell may be either greater or less than the heat equivalent of the chemical reactions. It is greater when the temperature coefficient of the cell is positive, and it is less when it is negative. If such a cell be connected in a circuit with an external resistance so large in comparison with the internal resistance of the cell that the Joule's heat due to the internal resistance is vanishingly small, then heat must be added to the cell to keep its temperature constant when a current passes through it if its temperature coefficient is positive. On the contrary, if its temperature coefficient is negative, it must give up heat to surrounding bodies to remain in thermal equilibrium. In the former case all the potential chemical energy transformed goes over into electrical energy, and in addition some heat undergoes a similar transformation. In the latter case only a part

¹ Sitzungsber. der Akad. der Wiss. zu Berlin, I., 1882, p. 24.

² Wied. Ann., Vol. XXVIII., pp. 21 and 491, 1886.

of the transformed chemical energy becomes electrical in form; the remainder appears as heat. The calomel cell devised by Helmholtz is an example of a cell with a positive temperature coefficient and a converter of heat into electrical energy. The Clark standard cell, on the other hand, has a negative coefficient and gives up heat or grows warmer when functioning as a primary cell. In the Daniell cell the electrical energy is almost the exact equivalent of the difference between the heat of combination of the zinc sulphate formed and the copper sulphate decomposed.

The Helmholtz principle has hitherto been applied to a Voltaic cell in bulk, as it were. In the investigation which I am about to describe I have applied it to the cell in parts—that is, the positive and negative sides of a Voltaic cell are treated separately. In other words, I have considered the thermodynamics of a cell more in detail than has hitherto been done. This treatment may be regarded as an extension of the Helmholtz principle.

A reversible cell is one of which it is at least theoretically true that the electrical energy obtained from its action, when applied inversely so as to reverse the chemical operations, exactly suffices to restore the cell to its initial condition. Imagine the electromotive force of a Daniell cell compensated by a second inverse electromotive force. If the latter is reduced, a current passes through the Daniell in the normal direction, zinc goes into solution and copper is deposited. If the opposing electromotive force is made to exceed that of the Daniell, copper goes into solution and zinc is deposited. When equal quantities of electricity have passed in the two directions, the cell has been restored to its initial condition and the cycle is complete. Hence the laws of thermodynamics may be applied to such a reversible process.

Let T be the absolute temperature and dH the quantity of heat which must be applied to the cell or be taken from it in order to keep its temperature constant during the passage of a quantity of electricity dq . Also let u be the total energy contained in the cell. It is a function of the temperature of both the positive and negative sides of the cell, the cell being constructed so that the two sides may be separately considered. It is also a function of the quantity of electricity q passing through the cell.

Then from the principle of the conservation of energy (indicating the positive side of the cell by p and the negative by n subscript, and letting E be the electromotive force),

$$J \cdot dH = \left(\frac{\partial u}{\partial T} \right)_p dT + \left(\frac{\partial u}{\partial T} \right)_n dT + \left[\frac{\partial u}{\partial q} + E \right] dq. \quad (1)$$

The change of entropy dS during the flow of dq is

$$dS = J \frac{dH}{T} = \frac{1}{T} \left[\left(\frac{\partial u}{\partial T} \right)_p dT + \left(\frac{\partial u}{\partial T} \right)_n dT \right] + \frac{1}{T} \left[\frac{\partial u}{\partial q} + E \right] dq. \quad (2)$$

Hence

$$\frac{\partial S}{\partial T} = \frac{1}{T} \left[\left(\frac{\partial u}{\partial T} \right)_p + \left(\frac{\partial u}{\partial T} \right)_n \right] \text{ and } \frac{\partial S}{\partial q} = \frac{1}{T} \left[\frac{\partial u}{\partial q} + E \right]. \quad (3)$$

Differentiating the first of equations (3) with respect to q and the second with respect to T ,

$$\begin{aligned} \frac{\partial^2 S}{\partial T \cdot \partial q} &= \frac{1}{T} \left[\left(\frac{\partial^2 u}{\partial T \cdot \partial q} \right)_p + \left(\frac{\partial^2 u}{\partial T \cdot \partial q} \right)_n \right] \\ &= \frac{1}{T} \left[\left(\frac{\partial^2 u}{\partial T \cdot \partial q} \right)_p + \left(\frac{\partial^2 u}{\partial T \cdot \partial q} \right)_n + \left(\frac{\partial E}{\partial T} \right)_p + \left(\frac{\partial E}{\partial T} \right)_n \right] - \left[\frac{\partial u}{\partial q} + E \right] \frac{1}{T^2}, \end{aligned}$$

or

$$T \left[\left(\frac{\partial E}{\partial T} \right)_p + \left(\frac{\partial E}{\partial T} \right)_n \right] = \frac{\partial u}{\partial q} + E. \quad (4)$$

Substituting in equation (1),

$$J \cdot dH = \left(\frac{\partial u}{\partial T} \right)_p dT + \left(\frac{\partial u}{\partial T} \right)_n dT + T \left[\left(\frac{\partial E}{\partial T} \right)_p + \left(\frac{\partial E}{\partial T} \right)_n \right] dq. \quad (5)$$

This last equation is the heat, expressed mechanically, which must be added to the cell or abstracted from it to keep its temperature constant while the quantity of electricity dq is passing through it. In fact if dT is zero, the equation becomes

$$J \cdot dH = T \left[\left(\frac{\partial E}{\partial T} \right)_p + \left(\frac{\partial E}{\partial T} \right)_n \right] dq. \quad (6)$$

$\left(\frac{\partial E}{\partial T} \right)_p$ is the temperature coefficient of the positive side of the cell, the temperature of the negative side remaining constant; $\left(\frac{\partial E}{\partial T} \right)_n$ is

the temperature coefficient of the negative side, the temperature of the positive side being maintained constant; the whole bracketed quantity is the temperature coefficient of the cell as a whole, neglecting any small coefficient due to the thermo-electromotive force at the junction of the two halves of the cell.

These positive and negative coefficients are the thermo-electromotive forces at the contacts between the two electrodes and the liquids bathing them respectively. Still neglecting the thermo-electromotive force at the junction between the two sides of the cell, the temperature coefficient of the entire cell is zero only when

$$\left(\frac{\partial E}{\partial T}\right)_p + \left(\frac{\partial E}{\partial T}\right)_n = 0,$$

that is, when the coefficients on the two sides are numerically equal and of opposite sign; or else when both are zero. The first condition is nearly realized in the Daniell cell. For $\text{Cu} - \text{CuSO}_4$, $\left(\frac{\partial E}{\partial T}\right)_p$

is 0.00073; for $\text{Zn} - \text{ZnSO}_4$, $\left(\frac{\partial E}{\partial T}\right)_n$ is 0.00079. The direction of

these electromotive forces is in each case from the liquid to the metal across the heated contact. Hence the former gives to the cell a positive temperature coefficient, and the latter a negative one, while the coefficient of the cell in its entirety is negative and small, as I have shown elsewhere.¹

A further consideration of equation (6) shows that the maintenance of a constant temperature on both sides of the cell during the flow of the quantity dq , requires that heat represented in mechanical measure by $\left(\frac{\partial E}{\partial T}\right)_p dq$ must be *added* to the positive side of the cell, and $\left(\frac{\partial E}{\partial T}\right)_n dq$ must be *withdrawn* from the negative side; or, in other words, these expressions represent the loss of heat on the positive side, and the gain on the negative respectively. Divide them by the thermal capacity of the two sides of the cell, and we have the *fall* of temperature on the positive side and the *rise* on the negative. These temperature changes are due to the thermal or Peltier elec-

¹ Primary Batteries, pp. 137-146.

tromotive forces at the two contacts. On the negative side of the Daniell cell, for example, the current from the zinc to the liquid flows against the Peltier electromotive force, and heat is generated. On the opposite side the current flows from the copper to the liquid, or with the Peltier electromotive force at the contact, and therefore heat is absorbed and converted into the energy of the current.

If a reverse current be sent through the cell, all the physical phenomena, except that of the Joule's heat, are reversed. The current on the positive side flows from the copper to the liquid, or against the thermo-electromotive force, and Peltier heat is generated. On the zinc side heat is absorbed. With a reverse current, therefore, the temperature of the positive side of the cell rises faster than that of the negative, while with a direct current the temperature of the negative side rises faster than that of the positive, that is, under practical conditions where the Joule's heat causes a rise of the temperature of the entire cell.

While equation (6) is perfectly general, the preceding conclusions are applicable only when the Peltier electromotive force at the contact of the electrode and the liquid is directed from the latter to the former across the heated junction, both on the positive and the negative side of the cell. There are some exceptions to this general rule. For example, the thermo-electromotive force of Fe—FeSO_4 is zero. Hence a cell consisting of $\text{Fe—FeSO}_4\text{—CuSO}_4\text{—Cu}$ has a positive temperature coefficient¹ due to the thermo-electromotive force on the copper side, and the Peltier phenomenon is confined to the positive side of the cell. In the case of the Voltaic series $\text{Ni—NiSO}_4\text{—CuSO}_4\text{—Cu}$, the two thermo-electromotive forces are in the same direction through the cell. The temperature coefficient is large—about 0.8 per cent., and heat is absorbed at both electrodes. Such a cell takes heat from the surroundings on both sides and converts it into electrical energy.

II. EXPERIMENTAL.

The general conclusions arrived at above I have not found it difficult to confirm qualitatively. It was only when quantitative de-

¹ A one-volt standard cell, *Am. Jour. Sci.*, Vol XLVI., p. 64.

terminations were attempted that serious difficulties were encountered. These I have in a large degree happily overcome. The results are highly interesting.

The Daniell cell was chosen as the most convenient one for the experimental work, particularly because the necessary constants pertaining to it are known with a good degree of accuracy.

The cell was made as follows : Two glass tubes 9.5 cm. long and 3 cm. in diameter were provided near the bottom with side tubes 18 mm. long and 18 mm. wide (Fig. 1).

Fig. 1.

Heavy, tight-fitting rubber collars served to connect the two halves of the cell together, with a plate of fine unglazed porcelain between them as shown. The edges of the porcelain plate were covered with paraffin after the rubber collars had been bound together with fine iron wire. No difficulty was found in making a water-tight joint.

In most of the experiments 10 per cent. water-free solutions of zinc and copper sulphates were used. These solutions have relative conductances of 321 to 320.¹ They were chosen with the object of eliminating as far as possible the inequalities of Joule's heat between the two sides of the cell. In every experiment 40 c.c. of each solution were placed in the double cell, which was supported by a stout cord in a large pasteboard box and completely surrounded and covered with eider down.

The earlier observations were made with two Haak thermometers reading directly to fifths, and by means of a telescope to hundredths of a degree. The copper and zinc plates were attached directly to the thermometers by rubber bands, and the liquids were stirred before taking observations by moving the thermometers and the attached plates back and forth. Since the internal resistance of the cell was over 100 ohms, it was necessary to put it in series with a few storage cells and some resistance, with the double object of varying the current and of causing a reverse current to traverse the experimental cell.

¹ Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, p. 151.

The current was measured as follows : The electromotive force of a Weston standard cell was balanced against the fall of potential over a portion of two resistance boxes containing 10,000 ohms and connected in series with a storage cell. By means of an appropriate switch, consisting of mercury cups in a plate of paraffin, this potential drop in the auxiliary circuit was balanced against the fall of potential over the requisite number of ohms in the main circuit. For example, for 0.03 ampère the fall of potential over 34 ohms was thus balanced indirectly against the electromotive force of the Weston cell, which was very nearly 1.02 volts. The current was not allowed to vary more than about 0.05 per cent.

Fig. 2 shows the results obtained with a current of 0.02 ampère. Curve I, I, I, belongs to the zinc sulphate and II, II, II, to the cop-

Fig. 2.

per sulphate, both of which in this case were fifteen-per-cent. solutions. These curves are valuable chiefly because they exhibit two facts rather strikingly. The current through the cell was reversed at the points indicated by the two vertical dotted lines. In the first place it is evident that the temperature always rises most rapidly on the side of the cell by which the current enters. The same fact

appears in every case and in every trial. In the second place the curves show how the phenomenon is complicated by the change in concentration. For this reason the difference in temperature between the two sides of the cell is less before reversal than it would otherwise be, for the concentration and conductance of the zinc sulphate increase while those of the copper sulphate decrease. After reversal this change in concentration accelerates the rise of temperature on the copper side and retards it on the zinc side. After reversing the current an established difference of temperature is reduced to zero in about half the time necessary to produce it. It is therefore obvious that some method had to be devised to eliminate the effect of this change of concentration as well as that of any difference in resistance on the two sides due to the dimensions of the apparatus, position of the plates, etc., if reliable quantitative results were to be obtained. For this purpose the following expedients were adopted: First, ten-per-cent. solutions of practically equal specific conductances were used. Second, the duration of any series of observations in either direction was taken inversely as the current, so that the same quantity of electricity was always transmitted with the same changes in concentration. This quantity was 72 coulombs,—0.03 ampère for 40 min., 0.04 ampère for 30 min.; etc.

Third, a curve was constructed from observations showing the equalization of any established difference of temperature between the two sides of the cell as a function of the time. This may be called for convenience a "cooling curve." By means of this curve it is not difficult to correct any series of observations so as to obtain the temperature differences which would have been observed if heat had not flowed from one side to the other during the time covered by the series. Fourth, to eliminate the effect of the change in concentration and the lack of equal resistance on the two sides, a series of observations was first taken with a direct current through the cell, and then after reducing the temperature difference again to about zero without any current, another series of equal duration was taken with the current through the cell reversed. After correcting both series by the "cooling curve," the half sum of the two maximum differences of temperature was taken as the correct value. The

difference between the heats generated on the positive and negative sides, with the current first direct and then reversed, may be expressed by the two equations (R' being the resistance of the zinc side and R'' that of the copper),

$$\begin{aligned} J \cdot H' &= I^2 R' t - I^2 dR' t + T \left(\frac{\partial E}{\partial T} \right)_n It \\ &\quad - \left[I^2 R'' t + I^2 dR'' t - T \left(\frac{\partial E}{\partial T} \right)_p It \right]. \\ J \cdot H'' &= I^2 R' t - I^2 dR' t - T \left(\frac{\partial E}{\partial T} \right)_n It \\ &\quad - \left[I^2 R'' t + I^2 dR'' t + T \left(\frac{\partial E}{\partial T} \right)_p It \right]. \end{aligned}$$

Half the algebraic differences of these two is

$$T \left(\frac{\partial E}{\partial T} \right)_p It + T \left(\frac{\partial E}{\partial T} \right)_n It = J \cdot dH,$$

and this is the quantity sought, considered arithmetically.

In the later experiments the thermometers were discarded and two thermal couples, consisting of thin iron and "constantan" wires, were substituted for them. The junctions were thickly covered with shellac and were then enclosed in thin glass tubes with enough mercury to cover the soldered junctions to aid in conductivity of heat. One junction was placed in the zinc sulphate side, the other in the copper sulphate. The plates of the cell were attached to the glass tubes containing the thermal junctions, and the tubes in turn were held by rubber bands to two long, thin rods of wood held firmly at their upper ends. The stirring of the liquids was thus easily accomplished by bending the wooden rods.

The galvanometer connected in series with the thermal couples was astatic and sufficiently sensitive, but its period was about 20 sec. The reading telescope was placed at a distance of 2.8 m., and the reduced deflection per degree difference of temperature was 138.3. The zero position was unfortunately a drifting one, so that the cross-wire of the telescope had to be set on it before every reading. The liquids were stirred for fifteen seconds before every reading. Five seconds intervened between the stirring and the observation.

With this arrangement I set out to determine, first, whether the temperature difference per second is proportional to the current, as equation (6) requires; second, how nearly the observed value of any established temperature difference agrees with the calculated value.

Fig. 3 shows the results of one series with a current of 0.05 ampère. Curve I belongs to the series of observations with a direct current, curve II to those with the current reversed, and III is the "cooling curve." Many other observations were taken for curve III, all of them agreeing well with this series.

Time in Min.	Reading, Deflection and Cooling Correction.					
	0.02		0.03		0.04	
0	3.6		4.0		1.0	
5	4.6		8.5	0.2	3.7	
10	6.0		11.0	1.1	5.0	
15	6.4		12.5	1.4	7.5	0.2
20	7.3	0.2	14.0	1.4	8.6	0.6
25	7.7	0.4	15.0	1.6	10.0	0.9
30	8.0	0.5	16.2	1.7	11.1	1.1
35	8.3	0.6	16.5	1.8		
40	8.5	0.7	16.8	1.9		
45	9.0	0.8				
50	9.1	0.9				
55	9.5	1.0				
60	10.0	1.1				
		6.4		12.8		10.1
Corrected Deflections,		12.6	23.9		12.9	
REVERSE CURRENT.						
0	2.8		-0.2		3.3	
5	6.9		3.0		8.7	0.2
10	10.0	0.7	5.0		13.2	1.2
15	12.0	1.2	7.7	0.2	16.9	1.6
20	13.3	1.3	9.2	0.3	20.0	2.1
25	14.4	1.5	10.9	1.1	22.8	2.4
30	15.5	1.6	12.0	1.4	24.8	2.8
35	16.8	1.8	13.7	1.5		
40	17.2	1.9	14.6	1.6		
45	17.5	2.0				
50	17.8	2.0				
55	18.5	2.1				
60	18.6	2.1				
		15.8		14.8		21.5
Corrected Deflections,		34.0	21.4		31.8	
Half Sum,		23.30	22.65		22.35	

Time in Min.	Reading, Deflection and Cooling Correction.					
	0.05		0.05		0.06	
0	2.0		3.6		0	
4	5.0		5.8		4.1	
8	7.0	0.2	7.9	0.2	6.8	
12	7.0	0.4	9.6	0.8	10.0	0.7
16	8.9	0.5	12.0	1.0	11.3	0.9
20	9.0	0.7	13.8	1.1	12.7	1.1
24	10.8	1.0	15.4	1.2		
		8.8		11.8		12.7
Corrected Deflections,		11.6	16.1		15.4	

REVERSE CURRENT.						
0	-4.0		4.8		1.0	
4	2.8		9.8	0.3	8.7	
8	8.0		14.1	1.1	13.2	1.0
12	12.5	0.9	18.2	1.4	18.5	1.4
16	16.6	1.3	21.5	1.8	22.8	1.8
20	19.4	1.6	23.3	2.1	26.0	2.3
24	23.0	2.0	26.0	2.3		
		27.0		21.2		25.0
Corrected Deflections,		32.8	30.2		31.5	
Half Sum,		22.20	23.15		23.45	
Mean of all,			22.85			

The above table contains all the essential data for the several currents used.

A deflection of 22.85 scale parts corresponds to a difference of temperature of $0^{\circ}.165$. If the phenomenon here measured is proportional to the current, then since the quantities transmitted with the above currents were all equal, the resulting corrected deflections should be equal. The results represented by the half sums show good agreement :

Current in Amperes.	Period in Min.	Half Sum.	Variation from Mean.
0.02	60	23.30	+0.45
0.03	40	22.65	-0.20
0.04	30	22.35	-0.50
0.05	24	22.20	-0.65
0.05	24	23.15	+0.30
0.06	20	23.45	+0.60

It is obvious that the heat generated on one side and the heat absorbed on the other are both proportional to the current in the case of a Daniell cell.

Fig. 3.

To calculate the difference of temperature between the two halves of the cell, it must be remembered that equation (6) expresses only the heat required to keep the temperature of the whole cell constant during the passage of a given quantity of electricity. To calculate the quantity corresponding to the observed mean of 22.85 or 0°.165, we must find the calories generated on one side of the cell and absorbed on the other and divide their sum by the thermal capacity of half the cell. For this purpose we have the following data :

$$I/J = 0.24 \quad T = 292$$

$$\left(\frac{\partial E}{\partial T}\right)_n = 0.00079 \quad \left(\frac{\partial E}{\partial T}\right)_p = 0.00073^1$$

$$dq \text{ or } Q = 72.$$

Hence $H = 0.24 \times 0.00079 \times 292 \times 72 = 3.99$ (zinc side)

and $H = 0.24 \times 0.00073 \times 292 \times 72 = 3.68$ (copper side).

¹ Primary Batteries, pp. 140, 141.

The specific heat per unit volume of the solutions is 0.99. The mean of two determinations of the thermal capacity of the unfilled cell was 16.5. Hence the thermal capacity of one-half the cell is

$$40 \times 0.99 + 8.25 = 47.85.$$

The temperature difference produced by the passage of 72 coulombs should then be

$$(3.99 + 3.68) \div 47.85 = 0^{\circ}.160.$$

The mean observed value is $0^{\circ}.165$.

I must reluctantly defer the application of the principles herein discussed to other types of cells for some later opportunity. It is obvious that the same method of investigation may be applied to a silver voltameter, a copper voltameter or a zinc voltameter. The essential fact involved in all is the presence of Peltier or thermo-electromotive forces.

My thanks are due to Professor H. F. Weber for his courtesy in welcoming me to his laboratory and in placing at my disposal the requisite apparatus for the work described in this paper.

ZÜRICH, April 3, 1900.