The Voltage-Current Curves Obtained with an Electrolytic Cell and Electric Oscillations

By

Tatsumi Terada

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Abstract

The voltage-current curves obtained when a fine platinum wire electrode came in contact with the surface of the electrolyte, the other platinum electrode being in the electrolyte, and thence a potential difference was applied between them, consists of two stages. The curves obtained for the conditions, under which the potential difference is first applied between the electrodes and thence the wire electrode nearly comes in contact with the electrolyte, consists of two stages when the wire is negative, and of three or four stages when the wire is positive. An explanation is given as to the mode of formation of these stages. Next, electric oscillations are produced with the cell described above, and it is shown that the evolution of chlorine or other gases at the end of the wire electrode which is in contact with the electrolyte is apparently sufficient to produce oscillations similar to those produced by hydrogen in the experiments of Schulgin, and that the sudden change of a current through our cell may excite the oscillations.

Some years ago, it was discovered by W. M. Schulgin[1] that electric high frequency-oscillations were produced by reversing the polarity of the Wehnelt interrupter, in an arrangement similar to that of an arc generator : that is, the platinum point of the interrupter was connected through a choke to the negative electrode of a battery and the lead plate of the interrupter was connected through a second choke to three incandescent lamps in parallel and thence to the positive terminal of the battery. Recently, using an improved form of the negative electrode, he[2] pointed out that the evolution of hydrogen at the platinum point was apparently necessary for the production of oscillations. The writer has investigated the voltage-current relation obtained with an arrangement which was essentially similar to that of Ferrié, Fessenden or Schloemilch electrolytic detector[3] and also observed the electric oscillations in a circuit with the detector. In Fig. 1, E_2 is a circular platinum plate of 1.5 cm. in diameter, placed horizontally in a glass vessel

1. W. M. Schulgin: Phys. Zeits. 29, 724 (1928).   2. W. M. Schulgin: Phys. Zeits. 30, 235 (1929); Wireless World 26, 251 (1930).   3. J. A. Fleming: "The Principles of Electric Wave Telegraphy and Telephony", 509 (1916).

Fig. 1
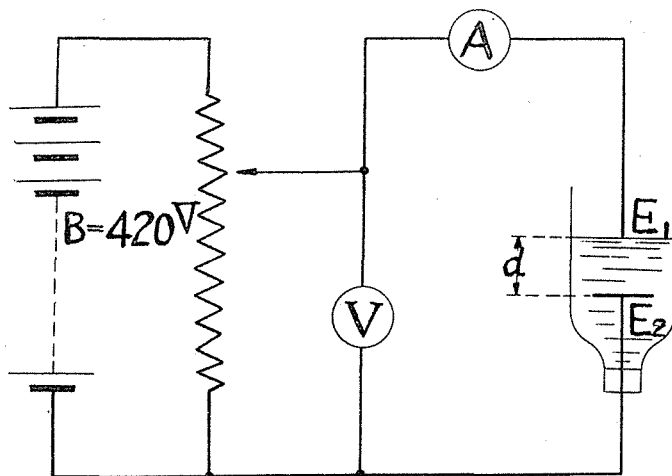
of 4.2 cm. in diameter and 6 cms. in height, which contains dilute acids or salt solutions, and it serves as an electrode. E_1 is the other electrode of fine platinum wire of 0.19 mm. or much less in diameter and soldered to the screw of a spherometer, by which the wire E_1 is adjusted to any required position. To begin with, the currents through 5 % hydrochloric acid solution were measured with various voltages which were applied after the electrode E_1 just touched the electrolyte, the values of the potential difference across the electrodes and the currents corresponding to them being read by a voltmeter V and an ammeter A respectively. The results obtained with the wire E_1, positive
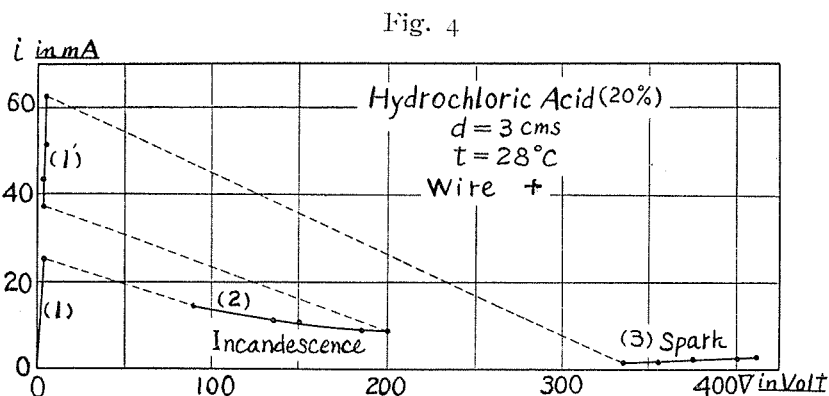
Fig. 2
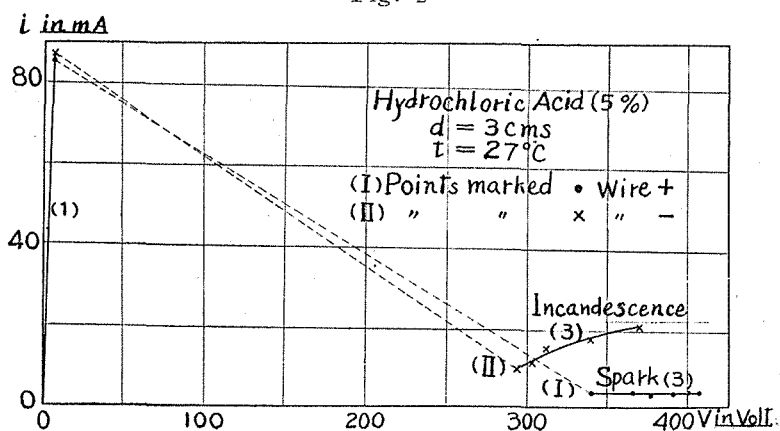
and negative, are shown by the curves (I) and (II) respectively of Fig. 2, in which the abscissae represent the potential differences and the ordinates the currents. Both curves consist of two distinct stages. For stage (1) in the curves, the current increases with the voltage and Ohm's law is generally applicable as is well known. For the stage marked (3), the character of the curve varied a little according as the wire E_1 was negative or positive. When the wire E_1 was negative, the current was suddenly reduced when the voltage reached about 6 volts, and as a result the voltmeter showed the higher value of about 294 volts (330 volts when there was no current). Just at this moment short purplish sparks appeared at the end point E_1, but they presently changed into reddish light as the point became hot. After this, with the increase of the voltage, the current increased again and the light emitted from the point electrode E_1 became stronger, the wire finally being melted by the heat generated by an explosion. This may be understood from the fact that with glow discharges through hydrogen produced arround the negative wire, practically the whole of the power supplied was converted into heat[1] and a chemical action then occurred between the hydrogen and the oxygen in the air. With the point E_1 positive, purplish sparks appeared at about 340 volts (350 volts when there was no current) through the gases produced around E_1, but the current did not increase even when the voltage was further increased. At this stage the electrolyte jumped up and down in both cases owing to the evolution of many bubbles at the point E_1 whatever the concentration of the electrolyte. The apparent difference between stage (3) of curve (I) and that of (II) in Fig. 2 seems to be due to the following facts : When the platinum wire E_1 is negative, it is wholly surrounded by wet hydrogen, and thermionic emission from its heated end, which is necessary for the discharges, will increase with the increase of voltage, but when the wire is positive it is surrounded by chlorine and other gases and its heating is more of a hindrance than a help for the conduction of electricity.

Next, the voltage-current curves were obtained by another method; a potential difference was first applied between the electrodes and then the screw of the spherometer was carefully turned until the current just passed through the electrolyte. The results obtained with hydrochloric acid (5%) are shown in Fig. 3. Curve (II) corresponding to the wire

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1. K. G. Emeléus : "The Conduction of Electricity through Gases," 38 (1929).

E_1 negative is similar to curve (II) in Fig. 2, but curve (I) corresponding to the wire E_1 positive differs a little from curve (I) in Fig. 2. Curve (I) in Fig. 3 consists of three stages : stage (2) is a new one and is obtained with voltages above 110 volts (210 volts without current), though the stages (1) and (3) are similar to those (1) and (3) of curve (I) in Fig. 2 respectively. The current in stage (2) was less than about 14 milliamperes, but the end point of the wire E_1 was at red heat after emission of a few sparks, the phenomenon being accompanied by a

Fig. 3

hissing noise. The light emitted from the end point became brighter with the increase of voltage as in the case of stage (3) of curve (II), though the current in the present stage was reduced with the increase of voltage. The voltage-current curves obtained with the electrolyte still stronger (20% hydrochloric acid solution) never differed for the wire E_1 negative, but they differed for the wire positive. With the wire positive, another stage (1') usually appeared as shown in Fig. 4, ; besides the stages (1), (2) and (3) corresponding to those of (I) in Fig. 3 respectively. In Fig. 4, stage (1) was obtained with voltages up to 190 volts, stage (2)—" incandescence "—in the range between 200 and 255 volts, stage (1') in the range between 260 and 330 volts and stage (3)—" spark "—with voltages above 340 volts (these voltage values show the potential difference between the electrodes when there is no current through the electrolyte). From many observations made with other electrolytes such as sulphuric acid, nitric acid, sodium chloride, sodium

Fig. 4

hydroxide and potassium chloride, it was known that the voltage-current curves obtained with comparatively weak solutions were the same as those shown in Fig. 3, but the curves obtained with strong solutions and with the wire positive were generally similar to that shown in Fig. 4, though the stage (1′) was unstable with some electrolytes owing to its shift to the " spark " stage. The exact form of the curves depended upon the kind of electrolyte and the diameter of the wire used. When a saturated solution of sodium chloride was employed, the light emitted from the positive point was comparatively strong and it was easily found with a direct vision spectroscope that the sodium spectrum was especially predominant in the light. With a wire of 0.6 mm or more in diameter these stages were never observed distinctly within our experimental range.

Now, we must consider the formation of curve (I) in Fig. 3. When the end point of the positive electrode E_1 is brought immediately over the surface of the electrolyte and to a distance of about 0.1 mm from it, the electrolyte under the end point rises up in the shape of a cone. As the end point approaches closer to the electrolyte the latter rushes up to the end point and a strong current flows as shown in stage (1). As the potential difference between electrodes E_1 and E_2 increases, the cone rises higher and a thin " gas-layer " consisting of chlorine, oxygen and water vapour is produced around the end point E_1 as a result of short sparks occurring at the moment when the end point E_1 comes nearly in contact with the apex of the cone. Among the ions produced in the gases the electrons and negative ions will be attracted and the positive ions repelled towards the electrolyte, forming an ionic wind. Consequently, the electricity which is small compared with that in stage

(1) may be conducted through gases, but the end point E_1 will be heated owing to the focusing of the electrons and the negative ions upon it. The reason why the current in stage (2) was reduced with the increase of the voltage is not simple, but the following seem to be the main causes. (i) With the increase of voltage the temperature at the end point E_1 rises, but the thermionic emission from the heated point is greatly obstructed as the wire is positive. (ii) The thickness of the gas-layer between the end point E_1 and the electrolyte increases inevitably with the increase of voltage and this results in an increase of the resistance in the circuit. When the voltage is higher than that used in stage (2), the sparks occur violently as seen in the experiments. In consequence of the strong instantaneous current, the positive end point will be entirely surrounded by a thick " gas-layer ". If so, as the conditions are similar to those in stage (3) of curve (I), Fig. 2, the " spark " stage should be formed.

Next, we shall consider the mode of formation of stage ($1'$) in Fig. 4. When the electrolyte is stronger, strong sparks pass through the gases between the positive end point and the electrolyte, and are accompanied by splashes. The splashes which adhered to the wire E_1 will aggregate into a drop and presently fall along it, as is clearly seen with sodium chloride solution. This is nothing but the formation of an electrolytic bridge over the end point E_1. If so, as the conditions are similar to those of stage (1) in Fig. 3, stage ($1'$), similar to the latter, should appear.

The problem still remaining is the apparent difference between curves (I) and (II) in Fig. 3. According to Wolcott[1], at ordinary pressures the spark potential between a positive point and a plane is only half that for a negative. If this is applicable to our case also, the electrolyte is more apt to come into contact with the negative point than with the positive, for the distance between the negative point and the electrolyte should be smaller than that for the positive. Consequently, the stage " incandescence " should appear with higher voltage for the negative point, as shown in curve (II), Fig. 3, and we see only two stages (1) and (3) in the curve. In Fig. 5, the direct current i_0 was led by a potentiometer through two choking coils Ch_1 and Ch_2 of about 30 henries to our cell which was shunted by an inductance L and a variable oil condenser C in series. When wire E_1 was connected

1. S. Whitehead, " Dielectric Phenomena," 78 (1927).

to the negative, and plate E_2 to the positive terminal, as in the case of Schulgin, oscillations occurred in the shunt circuit LC. If the mode of formation of the curve (I) in Fig. 3 was essentially the same as that of curve (II) in the same figure described above, it seemed to the writer that oscillations should also occur in the circuit even if the wire E_1 was positive. As a matter of fact it was quite possible to obtain oscillations of high frequency up to 100 meters in the wave-length

Fig. 5
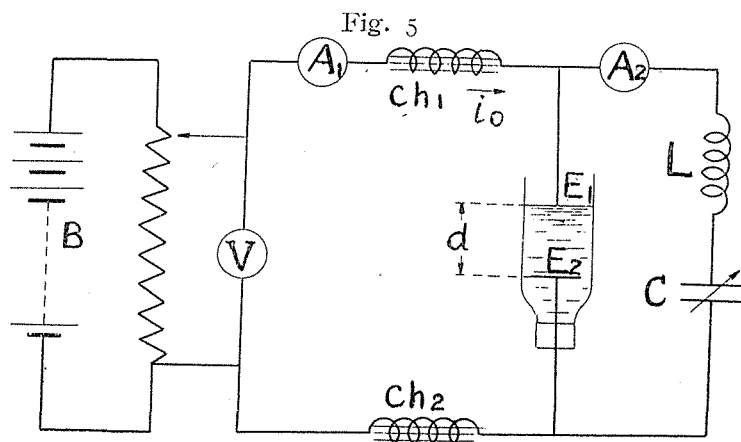
with an inductance of 31 microhenries and a voltage of 130 volts or more, though the oscillation was a little weak in comparison with that found with the wire E_1 negative. The oscillation-current which was measured by a thermoammeter A_2 increased with the capacity up to a certain value when the inductance was kept constant; if the capacity increased from about 30 to 3000 micro microfarads for a cell of ClH (20%), it increased from about 50 to 195 milliamperes under the conditions $L = 31$ microhenries, $V = 355$ volts, distance d between the electrodes $= 3$ cms and the diameter of the wire $= 0.19$ mm. Oscillation-currents also depended upon the concentration of the electrolyte, the diamter of the wire E_1 and the distance d, especially on the voltage as shown in the Table.

When solutions of different concentrations of the other electrolytes such as sulphuric acid, nitric acid, sodium chloride and potassium chloride were used instead of hydrochloric acid solution, it was also possible to get oscillations in the shunt circuit and it was noticed that there were successive strong sparks with the colour peculiar to the electrolyte at the point E_1 whenever the oscillation occurred.

Now, according to the experimental results so far obtained by

Table   ClH (20%)

(The wire positive and 0.19mm. in diameter)

$L=31$ microhenries, $C=0.0031$ microfarad, $d=1.5$cm.)

Potential difference between the electrodes (without current) V in volt	Main current i_0 in mA.	Oscillation-current i in mA.
270	85	110
300	90	125
335	105	160
360	110	210
370	110	215

the writer, it seems that the evolution of chlorine and other gases at the platinum point electrode is sufficient to produce oscillations, just as occurs with hydrogen in the experiments of Schulgin, and that the sudden starting, stopping or changing of a current through our cell excites oscillations.   To make the latter point clearer, another example may be cited.   An interrupting toothed disc was used instead of the cell in Fig. 5.   When the disc rotated intermittent discharges took place across the gaps, and it was quite possible to produce an oscillation-current of about 300 milliamperes in the shunt circuit with a condenser of 2 microfarads and a supply of 60 volts.