POLARIZATION IN THE ALUMINIUM RECTIFIER.

By Clarence W. Greene.

THE primary object of this investigation was to make a study of the potential difference between the electrodes of the aluminium rectifier at extremely short intervals after breaking the charging circuit. It was hoped that the investigation might also throw some further light on the action of electrolytic cells. The methods employed and results obtained are new and may be suggestive in the further study of the electrolytic cell.

The aluminium plates, which were used as electrodes, were prepared in the instrument shops of the University of Michigan and were hammered out of 98 per cent. pure aluminium ingots. They were 10 cm. long, 2.7 cm. wide and 0.3 cm. thick. The plates were so insulated with Bank of England sealing wax as to leave a definite area exposed as active electrode to the electrolyte. The cathode was a platinum plate of 20 sq. cm. exposed area, totally immersed in the electrolyte, the platinum wire leading out of the solution being thoroughly insulated from the solution. The insulation thus eliminated any possibility of surface effects, which are found to be present when the electrode surfaces are exposed at the surface of the electrolyte. The active surfaces of the aluminium electrodes were polished with fine sand paper and rinsed with distilled water before each experiment was begun. The electrolytes used were ammonium aluminium sulphate (40 grams per liter of water) and potassium dichromate (26.18 grams per liter of water).

After checking some of the results obtained by former investigators[1] by the ballistic galvanometer-condenser method, a potentiometer method for measuring the counter E.M.F. was devised and the results thereby obtained were compared with those obtained by the former method. The potentiometer method invariably gave larger values for the counter E.M.F. of the rectifier than did the condenser method, the differences being far beyond the range of experimental error. For instance, with a given E.M.F. the difference was consistently about 4.7 per cent. A

---

[1] Theory of the Electrolytic Rectifier, by S. R. Cook, Phys. Rev., 18, pp. 23–29, Jan., 1904; also Phys. Rev., 20, pp. 312–321, May, 1905; H. W. Morse and C. L. B. Shuddemagen, American Acad. Arts and Sciences, *Proc.*, 44, pp. 367–397, 1908–9.

repetition of comparative experiments gave a similar characteristic difference, which indicates that when the charged rectifier is connected to a condenser, a quantity of electricity required to charge the condenser being taken from the rectifier, the electrical condition of the rectifier is thereby disturbed and the difference of potential between the electrodes of the rectifier decreased. The potentiometer method was, therefore, used throughout the remainder of the experimental work.

The arrangement of apparatus for the measurement of the counter E.M.F. of the rectifier after the expiration of definite periods of open circuit is indicated in Fig. 1. *R* is the aluminium rectifier, in which *A* is

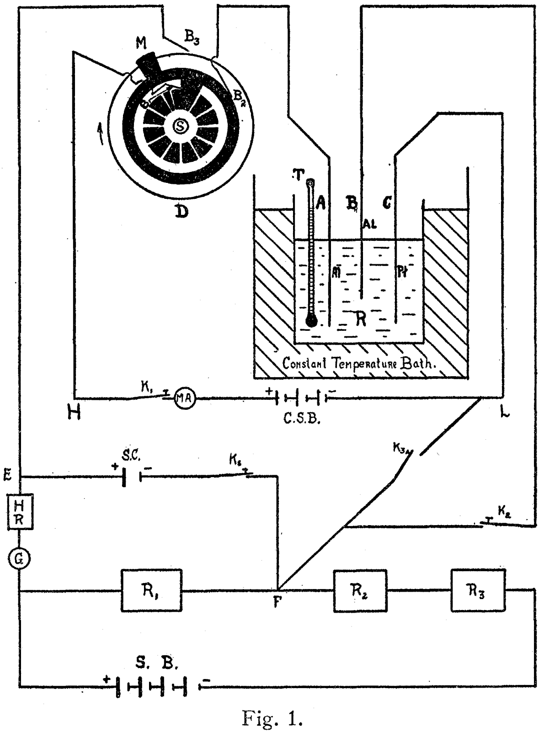

Fig. 1.

the aluminium anode; *C*, the platinum cathode; and *B*, an aluminium test electrode placed at one side and somewhat in the rear of the anode so as not to be in the path of the current between anode and cathode; *C.S.B.*, the charging storage battery; *MA*, a milliammeter; R_1 and R_2, two high grade Leeds and Northrup resistance boxes; R_3, a high grade Leeds and Northrup resistance box with travelling plug; *H.R.*, a 250,000 ohm resistance box; *S.C.* a cadmium standard cell; *G.*, a Leeds and, Northrup high sensibility galvanometer having a resistance of 1,600 ohms; *S.B.*, a storage battery; and *D*, a disc especially designed for this experimental work. The disc consisted of a single piece of hard rubber, 13.5 cm. in diameter and 1 cm. thick, to which were firmly riveted two concentric brass rings, 2 mm. thick and 1.5 cm. wide, the outside diameters being 7.5 cm. and 13 cm., respectively. The inner ring was divided into 30° sectors, one of which was subdivided into two 15° sectors; one of these 15° sectors was later soldered to the adjoining 30° sector, as indicated in the figure. These sectors could be connected, when desired, by inserting a brass plug between them. One of these sectors was electrically connected, as shown in the diagram, to the outer ring. The outer ring was in turn connected to the brass contact maker, *M*, which fitted closely over the rim of the rubber disc. The contact maker could be shifted along the rim by 15° intervals and was firmly held in place by a plug inserted through the contact maker and into the disc from the rear. The disc was rotated by a motor running at an approximately constant speed of 2,000 R.P.M. B_1, B_2, B_3 are spring brass brushes so adjusted as to make good electrical contact with the inner ring, outer ring and contact maker, respectively.

The division of the inner ring into sectors makes it possible to regulate the portion of the period of rotation during which the impressed E.M.F. is applied to the rectifier; the portion of the period finally adopted was the time required for the brush to sweep over a 45° sector. Regulation of the contact maker made it possible to vary the period of decay of the counter E.M.F. of the rectifier before this E.M.F. was balanced against the fall of potential over R_1. The sum of R_1 and R_2 was kept constant and the resistance in R_3 adjusted until the current flowing through R_1 was 0.001 ampere, as was shown, on closing K_s, by balancing the fall of potential over R_1 against the E.M.F. of the standard cell. This made it possible to read the counter E.M.F., on obtaining a balance, directly from the resistance in R_1. On closing K_1, *C.S.B.* charges the rectifier through the disc; on closing K_2 the counter E.M.F. of the rectifier is balanced against the fall of potential over R_1, while B_3 sweeps over *M*.

The arrangement of apparatus indicated in Fig. 1 is such, on closing K_2, as to give the data for the curve of decay between the aluminium anode and the aluminium test electrode, thus giving the effect at the anode only, due to the impressed E.M.F. By closing K_3 instead of K_2 the data for the curve of decay of E.M.F. between anode and cathode were obtained, thus giving the total effect of polarization. To obtain the effect of polarization at the cathode only the positive terminal of *C.S.B.* was disconnected from the disc and connected directly to the anode, while the negative terminal of *C.S.B.* was connected to the cathode through the disc.

It was ascertained that in order to obtain the maximum counter E.M.F. of the rectifier by charging it through the disc while revolving, it was necessary that the motor run for a period of from 10 to 15 minutes before the polarization was measured and 15 minutes was the interval accordingly adopted before any measurements were taken. One of the greatest difficulties met with in experimental work with the rectifier is the slow change in the character of the film with time; and it is therefore necessary (1) that the series of results be taken as rapidly as possible, (2) that the period of open circuit between the determinations of the balance for successive intervals of decay be kept constant, (3) that the points on the decay curve be determined in the same order. A cyclic order of performing the operations was followed, thus rendering it feasible for each series of results obtained to be checked. Yet the author believes that the curves obtained are characteristic of the general behavior of the anode film.

Table I. gives the mean corrected values obtained from a number of experiments and Fig. 2 gives the curves plotted therefrom for the decay of the counter E.M.F. between the anode and the aluminium test electrode (*A*–3), between the anode and cathode (*AC*) and between the cathode and aluminium test electrode (*C*–3), for an applied E.M.F. of 6.16 volts. Table II. gives the corresponding data and Fig. 3 gives the curves for an applied E.M.F. of 12.25 volts. Table III. and Fig. 4 give the corresponding results for an applied E.M.F. of 18.13 volts.

Table I.

Electrolyte: Ammonium Aluminium Sulphate.
Applied E.M.F.: 6.16 volts.
Temperature: 23° C.
Current: 0.00025 ampere.

Period of Decay, Second.	E_{A-3}, Volts.	E_{AC}, Volts.	E_{C-3}, Volts.	$E_{AC}+E_{C-3}$, Volts.	$E_{A-3}-(E_{AC}+E_{C-3})$, Volts.
0.0000	6.43	6.15	....	....	....
0.0013	6.20	5.90	0.31	6.21	—0.01
0.0025	6.02	5.66	0.36	6.02	0.00
0.0038	5.91	5.50	0.39	5.89	+0.02
0.0050	5.78	5.36	0.35	5.71	0.07
0.0075	5.57	5.17	0.36	5.53	0.04
0.0100	5.43	5.01	0.35	5.36	0.07
0.0150	5.24	4.80	0.38	5.18	0.06
0.0200	5.08	4.64	0.38	5.02	0.06
0.0250	4.90	4.51	0.40	4.91	—0.01

TABLE II.

Electrolyte: Ammonium Aluminium Sulphate.
Applied E.M.F.: 12.25 volts.
Temperature: 23.°2 C.
Current: 0.00035 ampere.

Period of Decay, Second.	E_{A-3}, Volts.	E_{AC}, Volts.	E_{C-3}, Volts.	$E_{AC}+E_{C-3}$, Volts.	$E_{A-3}-(E_{AC}+E_{C-3})$, Volts.
0.0000	12.52	12.31	....	.....	....
0.00083	11.92	11.72	0.31	12.03	—0.11
0.0021	11.32	11.07	0.31	11.38	—0.06
0.0033	11.00	10.69	0.31	11.00	0.00
0.0046	10.69	10.42	0.32	10.74	—0.05
0.0071	10.37	10.02	0.33	10.35	+0.02
0.0096	10.14	9.71	0.35	10.06	0.08
0.0146	9.60	9.28	0.36	9.64	—0.04
0.0196	9.37	8.89	0.37	9.26	+0.11
0.0246	9.23	8.75	0.36	9.11	0.12

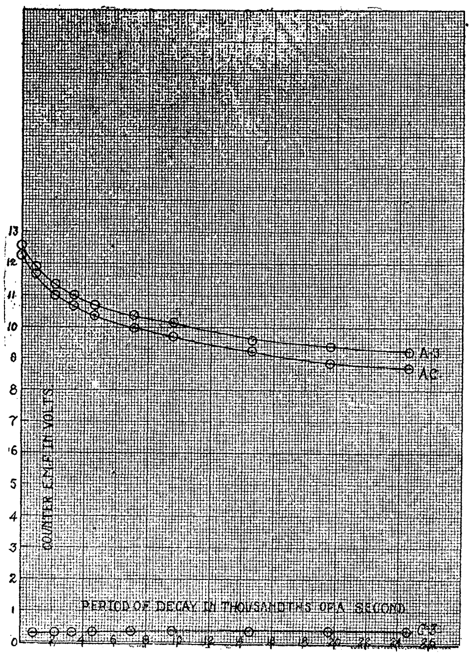

Fig. 2.

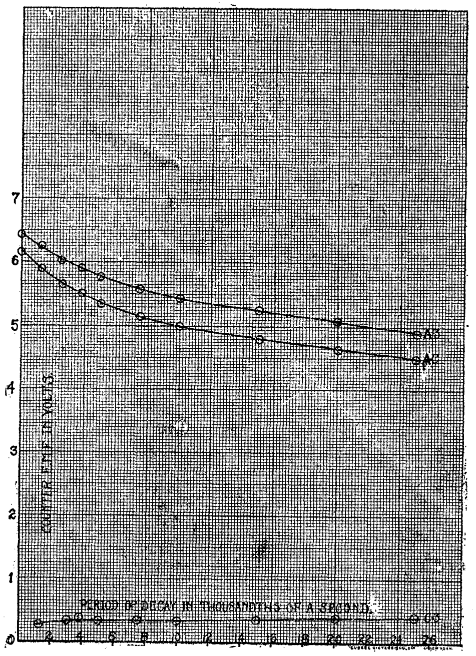

Fig. 3.

It is worthy of note that the polarization E.M.F. between the anode and the aluminium test electrode exceeds the applied E.M.F. by about 0.3 of a volt. The excess voltage is due to the fact that the electrolytic cell, acting as a primary cell, furnished an effective voltage of about 0.3

Table III.

Electrolyte: Ammonium Aluminium Sulphate
Applied E.M.F.: 18.13 volts.
Temperature: 23° C.
Current: 0.0005 ampere.

Period of Decay, Second.	E_{A-3}, Volts.	E_{AC}, Volts.	E_{C-3}, Volts.	$E_{AC}+E_{C-3}$, Volts.	$E_{A-3}-(E_{AC}+E_{C-3})$, Volts.
0.0000	18.43	18.02	....	....	.....
0.0013	17.01	16.59	0.34	16.93	+0.08
0.0025	16.11	15.68	0.32	16.00	0.11
0.0038	15.57	15.12	0.31	15.43	0.14
0.0050	15.29	14.70	0.31	15.01	0.28
0.0075	14.63	14.09	0.32	14.41	0.22
0.0100	14.00	13.67	0.31	13.98	0.02
0.0150	13.33	12.91	0.34	13.24	0.09
0.0200	12.98	12.53	0.36	12.89	0.09
0.0250	12.75	12.34	0.37	12.71	0.04

volt in series with the charging storage battery to assist in the process of polarization. The difference between E_{A3} and $E_{AC}+E_{C3}$ for corresponding decay intervals is also seen to be negligible, the error rarely exceeding 1 per cent., which demonstrates that the method used renders possible the attainment of a high degree of accuracy. The results show conclusively that the E.M.F. of polarization, at the instant when the charging circuit is opened, is equal to the polarizing E.M.F., and that there has been no considerable IR component in the surface film during the charging period.

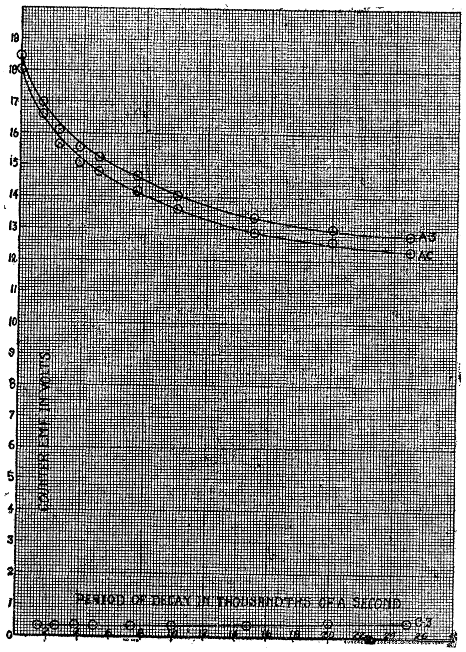

Fig. 4.

It has been proved by Schulze,[1] in an extensive series of experiments, that the effective anodic layer, in conformity with the suggestion of

---

[1] Ann. d. Physik, 21, 5, pp. 929–954, December 14, 1906; also 22, 3, pp. 543–558, March 5, 1907.

Guthe,[1] consists of oxygen gas. An extension of the gas film theory accounts for the slight residual current that flows through the electrolytic cell. The negative ions accumulate in the electrolyte next to the gas layer and electrons are forced from some of the carriers by the high potential gradient. These free electrons pass through the gas layer, thus causing the observed small residual current. The higher the value of the impressed voltage, under the experimental conditions maintained by the writer, the higher is the potential gradient through the gas film, and the larger should be the number of detached electrons and the resulting current. The results are seen to conform to this theory, since, for example, the residual current for an applied voltage of 6.16 volts was 0.00025 ampere; for 12.25 volts, 0.00035 ampere; for 18.13 volts, 0.00050 ampere.

The above way of looking at the counter E.M.F. of the aluminium cell very closely corresponds to our ideas of the process of charging a condenser and by many experimenters the aluminium anode is spoken of as a condenser. This comparison should, however, not be carried too far. When the two plates of a charged condenser are connected by a conductor of very high resistance, the potential difference between the plates decreases in accord with the well-known law: $V = V_0 e^{-t/RC}$. Passing to logarithms, $\text{Log } V = \text{Log } V_0 - t/RC$. If the action of the rectifier were that of an ordinary condenser, a straight line should be obtained by plotting the logarithms of V as ordinates and the corresponding periods as abscissæ. Applying this test to the data of Table IV., for instance, curve C, of Fig. 5, is obtained. It shows that the rate of decrease of counter E.M.F. is not such as to indicate that the rectifier conforms to the law of the ordinary condenser. The explana-

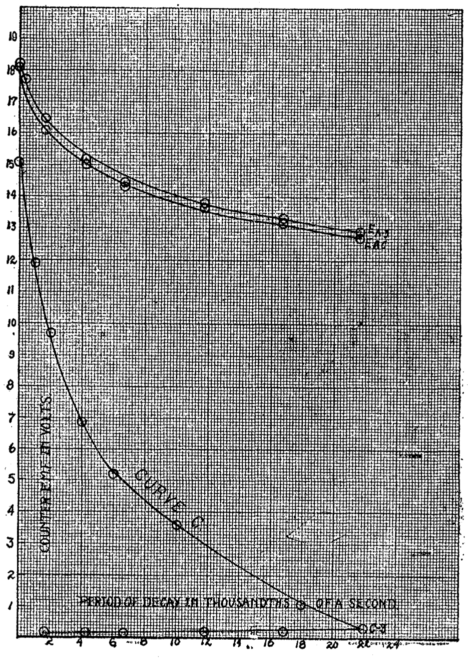

Fig. 5.

---

[1] Theory of Electrolytic Rectifier, PHYS. REV., 15, pp. 327–334, 1902.

tion of this discrepancy may lie in the fact that the decrease of potential in the rectifier is due to the diffusion of the ions back into the solution rather than to ordinary metallic conduction.

Table IV.

Electrolyte: Potassium Dichromate Solution.
Temperature: 23.1° C.
Applied E.M.F.: 18.16 volts.
Current: 0.0005 ampere.

Period of Decay, Second.	E_{A3} Volts.
0.0000	18.22
0.0004	17.70
0.0017	16.31
0.0042	15.17
0.0067	14.44

When the impressed voltage causing the polarization of the rectifier is increased the ionic concentration near the film is increased and with it the rate of change in the concentration passing from the film to the body of the electrolyte is increased. Therefore, when the impressed voltage is removed, the ions should disappear from the boundary of the gas layer the more rapidly the higher the impressed voltage. A comparison of the curves of Fig. 6 confirms this view. If the assumption that the rate of diffusion of the ions from the gas layer back into the solution is a function of the difference between the ionic concentration near the anode and that in the remainder of the electrolyte, is correct, — then as the process of diffusion proceeds and the difference in ionic concentration decreases, the rate of diffusion (or the rate of decay of the counter E.M.F. of polarization) should decrease. This is seen to be true of each of the curves of decay.

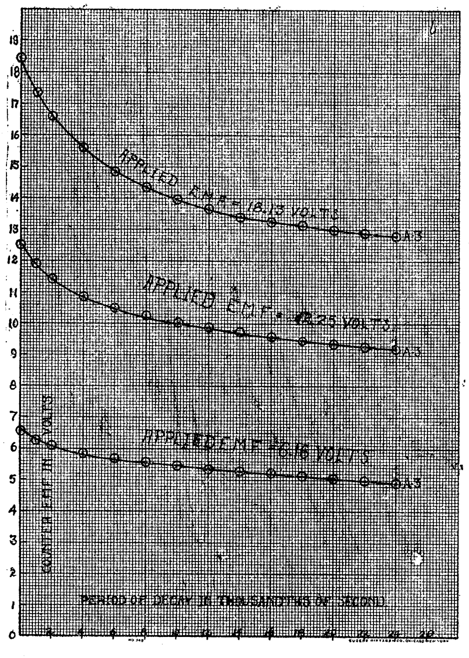

Fig. 6.

It is believed that the curves of decay obtained represent with a fair degree of accuracy no other effects than those of ionic diffusion, since during the extremely short intervals of decay used the effect of any disintegration of the film may be assumed to be negligible.

The results of this investigation may be summarized as follows:

1. The condenser method of measuring the counter E.M.F. introduces an error due to the taking of a charge from the rectifier.

2. The rectifier does not behave as an ordinary condenser.

3. When aluminium is used as the anode, the counter E.M.F. alone accounts for the reduction of the current to its exceedingly small value.

4. The results obtained in this investigation are apparently in accord with the gas film theory and the theory of ionic diffusion.

The writer is indebted to the University of Michigan for the special apparatus provided for the work and to Professor K. E. Guthe, of the University of Michigan, for many helpful suggestions received.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN.