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“Alternate Current Electrolysis.” By J. HOPKINSON, D.Sc.,
F.R.S., E. WILSON, and F. LYDALL. Received November 2,
—Read November 23, 1893.

Our attention has been called to the interesting work of Messrs. Bedell, Ballantyne, and Williamson on “Alternate Current Condensers and Dielectric Hysteresis,” in the ‘Physical Review’ for September—October, 1893. As experiments bearing upon an analogous subject were carried out in the Siemens Laboratory, King’s College, London, we think it may be of interest to publish them. Our experiments were commenced in June, 1892, and were discontinued in the following July with the intention of resuming them at a future time. They are therefore not exhaustive.

Suppose an alternating current to be passed through an electrolyte between electrodes, and that the current passing and the difference of potential are measured at intervals during the phase. If the electrolytic action were perfectly reversible, we should expect to find the potential difference to have its maximum value when the current was zero, that is to say, when the total quantity of electricity had also a maximum value. One object we had in view was to ascertain if this were the case, and, if not, to determine what amount of energy was dissipated under different conditions.

This is readily done, inasmuch as the work done on the voltameter or by the voltameter in any short time is the total quantity of current passed in the time multiplied by the potential difference. Let a curve be drawn in which the ordinates are the coulombs and the abscissæ the volts at corresponding times: the area of this curve represents the work dissipated in a cycle.

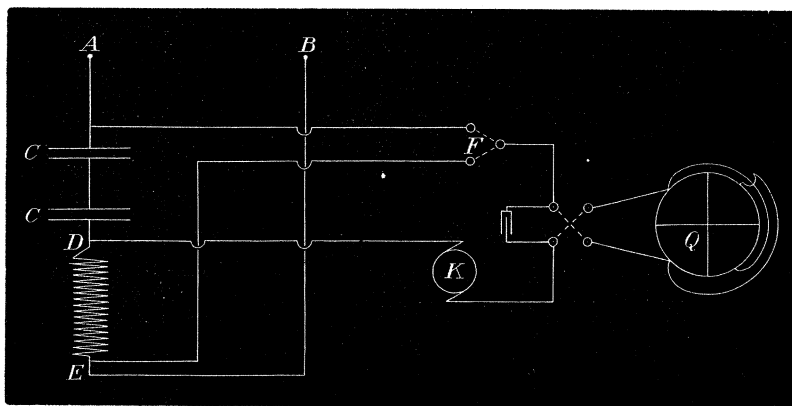
It is, of course, well known that if a current is passed through an electrolyte, the potential difference speedily attains a certain maximum value and there remains. If an alternate current is passed, we should expect to find that as the number of coulombs passed in each

half period increased, the potential difference would also increase, until it attained the value given with a continuous current, and that when this value was attained, the curve of potential and time would exhibit a flat top for all higher numbers of coulombs passed. We thought it possible that from the number of coulombs per unit of section required to bring the potential difference to its full value, we could obtain an idea of how thick a coating of the ions sufficed to secure that the surface of the plate had the chemical quality of the ion and not of the substance of the plate.

Platinum Plates.

Part I.—In the first instance, two cells having platinum plates for electrodes were used. We are indebted to Messrs. Johnson and Matthey for the loan of these plates. They have each an area of 150 sq. cm. exposed to one another within the electrolyte, and are placed in a porcelain vessel $\frac{1}{8}$ in. apart. Pieces of varnished wood were placed at the back of each plate so as to prevent conduction between the outside surfaces through the fluid. The solution used was of water 100 parts by volume, and H_2SO_4 5 parts. Fig. 1 gives a diagram of connections, in which A, B are the terminals of a Siemens

FIG. 1.



W12 alternator, C, C are the cells above described, in series with which is placed a non-inductive resistance, DE. By means of a two-way switch, F, one of Lord Kelvin's quadrant electrometers, Q, could be placed across the cells C, C or the non-inductive resistance DE through a revolving contact-maker,* K, fixed to the shaft of the alternator. A condenser of about 1 m.f. capacity was placed across the terminals of the electrometer.

* For description of contact-maker see 'Roy. Soc. Proc.,' vol. 53, p. 357.

From observations of the values of the E.M.F. across the cells C, C at different times in a period, a Curve A (figs. 2, 3, 4) was plotted, giving potential in terms of time.

FIG. 2.

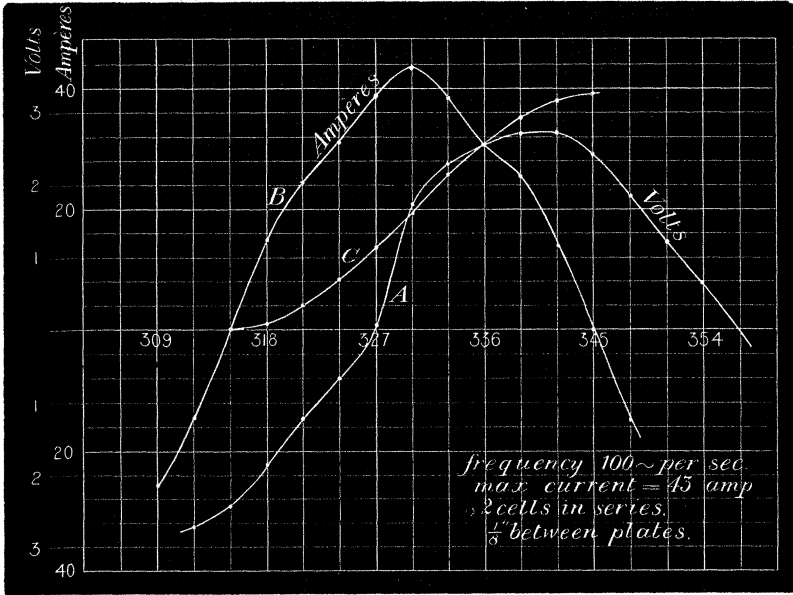


FIG. 3.

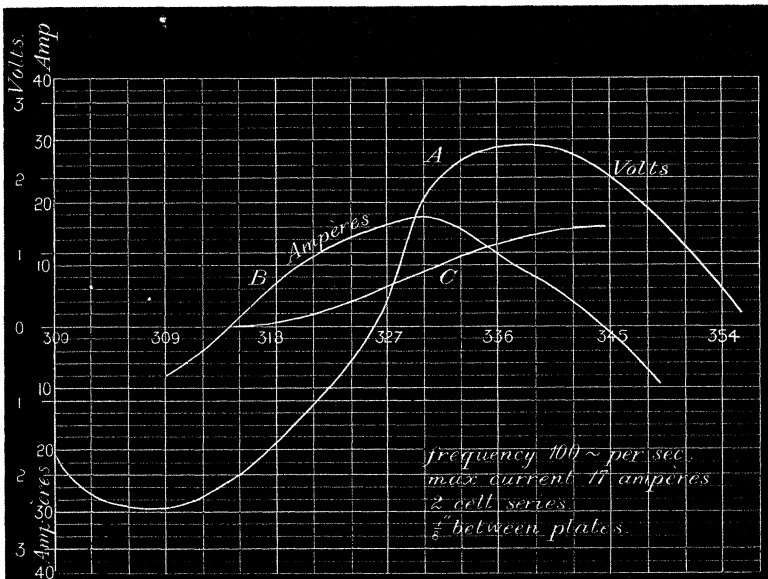
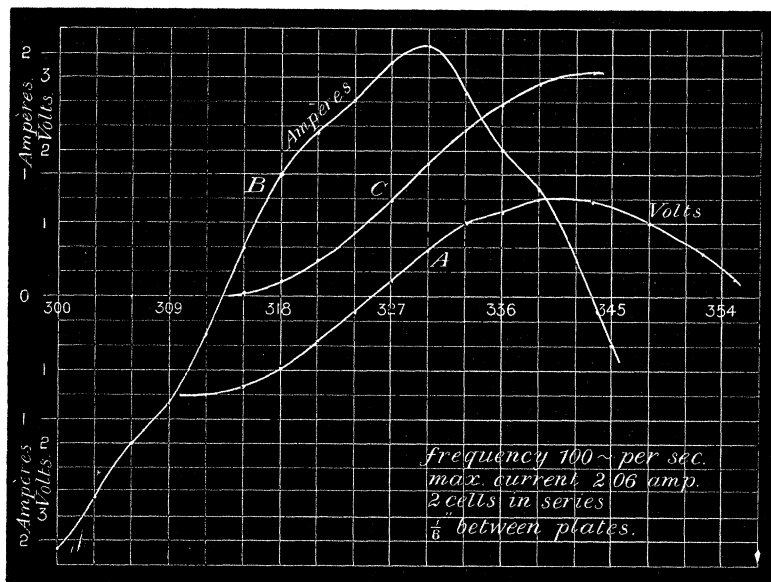


FIG. 4.



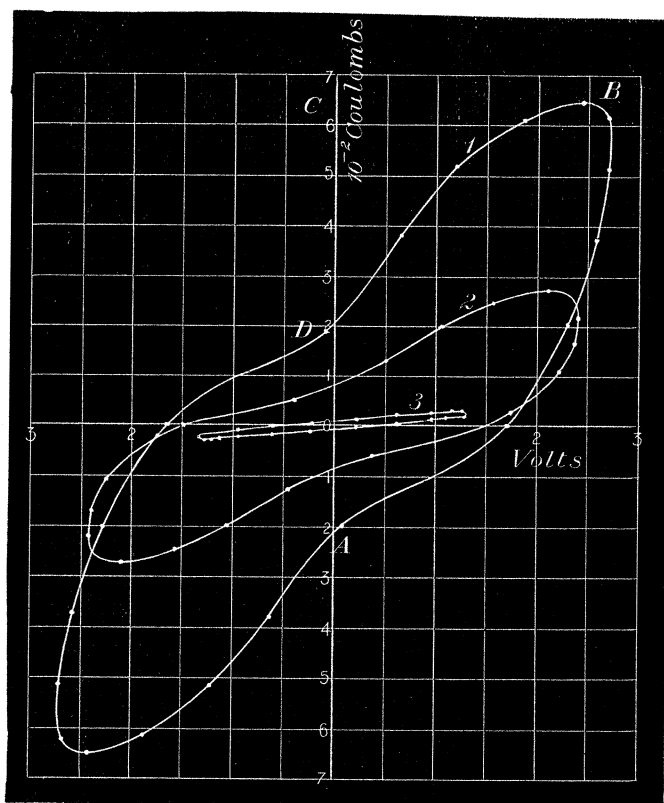
In the same way the Curve B was plotted for the E.M.F. between D and E, giving the current in terms of time. Hence the area of this Curve B up to any point, *plus* a constant, is proportional to the quantity of electricity corresponding to that point. This is shown in Curve C, which is the integral of B. The three curves, Nos. 1, 2, 3, in fig. 5, have been plotted from figs. 2, 3, 4 respectively, and show the cyclic variation of the potential across the cells in volts, and the

Table I.

	Frequency.	Maximum volts across cells.	Maximum ampères.	Maximum coulombs.	Area of cyclic curve in square centi- metres.*	Efficiency per cent.
Fig. 2 ..	100	2.7	43.3	0.065	53.8	23
" 3 ..	"	2.4	17.4	0.027	9.0	24
"	"	2.38	10.0	0.0164	—	34
"	"	1.93	5.7	0.0088	—	—
"	"	1.61	2.9	0.0048	—	32
" 4 ..	"	1.3	2.06	0.003	0.6	43

* 1 sq. cm. represents $\frac{1}{2}$ volt $\times 10^{-2}$ coulombs.

FIG. 5.



quantity of electricity in coulombs. The area of each curve (see Table I) is a measure of the energy dissipated per cycle, and since in this case there can be no accumulation of recoverable energy at the end of the cycle, it follows that the *whole* difference between what is spent during one part of the process and what is recovered during the other part is dissipated. In order to obtain an idea of the efficiency to be looked for when used as a condenser with platinum plates $\frac{1}{8}$ in. apart and dilute sulphuric acid, under varying conditions as to maximum coulombs, the area ABC (Curve 1, fig. 5) has been taken and is a measure of the total energy spent upon the cell; whilst the area DBC is a measure of the energy recovered—the ratio of these areas gives the efficiency.

Part II.—In the next set of experiments the frequency was varied, in addition to current; and in order to allocate the losses of potential in the cell, the platinum plates were placed $\frac{1}{4}$ in. apart for the

purpose of introducing an electrode into the fluid between the plates. This electrode consists of a platinum wire sealed into a glass tube which was capable of being placed in any desired position between the plates. The solution was, as before, of water 100 parts and H_2SO_4 5 parts by volume.

The arrangement of connections was similar to that shown in fig. 1, but, instead of observing the potential between the two platinum plates, observations were taken of the values of E.M.F. between one plate and the exploring electrode.

Table II gives particulars of the experiments tried, and two sets of results are shown in figs. 6 and 7, in each of which, from observations of the values of E.M.F. between the exploring electrode and the platinum plate at different times in a period, a Curve A_1 was plotted, giving potential in terms of time. This Curve A_1 is peculiar, in that the ordinates at corresponding points in the two half periods are not equal to one another, as is the case in Curve A, which gives the potentials across the two plates.

Table II.

	Frequency.	Maximum coulombs.	Maximum ampères.	Maximum volts per cell.
	100	0·090	58·6	1·83
	19·7	0·082	11·2	1·57
	20·5	0·054	7·1	1·39
Fig. 6.....	142·5	0·071	65·4	1·77
„ 7.....	2·4	0·120	1·9	1·37

The Curve A_1 gives, at any epoch, the potential taken up in the evolution of gas at the surface of the plate, *plus* the potential due to the current in overcoming the resistance of the electrolyte itself. To separate these quantities experiments were made upon the resistance of the electrolyte for varying frequencies and currents. To this end the plates were placed about 2 in. apart in the fluid, and two exploring electrodes, as already described, were placed within the fluid in a straight line drawn perpendicularly between the faces of the plates, the distance between the electrodes being 4·3 cm. Some difficulty was experienced, owing to the gases being given off at the plates more rapidly in some cases than in others. We, however, estimate that the resistance of a layer of the electrolyte, of a thickness equal to the distance between the electrode and plate, and of area equal to the area of plate submerged, in figs. 6 and 7, was approximately 0·0056 ohm.

In fig. 6 the Curve A_2 is the result of correcting Curve A_1 for

FIG. 6.

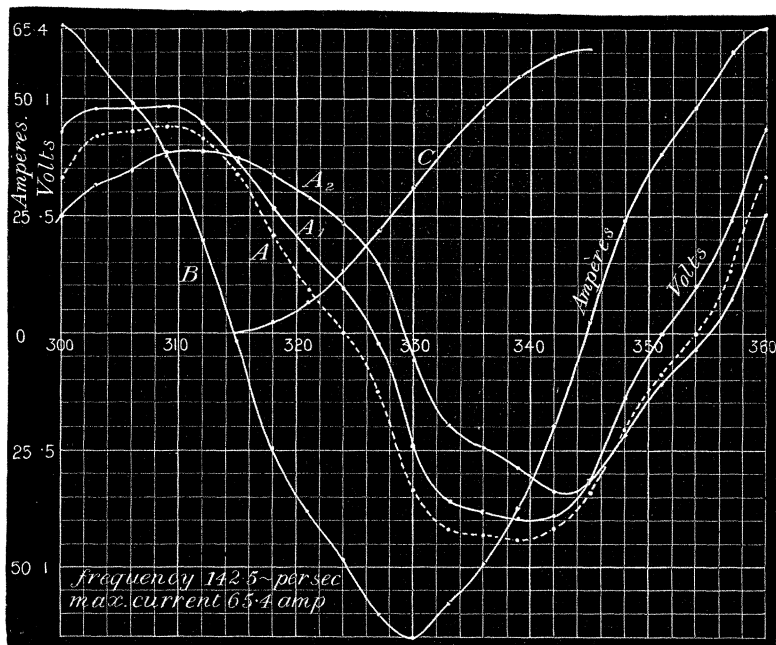
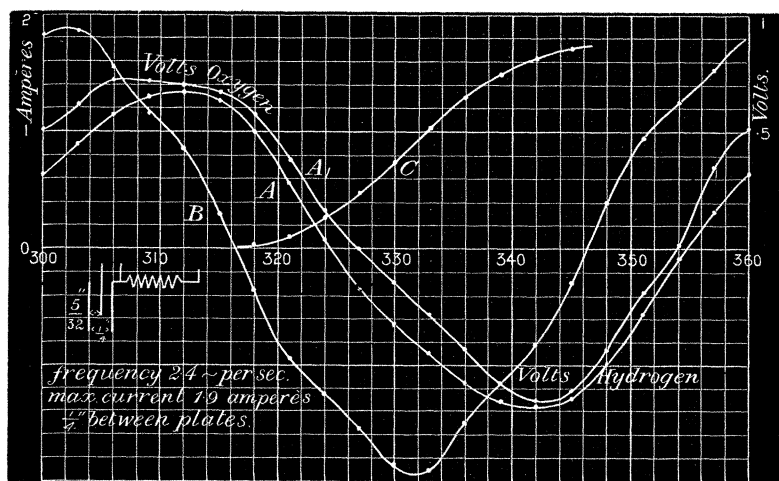


FIG. 7.

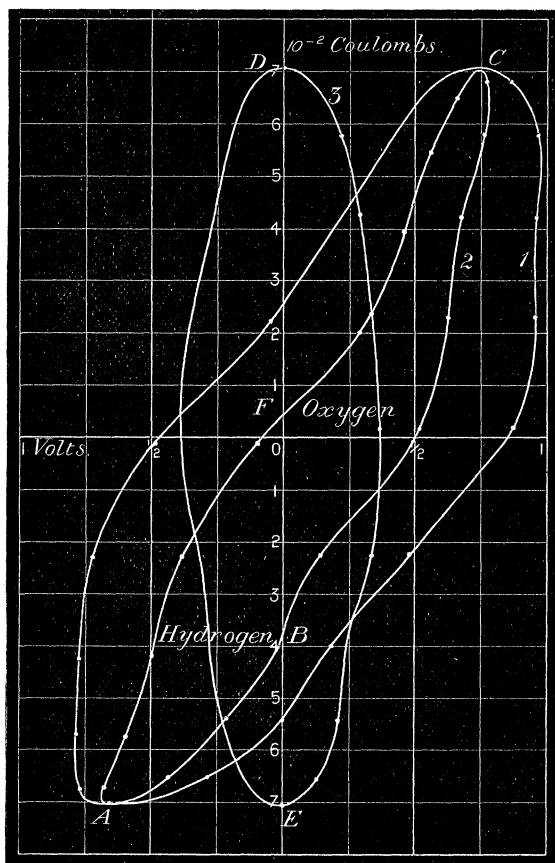


potential lost in the resistance of the electrolyte itself, and this curve therefore gives potential taken to decompose the fluid, in terms of

time. Curve B gives current in amperes in terms of time, whilst C is the integral of B and gives quantity in coulombs. With this frequency and current the energy dissipated on resistance of the electrolyte is a large proportion of the total energy dissipated; and only about 40 per cent. of the total energy is taken up in evolving oxygen and hydrogen at the plate, owing to the high frequency. The reverse of this is the case with lower frequency, as will be shown in connection with fig. 7.

From observations on the direction in which the electrometer needle was deflected for a given position of a Clark's cell connected to its terminals, we were able to state, for a given half period in the curves in figs. 6 and 7, which gas was being given off at the plate.

FIG. 8.



The abscissæ of Curves Nos. 1 and 2 (fig. 8) have been plotted from Curves A_1 and A_2 respectively in fig. 6, the ordinates being given for corresponding epochs by the integral Curve C.

Curve No. 1 (fig. 8) shows the cyclic variation of the potential between the electrode and the platinum plate, in terms of coulombs. Curve No. 2 shows the cyclic variation of the potential used in decomposition, also in terms of coulombs. Oxygen begins to be directed to the plate at the point A, as then the coulombs are a maximum and the current changes sign. But the oxygen is evolved on a hydrogen plate, and the E.M.F. aids the current; the work done on the plate is negative. This continues to point B (Curve No. 2). After this point (B) the character of the plate is that of a layer of oxygen and the work done becomes positive; this continues to the point C. The area AEB is the work returned by the plate, whilst oxygen is being evolved on a hydrogen surface. The area BCD is the work done on the plate, whilst oxygen is being evolved on an oxygen surface. In like manner the area CDF is the work returned by the plate whilst hydrogen is being evolved on an oxygen surface, and FAE the work done on the plate whilst hydrogen is being evolved on a hydrogen surface. The above areas have been taken in square centimetres, and are given in Table III. The area inclosed by Curve No. 2 (25.3 sq. cm.) represents the total energy dissipated by electrolytic hysteresis, whilst the area of Curve No. 1 (63.5 sq. cm.) gives the total energy spent in the cell. The abscissæ of Curve No. 3 are the differences of potential differences of Curves Nos. 1 and 2, the ordinates, as before, being coulombs. In fig. 8, 1 sq. cm. = $\frac{1}{5}$ volt $\times 10^{-2}$ coulomb.

In fig. 7 the frequency is 2.4 per second, and this is the case in which practically the whole of the energy dissipated in the cell is spent in decomposing the electrolyte at the plates. The correction to be applied to Curve A_1 for resistance is so small as to be almost negligible. The cyclic curve in fig. 9 has been plotted from Curve A_1 and the integral Curve C, and its area (146.7 sq. cm.) represents the energy dissipated per cycle by electrolytic hysteresis. Areas have been taken in square centimetres from the curve, as in the preceding case, and are given in Table III. In fig. 9, 1 sq. cm. = $\frac{1}{10}$ volt $\times 10^{-2}$ coulomb.

The potential curve in fig. 7 does not exhibit a level part at the highest potential; this is possibly due to the resistance of liberated gas.

A general conclusion of the experiments is that about one-tenth of a coulomb suffices to fully polarise 150 sq. cm. of platinum. This will liberate 0.00001 of a gram of hydrogen; hence 0.00000007 gram of hydrogen serves to polarise 1 sq. cm. of platinum. 0.00000007 cm. is probably a magnitude comparable with the distance between mole-

FIG. 9.

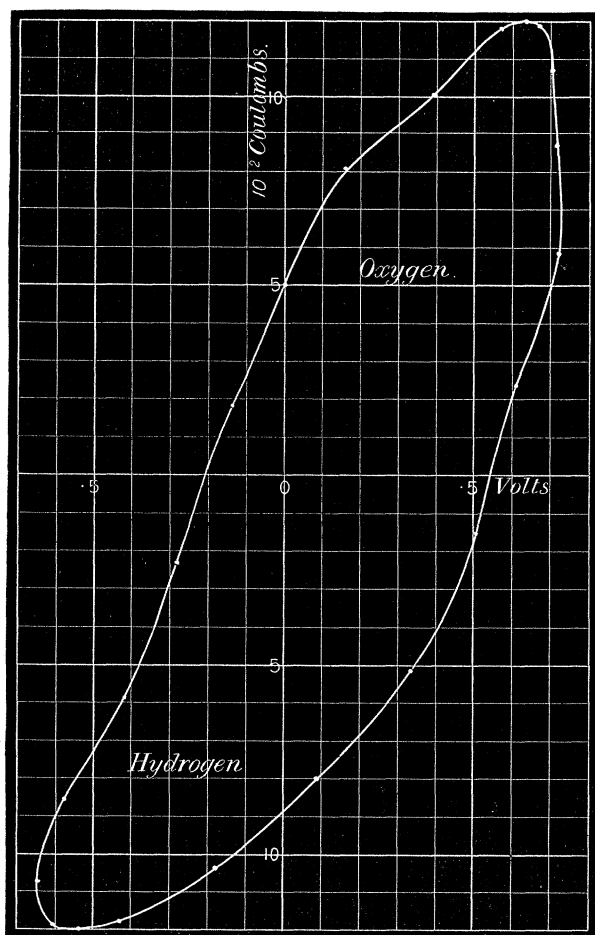


Table III.

	Oxygen on hydrogen surface, AEB.	Oxygen on oxygen surface, BCD.	Hydrogen on oxygen surface, FCD.	Hydrogen on hydrogen surface, FAE.
Fig. 8, Curve No. 2	3.65	27.25	13.8	15.6
Fig. 9	5.8	111.3	17.2	58.4

cules of hydrogen when this body is compressed to a density comparable with the density of liquids.*

“The Experimental Proof that the Colours of certain Lepidopterous Larvæ are largely due to modified Plant Pigments derived from Food.” By EDWARD B. POULTON, M.A., F.R.S.
Received May 12,—Read June 8, 1893.

[PLATES 3 AND 4.]

In a paper printed in the ‘Proceedings of the Royal Society’ for 1885 (pp. 269—315), I brought forward many reasons for regarding certain elements of the colouring of Lepidopterous larvæ as modified chlorophyll derived from the food plant. For this altered pigment the name metachlorophyll was suggested (*loc. cit.*, p. 270). Many other observations, subsequently made, supported the same conclusion; but it was not until the summer of last year (1892) that I was able successfully to carry out the critical experiment, viz., selecting a species of larva which normally eats green leaves, to feed it from the egg upon parts of the plant from which all colouring matter is absent.

This experiment was carried out in the following manner:—

A captured female of *Tryphæna pronuba* laid many hundreds of eggs in a chip box. The first larvæ began to appear September 7, 1893. On this and the subsequent dates, the larvæ intended for the purposes of these experiments were arranged in three sets, fed respectively upon—(1) the yellow etiolated leaves from the central part of the heart of the cabbage, (2) the white mid-ribs of such leaves from which the yellow blade was carefully removed with scissors, (3) the deep green external leaves of the same plant.

In all other essential respects the conditions of the three sets were the same. All were kept in the dark to prevent the change of the etiolin into chlorophyll. They were only exposed to light during the times necessary for comparison and feeding, and these are indicated below. A few were kept in glass cylinders standing on plates, the majority being confined in white earthenware pots covered at first with white muslin, but subsequently with glass sheets. Eventually all were kept in pots.

It is clear that the only essential difference between the conditions of the sets was the fact that the food of the first contained etiolin but

* Lord Kelvin states that in “any ordinary liquid” the mean distance between the centres of contiguous molecules is, with a “very high degree of probability,” less than 0·0000002 and greater than 0·000000001 of a centimetre. See ‘Roy. Institution Proc.’ vol. 10, p. 185.

FIG. 1.

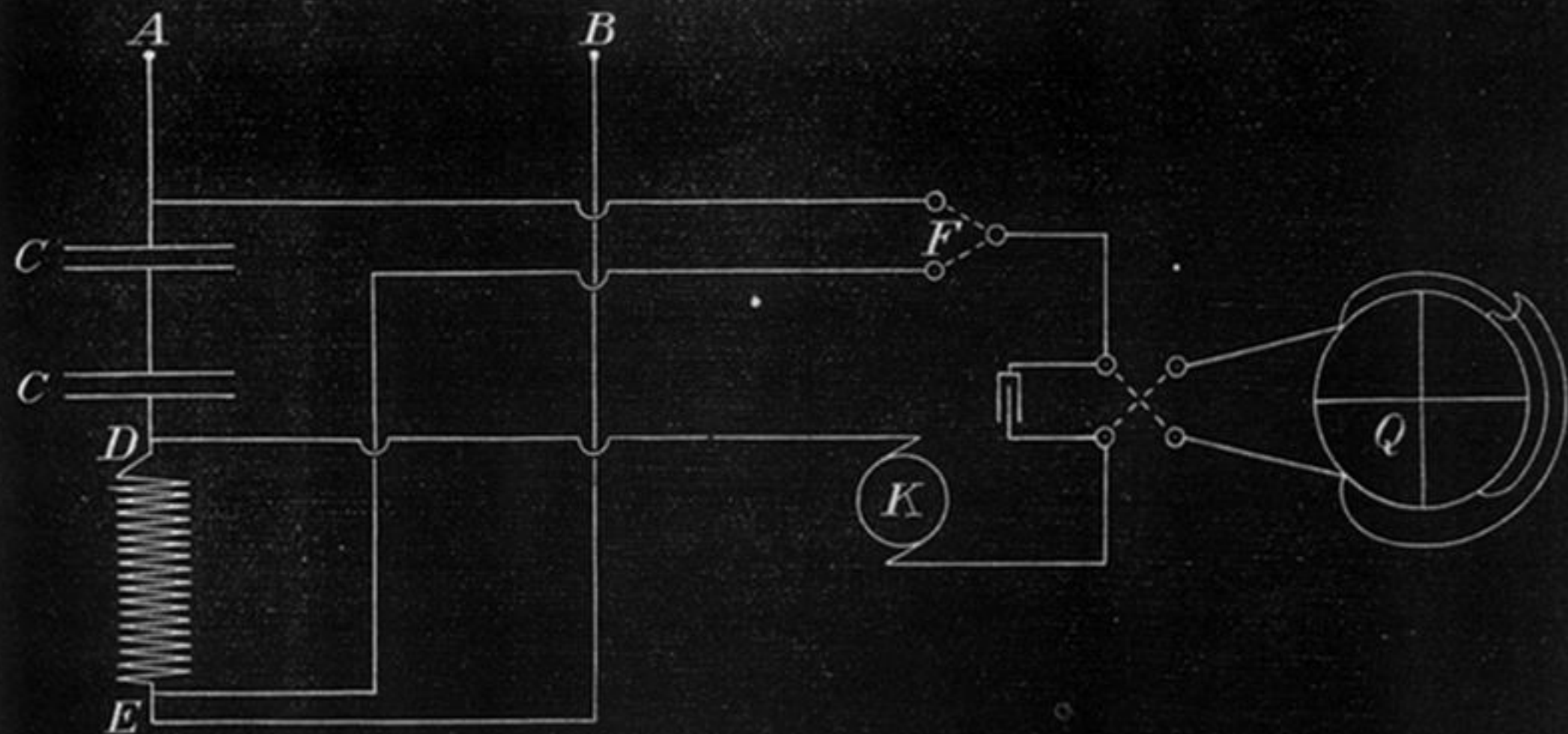


FIG. 2.

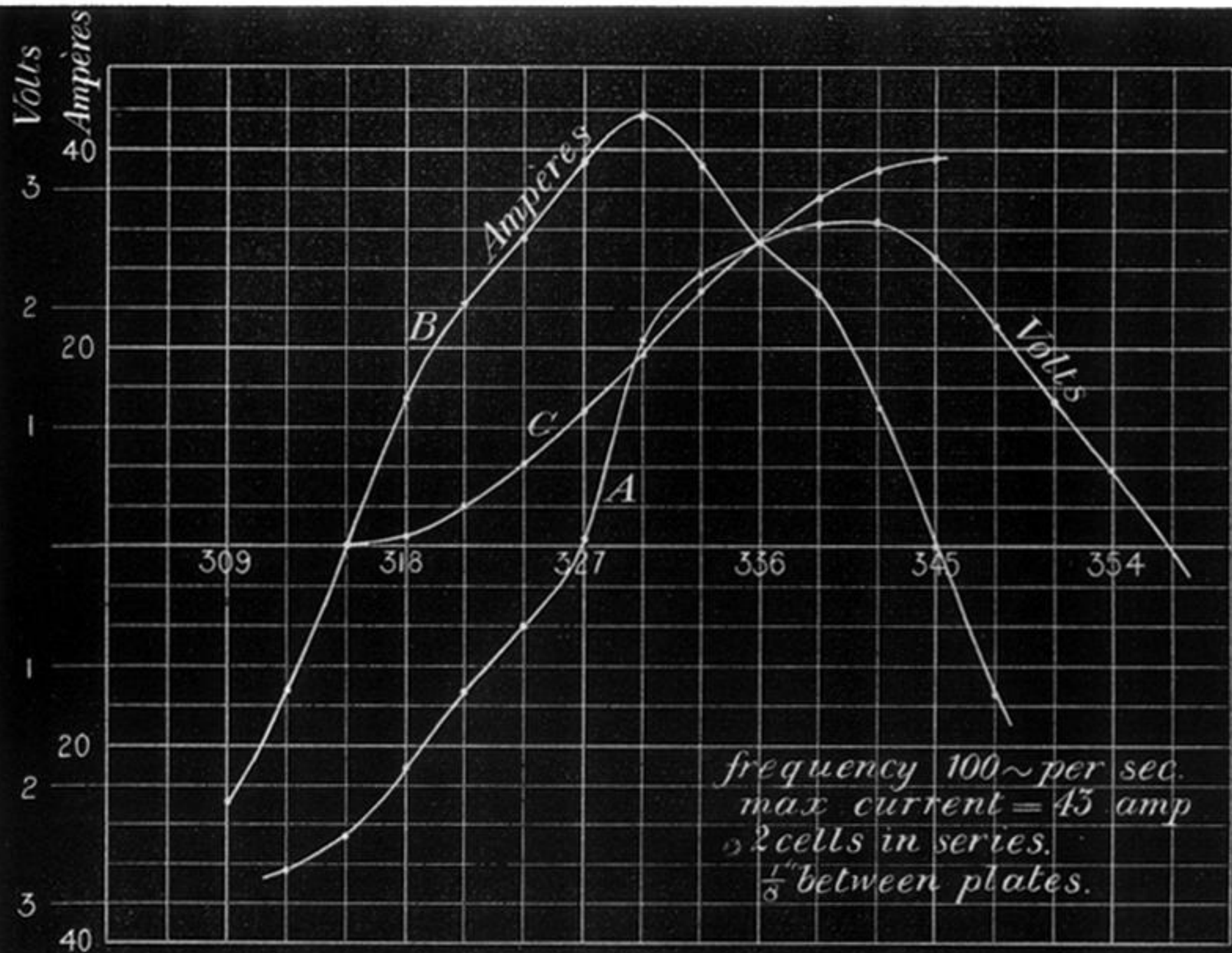


FIG. 3.

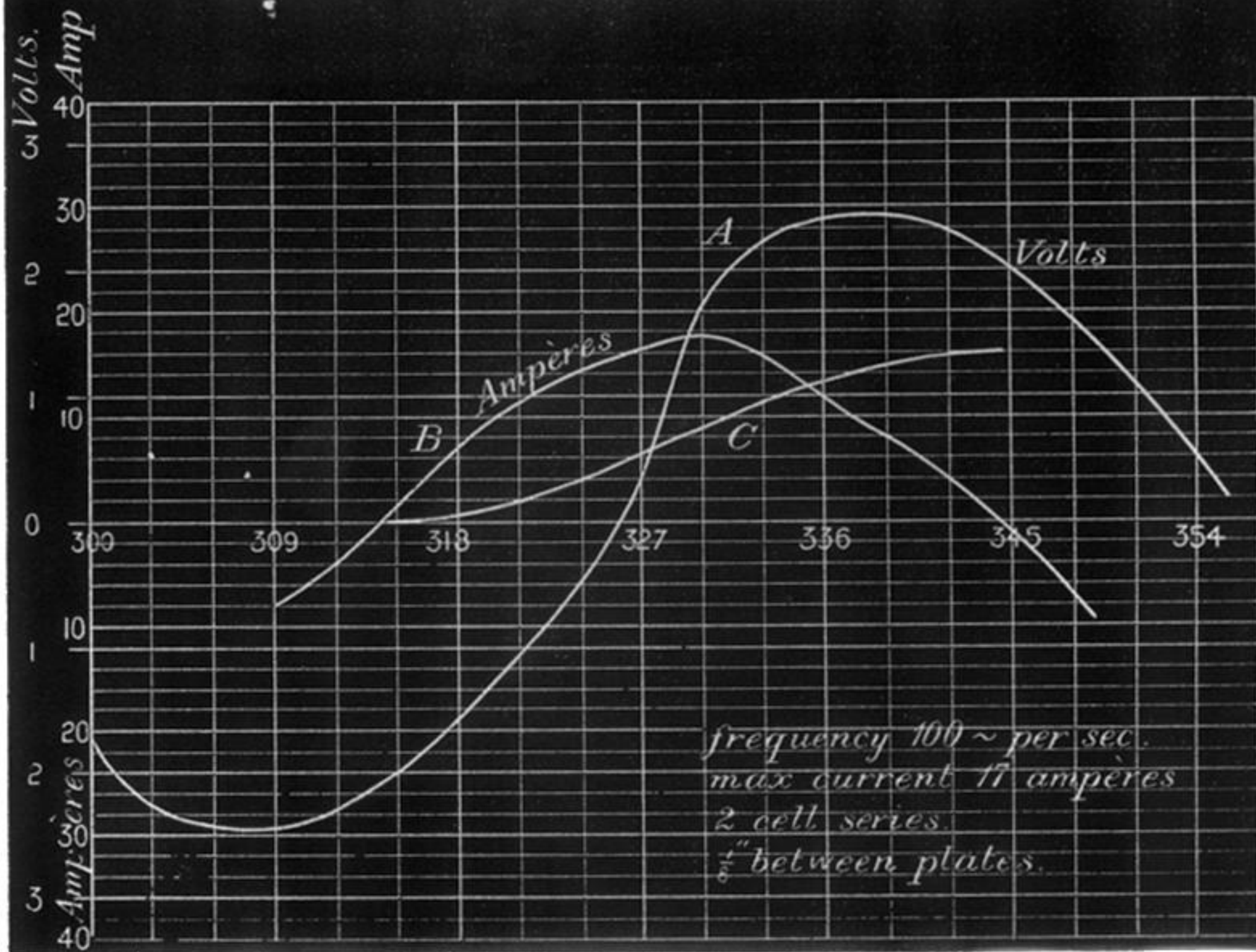


FIG. 4.

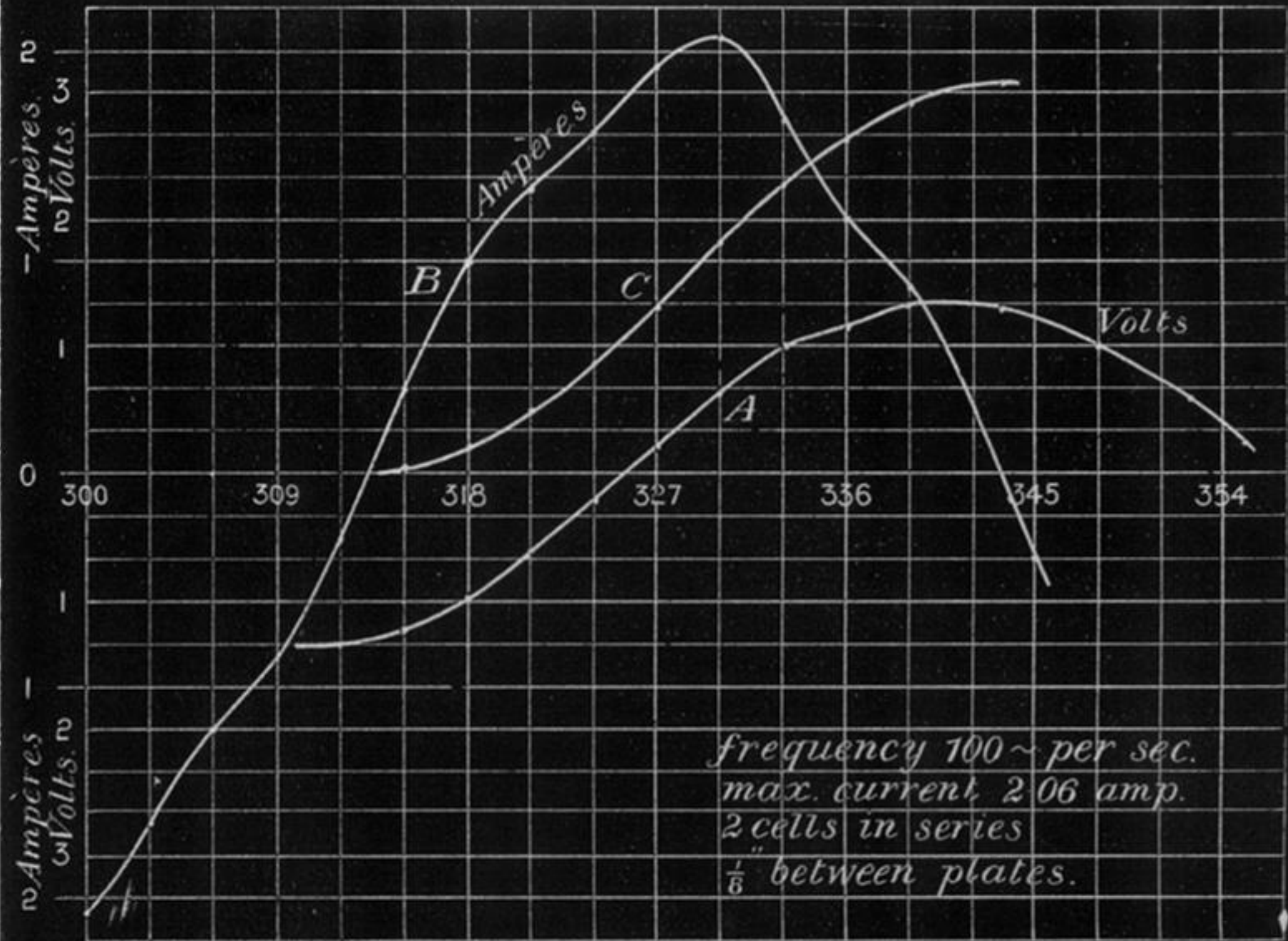


FIG. 5.

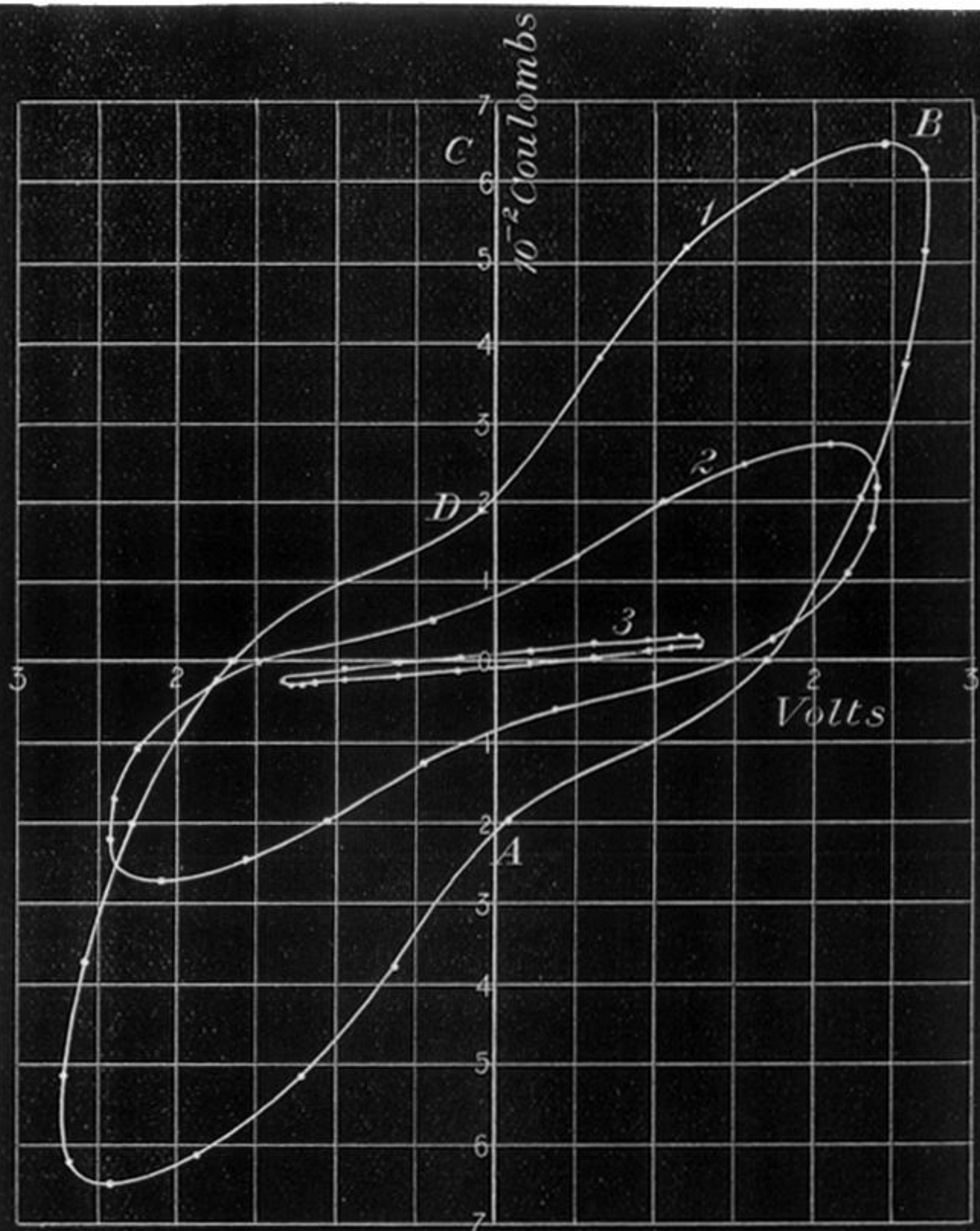


FIG. 6.

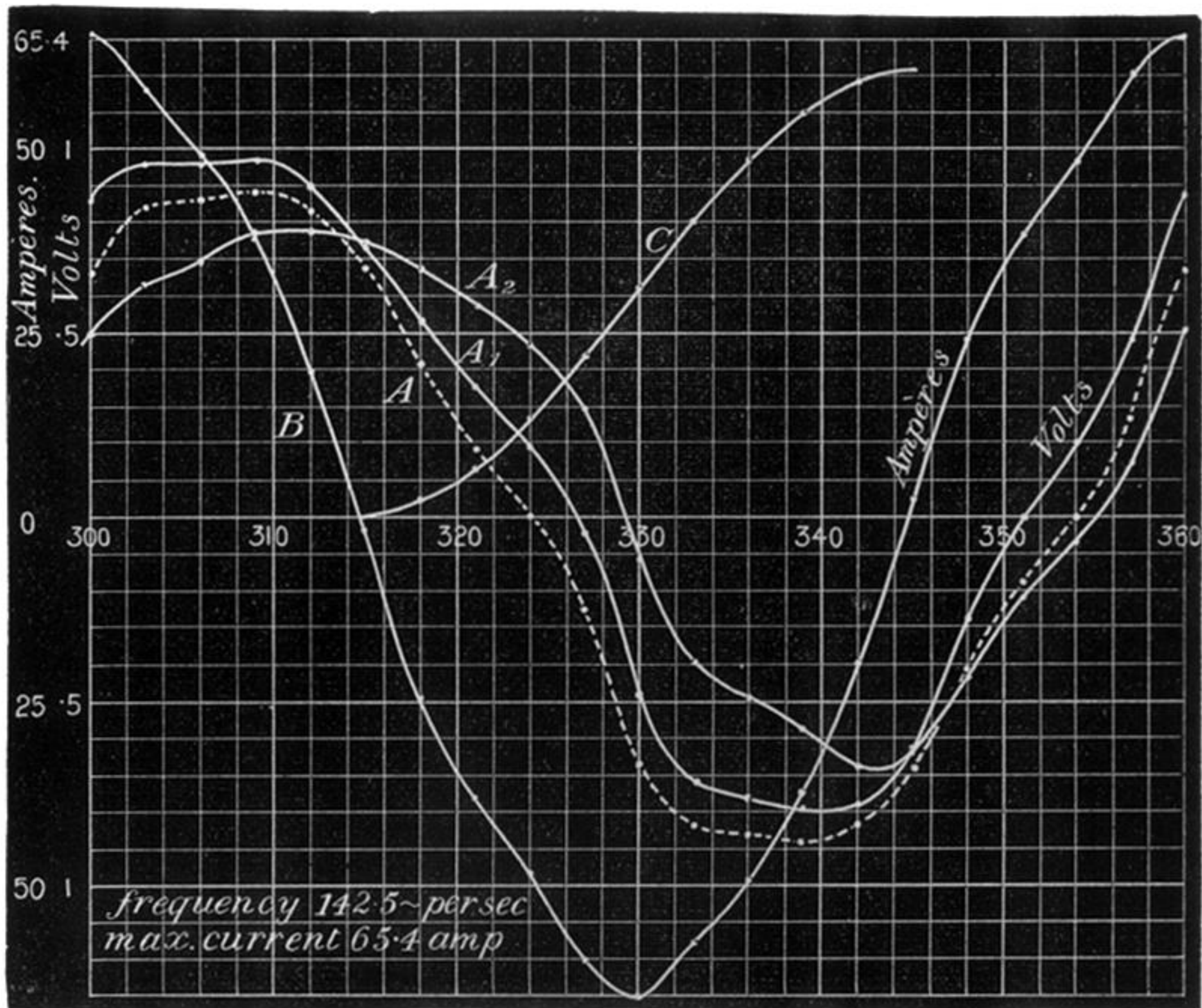


FIG. 7.

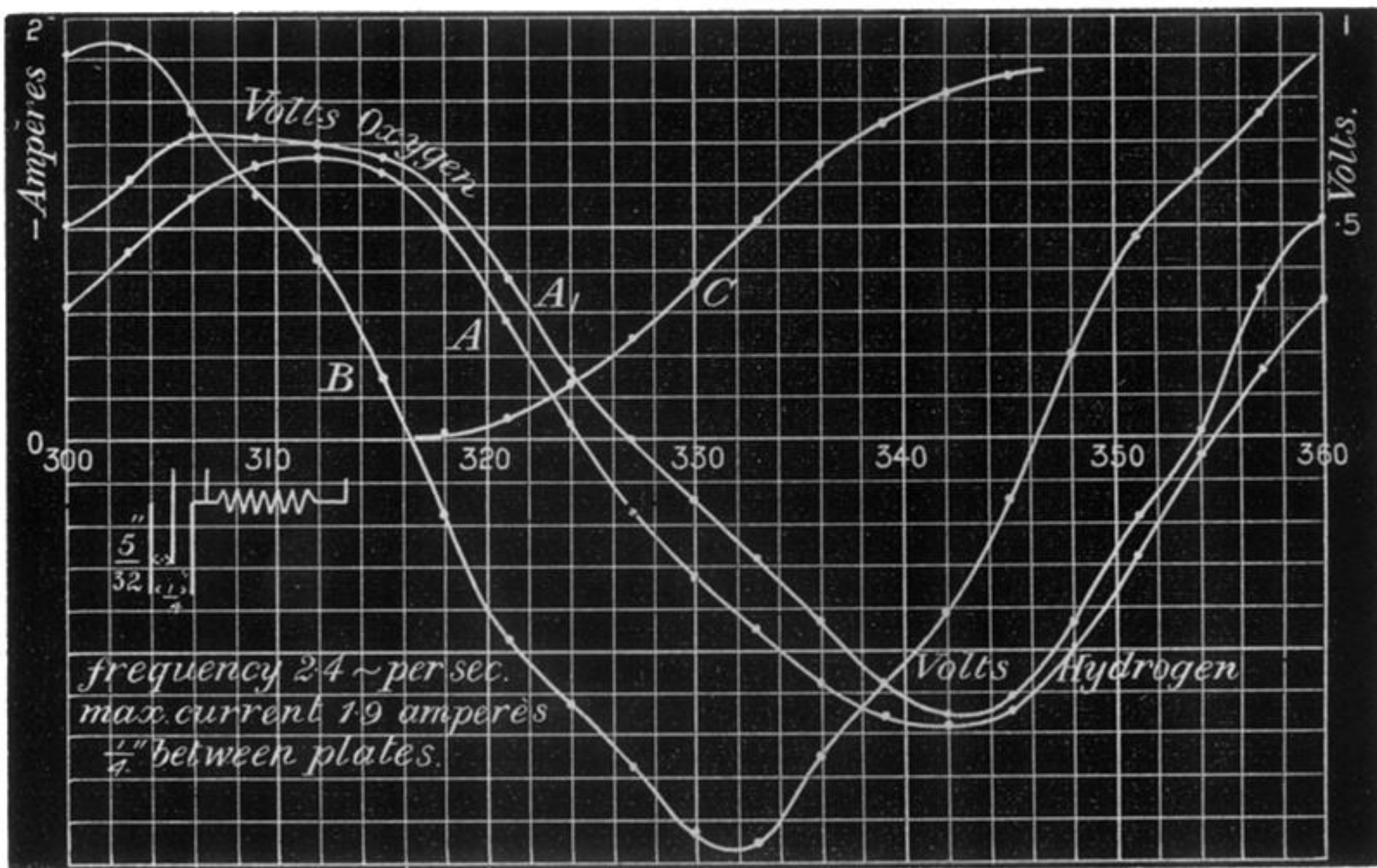


FIG. 8.

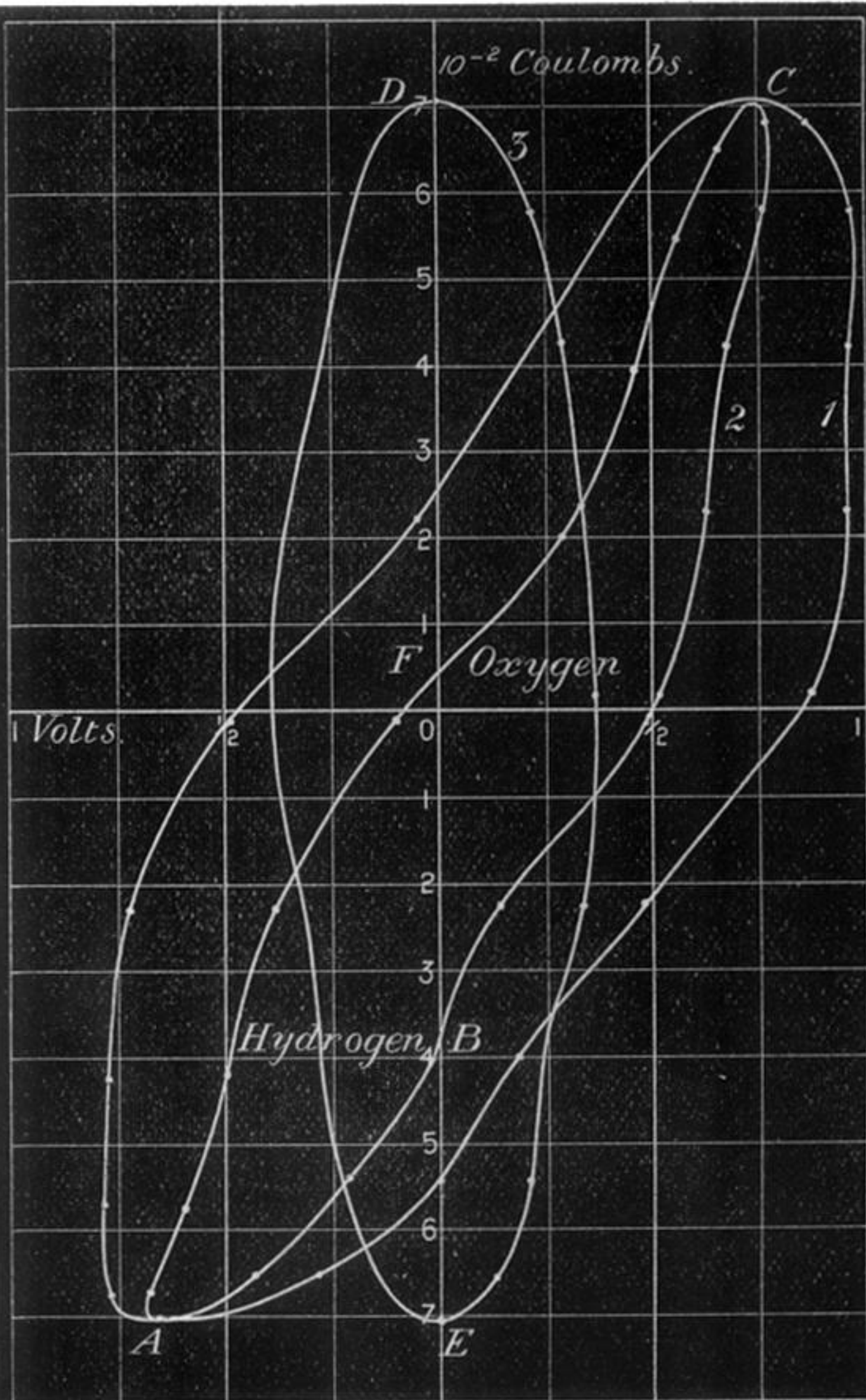


FIG. 9.

