The Reversibility of Voltaic Cells

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XI. *The Reversibility of Voltaic Cells.**By T. SIDNEY MOORE*.*

THE experiments described in this paper were carried out in order to test the reversibility of certain voltaic cells. Five cells have been treated:—Copper-zinc in sulphates, copper-cadmium in sulphates, copper-zinc in chlorides, and copper-cadmium in chlorides, in addition to the Clark cell. Preliminary experiments were carried out with nitrate cells, but the surfaces of the electrodes were spoiled by the nitrate solutions, and these cells have been put aside.

The diagram of the apparatus is shown in fig. 1.

ABCDEF shows the ordinary potentiometer arrangement, F being the experimental cell and E the Clark standard. G is an adjustable resistance, and by means of its three-way key H either the cell F may be placed in closed circuit with G, or the accumulators may be opposed to the experimental cell through the resistance G.

Fig. 1.

By means of this arrangement it is easy to get two determinations of the internal resistance of the cell F. Firstly, by means of the direct current when the cell F is in circuit with G, and, secondly, by means of the reading of the potentiometer when a current is running through F and in opposition to it.

* Read March 2, 1900. (Communicated by Dr. Lehfeldt.)

But to calculate the internal resistance from the latter experiment it is necessary to assume that the experimental cell is reversible. Thus, if we assume that the cell is reversible, the difference between the values obtained for the internal resistance will measure the divergence of the cell from reversibility.

The results were calculated from formulæ which are easily deduced.

Let D = E.M.F. of experimental cell on open circuit.

D_1 = " " " when running through
resistance R ohms.

D_2 = " " " when reversed through
 R ohms.

B = " " the accumulators.

Current from cell through $R = \frac{D}{R+r}$, where r is internal resistance of cell.

$$\therefore \text{E.M.F. between poles of cell} = \frac{D}{R+r} \times R = D_1;$$

$$\therefore r = \frac{D-D_1}{D_1} \times R. \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Or, if we regard the internal resistance as known, we have

$$D_1 = \frac{RD}{R+r}. \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Now the reverse current through cell and resistance R ohms

$$= \frac{B-D}{R+r}, \text{ if the cell is reversible;}$$

$$\therefore \text{External E.M.F.} = R \times \frac{B-D}{R+r};$$

$$\therefore \text{E.M.F. between poles} = B - \frac{R(B-D)}{R+r} = D_2;$$

$$\therefore r = \frac{D_2-D}{B-D_2} R. \quad . \quad . \quad . \quad . \quad . \quad (c)$$

Or, if we regard the internal resistance as known,

$$D_2 = \frac{rB+RD}{r+R}. \quad . \quad . \quad . \quad . \quad . \quad (d)$$

For the experiments a Crompton potentiometer was used,

the arrangement of which is shown in fig. 2, together with the arrangement of the experimental cell and the resistance-box.

The accumulators *L* are connected with the circuit *ABDEFG*, and by means of the rheostat *F* and by balancing a Clark cell against the accumulators it is easy to so adjust the current that 1 millimetre of the bridge-wire shall correspond to a change in E.M.F. of 1 millivolt. The bridge-wire is 1 metre long, and thus corresponds to 1 volt. Also the coils (1) and

Fig. 2.

(2) (see figure) are each of the same resistance as the bridge-wire, and thus each of these corresponds to 1 volt. So that it is very easy to get readings of any E.M.F. up to 3 volts.

The scale-wire extends to B, and the wire AB had a resistance equal to that of 43.4 millimetres of the scale-wire. Thus if the reverse current was taken between A and D, its E.M.F. was 2.0434 volts. If, however, as was sometimes the case, the coil (1) was taken out of the circuit, B was equal to 1.0434 volts.

The cell consisted of two glass vessels (short boiling-tubes) which had side-tubes blown in them. These side-tubes were connected by a short piece of indiarubber tube, to which was attached a screw-clip. It was found that, unless wads of cotton-wool were placed in the connecting-tubes, it was necessary to have solutions whose densities only differed in the fourth place. With the wads there is practically no diffusion, and the internal resistance is not unduly high. The solutions were made up approximately to the formula $R \cdot 100 \text{H}_2\text{O}$, where *R* is the molecular formula of any salt. The densities were then adjusted until they were approximately equal.

Solution.	Density at 13°·5 C.	Solution.	Density.	Temp.
Copper sulphate ...	1·081	Copper chloride ...	1·074	25 ⁰
Cadmium „ ...	1·082	Cadmium „ ...	1·079	16
Zinc „ ...	1·082	Zinc „ ...	1·076	25

Results:—(1) Cu, CuSO₄, ZnSO₄, Zn. (Daniell's cell.)

R.	r (direct experiment).	r (reverse experiment).	D ₁ (observed).	D ₁ (calculated).	D (observed).	D ₂ (calculated).
4000 ...	ohms. 1389	ohms. 1392	volt. 0·8135	volt. 0·8135	volt. 1·3405	volt. 1·3397
6000 ...	1401·2	1389	0·8885	0·8895	1·2740	1·2736
12000 ...	1380·0	1378	0·9819	0·9835	1·1935	1·1937

For this cell $D = 1·096$ volt, $B = 2·0434$ volts.

The second column of the above was calculated from the observations by means of formula (a), the third column by (c), the fourth by (b), and the sixth by (d). The value of r used in the formulæ (b) and (d) was 1388·2, the mean of the six values obtained above.

In this experiment (and in all following) the copper electrode was electroplated and the zinc electrode cleaned with emery-paper and dilute sulphuric acid.

(2) Cu, CuSO₄, CdSO₄, Cd.

R.	r (direct experiment).	r (reverse experiment).	D ₁ (observed).	D ₁ (calculated).	D ₂ (observed).	D ₂ (calculated).
4000 ...	ohms. 1149·6	ohms. 1150·6	volt. 0·5740	volt. 0·5746	volt. ·8070	volt. ·8068
6000 ...	1128·6	1151·1	0·6220	0·6206	·7880	·7878
12000 ...	1118·4	1168·0	0·6760	0·6746	·7660	·7654

For this cell $D = 0·739$ volt at 14° C., $B = 1·0434$.

Mean value for $r = 1144·4$.

The cadmium used was a rod prepared by Johnson and Matthey, and was warranted to be over 99 per cent. cadmium.

It was cleaned before each experiment by emery-cloth and dilute sulphuric acid.

(3) Cu, CuCl₂, ZnCl₂, Zn.

R.	r (direct experiment).	r (reverse experiment).	D ₁ (observed).	D ₁ (calculated).	D ₂ (observed).	D ₂ (calculated).
	ohms.	ohms.	volt.	volt.	volt.	volt.
4000 ...	304.9	301.4	0.997	0.9997	1.141	1.1332
6000 ...	286.8	298.5	1.025	1.0230	1.119	1.1182
12000 ...	262.0	304.3	1.051	1.0474	1.097	1.0961

For this cell $D = 1.073$ at 23°C ., $B = 2.0434$.

Mean value of $r = 293.1$.

(4) Cu, CuCl₂, CdCl₂, Cd.

R.	r (direct experiment).	r (reverse experiment).	D ₁ (observed).	D ₁ (calculated).	D ₂ (observed).	D ₂ (calculated).
	ohms.	ohms.	volt.	volt.	volt.	volt.
4000 ...	479.9	482.0	0.671	0.6704	0.782	0.7836
6000 ...	487.8	487.3	0.695	0.6956	0.7725	0.7738
12000 ...	493.1	490.4	0.722	0.7227	0.762	0.7633

For this cell $D = 0.752$ at $16^{\circ}.5\text{C}$., $B = 1.0434$.

Mean value of $r = 486.75$.

During the experiments, so long as diffusion was prevented, the E.M.F. of the cells remained constant. Even under the most unfavourable circumstances, viz. when the reverse current through 4000 ohms was running through the cell, the E.M.F. only altered about two millivolts. The conclusion to be drawn from the preceding results is that the cells treated, and consequently all similarly constituted cells, are reversible; for the differences in the values of the E.M.F.'s when calculated and when observed are not greater than might be expected as errors of experiment.

(5) A few experiments were also carried out with the Clark cell.

In the foregoing experiments the Clark standard consisted of two Clark cells in parallel. These were now

separated, and one used as a standard and the other as the experimental cell. The internal resistance of this cell is, of course, comparatively small, so that it was necessary to use smaller resistances for R than were used in the previous cases. R was therefore made equal to 3000, 2000, and 1000 ohms respectively.

R.	r (direct experiment).	r (reverse experiment).	D_1 (observed).	D_1 (calculated).	D_2 (observed).	D_2 (calculated).
3000 ...	ohms. 92.9	ohms. 98.8	volt. 1.389	volt. 1.3875	volt. 1.4515	volt. 1.4496
2000 ...	88.3	95.7	1.370	1.3667	1.4580	1.4585
1000 ...		95.1			1.4825	1.4837

For this cell $D=1.4315$ at 16°C. , $B=2.0434$.

Mean value for $r=94.16$.

With $R=1000$ ohms, it was found that the current was much too large, as the E.M.F. of the cell decreased very rapidly when running the current. But the reverse current gave a fairly good result, as might be expected. For the direct current would cause the solution of Hg_2SO_4 to become weaker, and the solid present would not immediately saturate the solution. But the reverse current would cause Hg_2SO_4 to be formed in the solution, which would therefore deposit some solid, but would at the same time remain saturated. Thus, all the results from the reverse experiments are better than the corresponding direct results; but considering the nature of the cell, these latter are fairly good.

Thus we may say that the Clark cell, besides the others treated here and those similar to them, is reversible.

These experiments were carried out at the suggestion and under the direction of Dr. Lehfelddt, of the East London Technical College, to whom I gladly acknowledge my debt.

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E. Lond. Tech. Coll., Oct. 1899.

DISCUSSION.

Prof. S. P. THOMPSON asked if experiments had been made upon Leclanché cells, where the products of the action escape.

Dr. LEHFELDDT said that experiments were not made upon these cells, because they were known not to be reversible.