

On the Polarization of Electrodes in Water free from Air

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II. *On the Polarization of Electrodes in Water free from Air.*

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In the 'Electrical News' for September 2, 1875, I published a short paper, previously read at the Meeting of the British Association at Bristol, entitled "The Decomposition of an Electrolyte by Magneto-electric Induction." In it experiments were described showing that when an electrolyte (viz. dilute sulphuric acid) flows in a very strong magnetic field, the electromotive force generated by its motion effects the electrolysis of the liquid, such electrolysis being held to be proved by the subsequent polarization of the electrodes. No actual liberation of gases was observed, since the electromotive force brought into play was insufficient to effect free decomposition. At the time it was read Professor H. A. Rowland raised certain doubts as to the correctness of the conclusions drawn; and his remarks were published, appended to my paper, in the 'Electrical News.' As these objections would, if correct, have deprived the experiments entirely of any little interest they might otherwise have had attaching to them, it was obviously necessary to examine them carefully.

Professor Rowland's remarks amounted practically to saying that he thought the electrolyte was not really decomposed, but that the polarization observed was in some way or other due to the presence of dissolved air, and that in air-free liquid the effect would not have been observed, at any rate with the electromotive force (about $\frac{1}{800}$ of a Daniell's cell) which came into play.

To meet these doubts two very definite questions have to be examined.

(i) In air-free water, can platinum electrodes be polarized by very small electromotive forces to the same degree and with the same facility as in ordinary aerated water?

(ii) Is this very feeble polarization really a decomposition of the electrolyte?

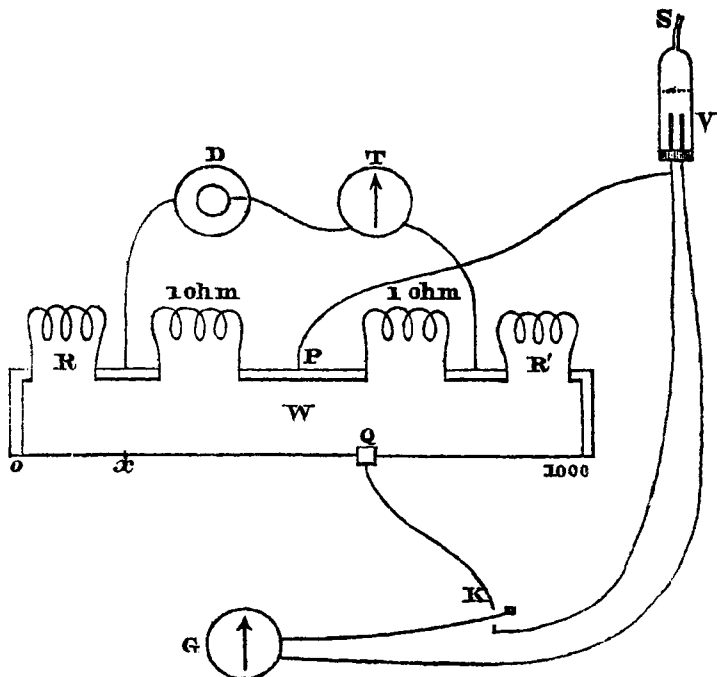
If the following facts are held to give an affirmative answer to both the above questions, the objections raised are invalid and may be dismissed.

To test the first point, it was necessary to compare the effect of a small known electromotive force acting through platinum electrodes, first in air free, next in aerated acidulated water, under identical conditions. In the former experiments the electromotive force was generated *in* the liquid by its motion ; for my present purpose it was sufficient to act on it by an *external* electromotive force of measurable amount, since it is obvious the results hold good no matter how it is produced. The arrangement consisted of the following parts.

The decomposing cell or voltameter was a glass tube 30 centims. long, $2\frac{1}{4}$ centims. wide, stopped at one end by an india-rubber stopper, through which passed two platinum wires having welded to them on the interior platinum plates 8 centims. long, 2 centims. wide, placed so as to lie against the walls of the tube. The other end of the tube was connected by a narrow tube with the Sprengel pump. The platinum plates having been rendered chemically clean, the tube was three parts filled with dilute sulphuric acid, which had been previously boiled for six hours so as to expel some of the dissolved air. A vacuum was then made in the voltameter ; and the apparatus remained untouched for five days, the pumping being carried on at intervals and continued during the experiments.

To obtain a small electromotive force a well-known method was made use of. A Wheatstone's bridge had its branches filled up with previously measured resistances, and the other connexions made as in the figure (p. 17). Between the points P and Q any small difference of potentials can be produced whose value is known when the distance x Q of the block from the point of equilibrium x is known. The galvanometer employed was a very sensitive mirror-galvanometer, with short needle and a long suspending fibre. The image of a fine wire across the slit was reflected on to a scale in the usual way, and the image viewed through a telescope placed behind the galvanometer. By this means it was found possible to detect and read deflections of the needle amounting only to $\frac{1}{16}$ of a degree with great ease. With this delicate arrangement it was a matter of great difficulty to get the platinum plates perfectly neutral. The last traces of polarization from previous experi-

ments subsided with extreme slowness. The following operations were then performed :—



- W. Wheatstone's bridge.
 D. Daniell's cell.
 T. Tangent-galvanometer.
 V. Voltmeter.
 G. Mirror-galvanoscope.
 K. Key.
 S. Tube to Sprengel pump.

- (i) The electrodes were made perfectly neutral.
- (ii) The galvanometer excluded from the circuit, and a direct current sent through the decomposing-cell for one minute.
- (iii) The polarization measured by the swing made by the galvanometer-needle when the electrodes were suddenly connected with it.
- (iv) The swing or excursion made by the needle when the same direct current was started through the cell and galvanometer in one circuit, previously bringing the platinum plates to a neutral condition.

The first column in the subjoined Table gives the bridge-reading, the second the electromotive force which this is equivalent to in absolute units (C. G. S.), the third the swing of the needle with the direct current (charging), fourth the same with the polarization current (discharge).

TABLE I.—Polarization in Acidulated Water free from Air and kept *in vacuo*.

Bridge-reading.	Electromotive force.	Excursion of needle in degrees or fractions.	
		Direct current.	Polarization ⁿ current.
275	12110	0	0
280	18165	$\frac{1}{2}$ barely.	$\frac{1}{2}$ nearly.
285	24220	full.	full.
290	30275	nearly.	nearly.
300	42385	1	1
310	54495	$1\frac{1}{2}$	$1\frac{1}{2}$
320	66605	2	nearly.
330	78715	$2\frac{1}{2}$	$2\frac{1}{2}$
340	90825
350	102935	3	3
400	115045	5	1
450	224035	7	$1\frac{3}{4}$
500	284585	10	$2\frac{1}{2}$

Since a Daniell's cell is about 100,000,000 units in electromotive force, the above Table shows that, with the galvanometer employed, the least electromotive force which, acting for one minute under these circumstances on platinum plates of 16.39 centims. surface, would leave a detectable polarization, was about $\frac{1}{8000}$ of a Daniell's cell.

The observations having been repeated several times with the same results, the dilute acid was then removed, and thoroughly aerated by shaking it up with air under pressure, and by bubbling air through it for some time. This aerated water was then returned to the voltameter, all other arrangements remaining the same, and the same observations repeated in this case as in the last. The results are appended.

TABLE II.—Polarization in Acidulated Water thoroughly well aerated.

Bridge-reading.	Electromotive force.	Excursion of needle in degrees or fractions.	
		Direct current.	Polarization current.
275	12110	0	0
280	18165	$\frac{1}{2}$ barely.	$\frac{1}{2}$ barely.
285	24220	$\frac{1}{2}$	$\frac{1}{2}$ barely.
290	30275	$\frac{1}{2}$	$\frac{1}{2}$
300	42385	$1\frac{1}{2}$	$1\frac{1}{2}$ barely.
310	54495	$1\frac{1}{2}$	$1\frac{1}{2}$
320	66605	2 barely.	$2\frac{1}{2}$ barely.
330	78715	2	$2\frac{1}{2}$
340	90825
350	102935	3	$3\frac{1}{2}$
400	115045	5	1
450	224035	7	$1\frac{1}{2}$
500	284585	10	$2\frac{1}{2}$

An examination of these two Tables shows that there is very little difference between them which cannot properly be ascribed to errors in observation. There is *no* difference in the minimum electromotive force which could give in each case a visible polarization with the galvanometer employed. But now there was one very striking difference between the two sets of experiments, not shown in the Tables, viz. the time required after each experiment for the polarization to subside. In the case of the aerated water, the polarization disappears *very much* more quickly when the plates are short, circuited than in the case of the air-free water. With this latter it was most troublesome to get rid of the last traces, even with the smallest polarizing currents. This has been previously noticed and explained by Helmholtz*. It is, however, a point not involved in our present considerations.

A consideration of these observations leads apparently to the conclusion that the presence of air in the water has no effect in creating or assisting the polarization of the electrodes under a

* Phil. Mag. [IV.] vol. xlvii. p. 152, Dr. Helmholtz "On Galvanic Polarization in Liquids free from Gas."

feeble electromotive force (it is difficult to see any reason why it should), although it has a great effect in removing it when once formed. The process called by Helmholtz *electrolytic convection*, and in which dissolved air is essential, is the consequence and not the cause of polarization.

It is not true that it requires any definite electromotive force to begin to polarize electrodes in air-free water; any electromotive force, however small, will do it. Its detection is only a question of a sufficiently delicate galvanometer; and we may therefore say that any electromotive force, however feeble, acting on platinum electrodes, builds up a corresponding amount of polarization equally in air-free as in aerated water. But no liberation of free gas is possible under these circumstances, until the external electromotive force just exceeds the counter-electromotive force of the electrodes when polarized to their fullest extent.

With regard to the second question, whether polarization, however small, means literal chemical decomposition, I am not aware that it has ever been called into question. There is abundant evidence to show that it is not a mere physical state of the chemically unaltered electrolyte, but that there is *something* deposited on the electrodes which can only be the products, primary or secondary, of electrolysis. Although a voltameter charged by a weak electromotive force resembles very closely a condenser, yet there is something very different between the state of strain or electrical displacement in a condenser's dielectric and the electrolyte after having had a current passed through it.

That even very feeble polarization does really in every case consist in the deposition of products of an unseen electrolysis in or on the electrodes receives support, in addition to many other facts, from the following:—Platinum plates were placed in the inside of a vertical glass tube, and made to communicate with the outside by wires sealed through the glass. The tube was so arranged that dilute acid could be made to flow down through the tube from a reservoir, without the plates being ever exposed to air. The tube being full of acid, the platinum plates were now polarized feebly. If the acid was allowed to flow out *slowly*, so as to gradually replace the liquid which was between the plates when polarized by other fresh acid, the

plates gave, on discharge, a nearly equal current to that which they would have given if no replacement had been made ; but if the liquid was made to rush down *violently* and then stopped, little or no polarization was found, provided the plates had been only slightly polarized. If the plates were defended by strips of cloth laid over them, no such removal was effected by the liquid rushing down. This all seems to indicate that there is something on the plates which can be *wiped off* mechanically. This can only be the products of electrolysis. This experiment has no analogy in a condenser. These and many other facts seem to point out that polarization is in all cases only unseen electrolysis.

In conclusion I cannot but think that the objections raised to the former experiments were groundless, and that, when it is found that a stream of acidulated water flowing down between the poles of a magnet polarizes platinum plates placed in it, we are entitled to call it chemical decomposition, since it would only be necessary to exalt the magnet's power and increase the velocity of flow in order to see, under certain precautions, the liberated gases streaming from the plates.

III. *On a new Form of Wave-apparatus suitable for the Lecture-room.* By C. J. WOODWARD, B.Sc.*

The apparatus about to be described illustrates the motion of the air-particles when a sound-wave is propagated, and also the motion of the æther molecules in a wave of plane-polarized light.

Wave motion consists in the repetition by a number of particles of some prescribed motion which is given to the first of the particles and taken up successively by the others, a certain interval elapsing between the successive motions. If, for example, we have a number of pendulums of equal length hanging from a beam, but their lower ends supported so that they are out of the vertical, we shall find on releasing one of them, say the left-hand end one, it will commence swinging to and fro ; by the time the first pendulum has gone over one fourth of its path release the second, and then after equal intervals