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# The Electrolysis of Water [with discussion]

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*A paper read at the Third General Meeting  
of the American Electrochemical Society,  
at New York City, April 16, 1903, Vice-  
President Bancroft in the Chair.*

## THE ELECTROLYSIS OF WATER.

BY JOSEPH W. RICHARDS AND WALTER S. LANDIS.

The phenomena accompanying the passage of an electric current through acidulated water have been studied from the very beginning of electrochemistry. It is believed that a true explanation of them would clear up a great deal of the present incomplete state of our knowledge of the subject of electrolysis in general. Omitting the experiments of the early investigators, which were intended solely to show the actual decomposition of water, we will here review the work of a few of the later ones.

Helmholtz<sup>1</sup> was probably the first investigator to observe the passage of a current through water at a voltage below 1.5 volts. He mentions that a Daniell cell passed current through water for four or five months without visible decomposition. His results were somewhat incomplete because of his lack of measuring instruments.

Ernst Salomon<sup>2</sup> first developed, at the suggestion of Nernst, the idea that when using soluble electrodes, the difference of concentration produced at the two electrodes gave rise to an electromotive force whose intensity could be calculated from the difference in concentration at the two electrodes and the rate of diffusion of the salt in the electrolyte.

Sokolow<sup>3</sup> claims to have produced hydrogen gas bubbles on a platinum cathode by using 1.072 volts.

H. Danneel<sup>4</sup> took up Nernst's idea, as used by Salomon, and applied it to calculating the residual currents which pass through dilute aqueous solutions of acids and bases, from which higher

<sup>1</sup> Pogg. Ann., 150, 483 (1873); Wiss. Abhandl., I, 823.

<sup>2</sup> Zeit. für Elektrochemie, III, 264 (1896).

<sup>3</sup> Wien. Ann., 58, 209.

<sup>4</sup> Zeit. für Elektrochemie, IV, 211, 227 (1897).

voltages liberate hydrogen and oxygen. Danneel based his calculations on Fick's Law of the diffusion of a substance in a fluid,

$$S = \frac{q}{l} \cdot D(C_1 - C_2)Z,$$

in which  $S$  is the quantity of substance diffusing through a length  $l$  of solution, with a cross section  $q$ , in time  $Z$  (in days), with concentrations  $C_1$  and  $C_2$  at the respective terminals (in grams per cubic centimeter), and  $D$  is the quantity found by experiment diffusing through a 1 cm. cube, in one day, for a difference of concentration of 1 gram per cm. cube.

Since hydrogen diffuses so much faster than oxygen, the calculations were made for hydrogen, on the assumption of the solution being saturated at one pole (0.000002 gram per cubic centimeter) and containing no hydrogen at the other pole, and taking  $D$  as 4, from Hufner's figures. Calculating on the basis of oxygen diffusing from one electrode to the other, the saturation point is 0.000041 gram per cubic centimeter and  $D = 1.62$ .

Experiments were then made with dilute sulphuric acid, and the currents passing measured for voltages up to 0.08. The actual residual current measured was two to five times the calculated value for electrodes close together, and up to fifty times as much, for electrodes 26 cm. apart. It is to be regretted that the measurements were not made with higher voltages also. Danneel cannot be said to have proven his thesis.

Glaser<sup>1</sup> investigated at length the question of the passage of these residual currents. His first research was on the electromotive force of the gas battery. He made this to be over 1.09 volts, with a tendency to slowly reach a higher value. He then investigated the current passing through dilute sulphuric acid (N/10) with increasing voltages up to 1.20. His curves show a rapid increase in current, or nick in the curve, at 0.59 volt, and again at 1.09 volts, when the two electrodes used were of equal size. When the anode was large and the cathode small, a sudden rise occurred between 0.7 and 0.8 volt, and another at 1.10 volts. Other tests, however, showed only the rise at 1.10 volts, without any explanation of the absence of the lower bend in the curve. With dilute alkalis there was a slight rise at 0.5 to 0.6 volt and a decided rise at 1.10. By using a large cathode and small anode,

<sup>1</sup> Zeit. für Elektrochemie, 4, 355, 373, 424.

the curve began to rise steeply at 0.7 to 0.8 volt, and became nearly linear above 1 volt. Using caustic potash, a marked nick or turning point in the curve was found as follows:

With 10 normal KOH at 1.32 volts				
“ 4 “ “ “	“	“	“	1.38 “
“ 1 “ “ “	“	“	“	1.40 “
“ $\frac{1}{8}$ “ “ “	“	“	“	1.45 “
“ $\frac{1}{80}$ “ “ “	“	“	“	1.46 “

using a small cathode and a large anode.

Glaser's results were not conclusive since they neither show the cause of the residual currents nor their properties.

Emil Bose<sup>1</sup> has published a long and very interesting work on the decomposition voltages. He used a continuously increasing voltage, so that increasing measurements were obtained without breaking the circuit. He started out first to test Glaser's results, using electrodes of unequal size. He remarks that decomposition points are much more difficult to detect when gases are evolved, than when solids only are deposited. He found in five experiments a gradual bend in the current curve at the neighborhood of 1.08 volts, but not the sharp bend indicated by Glaser. Bose suggests the most probable value of this point of the reversible decomposition and formation of water, as 1.14 volts.

Bigelow<sup>2</sup> has made extensive tests, keeping the voltage constant at one volt, and measuring the current for as long as 82 days. The residual current falls for 50 to 70 days, from which it would appear that no one before him had measured the true residual currents. The values reach a minimum which Bigelow takes to be the true residual current. With platinum electrodes 17 mm. square and 11 mm. apart, in sulphuric acid (0.05 per cent.), the residual current, in micro-amperes, was 56.4 at the end of twenty-four minutes, but sank to 0.169 in seventy-two days. These results invalidate the figures of all previous investigators, since they measured their currents at thirty seconds or one minute in some cases, at five to twenty-four days in others.

We shall now take up in detail the experiments which we have made at the laboratory of the Lehigh University with a view of throwing some light upon many of the obscure points untouched upon by these previous investigators. It may seem strange to

<sup>1</sup> Zeit. für Elektrochemie, 5, 153.

<sup>2</sup> Journal of Physical Chemistry, Vol. 6, No. 9.

many to notice the widely varying experiments which we made, but we may say, as others may have already experienced, that each experiment led up to several others; in fact to a sort of a divergent series of experiments, and it is only the most striking which we have here reproduced. Following the scheme of presentation of the work of the other investigators we shall first describe the experiments and then return to a critical and comparative review of them afterwards.

#### ELECTROLYSIS IN CLOSED VESSELS.

Dilute sulphuric acid (0.1 per cent.) was boiled to expel dissolved gases, cooled in a closed vessel, and electrolyzed in thermometer bulbs, completely filled and sealed as full as possible. In every case, when a current at 3 volts tension was applied, the bulb exploded within thirty seconds, and it was impossible in this time to follow the course of the ampere meter. The apparatus was arranged as the upper design in Fig. 1.

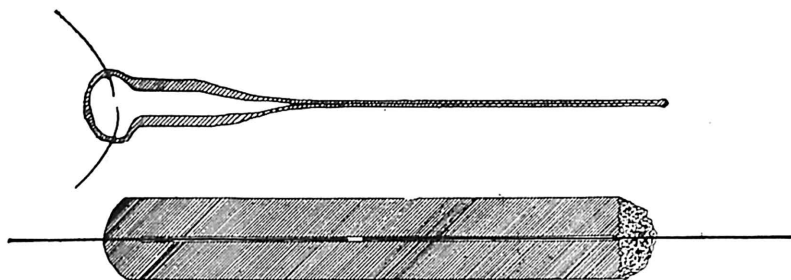


FIG. 1.

The platinum wires ( $\frac{1}{8}$  mm. in diameter) were then sealed inside a thermometer stem with a bore  $\frac{1}{4}$  mm. in diameter and with walls  $2\frac{1}{2}$  mm. thick around that bore. (See lower design, Fig. 1). Theoretically this should stand 25,000 atmospheres,—much more than the pressure of water if converted into hydrogen and oxygen in its own volume (1,830 atmospheres). The tube was filled, the platinum wires being within 1 mm. of touching each other and sealed by Canada balsam at the ends, without an indication of any clear space. Three and one-half volts applied electromotive force failed to send a current through it, the galvanometer in circuit being capable of indicating 0.07 micro-ampere. This was tried repeatedly, the connections being tested so as to make

certain that the resistance was surely in the tube. On breaking the seal at one end, current immediately began to flow from 0.3 volt upwards, and gas was visible on the cathode at 1.6 volts.

## ELECTROLYSIS OF PURE WATER.

Distilled water was boiled in a platinum dish, and then placed between two platinum electrodes. The galvanometer in circuit was sensitive to 0.07 micro-ampere. No observable current passed, using up to three volts potential. With 1 volt potential across the electrodes, mixed oxyhydrogen gas was bubbled in midway between the two electrodes. A current immediately passed, equal to several micro-amperes.

## CRITICAL VOLTAGE.

*I. Heat Value of Decomposition.*—A calorimetric experiment was made, electrolyzing dilute sulphuric acid with free disengagement of gases. Assuming 0.239 gram-calorie per second as the heat value of 1 watt, the heat obtained in the electrolyte corresponded to  $C \times (V - 1.50)$ . Or, in other words, the heat absorbed in chemical work corresponded to  $C \times 1.50$ , thus proving the energy absorbed in decomposing the water as 1.5 volts.

In detail the experiment was as follows: A water voltameter designed for the separate production of the gases was connected through resistance to an ordinary lighting circuit. 133 grams of 20 per cent. sulphuric acid at the temperature of the room was placed in it, the current was turned on and readings taken, at stated intervals, of the voltage, current and temperature. Below are the results and calculations.

Voltage absorbed by the cell .....	18.1 volts.
Current .....	0.51 ampere
Time in minutes.	Temp.
0 .....	22.3°
0.5 .....	22.8
1.0 .....	23.3
1.5 .....	24.0
2.0 .....	24.5
<hr/>	
Total time, 120 seconds.	Rise, 2.20
	Rise per second, 0.0183°.
Specific heat of 20 per cent. sulphuric acid .....	0.83
Heat received by cell per second, $133 \times 0.0183 \times 0.83 =$	2.021
gram-calories.	

Heat value of the current in calories per second  $18.1 \times 0.51 \times 0.239 = 2.206$ .

Heat absorbed in decomposition,  $2.206 - 2.021 = 0.185$  gram-calories.

Voltage absorbed in decomposition,  $\frac{0.185}{0.51 \times 0.239} = 1.51$  volts.

No corrections were made for the sensible heat of the evolved gases, or the losses by radiation. The sensible heat in the evolved gases was negligible in comparison with the heat capacity of the electrolyte. As to loss by radiation, the difference in temperature between the electrolyte and the external air was so small, and the time so short, that it was also considered negligible.

*II. Critical Voltage by Measuring Counter-electromotive Force.*—In the course of our experiments we happened upon this method of determining the critical voltage. We were using a cell 8.75 meters long (Fig. 2) with a resistance of about 10,000 ohms, and were constructing a current curve as will be described later. The cell was connected in series with a galvanometer and a 66-element Gülcher thermopile. The thermopile was lighted and simultaneous readings were taken of the current and the electromotive force. The electrodes used were small pieces of gold foil, and the electrolyte was dilute sulphuric acid of 10 per cent. strength. After reaching a maximum of 3.5 volts, the gas was turned off from the thermopile and it was allowed to cool. Simultaneous readings were again taken of the current and the applied voltage as before. As the thermopile cooled, the current dropped steadily and when the voltage had reached 1.5 exactly the current passing reached zero.

The same experiment was again repeated with platinum electrodes, and while the current did not drop quite as regularly as with the gold electrodes, still there was no doubt of the cessation of the current at 1.5 volts. The electrodes should be allowed to evolve gases freely for some time to give constant results in this class of work. If this precaution is taken, platinum electrodes give no trouble, and compare favorably with gold.

*III. Critical Voltage as Determined by Observing Gas under the Microscope.*—Two platinum electrodes, which had been running some time evolving hydrogen and oxygen, were immersed in a normal solution of sulphuric acid and placed under a microscope, magnifying 100 diameters. On applying 1.8 volts, gas was

generated freely at the cathode and the anode. On cutting off the current the gas bubbles grew smaller until they finally disappeared. This was repeated with the cathode in the field at 1.75, 1.70, 1.65, 1.60, 1.55 and 1.50 volts. At the latter voltage a distinct gas bubble appeared on first closing the circuit, and then gradually decreased in size until it finally disappeared. At 1.45 volts, no gas bubbles appeared; at 1.50, they were again produced as before, on closing the circuit.

*IV. Critical Voltage as Determined by Increase of Current with Increase of Voltage.*—The current curve, by which is meant the curve obtained by plotting current as ordinates and voltage as abscissas, was found to vary greatly with the distance apart of the electrodes. Also the nature of the electrolyte affects the curve to a great extent. Yet even with these variations it might be expected that a decided break should occur somewhere at about 1.5 volts. With this end in view we conducted the following experiments and plotted the accompanying curves. It should be here stated that these experiments were not undertaken solely with this end in view, but rather for the purpose of gaining a better understanding of the phenomena of the residual currents which pass through such a dilute solution of sulphuric acid.

*Experiment 1.*—A cell was constructed of  $\frac{3}{8}$ -inch glass tubing, using for electrodes two platinum wires having their ends 5 mm. apart. The electrolyte was 0.1 per cent. sulphuric acid. A varying voltage was obtained by changing the number of couples of a Gülcher thermopile, in circuit. The current was interrupted during the changing, and after closing the circuit, readings were taken every five seconds up to, in some cases, thirty seconds.

There were several kinks in the current curve, the only one with which we will concern ourselves at present being at about 1.45 volts, where a very decided rise took place, marking an increase in current.

*Experiment 2.*—The same experiment was repeated, using the same cell with the electrodes 5 cm. apart. The current curve for this cell shows an abrupt rise beginning at about 1.2 volts, instead of 1.5 as before, showing that the distance apart of the electrodes seems to affect the nature of the curve.

*Experiment 3.*—We tried the same experiment with extreme distance apart of the electrodes. In one case the electrodes con-



sisted of platinum wires 8.75 meters apart, in the cell shown diagrammatically in Fig. 2. With an electrolyte consisting of 0.1 per cent. sulphuric acid, the curve (marked Exp. I (a) Plate I) is a perfectly straight line with no kinks or breaks in its entire length. Being only concerned with this point, we will not discuss at present its other peculiarities. The experiment was repeated with an electrolyte containing 10 per cent. sulphuric acid. Here

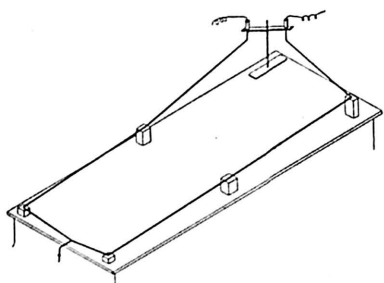


FIG. 2.

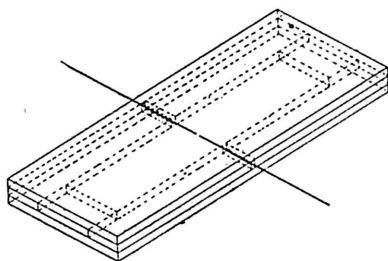


FIG. 3.

the curve rises somewhat steeply from the very beginning, with only a slight break at 2 volts.

Going to the other extreme, we employed a cell constructed as in Fig. 3, of glass, so that it could be used under the microscope. It consists of two microscope slides separated by pieces of glass, so as to leave a space in the middle for the reception of the electrolyte. By means of a scale in the eye-piece of the microscope the distance of the electrodes apart could be very accurately measured. We placed them  $\frac{1}{8}$  of a millimeter in this case, and first used 0.1 per cent. sulphuric acid for electrolyte. We found on this curve (see Plate I) two distinct inflections, one at 2 volts and the other at 2.35 volts. On repeating the experiment with 10 per cent. sulphuric acid electrolyte, the curve showed only one inflection at about 1.7 volts.

These experiments showed the existence of many unexpected conditions affecting the presence or absence in position of the points of inflection of the current curve. The distance apart of the electrodes, the strength of the electrolyte, and the time interval between the opening and the closing of the switch in the circuit all seemed to have a marked influence on the nature of the curve. On the whole this seems to be a very unsatisfactory method of obtain-

ing the critical voltage of an electrolyte. Method II is much more satisfactory.

#### RESIDUAL CURRENTS.

It has been known ever since the time of Helmholtz, that a current could be sent through an electrolyte, using insoluble electrodes at an applied voltage below that required for decomposition. We have already reviewed some of the work which has been done towards an explanation of this phenomenon, and it is now our purpose to discuss some of the results, and interpret them in the light of some of our own experiments.

Danneel, as has been previously stated, ascribed these small currents to the carrying capacity of the dissolved gases, oxygen and hydrogen, in his electrolyte, dilute sulphuric acid. Taking for instance the dissolved hydrogen he attempted to prove that the free ions took a certain charge from the cathode and by diffusion carried it over to the anode where a certain positive charge was neutralized when they came in contact with the anode. He made a calculation of the current which should thus flow through his cell and found a great discrepancy between his calculated and observed values.

Bigelow also made an extensive study of these residual currents his work being mainly a quantitative determination of them. His investigations covered a period of some eighty days, during which time he took readings at stated intervals, the results of which are carefully tabulated in his original paper. The great value of his work lies in the fact that it proves the theory upon which Nernst based his calculations. Bigelow had to wait between seventy and eighty days before the current became constant. On recalculating these results theoretically, using Danneel's formula, we have found the calculated value of this diffusion current to be 0.105 micro-ampere, against the minimum 0.088 micro-ampere found by Bigelow.

It may be that Danneel's figures would have corresponded more nearly with his calculated values, if he had taken readings like Bigelow, for seventy or eighty days, until the values had become constant. Danneel gives the time in only one instance, where he waited four days to get a constant value, but still obtained results thirty to fifty times as great as calculated. Bigelow's four-day results are forty times as great as his minimum obtained in

seventy-two days, so that if Danneel had taken that time to each of his measurements, with the tube 26 cm. long, he would probably have obtained a "beobachtet" corresponding to his "berechnet."

In thus confirming the diffusion formula we also confirm the application of Faraday's law to these diffusion currents because this law is embodied in the application of the diffusion formula. To keep the electrolyte so saturated that the required current will pass requires that an amount of gas be evolved proportional to that carried over to the other electrode. As to the exact condition of these gases, we have come to the conclusion that they are in solution in the electrolyte, and that their recombination furnishes the energy which was absorbed in the decomposition, thus causing no absorption of voltage.

These diffusion currents are no doubt very constant in their value and must therefore be quite independent of the comparatively large current which flows on first closing the switch, and gradually falls off in value for as much as eighty-two days, as observed by Bigelow. These currents are undoubtedly caused by the using-up of dissolved oxygen and hydrogen in the electrolyte. The electrolyte carries the current, just as it does above the critical voltage, and with an internal friction according to Ohm's Law, but the amount of such current which can flow is conditioned not by the voltage applied but by the rate at which dissolved hydrogen and oxygen can get to the electrodes and combine with the hydrogen and oxygen which may be there set free.

In support of this statement we shall again refer to an experiment of ours, which has been cited before. Two platinum wires  $\frac{1}{8}$  mm. in diameter were used as electrodes, heated to redness, and plunged 2 cm. into the electrolyte. The electrolyte was 0.1 per cent. sulphuric acid, made with distilled water and not used before, so nearly free from dissolved oxygen and hydrogen. The distance apart of the electrodes was 875 cm., cross section of the electrolyte 0.2 square centimeter. The theoretical resistance was about 1,000,000 ohms. A diagrammatic sketch of the cell is shown in Fig. 2. The curve is shown in Plate I. The current passing increased linearly with the applied voltage, without any kinks, no evolution of gas took place at the electrodes, and the amount of current passing was equal to the applied voltage divided by the ohmic resistance, within the errors of observation and cal-

ulation. But we cannot ascribe the whole of this current to true diffusion. The calculated diffusion current according to Danneel would be 0.0012 micro-ampere, whereas our lowest reading, at 0.3 volt, was 0.4 micro-ampere. With this long cell the limit which the current can reach is no doubt that set by Ohm's Law, because we have here gas enough in solution, aided by the diffusion current, to take care of all the current which this law would allow to pass.

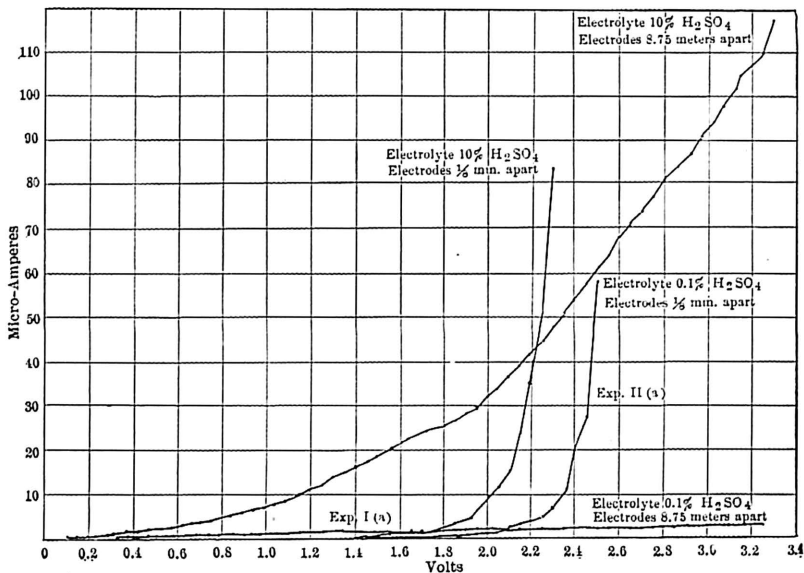


PLATE I.

Now as to the other case, that in which Ohm's Law will allow more current to pass than the dissolved gases and diffusion current can take care of, we have an example in the next experiment. The same platinum wires were placed as electrodes in the same kind of solution, with their ends  $\frac{1}{8}$  mm. apart, but with the active surfaces averaging virtually 2 cm. apart, the resistance (theoretical) was about 2300 ohms. The curve is shown also in Plate I. It will be noticed that no current passes until a voltage of 1.5 is reached, from that to 2.1 volts a smaller current than with the electrodes 875 cm. apart, from thence to 2.5 volts a rapidly increasing current with evolution of hydrogen at 2.4 volts, when the current flowing had reached 20 micro-amperes. In no case with

the voltage used was the current more than a small fraction of that which would be calculated from  $A = \frac{V}{R}$ . The current showed a very slight rise at 1.8 volts.

The cell used in this case is shown in Fig. 3. It does not contain over a half cubic centimeter of electrolyte, and so can contain but a very small amount of dissolved gas. As the diffusion current is a very small factor also we can easily see here that the total carrying capacity of these two agencies are the factors which here condition the current, and not Ohm's Law.

Returning again to the comparatively large currents due to the gases already in solution going to the electrodes and combining with the products of electrolysis, thus permitting a current to flow through the electrolyte, we must be careful not to confuse them with the true diffusion currents. For want of a better term we might call them extra residual currents in distinction to the very small normal residual current.

The extra residual current starts with a certain maximum value which falls off with the time, and as Mr. Bigelow found reached a constant between seventy and eighty days. The explanation of this phenomenon which we have to offer is as follows. These currents are due as before stated to the combination of the dissolved oxygen and hydrogen in the solution with the nascent products of electrolysis. This combination taking place at the electrodes, no voltage is absorbed, and still a current passes through the electrolyte. This combination can only take place at the electrodes. When the current is first turned on, the electrolyte just around the electrodes is well saturated with the gases which are immediately available for use. This causes the large initial currents. But as the solution becomes impoverished, the electrodes have to draw from a greater and greater distance, with the result that less and less gas reaches them in a given time and so causes the observed fall of current. When the gases in solution have all been combined with the products of decomposition, then we have the phenomenon of the true residual currents.

That this current also follows Faraday's Law was proven by some calculations made on Mr. Bigelow's results. In his experiment 1, for instance, a summation of the entire current passing through his cell, until the minimum—the diffusion current—was

reached showed that the extra residual current, above the diffusion current, could have consumed 0.00008 gram of hydrogen, or its equivalent in hydrogen plus oxygen, in the time given. If the solution was 10 cc. in volume (estimated; not given by Bigelow) it could have contained, if saturated, 0.00002 gram of hydrogen and 0.00048 gram of oxygen, equivalent altogether to 0.00008 gram of hydrogen.

There thus appears to be no doubt that Faraday's Law applies to the "Rest-strom" and that this current is composed of two factors:

I. A residual diffusion current, which is constant and is sustained by the diffusion of hydrogen and oxygen from one pole to the other.

II. A constantly decreasing extra current caused by the using-up of the dissolved hydrogen and oxygen, and which falls off as the concentration of the gases in the solution decreases.

It being manifestly impossible to conduct a series of experiments involving a large number of measurements at different voltages, if each single reading is to take seventy days, we consider that future investigators may take it as proven that the residual diffusion current is always to be counted on, and that its value may be calculated with sufficient accurateness by Danneel's formula. The second factor agrees very well with calculations based on the constantly decreasing current, the amount of oxygen and hydrogen it will consume, and the actual amount present.

#### CONCLUSIONS.

1. We have no explanation of the action in the closed tube.
2. There is no doubt that the actual voltage absorbed in the decomposition of water into free oxygen and free hydrogen is very close to 1.5 volts.
3. Faraday's Law applies to all currents passing through electrolytes, whether above or below the voltage absorbed in ultimate decomposition.
4. Ohm's Law applies to all currents passing through electrolytes, *i. e.*, the current in passing will lose in friction an amount of energy =  $C^2R$ .  $C$  will be equal to  $\frac{V}{R}$  only when  $R$  is so high that  $C$  is less than the amount of current which can be sustained

by the secondary actions taking place at the electrodes, *i. e.*, solution of a soluble anode or depolarization by dissolved gases.

5. Thomson's Rule applies to the decomposition of water. The voltage absorbed in decomposition can be calculated from the first and last states of the electrochemical system.

6. Gases in solution in pure water make it conducting, like salts in solution. All the phenomena of residual currents so far observed are explainable by the presence of gases in solution, by gaseous diffusion, and recombination at the electrodes.

ELECTROMETALLURGICAL LABORATORY,  
LEHIGH UNIVERSITY.

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### DISCUSSION.

MR. B. MACNUTT: Mr. Chairman, I would like to ask Dr. Richards if he consider that every term drops out of the energy equation except " $RI^2$ " when the current is small?

DR. J. W. RICHARDS: When the current is extremely small the only thing that is necessary is to consider the amount of products of electrolysis which can be taken care of or neutralized by recombination at the electrodes. The energy for decomposing  $H_2O$  to  $H_2$  and  $O$  does not enter into the question; the voltage of decomposition also does not enter into the question.

DR. H. S. CARHART:  $RI^2$  represents it all.

MR. MACNUTT: In regard to the polarization, do you consider it negligible with a very small current? A few years ago I made some experiments with electrolytic cells, using an extremely small current, about  $10^{-7}$  amperes, and measured the electromotive force with such current. The conclusions I drew from my experiments were that Ohm's Law did not apply in that case; that is to say, there was an electromotive force there which was not the product of the resistance and the current going through the cell and which did not become zero with a zero current, nor was it any simple function of the current. Did I understand you to say that Ohm's Law, in your experiment, did apply with a small current?

PRES. RICHARDS: It applies with very small currents when the resistance between the electrodes is so great that the voltage absorbed in frictional resistance in the electrolyte, as calculated by Ohm's Law, is greater than the depolarization which can take place

by residual gases. It applied in our experiments only to the electrolyte  $8\frac{3}{4}$  meters long and with a one-tenth per cent. solution of sulphuric acid.

MR. MACNUTT: That, of course, would mean that the factor RI is larger than anything else and the other becomes negligible.

PRES. RICHARDS: Yes.

MR. C. HERING: Do I understand that Prof. Richards used platinum in these experiments?

PRES. RICHARDS: Yes.

MR. HERING: It seems to me that the use of platinum complicates matters very much because there is a well-known tendency of platinum to absorb hydrogen and oxygen, combining with them and forming some sort of a chemical compound. Platinum is therefore, in my opinion, a very poor metal to use in any such work. On one occasion in connection with a liquid potentiometer, I had to use something which would not absorb oxygen and hydrogen and found that gold was quite satisfactory, while platinum was absolutely useless.

The test which Prof. Richards described with an absolutely closed vessel seems to me to be a very remarkable one, so remarkable that I should like to see it repeated a number of times. I understood that there was sulphuric acid in that solution, and that the highest voltage was only 3.5.

PRES. RICHARDS: Yes.

MR. HERING: It would be interesting to see at what voltage decomposition would start in that case. In the 8-meter test I understood the voltage was raised to only 3.5. Was there any evolution of gas, because that was above the decomposition voltage?

PRES. RICHARDS: No sign of gas.

MR. HERING: I did not hear Prof. Richards suggest that there may be actual decomposition and that the gases so formed might pass through the solution in suspension or solution to the other electrodes. I think he referred only to the gases that were originally in the solution. It seems to me that it is not impossible to suppose that gases might actually be formed even if there were none in the original solution and that they also might travel from one electrode to the other and therefore carry a current below the



decomposition voltage, because the oxygen traveling from the anode to the cathode would depolarize the cathode and the hydrogen would depolarize the anode.

In that test in which the amount of heat generated was measured, I would like to ask whether allowance was also made for the heat that passes out in the gases, or whether only the heat remaining in the liquid was measured. It seems to me that the gases themselves would carry off quite an appreciable amount of heat.

PRES. RICHARDS: I would like to reply to Mr. Hering's point. I think there is a great deal more difficulty made about platinum electrodes than is necessary, because of their supposed ability to absorb hydrogen or oxygen. They have not an indefinite ability to absorb an indefinite amount, and if the platinum electrodes are used until they have become saturated with oxygen and hydrogen they are practically then unalterable electrodes; they can not indefinitely absorb hydrogen and oxygen. By taking electrodes that have been used until they have freely given off hydrogen and oxygen, I take it that they are then in condition to act as unalterable electrodes. Regarding the amount of heat in the gases evolved in our calorimetric experiment, the rise of temperature was so very small—I think  $1^{\circ}$  in one minute—that it was from the rate of rise that we calculated the rate of evolution of heat; and the heat in the gases as compared with the heat in the solution was, I think, entirely negligible.

DR. CARHART: Did you correct for radiation loss?

PRES. RICHARDS: No, not for radiation; because the total rise of temperature was so small that the rate of rise was perfectly uniform. The experiment is one which needs the rate of rise of temperature to be determined, because that is proportional to the rate at which heat is being evolved in the electrolyte, and with a rise of  $0.1^{\circ}$ ,  $0.2^{\circ}$ , or  $0.3^{\circ}$  the rate of rise can be very accurately determined per minute, and the amount of heat radiated by the apparatus for a rise of  $1^{\circ}$  is practically negligible.

DR. CARHART: It is appreciable. You might have allowed for it by taking the rate of cooling.

PRES. RICHARDS: We determined the rate of cooling in another test, in which the temperature of the electrolyte was raised almost to boiling, and as the temperature sank asymptotally towards the

temperature of the room the final rate was so very slow that a correction for this in our experiment was a needless refinement, amounting to only a small fraction of 1 per cent.

MR. C. J. REED: If neither the oxygen nor the hydrogen is liberated, how do you know that the water is decomposed? How do you know it is not the other substances which are decomposed originally?

PRES RICHARDS: We have been decomposing dilute sulphuric acid and have considered the decomposition as practically the decomposition of water. We did not enter into the question as to whether it was primary or secondary.

MR. REED: I referred to your statement that if something else were present to combine with the oxygen or hydrogen so that they do not appear, you say in that case it would not take  $1\frac{1}{2}$  volts. I thought you referred to depolarizing agents, such as chromic acid, at the cathode and to a reducing agent, such as metallic lead, metallic zinc or something of that kind at the anode. In a case of that kind we have no ebullition of either oxygen or hydrogen because, as I understand your statement, there would be a combination of oxygen and hydrogen with those depolarizing and reducing agents. I ask, how do you know that there is any decomposition of the water at all in those cases? How do you know it is not simply an electrolysis of those other chemicals, the depolarizing and reducing agents, which are present. In other words, how do you know it is not an oxidation of lead or zinc at the anode and reduction of the chromic acid at the cathode?

I would like to say that it seems to me platinum electrodes are the very worst metals that could be used for any experiment of this kind. If we can imagine an experiment with electrodes which, in the beginning consist, one of zinc and the other of copper, and which, as the electrolysis proceeds, gradually change the zinc electrode into copper, and the copper electrode into zinc, so that as a final result they are both reversed,—you could not then have much worse conditions than you have in starting with two platinum electrodes (which are similar) and finally stopping your experiment when one has combined with oxygen and the other with hydrogen. The trouble with any experiment of that kind is that you have got a continuously varying electrode; and consequently it seems to me

any experiments performed in that way are of exceedingly doubtful value as settling this question of electromotive force. It is well known that platinum combines chemically with oxygen and also with hydrogen, forming chemical compounds which look exactly like the metal, but have very different chemical properties, for instance, platinum combines with electrolytic oxygen in the same proportion as that in which they combine to form platinum oxide, evolving also the same amount of heat and yet the compound has the same general appearance and most of the physical properties of metallic platinum. We know also that two such platinum plates, one charged with oxygen and the other hydrogen, will form a galvanic battery in acids and will act like a zinc plate and a peroxide plate and will give an electromotive force of over one volt.

Dr. Richards states that the so-called "residual current" is sustained by dissolved gases, agreeing with the conclusion of Dr. Bigelow.

It seems to me there is no proof of that statement in any of the experiments cited. Faraday found that with very minute currents there was no electrolysis or chemical change in any solution, unless the intensity or electromotive force exceeded a certain minimum for each solution. He found that for each substance there was a certain electromotive force, above which it would conduct the current with decomposition according to the law of electrochemical equivalents, but below which it conducted exactly like a metal, that is, without decomposition. That was one of his generalizations. In proof of this he arranged a potassium iodide cell in series with a number of other cells containing various solutions and passed a minute current through the series for several weeks. The amount of KI decomposed was proportional to the quantity of electricity transferred, but there was no decomposition in the other cells.

DR. S. L. BIGELOW: I have recently made a few experiments, using gold electrodes and the general character of the results is the same as with platinum electrodes, although the current quantity is much less, no doubt because there is less occlusion.

As to this other question, whether dissolved gases really conduct or not, it has been suggested that they act simply as depolarizers,

uniting with what is separated at the electrodes. I have carried out experiments as nearly identical as possible, excepting that in one my electrolyte was  $\frac{1}{200}$  normal sulphuric acid and in the other was normal sulphuric acid; in other words, I increased the concentration of the acid 200 times, and yet observed practically the same current strength. If the dissolved gases act merely as depolarizing agents it seems to me that such a great increase in the concentration of the ions, while the amount of dissolved gas remains about the same, should be accompanied by a marked increase in the current. This is evidence, as far as it goes, in favor of the view that dissolved gases conduct as such.

DR. W. D. BANCROFT: In the remark of Dr. Richards on Ohm's Law it would have been much better to have said those experiments showed that the ratio of the counter-electromotive force of polarization to the applied potential difference approached zero as the resistance of the solution became very large. It seems to me that that is what has been actually found and that that is another way to put it than to speak of the applicability and inapplicability of Ohm's Law.

As regards the platinum electrodes it seems to me that we can hardly speak of a platinum electrode as being a definite unalterable electrode after a little hydrogen has been set free, since Bose's measurements showed that the potential of the platinum electrode is still changing after hydrogen has been bubbled over it for two weeks. Lastly, I think the experiments are hardly accurate enough to justify us in saying that Thomson's Law holds exactly, in view of the evidence that we have against the accuracy of Thomson's Law.

PROF. C. F. BURGESS: Some results which Dr. Richards has described can be exaggerated if the process is carried on under very high pressures. I carried out, at one time, some experimental work which seems to have a bearing along this line; a steel cylinder into which one electrode was fixed by means of hard rubber was filled almost completely with a solution of sodium hydroxide, the cylinder constituting the other electrode. By passing a current through this cell, a pressure was developed which was estimated to be over 1,000 pounds per square inch. Measurements were made with an ammeter and it was found that a current could be made to flow at

a pressure considerably below one volt. I assume that the reason for this was that the high pressure of the gases caused an increase in the solubility and therefore acted as a more efficient depolarizer than under atmospheric pressure. I also obtained an effect which is similar to that which was described in connection with the enclosed thermometer tube. After a high pressure had been developed in the above apparatus, increasing the amount of current for a short time, it was found that the pressure necessary to force the current through rapidly increased to such a degree that a pressure as high as 60 or 70 volts could be applied and even then very little current would flow, as indicated by the ammeter. While not having sufficient data to explain this phenomenon, one of the suppositions which presented itself was that a layer of gas surrounded one of the electrodes and thereby insulated it, and that it was due to the high pressure that the gas layer was not destroyed. It was also noted that by shaking the cell the current would again flow for a short time and would then become interrupted. A measurement of the polarization at the time of the application of the 60 volts pressure showed that it was, as I remember it, something less than 1 volt.

MR. HERING: In that experiment it might have aided in explaining the result if Prof. Burgess had reversed the current at the time when he found he could get no more current through the cell; this would have depolarized both electrodes.

MR. H. E. HEATH: I would like to put Dr. Richards' information in a little different form. He has said that we get the decomposition of water at a voltage of less than 1.49. I do not think that he means exactly that. What he means is that we get this decomposition with an external voltage of less than 1.49, the idea being that we get a recombination or a counter-electromotive force in the solution itself, which causes an external voltage of merely the difference between the two.

MR. W. S. LANDIS: I would like to ask Mr. Burgess whether, taking a small thermometer tube such as we use (probably about an inch and a half long) there would be any appreciable advantage in shaking it if it was absolutely full of liquid. Our platinum wires very accurately fitted the bore of the tube; placing the tube under the microscope we could barely see any space between them

and the walls. By filling the end, the balsam was cooled and was drawn into the tube by capillary action, leaving practically no space we could see under the microscope. Would there be any appreciable effect in shaking that tube, considering the fact that the space was entirely filled with electrolyte?

MR. REED: I could not repeat that experiment with a closed tube because I was unable to get the tube sealed up that way. I found great difficulty, after getting in the wires and getting it full of acid, in getting any balsam or any other kind of cement that would actually fill the remaining space and keep it perfectly dry on the end so that I could be sure there was no leakage. I would ask Dr. Richards how he was sure there was no leakage and how he constructed that apparatus. I should like to be able to repeat that experiment, but confess that I was unable to do it.

MR. A. H. COWLES: Did you make an observation immediately at the beginning of the experiment, to note if there was not at first an impulse or flow of current followed by a falling off of the same, for there might have been a current for a few moments which fell off, and after that the leakage might not have been found?

MR. LANDIS: The instrument we used for measuring these small currents was a millivolt meter, reading, I believe, to about three-hundredths of a millivolt, with a resistance of 139 ohms, and in series with our cell. That would allow us to read two- or three-tenths of a micro-ampere. There was no appreciable motion of the needle in that instance. Of course, with a much finer galvanometer, reading more sensitively the current may have been of some appreciable value, but with our instrument there was no current shown.

PRES. RICHARDS: Mr. Landis is my assistant, who has made the experiments with me. The instrument we used would show at the closest reading a fraction of a micro-ampere—nearly, you can say, one-tenth of a micro-ampere at its highest delicacy; there was no appreciable motion of the needle at the beginning.

Replying to Mr. Reed, the tube was part of a very delicate thermometer that has been broken, and with a very fine bore and thick walls—which we selected, as I explained, in order that it would not be possible to break it. The tube was filled with electrolyte from one end to the other, the wires were inserted to within one

millimeter of each other, and then, the wires being bent over so as to be out of the way, liquid Canada balsam was dropped on the end of the tube and allowed to set. There was no empty space between the liquid and the balsam when the tube was sealed; under those conditions no current passed when over 3 volts was placed on it. On breaking the seal the current immediately passed.

MR. REED: How did you ascertain that there was none of the acid on the end of the tube under the balsam? You could not prevent the capillary attraction from causing the acid to follow the wire and thus get out over the end of the tube. I found it was impossible to get a seal that could be relied on as being perfect. Of course you might easily have it sealed so that you could not see any defect with the naked eye. I could not satisfy myself that there was no defect. I would also ask how you held the balsam against this enormous pressure which you subjected it to. How, in other words, did you know that there was not an expansion there that forced the balsam out a little at the end so as to relieve the pressure.

PRES. RICHARDS: I did not know many of those things. We observed no liquid oozing out at the end of the tube.

MR. REED: You would not expect to observe it from the amount of gas which would be formed by the minute current that you could not measure during the first instant.

PRES. RICHARDS: We observed no gases set free on the electrodes and we were able to get no current through. If there had been leakage we would have got the current through as we did every time that our tube leaked, which happened with some of the thermometer bulbs. Every time that the places, where it was closed, leaked we had no difficulty in getting the residual current through.

MR. REED: What test did you apply to see whether the tube leaked before you applied the current? Or was the current the test—the fact that you got current through, or did not? If that is so, then you are taking the thing proved as the proof.

PRES. RICHARDS: We used a piece of blue litmus paper and a hand lens, and carefully touched the end of the tube to see if there was any sign of acid. With capillary tubes that we had sealed we found considerable difficulty in getting a tight seal. Only one tube remained tight after the attempt to pass the current through it.

MR. COWLES: My question was directed to the point that at high pressure, say a thousand atmospheres, the quantity of gases a solvent will absorb should be a thousandfold greater than would be the case at one atmosphere pressure, and therefore there would be quite a little period, while the gases were being evolved and while they were going into solution, during and following which the pressure would be building up, and it seems to me that, during that period, or at the beginning of it at least, you ought to be able to get some observable reading from your milli-ampere meter indicating a current flow. After the pressure has built up it may act as a factor, reinforcing chemical affinity, and thus cause the stability of the water molecules to become so great that the electric force that is trying to break them down may not be sufficient, thus causing a stoppage of the process of electrolysis, and consequently of the flow of current. During the time that the pressure is raising in the tube, it seems to me that you ought to be able to note the beginning of the flow of a current, and then see it stop.

MR. LANDIS: In one experiment we used the drawn-out glass tube shown in the upper part of Fig. 1. of our drawings. It had a bulb at one end into which the two very fine platinum wires were sealed, and was drawn out to a capillary tube (possibly the size of the bore of the thermometer) and filled with liquid and sealed. Of course in sealing this end it left a small space, practically a vacuum. To fill that up all we had to do was simply to heat the tube, which expanded the liquid in the tube and filled it up completely to the top. It was placed on a 110-volt circuit. It is the only one all of glass that we sealed up successfully. The wires were probably 2 millimeters apart, very fine, and I suppose had a resistance of practically 10 ohms. There was also in series a 220-ohm lamp. Placed in a 110-volt circuit the tube broke; but the instrument, as I remember it, registered about 7 millivolts (equivalent to about 50 micro-amperes) and rapidly fell off until the tube broke—the whole thing exploded in twenty seconds after the current was put on and the glass was literally pulverized.

MR. REED: This shows, does it not, that the statement of Mr. Cowles was correct?

MR. LANDIS: There is a certain current going through the tube.



That is not an exactly similar bulb to the other one on account of the bore not being capillary, and the walls being somewhat elastic, whereas the other tube, I should say, did not permit of any great amount of elasticity.

MR. COWLES: I think it must be true that there were gases evolved at the beginning of the experiment at the two poles. It would take some little time for the full pressure to develop itself to its maximum amount throughout the thermometer bore. The act of diffusion of gases through a liquid is a slow process, and it may be that the time necessary for diffusion would be a factor that should be considered.

MR. REED: There are some statements and facts that I am unable to reconcile. In one experiment it is shown that current does pass at the initial stage. In the experiment of Prof. Burgess it is shown that after the pressure has been increased the current will still pass and at a lower voltage. The experiment which Mr. Hering and myself performed some years ago, and which Mr. Hering described at the last meeting, showed that as the pressure increased the voltage required to decompose water diminished. Now, according to these experiments, current will pass during the first instant and then cease, as the pressure rises. But, according to the experiments of Prof. Burgess, and those of Mr. Hering and myself, an increase in the pressure causes the current to flow at a lower electromotive force. I am not able to reconcile these results.

MR. COWLES: In your experiment you had a large volume of water and electrodes rather close, and I think there was a more ample chance for diffusion.

MR. REED: They were not as close together as in this case.

MR. COWLES: You had the ends of the two wires rather close together in the thermometer tube. You had a very small cross-section for the lateral diffusion of the gases evolved.

MR. REED: Our wires were farther apart than in this case. They were several millimeters apart in our experiment.

MR. HERING: At least 1 millimeter.

MR. REED: At least 1 millimeter, and the volume of liquid experimented on was very small, possibly not greater than in the case of the bulb in this case.

MR. COWLES: Was it greater than in the case of the narrow bore of the thermometer tube that Mr. Richards required?

PRES. RICHARDS: I think that the elasticity of the containing vessel explains the small current passing at first, since in the case of this thermometer bulb which Mr. Landis has spoken of there is a certain amount of elasticity of the walls which will allow of some expansion. In the small-bore thermometer tube with which we experimented, the expansion due to elasticity is, I think, negligible. With walls of the tube 2 millimeters thick and the bore only 0.25 millimeter, I think elasticity of the tube and the possibility of breaking it may be left out of consideration, whereas with the bulb the walls of the tube were certainly elastic, and after twenty seconds the elastic limit was passed and the tube was shattered.

MR. P. G. SALOM: What electromotive force was put on that?

PRES. RICHARDS: 110 volts.

MR. SALOM: Did you try lower voltages first?

MR. LANDIS: We tried the high one first to see if it was tight.

MR. HERING: It seems to me that Prof. Burgess' experiment in which he got no further current explains the experiment described by Prof. Richards, who also obtained no current. In Prof. Richards' experiment the amount of liquid was so small that the conditions of very great pressure was probably produced instantly, before he could even take a reading of his instrument.

MR. MOTT: I would like to ask Prof. Richards as to his conclusions concerning Ohm's Law. If a 0.2 per cent. sulphuric acid solution had been used instead of a 0.1 per cent. sulphuric acid solution would the conductivity have been doubled? In other words, does the sulphuric acid or the dissolved gases do the conducting?

PRES. RICHARDS: That was one of the experiments we might have tried. We filled our long tube ( $8\frac{3}{4}$  meters long) with a 10 per cent. solution of sulphuric acid for our next experiment and found that the current was not proportional to Ohm's Law. We made no intermediate experiment. I would like very much to make others, and hope, as soon as we have opportunity, to repeat some of those experiments with a strong acid and also very great resistance, to see if we do get current in that case proportional to Ohm's

Law, when the gases present in the solution are able to take care of all the current which flows.

PRES. RICHARDS (Communicated) : Mr. Landis and I have since tried Mr. Mott's suggestion of using differing strengths of dilute acid in our long tube, and find our first conclusion confirmed. The feeble currents flowing through these great resistances are proportional to the strength of the acid, and, in any one case, to the voltage applied. This has been found to be the case with our long tube for acids from 0.2 per cent. to 0.01 per cent. and for voltages from 0.1 to 110.

We feel more persuaded than ever that when the current which can flow through the electrolyte by Ohm's Law ( $C = \frac{V}{R}$ ) is *smaller* than the gases in solution can simultaneously take care of by depolarization, that then  $C = \frac{V}{R}$  is the law applying to the passage of electric current through the electrolyte. When, however, the voltage is so high or the resistance so low that  $C$  calculated as  $\frac{V}{R}$  is too large to be thus taken care of by depolarization, then the capability of the dissolved gases to get to the electrodes and perform the depolarization sets a limit upon the amount of current which can pass without expending the energy of decomposition. When this point is reached decomposition in its true sense begins, that is, some of the energy of the current begins to be applied to decomposing the electrolyte without simultaneous recombination or depolarization at the electrodes.

To make this clear, let  $C'$  be a current passing at voltage  $V'$  (the Ohmic resistance being  $R$ ), and assume that  $C'$  is smaller than should flow by the law  $C' = \frac{V'}{R}$ . This is the case where, according to our view of the matter, the current is limited below  $\frac{V'}{R}$  because the dissolved gases are not able to perform perfect depolarization. In this case the total energy of the current is  $E = C'V'$ . Of this, an amount equal to  $C'^2R$  is necessarily absorbed in overcoming Ohmic resistance, leaving  $C'V' - C'^2R$  excess energy to be accounted for. This excess energy is applied to *ultimate decom-*

*position* of the electrolyte, and will *liberate* oxygen and hydrogen at the electrodes in amount corresponding to  $C'' = \frac{C'V' - C'^2R}{1.5}$ , so that Thomson's rule is satisfied, as well as Faraday's.

When  $C''$  is small the liberated gases may all go into solution, and thus reciprocally increase the amount of depolarization possible. When  $C''$  is so large that the liberated gases cannot all get into solution they will become visible. *This* may occur at applied voltages much below 1.5 or may not occur until 100 volts are applied, according to the size of the electrodes, distance apart, resistance of electrolyte, nature of the electrolyte and its temperature.

LEHIGH UNIVERSITY,  
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