COUNTER ELECTROMOTIVE FORCE IN THE ALUMINUM RECTIFIER.

By Albert Lewis Fitch.

I. Introduction.

THE anomalous action of aluminum in the electrolytic cell was first discovered by Wheatstone in 1855. Soon after this, Buff found that an electrolytic cell one electrode of which was aluminum would rectify the alternating current. Among the other men who have been interested in this cell may be mentioned Ducretet,[1] Hutin and Leblanc,[2] Montpellier,[3] Nodon,[4] Guthe,[5] Greene,[6] and Schulze.[7] The latter has perhaps done the largest amount of work of any. His articles have appeared from time to time in a number of magazines.

The earlier experimenters with this cell confined themselves to the study of aluminum but later investigation[7] has shown that many other metals possess this same property to a greater or less degree. Among these may be mentioned iron, nickle, cobalt, magnesium, cadmium, tin, bismuth, zirconium, tantalum, etc.

A great many electrolytes may be used in the rectifier. The most commonly used are the alums, phosphates, and carbonates; however Greatz and Pollak[8] have shown that any electrolyte which will liberate oxygen on electrolysis may be used more or less satisfactorily.

It has been found that the ability of the cell to rectify alternating current depends upon the current density at the aluminum anode,[9] the inductance and resistance of the circuit,[10] and its temperature.[11] The cell works best when the current density is high and the inductance, resistance, and temperature are low.

[1] Comptes Rendus, Vol. 80, p. 280.
[2] French Patents, No. 215945.
[3] Electrician, Vol. 22, p. 17.
[4] Comptes Rendus, Vol. 136, p. 445.
[5] Phys. Rev., Vol. 15, p. 327.
[6] Phys. Rev., Vol. 3, series 2, p. 264.
[7] Zeitschr. Elektrochem., Vol. 14, p. 333.
[8] Elektrotechnische Zeitschr., Vol. 25, p. 359.
[9] Elektrotechn. Zeitschr., Vol. 21, p. 913.
[10] Ann. der Physik, Vol. 39, p. 976.
[11] Zeitschr. Elektrochem., Vol. 14, p. 333.

Two prominent theories have been advanced to explain the action of this cell. The earlier theory, known as *the solid film theory*, ascribes this action to the electrolytic deposition and decomposition of a solid film of some oxide or hydroxide of aluminum on the aluminum anode. The deposition takes place while the current flows in at the aluminum and, being a high resistance material, the film soon grows to a thickness which shuts off the current in that direction. The decomposition takes place when the current is in the opposite direction and permits the current to flow unimpeded from the electrolyte to the electrode.

In 1902 Guthe[1] first gave us the later theory, known as *the gas film theory*. This theory ascribes the action to a film of oxygen gas which is spread over the solid layer. The free electrons of the metal are forced through the gas film by the very high potential gradient with very little difficulty, when the aluminum is the cathode, but when the current reverses, and the aluminum is the anode, no such thing can take place because there are no free electrons in the electrolyte. Instead, the current must be carried through the film by the ions of the electrolyte and these being relatively large as compared to the electrons are with difficulty forced through.

It has been known for a great many years that the aluminum cell acts to a certain extent like a condenser. Schulze[2] states that a cell $40 \times 40 \times 40$ cm. with both plates of aluminum had a capacity of 5,000 mfd. on 160 volts alternating current of a frequency of 50 cycles per second. It was possible, he states, to take an alternating current of 250 amperes through this cell. But one must not go too far in likening this cell to an ordinary leaking condenser as Greene[3] has shown.

This investigation was undertaken to determine if a more careful study of the counter electromotive force, which is produced when current enters at the aluminum, would throw some light on the action of the cell as a condenser and also on the theories advanced.

The cell used was composed of a lead plate with an area of approximately 90 sq. cm. and an aluminum wire .258 cm. in diameter and 10 cm. in length, immersed in a saturated solution of sodium phosphate. The aluminum wire was tested and found to contain .27 per cent. iron and some silicon in the form of silicates. It is about 99 per cent. pure. The lead is the same grade as that used in the chemistry department in qualitative experiments and is believed to be as pure as the aluminum. Both electrodes are heavily coated with a good grade of sealing wax where

[1] PHYS. REV., Vol. 15, p. 327.

[2] Zeitschr. Elektrochem., Vol. 14, p. 333.

[3] PHYS. REV., Vol. 3, series 2, p. 264.

they emerge from the solution to eliminate surface effects which were found to be present when the electrodes were not coated.

II. Experimental Work.

As a preliminary study, a potentiometer method was devised for the measurement of the counter electromotive force. The cell was placed directly across the storage battery terminals for a time with the aluminum as anode and then the counter electromotive force, after a certain period of open circuit, was compared directly with the storage battery voltage. This period of open circuit was adjusted and measured by means of the disk described in the following method. Although this potentiometer method gives very accurate measurements of time of open circuit and of counter electromotive force, it is too slow to give the desired results.

Since the time for taking the readings by the former method could not be decreased, the oscillographic method was devised. This method enables one to take a complete set of readings in about one second. This eliminates to a large degree the objection to the former method and also enables one to get readings for much shorter periods of closed circuit.

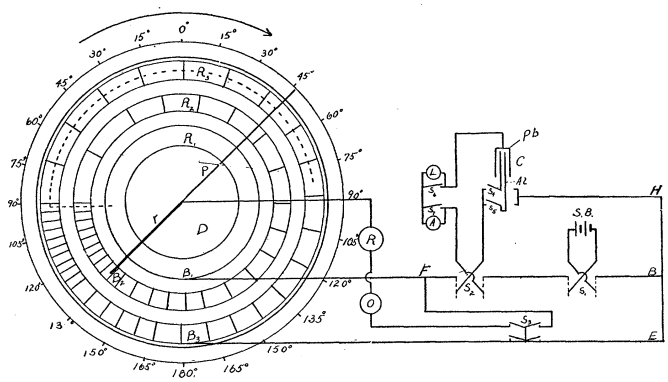

Fig. 1.

The diagram for the arrangement of apparatus is shown in Fig. 1. In this method the same disk was used as before with the same brush contacts and the same electrical connections on the disk. This disk is shown as D. It was designed for this work and made in the engineering shops of the University of Michigan. It is a solid, hard rubber disk of approximately 31 cm. radius. Firmly screwed to this disk are three concentric rings of brass. The inner ring R_1 has an inner radius of 12 cm. and an outer radius of 16 cm. It is made in one solid piece. The second ring R_2 has an inner radius of 19 cm. and an outer radius of 23 cm. It is divided into sectors ranging in magnitude from 5 degrees to

35 degrees. The outer ring R_3 has an inner radius of 26 cm. and an outer radius of 30 cm. It is divided into sectors ranging from 3.75 degrees to 28 degrees. Each sector on each ring is connected electrically to a binding post on the back of the disk. On the circumference of the disk is a steel tire. The disk is mounted on the shaft of a Roth motor, designed to run at 2,000 R.P.M. on 220 volts direct current. This disk is enclosed in a wooden box supported on sliding arms so that the box can be brought as near as desired to the disk and clamped fast. The front of the box holds the brush contacts B_1, B_2, B_3 made of spring steel with brushes of sheet copper. B_1 and B_3 are bolted directly to the box and allow the brushes fastened to them to bear on rings R_1 and R_3. B_2 is a movable brush contact supported on a brass rod bent at right angles and passing through the box front at a point directly in line with the center of the motor shaft. A long brass pointer P is fastened to this brush holder by heavy brass nuts and plays over a protractor of 8 inches radius divided into quarter degrees. On the back of the disk, the sectors are connected as shown by the dotted line. In the back of the box face, a large screw was placed to stop the rotating arm r at the same place each time.

As before, it was arranged to have the cell placed directly across the storage battery when readings were not being taken. S_1 and S_2 make an eight-pole double-throw switch. S_4 and S_5 are double-pole double-throw switches. C is the rectifier. L is a lamp for resistance. A is a Weston ammeter with .01 ampere divisions. L and A may be cut out of the circuit by switches S_6 and S_7. R is a Leeds & Northrup resistance box with a total resistance of 1,111 ohms and O is the vibrator of the Siemens & Halske Oscillograph. The oscillographic chamber was filled with oil to produce the proper damping effect. The cylinder of the oscillograph is connected directly to the motor shaft which rotates the disk. This makes the cylinder and disk rotate in exact synchronism.

The motor is connected with its field over the 220-volt direct current power line and its armature over the storage battery. By this arrangement, any speed up to 2,000 R.P.M. is attainable by varying the number of cells of the storage battery.

Electrical Connections.

It is evident from the figure that there are two paths for the current from the storage battery S.B. to the cell C if S_3 is thrown to the right. It can flow from S.B. to B and H to the cell through either of the switches S_4 or S_5, or it can flow by the path B, E, S_3, F, S_2 to C through either of the switches S_4 or S_5 thrown to the left. This arrangement enables one to use two anodes of different metals in the same cell and still have them electrically independent of each other. However in this work but the one switch was used and the one anode. If S_3, S_4, and S_5 are thrown to the left, current can flow from S.B. to B, E, S_3, B_3, along the wire on the back of the disk to R_1, and B_1, then to S_2, through the cell and back to the storage battery, while the brush B_3 is on the sectors connected by the wire. When the last connected sector has passed B_3, the cell is on open circuit until the sector on R_2 connected to R_1 passes under B_2. Current then flows from S.B. to B, E, S_3, O, R, r, B_2, through the connecting wire to R_1, and B_1, then to S_2 and through the cell to the storage battery. It is to be noticed that no matter by which path the current comes to the cell it is in the same direction through it, *i. e.*, from the aluminum to the lead. If there is a counter electromotive force in the cell, the fall of potential over the oscillograph and its resistance must then be equal to the difference between the storage battery voltage and this counter electromotive force. This difference of potential will be registered on the photographic film on the cylinder of the oscillograph.

A flash is registered on the film whenever the small sector on R_2, which is connected to R_1 and R_3, passes under B_2. Then if we rotate B_2 about its axis the resulting flashes on the film will register at exactly corresponding points of the film. Knowing the speed of the motor, we can compute the length of time between any two flashes by measuring the distance between them and comparing with the total film length. One mm. distance between flashes corresponds to 0.00037 sec. when the motor is running at 750 R.P.M. In most cases the flashes are very distinct so that one can measure accurately to 0.0002 sec. If still greater accuracy is desired one has but to increase the speed of the motor.

A calibration curve for the measurement of the voltage recorded by the flashes was made by sending current from a known voltage through the oscillograph and its accompanying resistance when the disk was in rotation. Since the deflections of the oscillograph are proportional to the current through it, they are also proportional to the difference of potential across its terminals. One has but to measure each ordinate and compare it with the deflection from the known source. The value of this ordinate subtracted from the applied voltage gives the counter electromotive force of the cell for that period of open circuit.

If one plots the counter electromotive force as ordinates and the time of open circuit as abscissæ, a curve is obtained which in general appearance resembles the curve of decay of electromotive force in a leaking condenser. But if the equation $V = V_0e^{-ct}$ is assumed and the value of c computed for several points of the curve, it is found that c is not a constant throughout the same curve nor the same value in successive curves for the same period of open circuit. It is evident then that this c depends on the time of open circuit and also on the time of closed circuit. But the above formula was derived on the assumption that c is a constant, it is therefore not proper merely to replace c by a function of the times of open and closed circuits. One must go back to initial conditions and construct a formula which will embrace the fact that the counter electromotive force depends both on the time of open circuit and on the time of closed circuit.

Theory Proposed.

Let us assume with Guthe and Schulze that the aluminum anode becomes coated with a layer of some oxide or hydroxide of aluminum and that this solid layer is covered with a very thin film of oxygen gas whose thickness depends on the applied voltage and on the time of open circuit. If this layer of oxygen gas attains a definite thickness for each applied voltage, the thickness of the solid layer must increase with increasing time of closed circuit, for if one places a milliammeter in the circuit with the cell and storage battery, it will be seen that while the current does attain a very low value in a very short time after the circuit is closed, it does not remain at that value but is constantly dropping lower and lower. Even after a whole day on closed circuit, it can be seen that this current is growing smaller, although at a very slow rate. This solid layer is deposited electrolytically, and therefore its thickness must be proportional to the quantity of electricity passing through the cell, which in turn depends on the length of time the cell is left on closed circuit. The drop in counter electromotive force after a period of open circuit is due to the leakage of electricity through the combined thickness of solid layer and oxygen. It has been shown by Schulze that this oxygen film decreases in thickness with increasing time of open circuit. We have here then a clear case of a condenser with a double dielectric, both parts of which leak slightly and change in thickness, the solid layer increasing in thickness with the time of closed circuit and the gas film decreasing in thickness with the time of open circuit.

From the theory of condensers we have

$$i = \frac{-dq}{dt} = \frac{-d(CV)}{dt},$$

where i is the current leaking through the dielectrics, q is the quantity of electricity stored in the condenser, C is the capacity of the condenser at that instant and V is the difference of potential between the two plates. With a double dielectric, we have the formula

$$C = \frac{Sc'c''}{4\pi(c''d' + c'd'')},$$

in which S is the area of the plates, c' is the dielectric constant of the substance whose thickness is d', c'' is the dielectric constant of the substance of thickness d'', and C is the capacity. Dividing both numerator and denominator by c'' and placing $Sc'/4\pi = K$ we have

$$C = \frac{K}{d' + \frac{c'}{c''}d''}.$$

Now let d', c' and d'', c'' apply to the solid layer and gas film, respectively, and call the maximum thickness of the gas film d_0. If we assume the rate of change in thickness of the gas film proportional to the thickness, we have

$$\frac{dd''}{dt} = -cd''; \quad \frac{dd''}{d''} = -c\,dt; \text{ integrating } [\log d'']_{d_0}^{d} = -c[t]_0^t.$$

Therefore $\log d''/d_0 = -ct$ or $d'' = d_0 e^{-ct}$. By substitution of this in the equation for i, we get

$$i = \frac{-d}{dt}\frac{KV}{d' + he^{-ct}},$$

where $h = (c'/c'')d_0$.

But the current leaking through a high resistance is equal to the quotient of the electromotive force over the resistance divided by the resistance.

$$i = \frac{V}{r + se^{-ct}},$$

where r equals the resistance of the solid layer and s equals the maximum resistance of the gas film. Equating these two values for i we have

$$\frac{-d}{dt}\frac{KV}{d' + he^{-ct}} = \frac{V}{r + se^{-ct}}.$$

If we carry out the indicated differentiation, separate our variables and integrate from $V = V_0$ when $t = 0$ to $V = V$ when $t = t$ we obtain

$$V = V_0 e^{-at}(A + Be^{-ct})^f(C + De^{-ct}),$$

where

$$A = \frac{r}{r+s}, \quad B = \frac{s}{r+s}, \quad C = \frac{d'}{d'+h}, \quad D = \frac{h}{d'+h}, \quad a = \frac{d'}{rK},$$

and

$$f = \frac{\frac{d'}{rc} - \frac{h}{cs}}{-K}.$$

Then

$$a = \frac{d'}{rK} = \frac{d'}{\frac{s'd'}{S}\,\frac{Sc'}{4\pi}} = \frac{4\pi}{s'c'}$$

and

$$f = \frac{\frac{d'}{rc} - \frac{h}{cs}}{-K} = \frac{\frac{d'}{s'd'c/S} - \frac{h}{s''c'ch/c''S}}{\frac{-Sc'}{4\pi}} = \frac{-4\pi}{s'c'c} + \frac{4\pi c''}{s''c(c')},$$

where s' and s'' are the specific resistances of the solid layer and gas layer, respectively. This s'' must be far greater than s' owing to the nature of the substances. It thus appears that a is very small and that f is negative and smaller even than a. Schulze has given us values for r and s, and also values for d and h. These values substituted in the equations above give $A = 1/51$, $B = 50/51$, $C = 100/101$, and $D = 1/101$. Now assuming that these values are at least of the correct order of magnitude, let us expand $(A + Be^{-ct})^f$ by the binomial theorem. We find

$$(Be^{-ct} + A)^f = B^f e^{-fct} + fB^{f-1}e^{-ct(f-1)}A + \frac{f(f-1)}{2}B^{f-2}e^{-ct(f-2)}A^2 + \cdots.$$

Since f is so extremely small and A is also small, we do not introduce any great error if we neglect all terms after the second. Factoring we have $(Be^{-ct} + A)^f = e^{-fct}(B^f + fB^{f-1}e^{ct}A) = (X - Ye^{ct})$, where $X = B^f$, $Y = -fB^{f-1}A$ and we put $e^{-fct} = 1$ since f is so very small. This simplifies our formula to

$$V = V_0 e^{-at}(X - Ye^{ct})(C + De^{-ct}).$$

Expanding and substituting $e^{-at} = 1$, since a is small, we obtain

$$\begin{aligned} V &= V_0(CX - CYe^{ct} + DXe^{-ct} - YD) \\ &= V_0(H - Ge^{ct} + Ke^{-ct}), \end{aligned}$$

which will be shown to fit the curves very closely.

In the above formula c is a constant which must fit all the curves obtained from this cell while H, G, and K are constants for each curve but vary from curve to curve.

To determine these constants we write $v_1 = V_1/V_0$, $v_2 = V_2/V_0$, etc. Then we have

$$\begin{aligned} v_0 &= H - G + K = 1, \\ v_1 &= H - Ge^{ct'} + Ke^{-ct'}, \\ v_2 &= H - Ge^{2ct'} + Ke^{-2ct'}, \\ v_3 &= H - Ge^{3ct'} + Ke^{-3ct'}, \end{aligned}$$

where t' is taken as a certain definite interval of time and we begin to count time from $t = 0$. These equations solved simultaneously give us

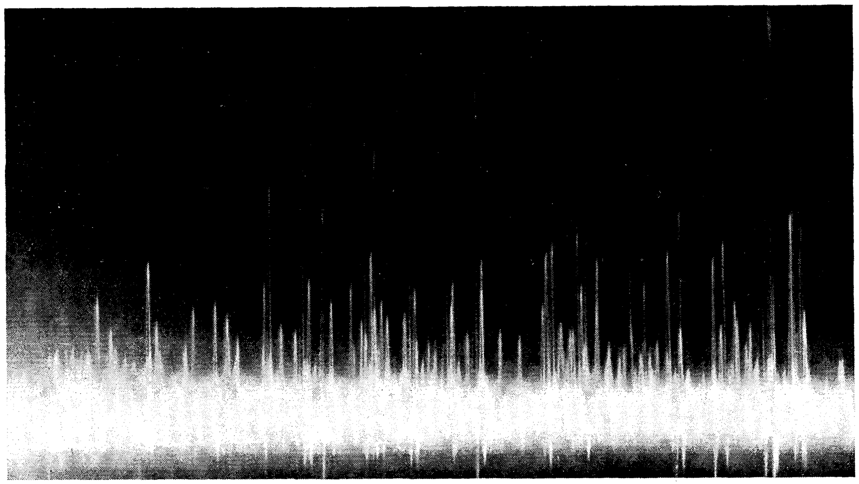

FIG 2.

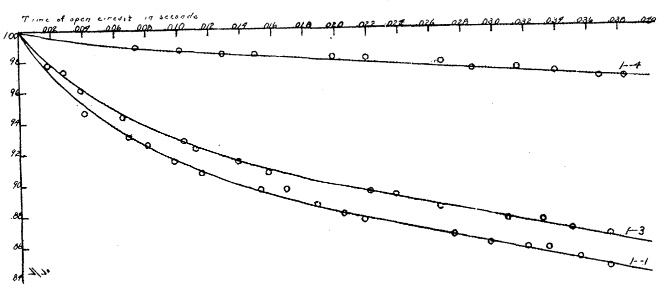

Fig. 3.

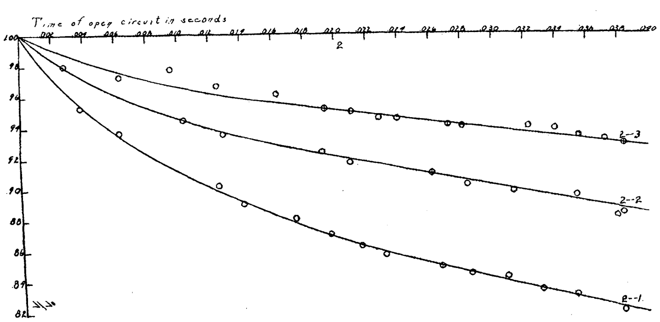

Fig. 4.

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$$K = \frac{(v_3 - v_2) - (v_2 - v_1)e^{ct'}}{(e^{-ct'} - e^{ct'})(e^{-ct'} - 1)},$$

$$G = \frac{(v_3 - v_2) - (v_2 - v_1)e^{-ct'}}{(e^{ct'} - e^{-ct'})(1 - e^{ct'})},$$

$$H = 1 + G - K$$

and

$$\frac{(v_4 - v_3) + (v_2 - v_1)}{(v_3 - v_2)} = e^{-ct'} + e^{ct'} = \text{a constant, } M.$$

Then $e^{2ct'} - Me^{ct'} + 1 = 0$. The solution of this last equation gives us the value of c when we know the values of t' and M. It also shows that M must be a constant for all the curves provided only that we take t' the same. Using t' equal to .0125 sec., the following values are derived for M from six representative curves 3.53, 3.36, 2.96, 3.11, 3.31, and 3.10. The mean value is 3.23 which gives $c = 84$. Likewise using t' equal to .010 sec. we obtain M from the same curves equal to 3.18, 2.87, 2.58, 2.63, 2.75, and 2.93. The mean of these is 2.82 which gives a value of c equal to 88. The mean of these two values of c, 86, was used in all the computation which follows.

1—1.

On closed circuit 16 min.
Applied E.M.F., V_0 = 99 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
$K = .138$, $H = .8629$, $G = .00094$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0018	96.9	.978	.981	+3
.0041	93.8	.947	.959	+12
.0069	92.2	.931	.938	+7
.0081	91.7	.926	.930	+4
.0098	90.6	.915	.920	+5
.0115	89.8	.907	.912	+5
.0152	88.7	.896	.897	+1
.0169	88.7	.896	.891	−5
.0188	87.7	.886	.886	−0
.0205	87.1	.880	.881	+1
.0218	86.7	.876	.878	+2
.0275	85.7	.866	.863	−3
.0298	85.1	.860	.862	+2
.0322	84.8	.857	.857	−0
.0335	84.8	.857	.854	−3
.0355	84.2	.850	.849	−1
.0374	83.6	.844	.845	+1

1—3.

On closed circuit 3 hrs.
Applied E.M.F., V_0 = 99 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
$K = .121$, $H = .8798$, $G = .00087$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0028	96.4	.974	.974	0
.0039	95.1	.961	.966	+5
.0065	93.5	.944	.948	+4
.0104	91.9	.928	.927	−1
.0111	91.4	.923	.924	+1
.0138	90.6	.915	.914	−1
.0157	89.8	.907	.908	+1
.0222	88.5	.894	.892	−2
.0238	88.3	.892	.889	−3
.0266	87.5	.884	.883	−1
.0309	86.7	.876	.877	+1
.0331	86.6	.875	.872	−3
.0350	86.1	.869	.869	−0
.0374	85.6	.865	.864	−1

DATA FROM PHOTOGRAPHS.

Since the actual figures are difficult to reproduce but one sample figure will be given. However the measured data will be given for several curves and curves drawn from the data which show the general form of the curves and the rise with time of open circuit.

1—4.

On closed circuit 24 hrs. 15 min.
Applied E.M.F., $V_0 = 99$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .0215$, $H = .979$, $G = .00046$.

2—1.

On closed circuit 2 min. 30 sec.
Applied E.M.F., $V_0 = 49$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .150$, $H = .8515$, $G = .00145$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.	t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0074	97.9	.989	.989	0	.0038	46.7	.953	.957	+4
.0102	97.7	.987	.987	0	.0063	45.9	.937	.937	0
.0129	97.5	.985	.985	0	.0126	44.2	.902	.899	−3
.0150	97.4	.984	.983	−1	.0142	43.6	.890	.891	+1
.0156	97.2	.982	.983	+1	.0175	43.1	.880	.878	−2
.0199	97.2	.982	.980	−2	.0197	42.6	.870	.870	0
.0220	97.1	.981	.979	−2	.0217	42.3	.863	.866	+3
.0268	96.9	.979	.977	−2	.0232	42.0	.857	.860	+3
.0287	96.4	.974	.975	+1	.0268	41.6	.850	.852	+2
.0316	96.4	.974	.973	−1	.0287	41.4	.845	.847	+2
.0340	96.1	.971	.972	+1	.0310	41.3	.843	.841	−2
.0368	95.8	.967	.969	+2	.0332	40.8	.834	.835	+1
.0384	95.8	.967	.967	0	.0354	40.6	.830	.829	−1
					.0384	40.1	.820	.818	−2

2—2.

On closed circuit 9 min. 30 sec.
Applied E.M.F., $V_0 = 49$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .0945$, $H = .9064$, $G = .00087$.

2—3.

On closed circuit 1 hr. 32 min.
Applied E.M.F., $V_0 = 49$ volts.
Counter E.M.F., V.
On open circuit t sec.
725 R.P.M.
$K = .0568$, $H = .9438$, $G = .000645$.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.	t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0028	48.0	.980	.980	−0	.0096	47.85	.978	.967	−11
.0063	47.6	.973	.960	−13	.0125	47.36	.967	.961	−6
.0104	46.4	.945	.943	−2	.0163	47.04	.961	.955	−6
.0129	45.9	.936	.935	−1	.0194	46.70	.952	.951	−1
.0192	45.23	.924	.920	−4	.0211	46.54	.950	.948	−2
.0210	44.9	.917	.917	−0	.0228	46.38	.946	.947	+1
.0262	44.57	.910	.908	−2	.0240	46.38	.946	.946	0
.0284	44.2	.902	.905	+3	.0272	46.13	.941	.943	+2
.0314	44.0	.898	.900	+2	.0281	46.05	.940	.942	+2
.0354	43.86	.895	.893	−2	.0323	46.05	.940	.937	−3
.0380	43.18	.881	.887	+6	.0340	45.88	.938	.936	−2
.0384	43.26	.883	.886	+3	.0355	45.72	.933	.933	0
					.0372	45.56	.931	.930	−1
					.0384	45.48	.928	.928	0

4—1.

On closed circuit 15 min.
Applied E.M.F., V_0 = 100 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
K = .101, H = .9002, G = .00124.

4—2.

On closed circuit on 100 volts 15 min. and on 75 volts 5 min.
Applied E.M.F., V_0 = 75 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
K = .0329, H = .9675, G = .000422.

t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.	t.	V.	V/V_0 Obs.	V/V_0 Comp.	Error.
.0058	95.6	.956	.960	+4	.0122	73.3	.978	.978	0
.0098	94.2	.942	.941	−1	.0166	73.1	.975	.974	−1
.0133	92.9	.929	.929	0	.0190	73.1	.975	.972	−3
.0174	91.9	.919	.917	−2	.0219	72.8	.971	.970	−1
.0200	90.8	.908	.911	+3	.0273	72.4	.965	.966	+1
.0233	90.2	.902	.905	+3	.0308	72.0	.960	.964	+4
.0270	89.5	.895	.897	+2	.0332	72.0	.960	.962	+2
.0302	88.8	.888	.891	+3	.0365	72.0	.960	.960	0
.0338	87.8	.878	.883	+5	.0374	72.0	.960	.958	−2
.0374	87.4	.874	.973	−1					

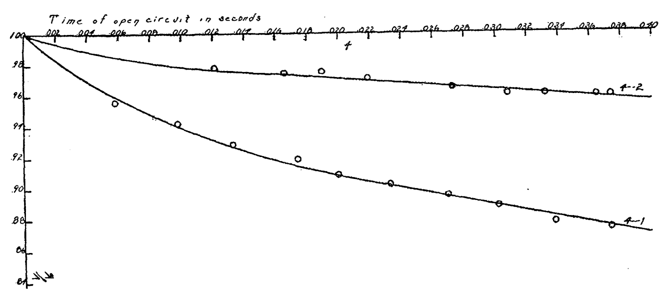

Fig. 5.

5—1.

On closed circuit 1 min.
Applied E.M.F., V_0 = 10 volts.
Counter E.M.F., V.
Time of open circuit t sec.
750 R.P.M.
K = .265, H = .735, G = .00003.

5—2.

On closed circuit 10 min.
Applied E.M.F., V_0 = 10 volts.
Counter E.M.F., V.
On open circuit t sec.
750 R.P.M.
K = .0615, H = .9392, G = .000695.

t.	V	V/V_0 Obs.	V/V_0 Comp.	Error.	t.	V	V/V_0 Obs.	V/V_0 Comp.	Error.
.0022	9.16	.916	.955	+37	.0076	9.70	.970	.970	0
.0107	8.20	.820	.840	+20	.0126	9.55	.955	.958	+3
.0142	8.08	.808	.813	+5	.0188	9.52	.952	.948	−4
.0196	7.85	.785	.784	−1	.0218	9.41	.941	.944	+3
.0246	7.78	.778	.767	−11	.0283	9.40	.940	.938	−2
.0307	7.48	.748	.754	+6	.0320	9.34	.934	.932	−2
.0342	7.48	.748	.748	0	.0336	9.34	.934	.930	−4
.0374	6.40	.640	.745	+105	.0365	9.28	.928	.926	−2
					.0374			.934	

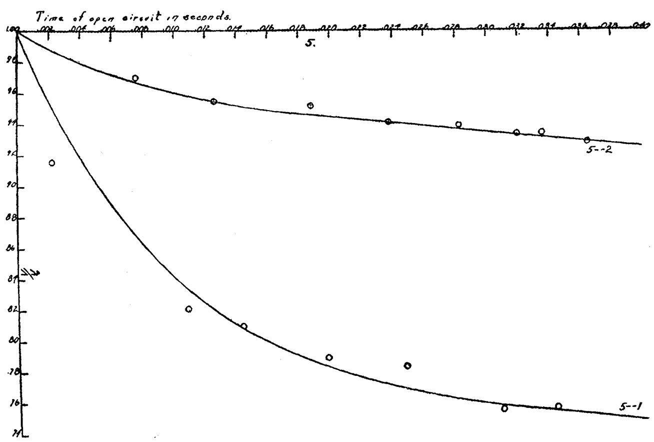

Fig. 6.

Discussion of Formula and Curves.

In the foregoing data but a portion of the data taken is given. The curves taken for longer periods of closed circuit lay so close to the axis that accurate measurement is impossible; however they do show the rise of the curve with time of closed circuit.

If one expresses the values of H, G, and K in terms of the thicknesses and resistances of the solid layer and gas film one will find that H should increase, K should decrease, and G should increase with time of closed circuit. The data given show that the H and K fulfill these requirements but that the G actually decreases. This apparent failure of the formula is explained however if we take account of one more term in the binomial expansion.

In every case, the curve of counter electromotive force plotted against time of open circuit rises with time of closed circuit. It seems evident that this counter electromotive force is not due entirely to a gas film as Guthe supposed. It is evident also that a permanent change must take place in the cell with time of closed circuit, for the current which leaks through the cell does not attain a minimum value but is constantly dropping lower and lower. Both of these effects are explained if we assume the cell's action depends upon the thickness of the solid layer which increases in direct proportion to the quantity of electricity passing through the cell, and also upon the thickness of the gas film, which quickly reaches a maximum value for each applied electromotive force and then gradually decreases in thickness with the time of open circuit. The increase in thickness of the solid layer results in an increase in the resistance of the combined layer, which accounts for the gradually decreasing value of the leakage current on closed circuit and also for the rise of the curves with time of closed circuit. The decreasing thickness of the gas film results in a decrease in the resistance of the combined layer which in turn accounts for the drooping curve.

This way of looking at the cell explains why it acts differently from the ordinary electrolytic cell with both electrodes of some inactive substance, such as platinum. With inactive electrodes, there will be no solid layer deposited; for the electrolytically produced oxygen can not combine with the electrode. In such a cell, the current will drop to a very small value and remain at that value provided the applied voltage is low enough, since the electrodes are unaffected by the passage of the current. But with an aluminum anode there is always deposited some of this solid layer and a drop in current results.

This way of looking at the cell is in accord with the results of Graetz and Pollak, that any electrolyte which will liberate oxygen on electrolysis may be used. It is also in accord with the results of Schulze, that other metals than aluminum may be used, since it only requires that the anode form a compound with the liberated oxygen which has a rather high resistance.

When the cell is used to rectify the alternating current, there is a slight deposit of this solid layer every time the aluminum is the anode. However when the current reverses, this deposit is not decomposed for to decompose the compounds of aluminum by electrolysis a rather high temperature is required. As this process goes on, we may reach a stage where the heat produced in the resistance of this solid film is sufficiently great to raise the temperature of the whole cell to a point where this solid film begins to decompose on the reversal. When this temperature is reached the cell fails to work satisfactorily. This is in accord with the results of others who state that the cell works best at the lower temperatures.

Summary.

1. This investigation has shown that any method of experimentation in which an appreciable length of time must elapse during the taking of data, the cell being on closed circuit with the battery at least a part of this time, will introduce serious errors due to the change taking place in the cell itself.

2. So far as the author is aware, no attempt has ever been made to explain the action of the cell on the theory that the action is due to a double dielectric, one part of which changes with the time of open circuit and the other with time of closed circuit. This investigation has shown such a theory is plausible and fully explains all the cases investigated.

3. The cell does not attain a steady state after a short time of closed circuit, nor does the single dielectric theory seem plausible.

4. The theory leads to the conclusion that any electrolyte which liberates oxygen on electrolysis may be used in the rectifier. It also shows that other metals than aluminum should be available as anodes, since it only requires the metal to form a compound with the liberated oxygen and that this compound have a rather high resistance.

The author is indebted to the University of Michigan for the apparatus provided, to Prof. N. H. Williams for many helpful suggestions, and to Mrs. Fitch for help in the computations.

ANN ARBOR, MICH.,
June 24, 1916.

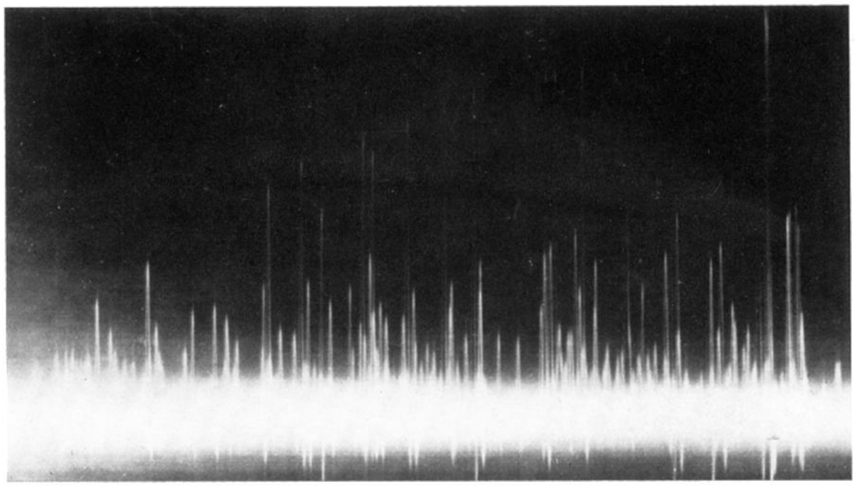

FIG 2.

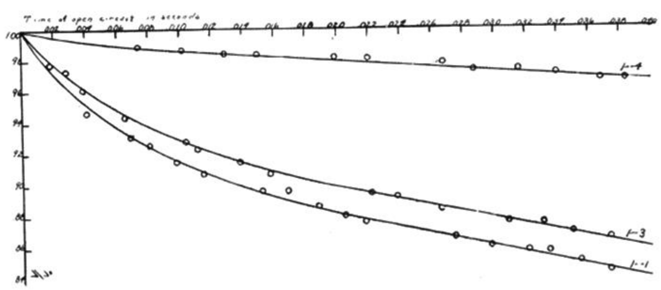

Fig. 3.

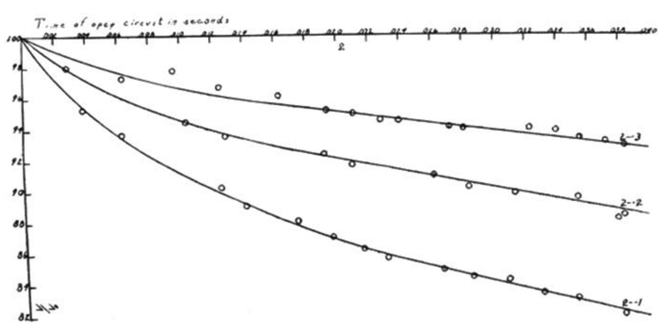

Fig. 4.