

VII. *Polarization of Metallic Surfaces in Aqueous Solutions. On a new Method of obtaining Electricity from Mechanical Force, and certain relations between Electrostatic Induction and the Decomposition of Water.* By CROMWELL FLEETWOOD VARLEY. Communicated by Sir W. THOMSON, F.R.S.

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IN 1860, having need of condensers of enormous capacity, the author found that platinum plates immersed in a solution of sulphuric acid and water had enormous capacity, and could, under certain conditions, be used as condensers with potentials below that necessary for decomposing water.

When one of the platinum plates was replaced by mercury, and a powerful battery was applied so as to make the mercury negative, the latter flattened out and increased its surface.

When a pasty amalgam was employed of the proper consistency on a flat surface, this flattening out was sometimes increased to more than double the original surface. The reversion of the current immediately brought the amalgam to its original dimensions.

This experiment suggested a means of obtaining dynamic electricity by reversing this process.

Plate II. fig. 1 represents a large glass vessel (A) cemented into a groove in the board B. The funnel-shaped glasses C and D, which are inside A, are connected with E and F outside of A. Under the board B is fixed a transverse bar of wood, so that the whole can be rocked from side to side. When tilted to the right the mercury in C runs into E, while that in F runs into D. The reverse operation takes place when the board is tilted to the left; consequently when the surface of mercury in C is diminished, that in D is augmented, and *vice versa*. The galvanometer G connects the two by the spiral wires W.

The glass vessel (A) is filled half full with diluted sulphuric acid. If the two poles of a voltaic battery be immersed in A, the positive pole in connexion with the acid and water, the negative in connexion with the mercury in C, the latter becomes polarized with “nascent hydrogen.”

The mercurial surface in C will retain its polarity for a long time after the removal of the polarizing-battery.

If the two cups E F be now connected by the galvanometer G, a current of electricity will be seen to flow between them, the polarization will be equally shared by the two mercurial surfaces, and then the current will cease. If, now, the board be rocked from right to left, and *vice versa*, the mercury surface in the one vessel will diminish, while

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that in the other increases. During this change of surface-dimensions currents of electricity will be found to pass from one to the other, the diminishing surface acting as the zinc plate, and the increasing surface as the copper plate of a voltaic couple.

All attempts to polarize the mercury with oxygen have entirely failed. This experiment enables one to obtain a mercurial surface neutral to the fluid in which it is placed, *i. e.* free from polarization, or very nearly so indeed.

All the specimens of mercury which were tested showed traces of this hydrogen polarization, but they can be almost absolutely depolarized (if the mercury be pure) by connecting it with the positive pole of a very feeble battery through a large resistance, and the aqueous solution with the negative pole, until the rocking to and fro of the vessel ceases to generate a current, or shows hardly any trace of one. The mercury-surfaces are then neutral, or very nearly so, to the fluid; if, however, they have been previously charged highly with hydrogen, this depolarizing process must be repeated over and over again until, after resting, the mercury is found not to yield a current by rocking. This "neutral" surface is likely to be of use in investigating the source of force in batteries.

The following arrangements will be found to give a continuous electric current. The three vessels A, B, and C are arranged as shown in figure 2 (Plate II). The vessel A receives mercury which issues from the jet J into the acid and water in the middle vessel B. The mercury at the bottom of B runs through a siphon into the vessel C. The mercury in A and B is connected through a galvanometer (G) by means of platinum wires.

If the mercury be pure and not polarized, the running of the mercury from A into B gives rise to no current. If, now, the larger surface of mercury in B be polarized as before, it will share its polarization with each drop of mercury that falls from J, and thus produce a current from A through the galvanometer to B; each drop as fast as it is polarized falls by gravitation into B, and so gives back the polarization it had received. By carrying the mercury from C back to A, this current is continued for a very long time.

The following method (fig. 4) is a convenient one for showing the experiment on a larger scale; and on this principle, several years ago, the author constructed an apparatus of twelve cells (which has never been published), which was worked by clock-work and gave a current of a potential rather greater than one cell of a DANIELL'S battery.

When clean platinum plates are polarized with hydrogen, and dipped into polarized mercury, they instantly amalgamate all over.

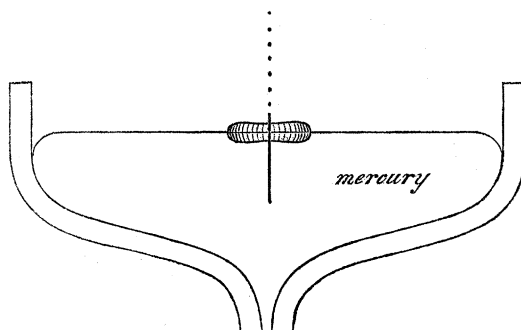
If a gutta-percha trough of the form shown in fig. 3 in section be constructed, so as to contain two separate cells of mercury covered and united together by the supernatant aqueous solution, and a bunch of platinum plates be inserted in each parcel of mercury and amalgamated, the mercurial surface exposed to the fluid will be augmented when the amalgamated plates are partially withdrawn from the mercury, and will diminish when they are inserted again; in this way, in a small space, a large extent of mercurial surface is easily obtained. If the platinum plates be well polarized, it will be found that, on raising those in the one cell and simultaneously immersing those in the other,

a current of considerable volume will flow from one to the other cell through the galvanometer. If a grain of zinc be added to the mercury this effect will be very persistent, and is more powerful, the zinc maintaining the polarization. Only one platinum plate in each vessel is shown in fig. 3.

When the funnel-shaped vessel C in fig. 1 was 5 inches in diameter, and the tube connecting it with E the  $\frac{1}{30}$  of an inch in diameter, and the galvanometer connexion between E and F was severed, it was found, after having polarized the mercury surface C by the power of rather less than one DANIELL'S cell (a power too small to evolve hydrogen gas), that on tilting the vessel so as to let the mercury run from C to E, a few small bubbles of hydrogen gas were given off just as the last drop of mercury ran out of C; *thus the contraction of the surface concentrated the polarization* until it had power enough to evolve the hydrogen as gas. The other funnel might have been removed, the surface D having no influence on the result.

This evolution of gas is better shown by floating a minute piece of fine platinum wire on the mercury, which gives off the gas as the surface of mercury becomes reduced.

In this experiment the piece of platinum wire was about 0.002 inch in diameter and 0.5 in length. It was floated on the mercury by a small lump of shellac, thus:



The exposed portion of the wire was as short as possible. The contracting polarized mercurial surface acted like zinc to the platinum, which evolved hydrogen as it would have done when in contact with a piece of zinc.

The author had many times endeavoured to ascertain the electrostatic capacity of metallic surfaces exposed to an aqueous solution, but has only recently, and by the following means, been able to get sufficiently reliable results.

A reflecting galvanometer was constructed with copper wire, No. 18 gauge, and having 20 Ohms resistance; this was again reduced by a shunt to 4 Ohms; the mirror and magnet are hung in water to destroy the oscillations rapidly.

Two sets of platinum surfaces were used:—1st. Two platinum spheres about  $\frac{3}{4}$  of an inch in diameter, and having each about 1.6 square inch of surface exposed to the acid and water, the two bulbs being placed in a glass of diluted sulphuric acid and water. 2nd. To reduce the resistance as much as possible two platinum plates, each of 1 square inch surface, were coated on one side with bees'-wax and paraffin, so as to leave only the one surface exposed to the fluid; these two plates were made to face each other at a very

short distance by placing one on each side of a double thickness of blotting-paper, and immersing the whole in diluted sulphuric acid, one volume of pure acid to four volumes of distilled water. By these means the resistance of the *fluid* between the plates was reduced to about  $\frac{1}{25}$  part of an "Ohm," according to *calculation* from BECQUEREL'S data. These plates were connected as shown in fig. 4 (Plate II.).

The current from two cells of DANIELL'S battery was made to pass through the adjustable resistance-coils R and R'. The united resistance of these coils, when the platinum bulbs were used, was made 1000 Ohms; when the platinum plates were used, it was made 100 Ohms.

The two cells of DANIELL'S battery had a resistance of about 12 Ohms, and by experiment their potential was found to be reduced from 344 to 317, or 8 per cent., by the resistance-coils R + R' connecting the poles of the battery when R + R' = 100 Ohms, and therefore the potential of them was reduced to about two volts.

By varying the resistance in R and R', it is easy to get any desired subdivisions of the potential of the two volts, as Sir WILLIAM THOMSON and Sir C. WHEATSTONE have shown.

The apparatus was sufficiently rapid and sensitive to read the discharge from the platinum bulbs and from condensers of 311 microfarads capacity for comparison therewith, when they were charged with a potential not greater than 0.02 volt.

Table II. shows the discharge from the platinum plates when charged by potentials varying from 0.2 of a volt up to 1.6 volt, also the discharge obtained from the condensers of 311 microfarads capacity for comparison therewith.

During each of the experiments in Table I. the sensitiveness of the galvanometer was maintained constant, and the results are directly comparable with those obtained from the condensers; the same is the case in Table II.; but Table I. is not comparable with Table II., excepting by means of the last column. They were made at different dates, when the sensitiveness of the galvanometer was not the same. Thus it will be seen by reference to column 6 that, while the electrostatic capacity of the ordinary condensers remains constant (*i. e.* the discharge varies directly as the "potential"), with the fluid plates this regularity is only observed while the charge is very low, not more than 0.08 volt (see Table I.). As the potential increases from  $\frac{1}{10}$  of a volt upwards, the discharge from the platinum plates increases in a greater ratio, as will be seen by column 6, which shows the deflection of the galvanometer divided by the "potential" to give the ratio; and it will be seen in Table I. that with potentials from .02 to .08 the capacity was 1 as against 3.5 with a potential of about 1.6.

An inference which the author thinks these experiments suggest is, that the water does not actually touch the platinum surface, and as the potential increases the water is attracted nearer to the electrified plate, thereby augmenting its electrostatic capacity as the distance between the platinum and the water is diminished by the electric attraction.

When, however, the repulsion between the platinum plate and the water is overcome by the electric attraction, then conduction of the current would seem to take place,

accompanied by decomposition of the water. If there be such a film between the water and platinum, the following considerations will enable us to get an idea of its depth. The electrostatic capacity of a layer of pure gas is sensibly the same as that of a vacuum. Gutta percha has a capacity of between three and four times this amount.

If we assume that the film between the platinum and the water is a pure gas, the comparison of the capacity of the 1 inch of platinum in water with the surface of air necessary to produce at a distance of 1 inch a similar capacity will give an idea of the thickness, or rather the extreme thinness, of this hypothetical film separating the water from the platinum.

The capacity of the French Atlantic Telegraph-Cable, Brest to St. Pierre, is 0.4 microfarads per nautical mile; each nautical mile has 400 lbs. of gutta percha, specific gravity 0.98, and 400 lbs. of seven-strand conductor filled with gutta-percha compound, giving it a specific gravity of about 8.8.

Calculating from this how large a sheet of gutta percha, 1 inch in thickness, and coated on each side with metal, is necessary to give an inductive capacity of one microfarad, we shall find that a sheet built up out of 1,040,000 cubic inches of gutta percha will have the capacity sought.

The condensers used for comparison with the two sheets of platinum, offering each 1 square inch of surface, had a capacity of 311 microfarads—that is to say, they were equal to a sheet of gutta percha 1 inch in thickness, and having a surface of 323 millions of square inches; and as gutta percha has about  $3\frac{1}{2}$  times the capacity of pure gas, 1131 million square inches of metal separated from another such surface by 1 inch of pure gas would about give the capacity sought, viz. 311 microfarads.

At the commencement of the experiment with the platinum plates in fluid, when the potential was very small, the capacity was about 175 microfarads per square inch of (double) platinum surface; and as a sheet of air one inch thick and having a surface of  $1,040,000 \times 3\frac{1}{2} = 3,640,000$  square inches has a capacity of 1 microfarad,  $3,640,000 \times 175 = 637,000,000$  square inches will have the same capacity as the two platinum plates 1 inch square.

If the two hypothetical films have the same thickness on each platinum plate, the film on each will, if a pure gas, be  $\frac{1}{1274,000,000}$  of an inch, with small potentials, and decrease to  $\frac{2}{7}$  of this amount with a potential of 1.6 volt.

A useful inference can be drawn from these experiments by the telegraph engineer.

It has been repeatedly proposed to telegraph by means of a naked wire laid in the Ocean.

The speed of a long telegraph-cable varies inversely as the square of its length for similar sectional dimensions.

If L be its length, I its inductive capacity, R its resistance, and A a constant, its speed will be  $\frac{A}{L^2} \times \frac{1}{I \times R}$ .

Thus, then, if the product of  $I \times R$  remain constant, their ratio to one another may vary without varying the speed of the cable.

The French Atlantic conductor consists of 400 lbs. to the nautical mile, and if made into a *solid* wire would in a length of 8.1 inches have the surface of  $3\frac{1}{3}$  square inches.

The cable in round numbers is 2500 nautical miles long, and this length has a capacity of 1000 microfarads, the same as  $3\frac{1}{3}$  square inches of platinum surface in water at a potential of .6 or .7 volt.

$I = 3\frac{1}{2}$  inches,  $R = 2500$  miles; by varying these until  $I = R$  in length (their product remaining constant), we get the length in round numbers of rather less than 1100 yards (or, say, half a mile) as that at which the bare wire if coated with platinum would equal in speed the cable now working from France to St. Pierre, the longest cable in the world.

As the surface of the wire increases with its diameter, and its conducting-power with the square of the diameter, the speed of transmission through a bare wire varies only as its diameter and not as its mass; therefore a bare solid conductor capable of working ten words a minute through 2500 miles of ocean must be more than 250,000 feet in diameter to have the same speed as the present French Atlantic Cable.

This mode of telegraphing is only practically available within distances of less than a mile, and this explains why Lord DUDLEY'S uninsulated cable between Dover and Calais would not work. The distance being 20 miles ( $40 \times \frac{1}{2}$  miles) and the conductor about half the diameter of the French Atlantic (which gives on an average ten words a minute in actual practice), the speed would be  $\frac{10}{(40)^2} \times \frac{1}{2} = 1$  word of five letters in 320 minutes = 1 letter of three signals in 53 minutes = 1 simple signal in 18 minutes.

The measures in the Tables of the capacity of the platinum surfaces in the water are only approximately true.

There is considerable difficulty in these experiments, owing to the discharge not being sensibly instantaneous, and the absorption being very large.

The general truth that the capacity increases when the potential increases is, however, beyond all manner of doubt established.

This is the very reverse of what was expected by the author when he commenced the investigation.

TABLE I.

Two platinum bulbs about 0.75 inch in diameter in diluted sulphuric acid.

Owing to the large resistance (1000 Ohms) used in R and R' the actual potential is uncertain in this experiment, because the conduction across the fluid reduces it.

1. Potential in terms of a cell of Daniell's battery.	2. Duration of electrification in seconds.	3. Swing of reflecting galvano- meter by the discharge of the bulbs on raising the key.				4. Current after magnet came to rest.	5. Mean <i>minus</i> the remaining current.	6. Mean divided by potential and 100 to give relative capacity for various potentials.	7. Approximate capacity in microfarads.
0.02	10	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$\frac{1}{2}$ }	2	1	348
"	20	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	" }			
0.04	10	$4\frac{1}{2}$	$4\frac{1}{2}$	$4\frac{1}{2}$	$4\frac{1}{2}$	" }	4	1	"
0.06	10	$6\frac{1}{2}$	$6\frac{1}{2}$	$6\frac{1}{2}$	$6\frac{1}{2}$	" }	6	1	"
0.1	10	$11\frac{1}{2}$	$11\frac{1}{2}$	$11\frac{1}{2}$		1 }	$10\frac{1}{2}$	1.05	365
"	20	11	12	$11\frac{1}{2}$		" }			
0.16	10	18	$17\frac{1}{2}$	18		$1\frac{1}{4}$ }	$16\frac{3}{4}$	1.09	379
"	20	18	18	18		" }			
0.2	10	24	24	24		$1\frac{3}{4}$ }			
"	20	24	24	24		$1\frac{1}{2}$ }	$22\frac{1}{2}$	1.12	390
"	30	24	24	24		" }			
0.4	10	59	58	58		$2\frac{1}{4}$ }			
"	20	58	57	58		$2\frac{1}{2}$ }	$55\frac{1}{2}$	1.39	484
"	30	58	58	57		" }			
0.6	10	105	$105\frac{1}{2}$	104		" }			
"	20	105	104	105		" }	$104\frac{1}{2}$	1.74	606
"	30	104	105	103		" }			
0.8	10	164	163	162	162	3 }			
"	20	162	162	161		" }	159	1.99	693
"	30	162	162	161		" }			
1.0	10	230	235	230	230	5 }			
"	20	232	231	230	231	" }	226	2.26	786
"	30	231	231			" }			
1.2*	30	318	320	314		14 }	303	2.53	880
1.4*	30	440	446	451		23 }	426	3.04	1057
1.6* }	30	about 603 .....				30 }	562	3.5	1218
						41 }			
						52 }			

TABLE I. (continued).

Condensers of 311 microfarads.

Potential in terms of a cell of Daniell's battery.	Throw of image by discharge of condensers.			Mean.	Ratio of capacity with different potentials as observed.	Value in microfarads.
0.02	$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	$1\frac{1}{2}$	1.03	311
0.04	3	3	3	3	"	"
0.06	$4\frac{1}{2}$	$4\frac{1}{2}$	$4\frac{1}{2}$	$4\frac{1}{2}$	"	"
0.08	6	6	6	6	"	"
0.10	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$	$7\frac{1}{2}$	"	"
0.20	$14\frac{1}{2}$	$14\frac{1}{2}$	$14\frac{1}{2}$	$14\frac{1}{2}$	1	"
0.40	29	29	$28\frac{1}{2}$	29	"	"
0.60	43	$43\frac{1}{2}$	44	$43\frac{1}{2}$	"	"
0.80	58	58	58	58	"	"
1.00	$72\frac{1}{2}$	73	73	73	"	"
1.60	116	116	116	116	"	"
2.00	143	143	143	143	"	"

\* Last three readings doubtful, the current remaining after the discharge being considerable. The true reading would be greater than indicated.

The condensers of 311 microfarads capacity consisted of 24300 square feet of metal surface, insulated by thin paper and paraffin-wax.

TABLE II.

Two platinum plates in acid and water, each exposing 1 square inch surface. The resistance of  $R+R'=100$  Ohms in this Table; by experiment the potential of the two cells was found to be reduced 8 per cent., and was therefore very nearly 2 volts instead of two cells DANIELL'S.

1. Approximate potential in volts.	2. Time of electrification.	3. Throw of image by discharge of plates on raising the key.	4. Current remaining after discharge.	5. Mean <i>minus</i> the current.	6. Ratio of capacity with different potentials.	7. Value in microfarads.
0.2	seconds. 10	19 20 19	1 }	18	1	175
"	20	18 19 19	" }			
0.4	10	45 46 46	3 }	43	1.2	210
"	20	46 46	" }			
0.8	10	175 170 170 165	11	159	2.2	385
1.0	"	230 228 226	18	210	2.33	408
*1.2	"	310 308 311	22	288	2.67	467
*1.4	"	373 380 382	30	350	2.77	484
*1.6	"	460 460 467 475	33	428	3.10	542
Condensers of 311 microfarads.						
0.2	.....	32 32 32	0	32	1	311
0.4	.....	63 64 63½	"	63½	"	"
0.8	.....	127 127	"	127	"	"
1.0	.....	159 159	"	159	"	"
1.2	.....	188 187 189	"	188	"	"
1.4	.....	220 220 221	"	220	"	"
1.6	.....	252 254 252 254	"	253	"	"
1.8	.....	284 283 284	"	284	"	"
2.0	.....	316 317 317	"	317	"	"

\* The author considers these readings uncertain, having been obliged to guess how much current remained after the image had swung out and back, the momentum of the galvanometer lasting longer than with smaller deflections; the true reading would be greater than those observed.



