THE EFFECT OF PRESSURE ON THE ALUMINUM RECTIFIER.[1]

By A. P. Carman and G. J. Balzer.

THE peculiar action of the electrolytic cell with aluminum anode has been the subject of much investigation since it was first observed by Buff in 1857,[2] but the interest has been heightened within recent years, because of the increasing demand for a rectifier for alternating currents, and because the newer theories of solution and of electrons have suggested new explanations of the cell. Within a half dozen years, the important part played by the gas formed on the anode has been urged by several writers on the action of the cell.[3]

It suggested itself to the writers of the present paper, that light would be thrown on the problem by determining the exact effect of pressure on the action of the cell when traversed by an alternating current. For this purpose small cells were made, and placed under a cast-iron bell jar, so that the pressure could be raised from nearly zero to several atmospheres. The wave forms of the alternating current were photographed with an oscillograph, and at the same time, readings were made of the current and the electromotive force with Weston ammeter and voltmeter. All the cells had aluminum anodes and carbon cathodes. Fig. 1 gives all the description needed of the mechanical features of the cell. The evaporating dishes used were 10.5 cm. in diameter, and as indicated in the figure, were placed inside of larger dishes for packing the cell in ice. In most of the experiments, the temperature of the cell was kept about 2° C. The resistance of the cell was varied by varying the size of the anode; in some cells an aluminum wire of about 1 mm. diameter

[1] Paper read before the American Physical Society, Boston, December, 1909.

[2] Buff, Liebig's Ann., 1857, p. 296.

[3] Guthe, Phys. Rev., Vol. XV., p. 327, 1903. Schulze, Ann. d. Physik, 21, p. 955; 22, p. 543; 26, p. 372; 28, p. 787.

was used, and in others a vertical plate. Electrolytes used in the experiments were solutions of alum, of sodium borate, of bichromate of potassium and of potassium phosphate. When such a cell is placed in an alternating current circuit, the current becomes apparently unidirectional. The oscillograph curves show that the resulting current is practically a series of unidirectional pulses. That is, provided the impressed E.M.F. is not above a certain critical value, the current wave in one direction is practically cut out, the current passing freely from carbon to aluminum, but not from aluminum to carbon. To get this rectifying action quickly we employed the usual device of first forming the cell with a direct

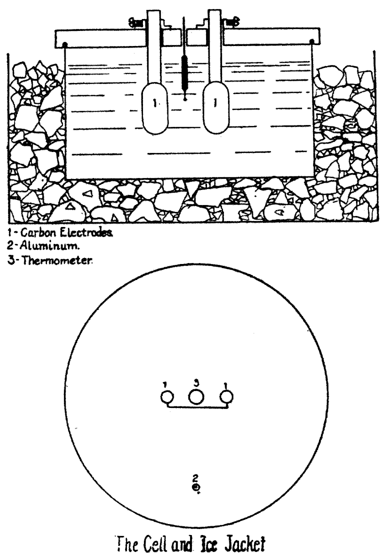

Fig. 1.

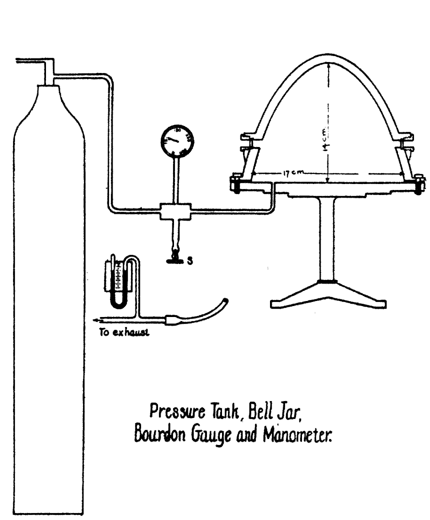

Fig. 2.

current. The alternating current was taken from the lighting and power circuits of the university system. The loads on the line were frequently changing, and so the wave forms changed. This hampered the work, and our curves often had to be taken late at night when the load on the lines was constant. In future work, a motor generator set, driven by a current from a storage battery, is to be used, but this was not available for the present experiments.

To vary the pressure, the cell was placed under a cast-iron bell jar, the arrangement being shown in Fig. 2. Small windows of heavy glass were placed so that the cell would be watched, and the temperatures read. To obtain uniform pressure, compressed air was taken from a cast-iron cylinder which had been charged to a pressure of about 1,000 lbs. per sq. in. from the compressor of the liquid air plant. The Duddell oscillograph was fitted with a home-made vertical slide, and the photographs were taken on 4×5 inch glass plates, the amplitude of the waves on the plate being generally about 4 cm. Fig. 4 shows the effect on the alternating current of the increase of pressure on a cell with a solution of sodium borate, the temperature being kept constant at 2.1° C. The pressures here increase successively from 8 mm. of mercury to 21 atmospheres. Fig. 5 shows the successive curves for the same cell as the pressure increases. These curves show that the rectifying action decreases with increasing pressure, and that the cell practically recovers its action when the pressure is removed. Similar curves were taken for cells with other electrolytes, showing that pressure decreased the rectifying action, though not always as much as in this case. In Fig. 6 we have curves for increasing pressures with a potassium bichromate cell, and in Fig. 7 we have similar curves for an alum cell. Readings of the current and of the electromotive forces were also made, in most cases, the instruments being kept in only during the times of reading. The readings of the voltmeter placed across the cell show only relative values, because the resistance of the low reading Weston voltmeter was not large compared with the resistance of the cell. A low reading electrostatic voltmeter was not available. Table I. shows the course of these readings for the alum cell with increasing and decreasing pressures.

These readings show the apparent decrease of resistance with increasing pressure, but the oscillograph curves are needed in any interpretation of the readings.

The experiments described above were all made at practically the same temperature, about 2° C. It suggested itself to us to try the effect of changes of temperature. Fig. 8 gives a series of oscillograph curves made for an alum cell, with temperatures increasing from 2.1° C. to 50° C. It is seen that the increase of temperature

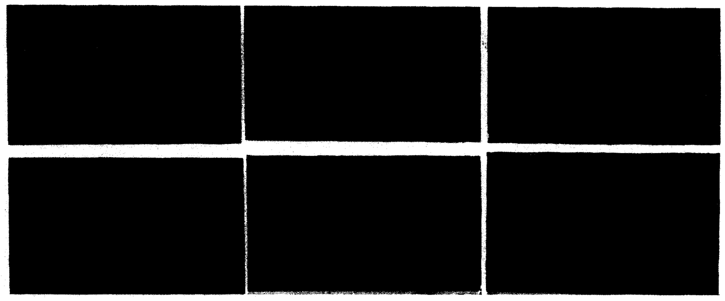

Fig. 3.

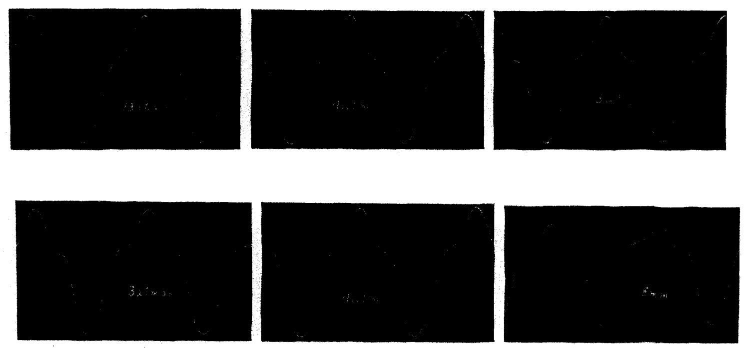

Fig. 4.

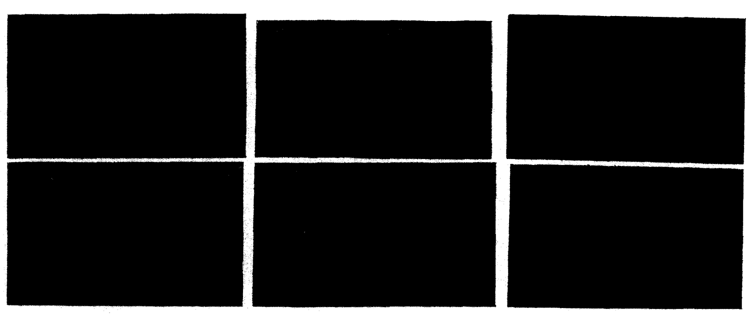

Fig. 5.

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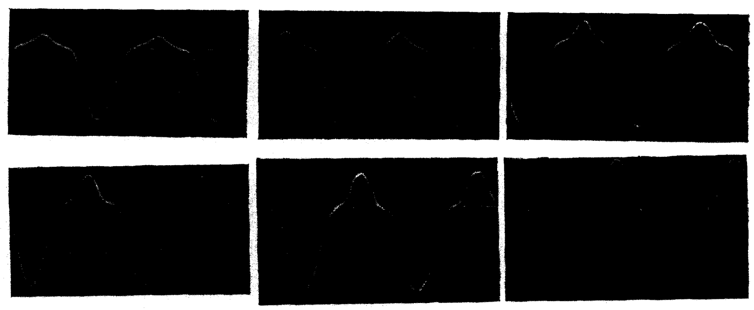

Fig. 6.

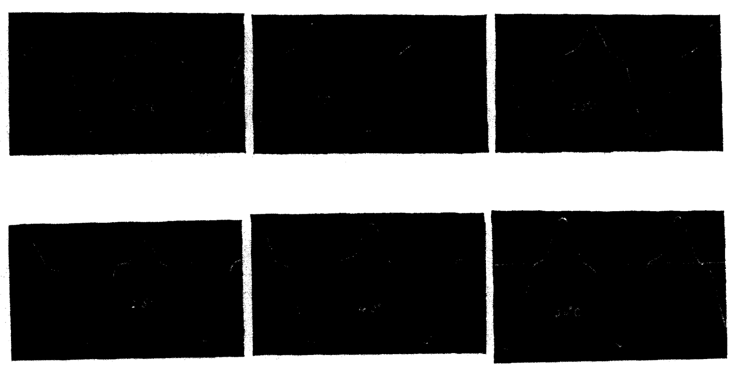

Fig. 7.

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TABLE I.

Cell with Aluminum Anode and with Alum Solution.

Pressure.	E.M.F. Across Cell.	E.M.F. Impressed.	Current (Amp.).
.8 cm.	24.5	32.2	.21
1 atmosph.	23.5	32.3	.22
2	22.1	32.2	.24
3	21.5	32.1	.25
5	19.7	32.2	.26
7	19.0	32.3	.27
9	18.5	32.4	.28
11	17.8	32.5	.29
13	17.4	32.3	.29
15	17.0	32.2	.29
17	16.5	32.3	.30
21	16.3	32.2	.31
17	16.4	32.3	.33
15	16.8	32.3	.33
13	16.9	32.2	.33
11	17.0	32.2	.32
9	17.0	32.1	.32
7	17.5	32.2	.30
5	18.2	32.2	.29
3	18.6	32.2	.28
2	19.3	32.3	.27
1	20.5		.26
.8 cm.	25.6		.17

decreases the rectifying action for this particular solution. The cell did not recover the rectifying action when the temperature was lowered again—a fact which has perplexed us. Of course the temperature fall was slow, and during this fall it was difficult to keep other conditions perfectly steady, but there was certainly a permanent change following the rise in temperature. This temperature effect probably depends also upon the temperature at which the cell is originally formed.

Numbers of investigators of the action of the aluminum cell have studied the character of the solid oxide film which is formed on the aluminum anode. The differences in the explanations of the cell are largely differences in the part ascribed to this solid film. Some writers have thought that the cell's action depended upon active selective properties of the film, while Schulze, who has published five or six investigations on this within the last few years, makes the action of the film wholly or almost wholly mechanical. According to him, it supports the gas film, which forms between the solid oxide deposit and the aluminum plate.

He says:[1] "The electrolytic valve action is not due to the rigid layer, which forms on the valve metals, but to a much thinner gas film which exists in the pores of the rigid layer and separates the electrolyte from the metal. If the valve metal is the kathode, then the free electrons contained in it pass through this gas layer with a comparatively small fall of potential. If the valve metal is the anode, a high difference of potential is necessary because there are then no free electrons in the electrolyte. I conclude, that the negative electrolytic ions then take the place of the electrons, and the ions, on account of their greater mass, experience a much higher resistance in the gas layer than that which the free electrons encounter in the opposite direction. This explains the so-called valve action."

The effect of pressure on the rectifying action, or "valve action" (Ventilwirkung), as Schulze calls it, is readily explained in accordance with Schulze's conceptions. The gas layer is reduced in thickness by the pressure and hence the resistance of the layer is decreased. We also observed a phenomenon which puzzled us at the time, but which is readily explained on the supposition of gas layers imprisoned in the body of the rigid film or behind it. The phenomenon was that at higher pressures a white fluffy deposit resembling in appearance the white of a boiled egg began to form at the aluminum anode and this increased as the pressure increased. This fluffy deposit would sometimes leave the electrode and rise to the top, or sink to the bottom. As the pressure was released the deposit decreased, and at low pressure dropped to the bottom almost entirely. Evidently the solid film was broken by the pressure of the gas, and the fluffy deposit was the disintegrated film.

The effect due to rising temperature which we observe is not explained so evidently. It would seem that the solid oxide film was rendered more porous by the temperature increase, and hence

[1] Schulze, Ann. d. Physik, 28, p. 787.

the gas layers were dissipated, that is, the formation on the plate was destroyed. This would accordingly not recover immediately. The temperature effects however require more investigation.

Laboratory of Physics,
University of Illinois,
December, 1909.

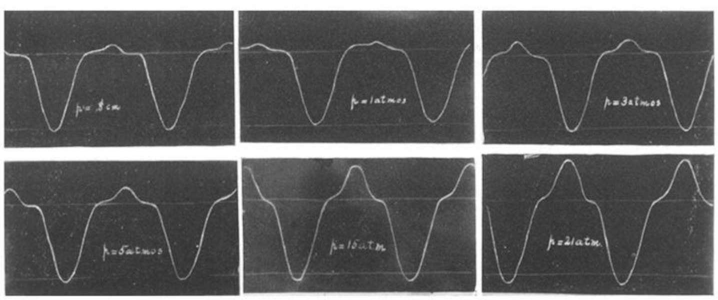

Fig. 3.

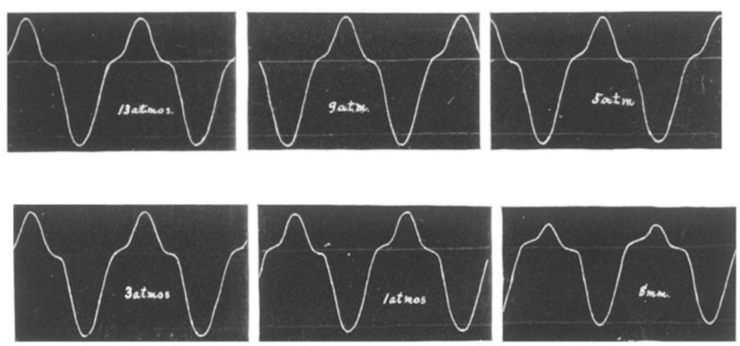

Fig. 4.

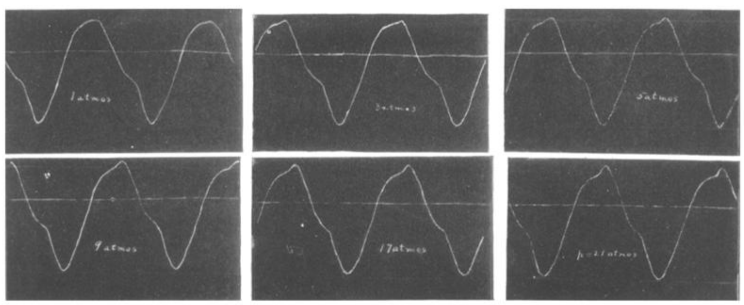

Fig. 5.

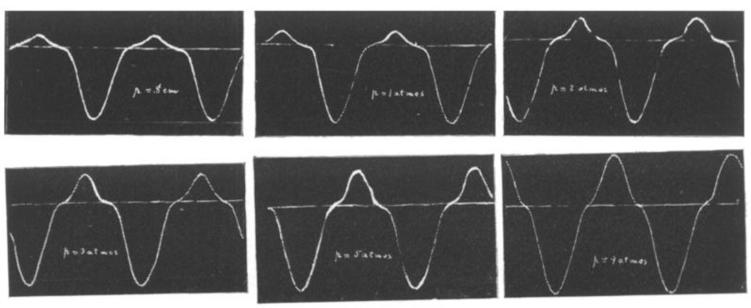

Fig. 6.

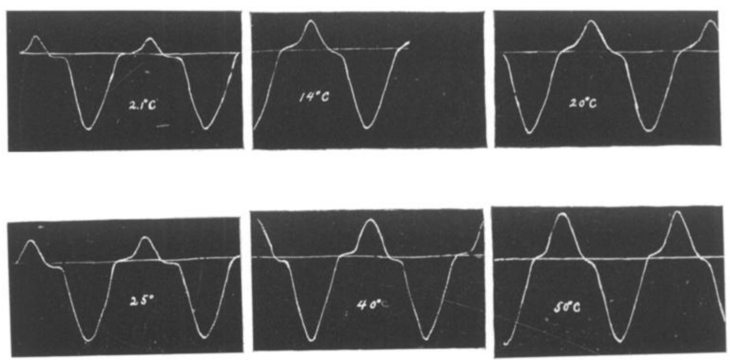

Fig. 7.