LXX. The unilateral conductivity of sulphated accumulator plates

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than a dozen years ago. The bearing of this theory upon Chemistry and other branches of Natural Science has already been pointed out*. Suffice it to say here that the solvate theory of solution is not at all at variance with the theory of electrolytic dissociation, but beautifully supplements it.

Johns Hopkins University, 1911.

LXX. *The Unilateral Conductivity of Sulphated Accumulator Plates.* By ROBERT G. LUNNON, B.Sc.†

THE high electrical resistance of accumulator plates which have been left unused for a considerable time is well known, and is due to the presence of a film of a sulphate of lead on the negative plate. This resistance becomes normal on the application of a high potential for a few minutes, and the experiments to be described were carried out to investigate this change. This object was attained, and it was further found that the layer of sulphate exhibits the property of aluminium anode-films in having a resistance dependent upon the direction of the current.

The accumulators used were of the simplest Planté type, as used in large numbers for obtaining a high potential. A different plate was necessarily used for each experiment, but the properties of the cells in one tray were found to be sufficiently identical to make this of no consequence. The connexion between the rate of decrease of the resistance and the applied potential difference was examined by including

Fig. 1.

the cell in a circuit, as shown in fig. 1. With this arrangement, any desired p.d. could be initially applied to the cell, and its diminution with time, together with the current going

* *Zeitschr. phys. Chem.* lxxiv. p. 377 (1910). *Journ. d. Chim. phys.* ix. p. 217 (1911). *Amer. Chem. Journ.* xlv. p. 146 (1911).

† Communicated by Prof. F. T. Trouton, F.R.S.

through the cell, recorded. The curves so obtained are the continuous curves of fig. 2.

Fig. 2.

If V denote the potential measured by the voltmeter, we have

$$V = CR - E',$$

where E' is any back e.m.f. that may arise in the cell. No evidence could be found of a larger back e.m.f. than the two volts which develops when the cell is charged. Cook * has suggested the presence of a back e.m.f. to explain the properties of the aluminium anode-film, but this is not now generally accepted. Accordingly the variation of R with t may be found by keeping constant the current through the cell, or by dividing values of V by simultaneous values of C .

* Cook, Phys. Rev. xviii. p. 23 (1904)

The curves so obtained are given in fig. 3; they are, except at first, approximately exponential.

Fig. 3.

These results can be explained on the assumption that the resistance is proportional to the amount of substance on the electrode, and that the rate of removal of the latter is proportional to the applied p.d. The relation between V and t can then be obtained as follows:—

With the symbols of the diagram (fig. 4), we have

Fig. 4.

$$Cr_2 = C_1(r_2 + r_3) - E,$$

$$C_1r_2 = C(R + r_1 + r_2).$$

$$\therefore C = \frac{Er_2}{(R + r_1 + r_2)(r_2 + r_3) - r_2^2}.$$

$$\therefore V = RC = \frac{R}{AR + b},$$

where

$$A = \frac{1}{E} \left(1 + \frac{r_3}{r_2} \right), \quad b = \frac{1}{E} \left(r_1 + r_3 + \frac{r_1 r_3}{r_2} \right).$$

$$\begin{aligned} \therefore \frac{dV}{dt} &= \frac{b}{(AR + b)^2} \frac{dR}{dt} \\ &= \frac{b}{(AR + b)^2} \cdot (-k^2 V), \text{ if } \frac{dR}{dt} = -k^2 V, \\ &= -\frac{k^2}{b} V(1 - AV)^2. \end{aligned}$$

Integrating, and putting $V = V_0$ when $t = 0$, we obtain

$$\frac{V_0}{1 - AV_0} \cdot \frac{1 - AV}{V} = e^{\frac{k^2 t}{b} - \frac{1}{1 - AV} + \frac{1}{AV_0 - 1}},$$

or, with a new constant B ,

$$V = \frac{1}{A + Be^{\frac{k^2 t}{b} + \frac{1}{1 - AV}}}.$$

This equation is found to fit the curves of fig. 2 with considerable accuracy. Specimen curves plotted from it are given by the broken lines of the diagram.

In the case of constant current through the cell, we have

$$\frac{dR}{dt} = -k^2 V = -k^2 CR.$$

$$\therefore R = R_0 e^{-k^2 C t}.$$

This corresponds to the curves of fig. 3.

Finally, if we assume that the final resistance of the cell is always the same, since

$$\frac{dR}{dt} = -k^2 V,$$

$$\therefore R_0 - R_T = -K^2 \int V dt = \text{constant}.$$

Values of this integral can be obtained by computing the areas under the curves of fig. 3, and, as shown by the

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following table, are approximately constant:—

Current.	$\int V dt.$
·73	638
·81	734
·90	696
1·11	803
1·43	646
1·60	785
2·36	720
Mean value 717	

In all the above experiments the current was sent in that direction for which the negatively formed plate is the anode. When the p.d. is applied in the reverse direction, the curve obtained for the decrease of V is similar in type, but the initial value, V_0 , is much lower, the reading is very unsteady, and visible sparking occurs at the cathode, apparently across the resisting film. The cell thus possesses, temporarily, the property of unilateral conductivity, offering a much larger resistance to a current sent outwards from the "formed" plate than to one in the reverse direction. The gas-layer theory developed by Schulze * for the corresponding property of the aluminium anode-film involves assumptions which are not possible in this case, and the more recent suggestion, of Corbino and Maresca †, of a perforation of the film of metallic salt is also unsatisfactory. The effect persists in the absence of any electrolyte; as, for example, in the case where the dry cathode with its film is pressed against a clean sheet of metal, and a current passed between the two. It is possible that the original electric deposition of the film involves a directional property in the substance of the film, which would not appear if the lead sulphate were chemically deposited; but, unfortunately, it has not been found possible to obtain a film deposited by chemical means alone to test this point.

A physical basis may be found for the assumption we have made regarding the rate of breaking down of the film, for we may consider that breaking down as a mechanical effect produced by the passage of electrons through the film. This effect would be proportional to the velocity of the electrons, and hence to the potential difference across the film, producing this velocity.

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* Schulze, *Wied. Ann.* xxi. p. 929 (1906).

† Corbino & Maresca, *Electrician*, Dec. 28, 1906.