The Silver Voltameter. Part I. Part II

F. E. Smith, T. Mather and T. M. Lowry

Phil. Trans. R. Soc. Lond. A 1908 **207**, 545-599
doi: 10.1098/rsta.1908.0013

XIII. *The Silver Voltameter.*

PART I.—*By* F. E. SMITH, *A.R.C.Sc.*, *and* T. MATHER, *F.R.S.*

PART II.—*By* F. E. SMITH, *A.R.C.Sc.*, *and* T. M. LOWRY, *D.Sc.*

(*Communicated by* R. T. GLAZEBROOK, *F.R.S.*)

Received July 22,—Read November 21, 1907.

(*From the National Physical Laboratory.*)

[PLATE 9.]

PRINCIPAL CONTENTS.

PART I.

PART II.

INTRODUCTION.

IT has been known for several years that the measurement of electric quantity by the electro-deposition of silver is liable to inaccuracies which appear to be dependent on the condition of the anode, kathode, and electrolyte of the voltameter (or coulometer) employed. In 1884 Lord RAYLEIGH* and Mrs. SIDGWICK found that a small quantity of silver acetate added to a solution of silver nitrate or of silver chlorate apparently increased the mass of silver deposited per ampere-second, and in 1895 RODGER and WATSON† showed that the silver voltameter was liable to give results varying by as much as 1 part in 1000 when the same solution of silver nitrate was repeatedly used. The latter effect was thought to be due to the formation of a complex silver salt, and in 1899 RICHARDS, COLLINS, and HEIMROD‡ practically confirmed this view. A new form of silver voltameter was suggested by the latter observers, and this has been frequently used for observations of precision. In 1898 KAHLE§ made a very large number of measurements, using platinum and silver bowls as kathodes and silver nitrate solutions, treated in various manners and from many sources, as electrolytes. He found that the deposit of silver per colomb was greater on a silver surface than on one of platinum; that it increased with the continued use

---

* RAYLEIGH and SIDGWICK, 'Phil. Trans.,' 175, p. 411, 1884.

† RODGER and WATSON, 'Phil. Trans.,' A, 186, p. 631, 1895.

‡ RICHARDS, COLLINS, and HEIMROD, 'Proc. Am. Ac.,' 35, p. 123, 1899.

§ KAHLE, 'Zeitschr. Inst.,' 18, pp. 229–267, 1898.

of a solution, and that the nature of the deposit also varied with the solution employed. In 1892 SCHUSTER and CROSSLEY* discovered that the mass of silver deposited was related to the pressure and also to the size of the silver anode; the pressure effect was verified by KAHLE,† RICHARDS,‡ and MYERS,§ and the latter observer found an increase when the liquid was saturated with nitrogen, but a decrease when the dissolved gas was carbon dioxide. MERRILL|| repeated the pressure experiments and found no effect due to change of pressure alone. Lord RAYLEIGH and Mrs. SIDGWICK observed an increase of deposit with increase of temperature; RICHARDS, COLLINS, and HEIMROD obtained greater deposits at 60° C. and at 0° C. than at 20° C. LEDUC¶ found a decrease with increasing temperature, and MERRILL|| suggests that the mass is independent of the temperature.

In more recent years GUTHE** and VAN DIJK†† have made a special study of various forms of voltameters. The form suggested by RICHARDS was found by him to give a smaller deposit of silver than the form originally devised by Lord RAYLEIGH. The difference between the two forms found by RICHARDS in 1899 was 80 parts in 100,000; in 1902 he found 44 parts in 100,000; WATSON,‡‡ in 1901, obtained a difference of 26; GUTHE, in 1904, found 48, and in the same year VAN DIJK observed a difference of 23. VAN DIJK also compared the syphon and Rayleigh types and found a mean difference of 8 parts in 100,000, the latter form giving the heavier deposit; if a very doubtful observation is excluded, the mean difference is 18 parts in 100,000. In addition, VAN DIJK observed a difference due to the size of the platinum bowls, the smaller one invariably containing the lighter deposit for the same form of voltameter. There are many other interesting differences which need not now be enumerated; sufficient has been written to show that the silver voltameter could not be regarded as an instrument of high precision. The international ampere is, however, defined in terms of the deposit of silver, and the Conference on Electric Units at Charlottenburg in October, 1905, reaffirmed this definition, but expressed the opinion that the information before it was not sufficient to enable it to lay down exact directions in respect to the silver voltameter to be employed. Hence the necessity for an enquiry to ascertain the possibility of specifying a voltameter which is easily reproducable and in which an ampere-second always deposits the same mass of silver.

[*] SCHUSTER and CROSSLEY, 'Roy. Soc. Proc.,' 50, p. 344, 1892.

[†] KAHLE, 'Brit. Assoc. Report,' Section A, 1892.

[‡] RICHARDS and HEIMROD, 'Proc. Am. Ac.,' 37, p. 415, 1902.

[§] MYERS, 'WIED. Ann.,' 55, p. 288, 1895.

[||] MERRILL, 'Phys. Rev.,' 10, p. 167, 1900.

[¶] LEDUC, 'Journ. de Phys.,' 1, p. 561, 1902.

[**] GUTHE, 'Phys. Rev.,' 19, p. 138, 1904. 'Bull. Bureau of Stands.,' vol. 1, No. 1, p. 28, 1906.

[††] VAN DIJK and KUNST, 'Ann. der Phys.,' 14, p. 569, 1904. VAN DIJK, 'Ann. der Phys.,' 19, p. 249, 1906.

[‡‡] WATSON, 'Phil. Trans.,' 1898, p. 445, 1902.

For convenience this communication is divided into two parts. In some of the very early experiments it was found that the mass of the deposit was dependent on the mode of preparation of the silver nitrate. A considerable quantity of the crystallised salt was necessary for the observations, and for economy and experience the salt was recovered from the used solutions by recrystallising. The first products gave very remarkable results, both as regards the deposited mass and its appearance, but on further purification the normal salt giving normal deposits was obtained. The abnormal results were found to be due to impurities hitherto unsuspected, and which are not usually contained in the salt purchased as pure in the ordinary way; they appear to arise in the manipulation of the solution, the fusion of the salt, and its long exposure to the air. These impure solutions are dealt with in the second part of this communication. In the measurements discussed in the first part the pure salt only was used.

PART I.

A Comparison of Various Forms of Silver Voltameters, by F. E. Smith, *A.R.C.Sc.; and a Determination of the Electrochemical Equivalent of Silver,*

by F. E. Smith, *A.R.C.Sc., and* T. Mather, *F.R.S.*

Description of the Voltameters.

Eleven platinum vessels and two silver ones have been used for the kathodes of the voltameters. The dimensions, approximate masses, capacities, &c., of these vessels are given in the following table. We are indebted to Messrs. Johnson, Matthey and Co. for the loan of the vessels A, B, C, D, L, and M.

Letter by which the vessel is indicated in Table I.	Shape.	Approximate mass in grammes.	Diameter at mouth, in centimetres.	Depth, in centimetres.	Maximum capacity, in cubic centimetres.	Convenient volume of electrolyte, in cubic centimetres.
A	Bowl	80	10	8·2	570	300–450
B	,,	80	10	8·2	570	300–450
C	,,	83	10	8·2	570	300–450
D	,,	87	10	8·2	570	300–450
E	,,	78	10	3·8	250	150–200
F	,,	30	10	4·5	280	150–200
G	,,	30	10	4·5	280	150–200
(Silver) HS	,,	85	10	6·5	450	300–400
(Silver) KS	,,	90	10	6·5	450	300–400
L	,,	65	6·3	6·0	170	100–130
M	Ring	65	7·7	5·7	—	—
N	Bowl	39	6·0	4·1	75	50
O	Crucible	39	4·1	5·0	50	40

L, M, and N are platinum vessels with lateral projecting ears to support them during electrolysis. L is nearly cylindrical in shape, M is a cylindrical *ring* only, and N is hemispherical. The vessels N and O were very kindly lent to the National Physical Laboratory by Professor G. VAN DIJK; N is the small bowl referred to as B in Professor VAN DIJK'S papers,* and O is one of the crucibles indicated by I. and II. For the vessel E we are indebted to Professor AYRTON.

The Anodes.

An anode usually consisted of a pure silver plate, 5·0 × 5·0 × 0·4 centims., held by a silver rod riveted through its centre. The silver was obtained from Messrs. Johnson, Matthey and Co. Before employing it for a determination of the electrochemical equivalent of silver, about 10 grammes of silver were deposited electrically on the plate, and on these occasions a platinum bowl with a deposit of silver on its inner surface was generally used as the anode. In this way the silver was always removed from the platinum bowls, but not from those of silver. When new, the surface of a platinum vessel is free from scratches, and silver deposited on it adheres much better than to a scratched surface; it is important, therefore, to avoid the use of a spatula. The electrical method removes the deposit, cleans the platinum, and at the same time prepares the anode. Shortly before using, the latter was washed with distilled water and dried in an electric oven. The platinum bowls were rinsed with distilled water and strong nitric acid, and if much of the dark silver salt Ag_7NO_{11} adhered to the platinum the washing with nitric acid was repeated. Distilled water was finally used and the bowls dried in an electric oven at 160° C.

For the Richards form of voltameter silver rods of two sizes were used; some of the rods were 1 centim. in diameter and the others 2·5 centims. These rods were also coated with electrically deposited silver.

The Electrolyte.

For the comparison of various types of voltameters the electrolyte was usually a 15 per cent. solution of pure silver nitrate in water. The silver nitrate was sometimes purchased and sometimes recovered from used solutions. A description of the preparation of the pure salt is given in Part II., p. 585, of this communication.

Form of Voltameters.

The following types were used:—

(1) *The Rayleigh Form* (fig. 1).—In this the kathode was usually a platinum bowl and the anode a silver plate or rod coated with electrically deposited silver. The anode was inserted in a cup made of filter paper, the folds in the paper being secured

---

[*] VAN DIJK and KUNST, 'Ann. der Phys.,' 14, p. 569, 1904. VAN DIJK, 'Ann. der Phys.,' 19, p. 249, 1906.

with a little sealing-wax. The silver plate was immersed in the solution just below the surface, and the sealing wax which secured the folds of the filter paper was at least 2 centims. above the surface of the electrolyte. The filter cup was supported by three platinum wires from an ebonite ring.

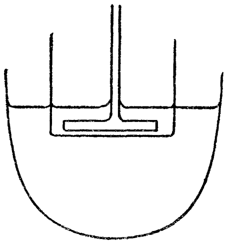
Fig. 1.

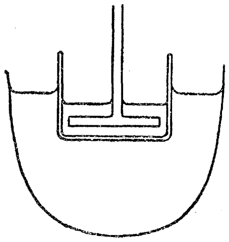
Fig. 2.

(2) *The Richards Form* (fig. 2).—A platinum bowl was in general used for the kathode, and the anode was of the same form as that of the Rayleigh voltameter. It was, however, surrounded by a fine-grained porous pot instead of a filter paper, and the electrolyte inside the pot was maintained at a lower level than the electrolyte in contact with the kathode. Usually no appreciable change in the difference of level resulted during an experiment, but a small syphon was frequently employed to ensure an approximately constant difference. Two of the porous pots were made by the Akron Insulator and Marble Company, of the United States of America, and were obtained for us by Dr. GUTHE; several were made by PUKAL, of Berlin; and others were from an unknown source.

(3) *The Syphon Form* (fig. 3).—The kathode was a platinum bowl and the anode a silver plate or silver bowl coated with electrically deposited silver. When a silver plate was used, it was contained in a glass dish, the electrolyte in the latter being connected with that in the platinum bowl by a glass syphon. Two sizes of syphon were used; one was 30 sq. centims. in its narrowest part and 30 centims. in axial length, the other was 8 sq. centims. section and 20 centims. in axial length.

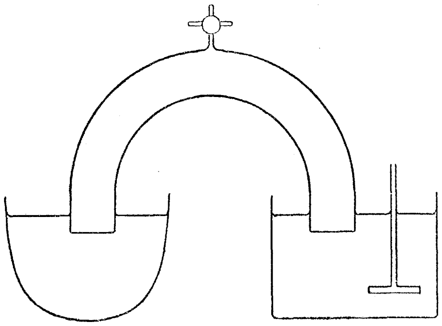
Fig. 3.

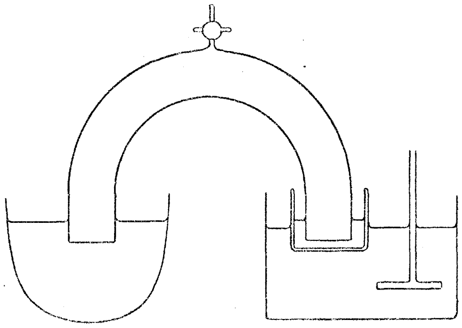
Fig. 4.

(4) *The Pot-Syphon-Bowl Form* (*P.S.B.*) (fig. 4).—In this the liquid in the syphon was separated from that in the anode vessel by a porous pot. Any *advantages* of the Richards form were thus combined with those of the syphon.

(5) *The Syphon-Pot-Bowl Form* (*S.P.B.*) (fig. 5).—In this the liquids in the syphon and kathode vessel were separated by a porous pot. Any *disadvantages* of the Richards form were thus introduced without eliminating any advantage of the syphon.

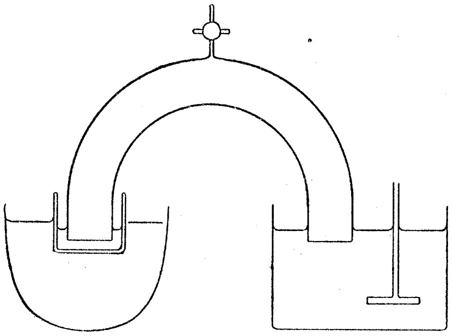

Fig. 5.

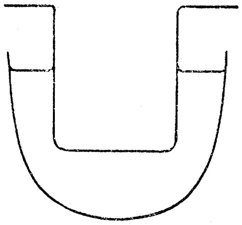

Fig. 6.

(6) *The Elevated Kathode Form* (fig. 6).—A silver bowl with electrically deposited silver formed the anode, and a platinum ring, or platinum bowl of smaller diameter than that of the silver bowl, formed the kathode. If a heavy anode liquid was formed, it would not come into such intimate contact with the kathode as in the Rayleigh form.

(7) *Several Modifications of the above.*—(*a*) The silver anode in the Rayleigh type was replaced by a platinum anode; (*b*) for the filter paper of the Rayleigh form a porous pot drilled with fine holes was substituted, and purified asbestos was placed in the pot to prevent any anode slime reaching the kathode; (*c*) in addition to the filter paper a china filter cup with very fine holes surrounded the anode of the Rayleigh form. The internal resistance was thus increased 100 times, and the potential difference between anode and kathode was correspondingly increased.

In all of the forms the platinum bowls used as kathodes were supported on brass rings mounted on ebonite, and the silver rods supporting the anodes were clamped to a metal arm projecting from a rod similarly mounted. From 300 to 400 cub. centims. of solution were used in the large bowls and about 30 to 40 cub. centims. in the small crucible loaned to us by Professor VAN DIJK. The solution was introduced by means of a pipette and was similarly removed after the required amount of silver was deposited. The liquid was carefully examined for loose silver, and if any was found, the solution and the water used for washing the deposit were filtered through a hard filter paper, the particles of the silver washed to the lowest part of the paper, and the latter dried in an electric oven. By the aid of a pointed glass rod the loose silver was transferred to the bowl. The main portion of the deposit was washed by rinsing three or four times with distilled water, after which the bowl was filled with water and left overnight. This last wash-water rarely showed more than the faintest bluish colour on addition of neutral NaCl solution. Two more rinsings with water followed, and then the bowl was dried by heating in an electric oven at 160° C.

Electrical Arrangements.

With the exception of that portion of the circuit which included the silver voltameters, the apparatus and its arrangement was the same as that used in the determination of current in absolute measure by the British Association (Ayrton-Jones) Ampere Balance.* The current which it was necessary to pass through a standard resistance at a known temperature in order that the potential difference on its terminals just balanced the E.M.F. of a Weston cadmium cell at a constant temperature, was determined by the balance, and for other slightly different temperatures of the coil and cell the change of current was calculated from their temperature coefficients. Neither cell nor coil was assumed to remain constant except over very short periods of time, and as the change in E.M.F. of the cell was determined to be not greater than 1 part in 100,000 in eighteen months and the secular change of the resistance coil was easily determined by comparison with the National Physical Laboratory Standards, no appreciable error was thus introduced. The probable error of the measure of the current in absolute units is shown in the communication dealing with the ampere balance to be about 2 parts in 100,000, and the mass of silver deposited per ampere-second in the silver voltameter is subject to the same error.

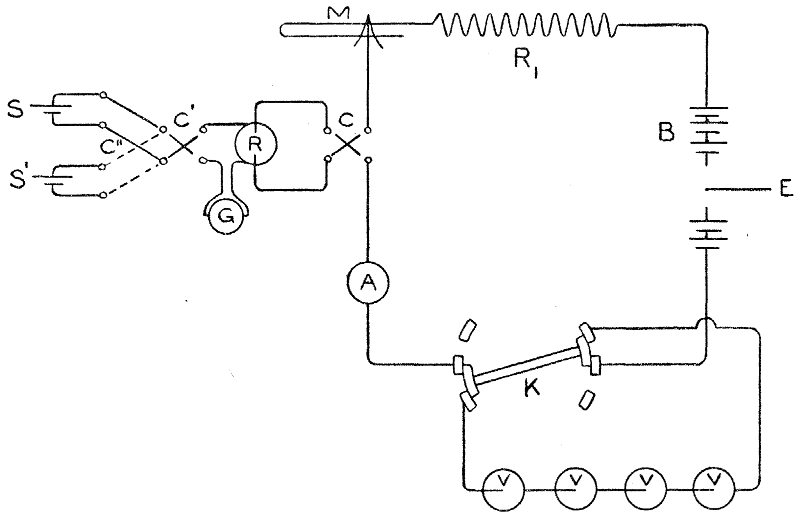

Fig. 7.

The arrangement of the apparatus is represented by fig. 7. The current was furnished by a battery B of 55 accumulators of 30 ampere-hours capacity, and in series with it were placed a three-dial adjustable resistance R_1 of 111 ohms, a double-groove mercury trough M for fine adjustment of the current, a standard resistance R of manganin strip built to carry a current of 10 amperes, an ammeter A, and the voltameters V. The latter were put in and out of the circuit by the switch K. This was specially designed to close the circuit of a chronograph at the same time as that of the voltameters and to close it again when the latter circuit

---

* Ayrton, Mather, and Smith, 'Phil. Trans.,' A 207, p. 518, 1908.

was opened. The precision with which this was secured was tested by placing a second chronograph and battery in place of the silver voltameters and noting the difference in the intervals of time recorded by the two instruments. The mean of 20 readings indicated a difference of a little less than one-hundredth of a second, which is equivalent to an error of 1 part in 600,000 in the observations made with the voltameters. The time was measured by the standard clock presented to the National Physical Laboratory by Lady Galton. The rate of the clock was determined by means of signals from Kew and Greenwich. The battery was earthed at such a point, E, that the mean difference of potential between the voltameters and the earth was very nearly zero, but the insulation of all the apparatus from earth was also very carefully attended to. The switches C and C′ were on one board and could not be separately operated; C reversed the current through the standard resistance, and C′ reversed the connections of the standard cell to the potential points of the resistance. C″ is a switch for placing either of two cells S, S′ in the potentiometer circuit; S′ was employed for the adjustment of the current before including the voltameters in the circuit, and S continually afterwards. No secondary potentiometer circuit was used. The resistance coils of R_1 were of manganin and were immersed in a large bath of paraffin oil. The double mercury trough M was bridged by a copper sliding piece which shunted a portion of the resistance of the trough and allowed of a fine adjustment. A change in current of 1 part in 1,000,000 was easily detected, and sometimes a current constant to this amount could be maintained for an hour or more. G was a galvanometer of the Broca type of 1000 ohms resistance.

The circuit was at first closed so as to exclude the voltameters, and remained closed for 1 hour or more before any adjustment for constancy of current was made. On many occasions a determination of current in absolute measure preceded the deposition of silver. This usually occupied 20 minutes; immediately afterwards R_1 was diminished by an amount comparable with that of the voltameters and the latter switched into the circuit. With the Rayleigh form of voltameter a current steady to 1 part in 100,000 was secured within 20 seconds after closing the circuit; a slightly longer time was necessary for the Richards type and longer still for the largest of the syphons.

Owing to the difficulty of maintaining a steady current through the syphon and other modified forms of voltameters, some of the observations are relative only. In these latter cases the standard is the Rayleigh form, but the constancy of this had been well established before any relative observations were made. In order to distinguish between the relative and the absolute values, we have placed an asterisk against all absolute determinations.

When Lord Rayleigh* determined the electrochemical equivalent of silver, the current that passed through the voltameters also passed through the standard current balance, and was thus directly determined in absolute measure. We also might have

---

* Rayleigh and Sidgwick, 'Phil. Trans.,' 175, p. 411, 1884.

adopted this method, but, owing to the ampere balance being less steady when a current passes through it for more than half an hour, the measurement of the current through the voltameters would have been subject to a comparatively large error. By frequently standardising a combination of resistance coil and cadmium cell (as already described) and employing these for the measurement of current through the voltameters, the probable error was appreciably reduced.

Mass of Deposits.

The large bowls were weighed on a balance by L. Oertling, sensitive to one-fiftieth of a milligramme; the small bowls were weighed on a more sensitive balance by Oertling, and very kindly lent by Mr. Oertling for this work, or on a balance by Ruprecht, which was loaned to the National Physical Laboratory by Dr. Scott, of the Davy-Faraday Laboratory. All weighings were made by the method of Gauss, a similar vessel being used as a tare. The mass of silver usually deposited was about 7 grammes in the large bowls and a single weight of 7 grammes was used to counterpoise; the difference was obtained by means of a rider. The weight employed was standardised by comparison with a 100-gramme weight from Sèvres. For difference determinations the four bowls A, B, C, D were largely used.

To reduce the error of weighing we have found it convenient to compare the masses of the bowls when empty and again with the deposits of silver. The following example is one with the bowls containing silver, and gives an idea of the error introduced:—

Observation.	Bowls.	Difference in mass in grammes.	Calculated from observations	Difference in mass. Mean value in grammes.
1	A and B	+0·49678 682 676	2 and 4 3 „ 5	+0·49679
2	A „ C	−3·94383 387 389	1 „ 4 3 „ 6	−3·94386
3	A „ D	−6·58421 419 415	1 „ 5 2 „ 6	−6·58418
4	B „ C	−4·44065 061 065	1 „ 2 5 „ 6	−4·44064
5	B „ D	−7·08097 099 097	1 „ 3 4 „ 6	−7·08098
6	C „ D	−2·64032 038 032	2 „ 3 4 „ 5	−2·64034

It is of interest to state that the diminution in mass of these four bowls from June, 1906, to June, 1907, is 0·8 milligram only. The electrical method of removing the deposit from the bowl does not take the platinum into solution, and the mass of any one bowl in a series of five or six experiments remains constant to 0·1 milligramme. We observed this constancy and found it a most useful check on our weighings of the empty vessels.

As the results of our observations differ very materially from those of nearly all other workers on the same subject, we include particulars of the kathode, anode, solution, current and deposit in Table I. These results are in chronological order and include the measurements discussed in Part II. of this paper.

When two or more voltameters were placed in series and the same current passed through each, the results of the observations are indicated by the same number, but by different letters. For those observations in which the current was maintained steady throughout the time of the deposit, the value of the current in amperes (10^{-1} C.G.S. unit) is stated to 1 part in 1,000,000. This is for the accurate comparison of results; the error of this measure is about 2 parts in 100,000. The time is recorded to one-hundredth of a second and is probably correct to 0·1 second. When the observations were made merely for the comparison of different forms of voltameters and the current was not maintained steady, the approximate value of the current only is given. Except in four special cases (43*a*, *b*, *c*, *d*) the electrochemical equivalent is calculated to 1 part in 100,000.

Under the heading of solution, letters are given which indicate the source of the silver nitrate crystals; H, M, G, and W are samples of silver nitrate purchased from four different manufacturing chemists, and when more than one sample was purchased from the same firm a number accompanies the letter. LR indicates that the salt was recrystallised by LOWRY, and SR that the same process was conducted by SMITH. WS is a solution from Professor WATSON, and the VD solutions were prepared from salt recrystallised by Professor VAN DIJK. The degree of electrolysis of the solution, *i.e.*, the ratio of the silver previously deposited by the passage of an electric current through the solution to that present in the solution is stated in column 8, and some brief notes on the appearance of the deposits appear in the last column. The pressure to which the electrolyte was subjected and its temperature are also stated, but only when these differed from the pressure and temperature of the air of the room in which the observations were made.

In column 4, R denotes the Rayleigh form of voltameter, P the Richards (porous pot) form, S the syphon form, P.S.B. and S.P.B. the arrangements we have called the pot-syphon-bowl, and syphon-pot-bowl forms, respectively, and EL.K. the elevated kathode form.

TABLE I.

Observation.	Date.	Kathode bowl.	Form of voltameter.	Solution.				Mass of silver deposit in grammes.	Time in seconds.	Current in amperes.	Milligrammes of silver per coulomb.	Remarks on deposit, pressure, temperature, &c.
				Source of crystals.	Concentration.	Added impurities.	Degree of electrolysis.					
	1905.				per cent.							
1*a*	2.12	F	P	Part recovered, part purchased.	15	—	0	7 ·00052	6147	1 ·01826$_5$	1 ·11842*	(1 to 13.) Many of the deposits were striated, and in the bowls E, F, G there was considerable trouble with loose silver. On several occasions the time was not accurately known.
1*b*	2.12	G	,,		15	—	0	126	6147	26_5	54*	
2*a*	16.12	F	,,		15	—	0	6 ·86359	6027 ·1	28_6	34*	
2*b*	16.12	G	,,		15	—	0	321	6027 ·1	28_6	28*	
	1906.											
3*a*	3.1	F	,,		15	—	0	6 ·99982	6147	19_7	39*	
3*b*	3.1	G	,,		15	—	0	7 ·00008	6147	19_7	43*	
4*a*	12.1	F	,,		15	—	0	6 ·99034	6141 ·8	16_2	786*	
4*b*	12.1	E	R		15	—	0	484	6141 ·8	16_2	858*	
4*c*	12.1	G	,,		15	—	0	564	6141 ·8	16_2	70*	
5*a*	27.1	F	P		15	—	0	6 ·98803	6138 ·2	19_6	10*	
5*b*	27.1	E	R		15	—	0	6 ·99070	6138 ·2	19_6	53*	
5*c*	27.1	G	,,		15	—	0	040	6138 ·2	19_6	48*	
6	10.2	HS	P		15	—	0	7 ·92422	6960 ·1	19_0	18*	
7*a*	17.2	F	R		15	—	0	7 ·00086	6147 ·9	16_4	42*	
7*b*	17.2	G	P		15	—	0	6 ·99911	6147 ·9	16_4	15*	
8	20.2	F	R		15	—	0	6 ·00786	5275 ·9	16_6	42*	
9*a*	24.2	A	P		15	—	0	7 ·00001	6146 ·93	21_9	41*	
9*b*	24.2	B	R		15	—	0	6 ·99975	6146 ·93	21_9	36*	
9*c*	24.2	E	,,		15	—	0	945	6146 ·93	21_9	32*	
10*a*	3.3	A	P		15	—	0	7 ·00081	6147 ·07	18_6	54*	Kathode rotated.
10*b*	3.3	B	R		15	—	0	280	6147 ·07	18_6	86*	,, ,,
10*c*	3.3	HS	P		15	—	0	6 ·99844	6147 ·07	18_6	17*	
10*d*	3.3	E	R		15	—	0	7 ·00243	6147 ·07	18_6	80*	
11*a*	10.3	A	,,		15	—	0	6 ·99647	6142 ·88	22_8	57*	
11*b*	10.3	B	P		15	—	0	492	6142 ·88	22_8	32*	
11*c*	10.3	HS	R		15	—	0	659	6142 ·88	22_8	59*	
11*d*	10.3	KS	P		15	—	0	439	6142 ·88	22_8	23*	
12*a*	17.3	A	R		15	—	0	7 ·00221	6147 ·87	17_9	63*	Kathode rotated.
12*b*	17.3	B	,,		15	—	0	240	6147 ·87	17_9	66*	,, ,,
12*c*	17.3	HS	P		15	—	0	6 ·99977	6147 ·87	17_9	24*	
12*d*	17.3	KS	,,		15	—	0	983	6147 ·87	17_9	25*	
13*a*	24.3	A	,,		15	—	0	768	6146 ·90	21_1	05*	
13*b*	24.3	HS	,,		15	—	0	807	6146 ·90	21_1	11*	
13*c*	24.3	B	,,		15	—	0	804	6146 ·90	21_1	10*	
13*d*	24.3	KS	,,		15	—	0	811	6146 ·90	21_1	12*	
14*a*	4.4	A	R	H_1	15	—	0	7 ·06863	6208 ·08	20_0	27*	No striæ.
14*b*	4.4	HS	,,	H_1	15	—	0	854	6208 ·08	20_0	25*	,, ,,
15*a*	9.4	KS	,,	H_1	15	—	0 ·5	6 ·99907	6147 ·01	19_8	26*	,, ,,
15*b*	9.4	A	,,	H_1	15	—	0 ·5	882	6147 ·01	19_8	22*	,, ,,

16*a*	9.4	HS	,,	H_1	15	—	0·75	6·99983	6147·95	16_5	1·11825*	Faint striæ.
16*b*	9.4	B	,,	H_1	15	—	0·75	961	6147·95	16_5	22*	,, ,,
17*a*	24.4	HS	,,	H_1	15	—	15	908	6147·16	21_5	22*	,, ,,
17*b*	24.4	KS	,,	H_1	15	—	1·0	977	6147·16	21_5	33*	,, ,,
17*c*	24.4	A	,,	H_1	15	—	1·0	938	6147·16	21_5	27*	,, ,,
17*d*	24·4	B	,,	H_1	15	—	0	930	6147·16	21_5	25*	No striæ.
18*a*	27.4	A	,,	H_1	15	—	1·25	942	6146·92	16_2	38*	Faint striæ.
18*b*	27.4	HS	,,	H_1	15	—	1·25	956	6146·92	16_2	40*	,, ,,
18*c*	27.4	B	,,	H_1	15	—	0	870	6146·92	16_2	26*	No striæ.
19	1.5	A	,,	H_1	15	—	0	908	6146·91	19_1	29*	Pressure = 8 centims. mercury.
20	2.5	B	,,	H_1	15	—	0	917	6147·12	20_6	25*	,, = 8 ,, ,,
21*a*	4.5	A	,,	H_1	15	—	1·50	7·00075	6148·12	18_8	34*	
21*b*	4.5	B	,,	H_1	15	—	0	042	6148·12	18_8	29*	,, = 2·5 ,, ,,
21*c*	4.5	HS	,,	H_1	15	—	1·50	047	6148·12	18_8	30*	
22*a*	9.5	A	P	H_1	15	—	0	6·92886	6086·87	21_1	797*	
22*b*	9.5	B	R	W_1	15	—	0	987	6086·87	21_1	813*	
22*c*	9.5	HS	,,	H_1	15	—	0	6·93057	6086·87	21_1	25*	
23*a*	16.5	A	,,	WS	15	—	?	7·00161	6146·93	16_2	72*	Striæ marked.
23*b*	16.5	B	,,	W_1	15	—	0	6·99821	6146·93	16_2	18*	
23*c*	16.5	HS	,,	Fused	15	—	0	7·00093	6146·93	16_2	61*	Striæ.
23*d*	16.5	KS	,,	H_1	15	—	30	6·99911	6146·93	16_2	32*	Solution-blue.
24*a*	21.5	A	,,	LR	15	—	0	897	6146·95	18_5	27*	
24*b*	21.5	B	,,	LR	15	—	0	880	6146·95	18_5	25*	
24*c*	21.5	HS	,,	H_1 fused	15	—	0	963	6146·95	18_5	38*	The crystals were just fused.
24*d*	21.5	KS	,,	H_1	15	Nitrite	0	926	6146·95	18_5	32*	Faint striæ.
25*a*	23.5	A	,,	W_1	15	—	0	824	6146·70	13_9	25*	Very small anode.
25*b*	23.5	B	,,	W_1	15	—	0	781	6146·70	13_9	18*	Very large anode.
25*c*	23.5	HS	,,	W_1 fused	15	—	0	888	6146·70	13_9	35*	Fused for 15 minutes.
25*d*	23.5	KS	,,	H_1	15	—	0	843	6146·70	13_9	28*	
26*a*	30.5	HS	,,	LR	15	—	0	7·00006	6148	1·0 variable	30	
26*b*	30.5	KS	,,	LR	15	—	0	6·99987	6148	1·0 ,,	27	
26*c*	30.5	A	,,	W_1	15	—	0·25	7·00049	6148	1·0 ,,	37	Very small anode.
26*d*	30.5	B	,,	W_1	15	—	0·25	031	6148	1·0 ,,	34	Very large anode.
27*a*	21.6	HS	,,	H_2	15	—	0	6·99858	6146·93	1·01812$_5$	28*	
27*b*	21.6	KS	,,	M. liquor	15	—	0	7·01817	6146·93	12_5	1·12141*	Very much striated.
27*c*	21.6	A	,,	LR	15	—	0	6·99861	6146·93	12_5	1·11828*	
27*d*	21.6	B	,,	LR	15	—	0	871	6146·93	12_5	30*	
28*a*	29.6	HS	,,	H_2	15	—	0	933	6146·93	18_9	33*	Loose deposit.
28*b*	29.6	A	,,	LR	15	—	0	903	6146·93	18_9	28*	,, ,,
28*c*	29.6	B	,,	LR	15	—	0	892	6146·93	18_9	26*	,, ,,
29*a*	3.7	A	,,	LR	15	—	0	938	6147·13	22_0	27*	Slight striæ.
29*b*	3.7	B	,,	H_2	15	—	0	952	6147·13	22_0	29*	
30*a*	7.7	HS	,,	G_1	15	—	0	854	6147·08	10_6	27*	
30*b*	7.7	KS	,,	LR	50	—	0	856	6147·08	10_6	27*	Coarse striæ.
30*c*	7.7	A	,,	M. liquor	15	—	0·25	7·01283	6147·08	10_6	1·12055*	Very much striated.
30*d*	7.7	B	,,	M	15	—	0	6·99832	6147·08	10_6	1·11823*	
31*a*	12.7	HS	,,	H_2	15	—	0	895	6147·09	15_5	28*	
31*b*	12.7	KS	,,	W_1	15	—	0	840	6147·09	15_5	19*	
31*c*	12.7	B	,,	—	?	Acetate solution	0	7·01935	6147·09	15_5	1·12154*	Fine matt deposit.
32*a*	16.7	A	P	M	15	—	0	6·99678	6147	1·0 variable	1·11813	Kathode solution acid.
32*b*	16.7	B	R	M	15	—	0	768	6147	1·0 ,,	27	
32*c*	16.7	KS	S	M	15	—	0	756	6147	1·0 ,,	25	
33*a*	21.7	KS	R	H_2	10	—	0	7·00018	6148	1·0 ,,	27	

TABLE I. (continued).

Obser-vation.	Date.	Kathode bowl.	Form of volta-meter.	Solution.				Mass of silver deposit in grammes.	Time in seconds.	Current in amperes.	Milli-grammes of silver per coulomb.	Remarks on deposit, pressure, temperature, &c.
				Source of crystals.	Concen-tration.	Added impurities.	Degree of electro-lysis.					
	1906.				per cent.							
33*b*	21.7	A	PSB	H_2	10	—	0	7 ·00005	6148	1 ·0 variable	1 ·11825	Pot, Akron. Cruc. Co.
33*c*	21.7	B	P	H_2	10	—	0	026	6148	1 ·0 ,,	28	,, ,, ,,
34*a*	25.7	HS	R	H_2	10	—	0 ·25	6 ·99681	6148 ·04	1 ·01812$_7$	779*	Platinum anode.
34*b*	25.7	KS	,,	H_2	10	—	0 ·25	988	6148 ·04	12$_7$	828*	
34*c*	25.7	A	P	H_2	10	—	0 ·25	869	6148 ·04	12$_7$	09*	Pot, Akron Cruc. Co.
34*d*	25.7	B	,,	H_2	10	—	0 ·25	841	6148 ·04	12$_7$	05*	Pot, W. and J. George.
35*a*	30.8	A	SPB	LR	10	—	0	6 ·97419	7860	0 ·8 variable	19	Pot, Akron Cruc. Co.
35*b*	30 8	B	PSB	LR	10	—	0	490	7860	0 ·8 ,,	31	,, ,, ,,
35*c*	30.8	C	R	LR	10	—	0	466	7860	0 ·8 ,,	27	
36*a*	4.9	A	SPB	H_2	10	—	0	7 ·02624	7900	0 ·8 ,,	01	Pot, Akron Cruc. Co. acid kathode liquid.
36*b*	4.9	B	PSB	H_2	10	—	0	812	7900	0 ·8 ,,	31	Pot, W. and J. George.
36*c*	4.9	C	R	H_2	10	—	0	787	7900	0 ·8 ,,	27	
37*a*	7.9	A	SPB	H_2	15	—	0 ·25	7 ·04973	7900	0 ·8 ,,	25	,, ,, ,,
37*b*	7.9	B	PSB	H_2	15	—	0 ·25	984	7900	0 ·8 ,,	27	Pot, Pukal.
37*c*	7.9	C	R	H_2	15	—	0 ·25	984	7900	0 ·8 ,,	27	Rotated kathode.
38*a*	11.9	A	,,	G_2	15	—	0	7 ·03110	6147	1 ·0 ,,	27	,, ,,
38*b*	11.9	B	,,	SR	15	—	0	096	6147	1 ·0 ,,	25	,, ,,
38*c*	11.9	C	,,	H_3	15	—	0	108	6147	1 ·0 ,,	27	Drilled porous pot, instead of filter paper around anode
39*a*	13.9	A	,,	M	15	—	0	7 ·00177	7900	0 ·8 ,,	27	
39*b*	13.9	B	P	M	15	—	0	133	7900	0 ·8 ,,	20	Pukal pot.
39*c*	13.9	C	S	M	15	—	0	186	7900	0 ·8 ,,	28	
40*a*	17.9	A	R	M	5	—	0 ·25	7 ·17006	8000	0 ·8 ,,	27	Very small anode.
40*b*	17.9	B	SPB	M	5	—	0 ·25	014	8000	0 ·8 ,,	28	
40*c*	17.9	C	PSB	M	5	—	0 ·25	7 ·16986	8000	0 ·8 ,,	24	
41*a*	24.9	A	P	M	15	—	0 ·50	6 ·99981	6147	1 ·0 ,,	20	Pot, W. and J. George.
41*b*	24.9	B	R	M	15	—	0 ·50	7 ·00029	6147	1 ·0 ,,	27	Very small anode.
41*c*	24.9	C	,,	M	15	—	0 ·50	026	6147	1 ·0 ,,	27	Usual anode.
41*d*	24.9	D	P	M	15	—	0 ·50	6 ·99982	6147	1 ·0 ,,	20	Pot, Akron Cruc. Co.
42*a*	28.9	A	,,	M	15	—	0 ·75	7 ·00463	7900	0 ·8 ,,	22	,, ,, ,,
42*b*	28.9	B	R	M	15	—	0 ·75	496	7900	0 ·8 ,,	27	
42*c*	28.9	C	P	M	15	—	0 ·75	462	7900	0 ·8 ,,	22	Pot, W. and J. George.
42*d*	28.9	D	S	M	15	—	0 ·75	507	7900	0 ·8 ,,	29	
43*a*	2.10	A	R	SR	15	—	0	6 ·99870	6147 ·00	1 ·01814$_1$	26$_9$*	Observations to get an idea of reproducibility of Rayleigh form.
43*b*	2.10	B	,,	SR	15	—	0	867	6147 ·00	14$_1$	26$_4$*	
43*c*	2.10	C	,,	SR	15	—	0	860	6147 ·00	14$_1$	25$_3$*	
43*d*	2.10	D	,,	SR	15	—	0	874	6147 ·00	14$_1$	27$_5$*	
44*a*	6.10	A	,,	LR	15	—	0	895	6147 ·16	15$_0$	27*	Coarse texture.
44*b*	6.10	B	,,	LR	15	—	0	890	6147 ·16	15$_0$	26*	
44*c*	6.10	C	,,	LR	15	—	0	825	6147 ·16	15$_0$	16*	
44*d*	6.10	D	P	LR	15	—	0	729	6147 ·16	15$_0$	00*	Pot, W. and J. George.

45*a*	11.10	A	R	SR	15	—	0 ·25	7 ·00382	7900	0 ·8 variable	1 ·11827	
45*b*	11.10	B	P	SR	15	—	0 ·25	345	7900	0 ·8 „	21	Pot, Akron Cruc. Co.
45*c*	11.10	C	„	SR	15	—	0 ·25	340	7900	0 ·8 „	20	Pot, W. and J. George.
45*d*	11.10	D	PSB	SR	15	—	0 ·25	402	7900	0 ·8 „	30	Pot, Akron Cruc. Co.
46*a*	18.10	A	P	SR	15	—	0 ·5	6 ·99775	6146 ·40	1 ·01820$_3$	16*	Pot, W. and J. George.
46*b*	18.10	B	R	SR	15	—	0 ·5	877	6146 ·40	20$_3$	32*	
46*c*	18.10	C	„	LR	15	—	0	866	6146 ·40	20$_3$	30*	
46*d*	18.10	D	P	LR	15	—	0	867	6146 ·40	20$_3$	31*	
47*a*	25.10	A	R	H_3	15	—	0	7 ·00297	6150 ·50	20$_0$	25*	
47*b*	25.10	B	„	Mother liquor	43	—	0	7 ·02974	6150 ·50	20$_0$	1 ·12252*	Very striated.
47*c*	25.10	C	„	LR	15	Hyponitrite	0	7 ·00954	6150 ·50	20$_0$	1 ·11930*	„ „
48*a*	31.10	A	„	W_2	15	—	0	7 ·01031	6147	1 ·0 variable	826	
48*b*	31.10	B	„	W_2	15	—	0	18	6147	1 ·0 „	24	
48*c*	31.10	C	„	H_3	15	—	0	38	6147	1 ·0 „	27	
49*a*	7.11	A	„	—	10	—	0	7 ·00121	6147	1 ·0 „	39	Chlorate solution. Striæ.
49*b*	7.11	B	„	LR	15	—	0 ·75	045	6147	1 ·0 „	27	
49*c*	7.11	C	P	LR	15	—	0 ·75	047	6147	1 ·0 „	27	Liquor 30 c. in pot (see p. 566).
49*d*	7.11	D	S	LR	15	—	0 ·75	060	6147	1 ·0 „	29	„ 30 c. in anode vessel (see p. 566).
50*a*	21.11	A	R	H_3	15	—	0	000	6147	1 ·0 „	27	
50*b*	21.11	B	„	—	10	—	0	124	6147	1 ·0 „	47	Chlorate solution.
50*c*	21.11	C	„	LR	15	Chloride	0	080	6147	1 ·0 „	40	
50*d*	21.11	D	„	LR	15	Oxide	0	157	6147	1 ·0 „	52	
51*a*	27.11	A	„	H_3	15	—	0	6 ·99907	6147 ·13	1 ·01821$_0$	23*	
51*b*	27.11	L	EL. K	H_3	15	—	0	46	6147 ·13	21$_0$	29*	
51*c*	27.11	C	S	H_3	15	—	0	21	6147 ·13	21$_0$	25*	
51*d*	27.11	D	EL. K	H_3	15	—	0	27	6147 ·13	21$_0$	26*	
52*a*	4.12	A	R	H_3	15	—	0	7 ·00108	6147	1 ·0 variable	27	No striæ.
52*b*	4.12	B	„	VD	15	—	0	233	6147	1 ·0 „	47	Striated.
52*c*	4.12	C	„	LR	15	—	0	165	6147	1 ·0 „	36	„
52*d*	4.12	D	„	LR	15	Nitrite	0	170	6147	1 ·0 „	37	„
53*a*	6.12	A	„	H_3	15	—	0 ·25	106	6150	1 ·0 „	27	
53*b*	6.12	B	„	LR	15	Carbonate	0	227	6150	1 ·0 „	46	
53*c*	6.12	C	„	LR	15	—	0	210	6150	1 ·0 „	44	
53*d*	6.12	D	„	LR	15	Acid	0	104	6150	1 ·0 „	27	0 ·01 per cent. acid.
54*a*	10.12	A	„	H_1	15	—	0 ·50	7 ·11542	6147	1 ·0 „	27	
54*b*	10.12	B	„	H_3	15	—	0 ·50	73	6147	1 ·0 „	32	
	1907.											
55*a*	1.1	C	R	H_3	15	—	0 ·50	7 ·00472	6147	1 ·0 „	27	
55*b*	1.1	B	„	H_3	15	—	0 ·50	372	6147	1 ·0 „	11	Platinum anode.
55*c*	1.1	A	S	H_3	15	—	0 ·50	500	6147	1 ·0 „	31	
56*a*	6.1	A	R	H_3	15	—	0 ·75	7 ·10382	50 hours	0 ·03 „	27	
56*b*	6.1	B	„	H_3	15	—	0 ·75	411	50 „	0 ·03 „	32	High resistance.
57*a*	8.1	A	„	H_3	15	—	0 ·25	6 ·02142	14 „	0 ·1 „	27	
57*b*	8.1	B	P	H_3	15	—	0 ·25	144	14 „	0 ·1 „	27	Pot, Akron. Cruc. Co.
57*c*	8.1	C	S	H_3	15	—	0 ·25	130	14 „	0 ·1 „	25	
58*a*	18.1	A	R	H_3	15	—	0	5 ·60118	4400	0 ·9 „	27	
58*b*	18.1	B	S	H_3	15	—	0	122	4400	0 ·9 „	28	
58*c*	18.1	C	„	H_3	15	Acid	0	051	4400	0 ·9 „	14	1 per cent. acid.
58*d*	18.1	L	R	H_3	15	—	0	119	4400	0 ·9 „	27	
58*e*	18.1	N	„	H_3	15	—	0	116	4400	0 ·9 „	27	

TABLE I. (continued).

Obser-vation.	Date.	Kathode bowl.	Form of volta-meter.	Solution.				Mass of silver deposit in grammes.	Time in seconds.	Current in amperes.	Milli-grammes of silver per coulomb.	Remarks on deposit, pressure, temperature, &c.
				Source of crystals.	Concen-tration.	Added impurities.	Degree of electro-lysis.					
	1907.				per cent.							
59*a*	23.1	A	R	H_3	15	—	0·50	10·10753	6147	1·0 variable	1·11827	
59*b*	23.1	B	,,	H_3	15	—	0·50	786	6147	0·9 ,,	30	B and C in parallel. Resistance in circuit with C.
59*c*	23.1	C	,,	H_3	15	—	0·50			0·1 ,,		
60*a*	25.1	A	,,	WS	7·5	—	?	6·21520	2400	2·3 ,,	50	300 cub. centims. electrolyte.
60*b*	25.1	B	,,	H_3	7·5	—	0	394	2400	2·3 ,,	27	300 ,, ,, ,,
61*a*	26.1	A	,,	WS	7·5	—	?	7·14289	17 hours	0·1 ,,	37	190 ,, ,, ,,
61*b*	26.1	B	,,	H_3	7·5	—	0	227	17 ,,	0·1 ,,	27	125 ,, ,, ,,
62*a*	30.1	A	,,	H_3	15	—	0·75	7·00867	6147	1·0 ,,	27	From A and D.
62*b*	30.1	B	,,	H_3	15	—	0·75	7·10563	12294	0·75 and 0·25	—	(B and C in parallel.)
62*c*	30.1	C	,,	H_3	15	—	0·75	6·91683	12294	0·25 and 0·75	1·11829	From B and C.
62*d*	30.1	D	,,	H_3	15	—	0·75	7·01348	6147	1·0 variable	—	
63*a*	1.2	A	,,	H_3	15	—	0	7·10404	17 hours	0·1 ,,	1·11830	Base of bowl protected.
63*b*	1.2	B	,,	H_3	15	—	0	382	17 ,,	0·1 ,,	26	Sides of bowl protected.
63*c*	1.2	C	,,	H_4	15	—	0	386	17 ,,	0·1 ,,	27	Normal.
64*a*	22.2	A	,,	H_4	15	—	0	385	17 ,,	0·1 ,,	27	
64*b*	22.2	B	,,	H_4	1·5	—	0	357	17 ,,	0·1 ,,	23	
64*c*	22.2	C	P	H_4	15	—	0	406	17 ,,	0·1 ,,	30	Pot, Pukal.
64*d*	22.2	HS	R	H_4	15	—	0	392	17 ,,	0·1 ,,	28	
65*a*	28.2	A	,,	H_4	15	—	0	7·00561	6147	1·0 ,,	27	
65*b*	28.2	B	,,	LR	15	—	0	582	6147	1·0 ,,	30	
65*c*	28.2	C	,,	LR	15	Acid	0	650	6147	1·0 ,,	41	0·1 per cent. acid.
65*d*	28.2	D	,,	LR	15	Acid	0	620	6147	1·0 ,,	36	1 per cent. acid.
66*a*	4.3	A	,,	H_4	15	—	0	301	6147	1·0 ,,	27	
66*b*	4.3	B	,,	LR	15	—	0	296	6147	1·0 ,,	26	
66*c*	4.3	C	,,	LR	15	Acid	0	510	6147	1·0 ,,	60	0·1 per cent. acid.
66*d*	4.3	D	,,	LR	15	Acid	0	382	6147	1·0 ,,	40	1 per cent. acid.
67*a*	6.3	A	,,	H_4	15	—	0	601	6147	1·0 ,,	27	
67*b*	6.3	B	,,	H_4	15	—	0	993	6147	1·0 ,,	90	Solution in pyridine.
67*c*	6.3	C	,,	LR	15	Sulphide	0	744	6147	1·0 ,,	50	Copper also added.
67*d*	6.3	D	,,	LR	15	Sulphide	0	587	6147	1·0 ,,	25	Ferric nitrate also added.
68*a*	8.3	A	,,	H_4	15	—	0	7·01542	6147	1·0 ,,	27	
68*b*	8.3	B	,,	M. liquor	?	—	0	917	6147	1·0 ,,	87	Mother liquor.
69*a*	15.3	A	,,	H_4	15	—	0	7·50141	6500	1·0 ,,	27	
69*b*	15.3	B	P	H_4	15	—	0	145	6500	1·0 ,,	28	
69*c*	15.3	C	,,	H_4	15	—	0	145	6500	1·0 ,,	28	
69*d*	15.3	D	S	H_4	15	—	0	144	6500	1·0 ,,	27	
70*a*	20.3	A	R	H_4	15	—	0	7·00401	6147	1·0 ,,	27	Temperature = 15° C.
70*b*	20.3	B	,,	H_4	15	—	0	406	6147	1·0 ,,	28	Pressure = 2·4 centims. mercury.
70*c*	20.3	C	,,	H_4	15	—	0	483	6147	1·0 ,,	40	Temperature = 65° C.
71*a*	22.3	A	,,	H_4	15	—	0	7·01085	6147	1·0 ,,	27	,, = 16° C.
71*b*	22.3	B	,,	H_4	15	—	0	210	6147	1·0 ,,	47	,, = 92° C.
72*a*	24.3	C	,,	H_4	15	—	0	7·05431	6147	1·0 ,,	27	,, = 16° C.

72*b*	24.3	D	R	H_4	15	—	0	7 ·05500	6147	1 ·0 variable	1 ·11838	Temperature = 46° C.
73*a*	13.5	A	,,	H_4	15	—	0	6 ·99840	6147	1 ·0 ,,	27	
73*b*	13.5	B	,,	LR	15	Acid	0	746	6147	1 ·0 ,,	12	0 ·2 per cent. acid.
73*c*	13.5	C	,,	LR	15	Acid	0	756	6147	1 ·0 ,,	14	1 per cent. acid.
73*d*	13.5	D	,,	LR	15	Acid	0	855	6147	1 ·0 ,,	29	1 ,, ,,
74*a*	16.5	A	,,	LR	15	Sulphide	0	673	6147	1 ·0 ,,	24	Copper also added.
74*b*	16.5	B	,,	H_4	15	—	0	693	6147	1 ·0 ,,	27	
74*c*	16.5	C	,,	LR	15	Sulphide	0	736	6147	1 ·0 ,,	34	Ferric nitrate also added.
74*d*	16.5	D	,,	M. liquor	15	—	0 ·5	7 ·01845	6147	1 ·0 ,,	1 ·12171	,, ,, ,,
75*a*	21.5	A	,,	H_4	15	—	0	6 ·99947	6147	1 ·0 ,,	1 ·11827	
75*b*	21.5	B	,,	H_4	15	—	0	901	6147	1 ·0 ,,	20	Pressure=2 ·4 centims mercury.
75*c*	21.5	C	,,	H_4	15	Acid	0	840	6147	1 ·0 ,,	10	1 per cent. acid.
76*a*	5.6	A	,,	H_4	15	—	0	7 ·00122	6147	1 ·0 ,,	27	
76*b*	5.6	B	,,	VD	20	—	0	328	6147	1 ·0 ,,	60	
77*a*	12.6	A	S	H_4	15	—	0	6 ·98754	15000	0 ·4 ,,	35	Temperature = 90° C.
77*b*	12.6	B	,,	H_4	15	—	0	703	15000	0 ·4 ,,	27	,, = 16° C.
77*c*	12.6	C	R	M. liquor	15	—	0	6 ·99828	15000	0 ·4 ,,	1 ·12007	450 cub. centims electrolyte.
77*d*	12.6	D	,,	M. liquor	15	—	0	303	15000	0 ·4 ,,	1 ·11923	150 ,, ,, ,,
78*a*	17.6	A	,,	H_4	15	—	0 ·75	6 ·98438	6147	1 ·0 ,,	1 ·11827	
78*b*	17.6	B	,,	H_4	15	Acid	0 ·75	387	6147	1 ·0 ,,	19	1 per cent. acid.
78*c*	17.6	C	,,	H_4	15	Acid	0 ·75	405	6147	1 ·0 ,,	22	0 ·1 per cent. acid.
79*a*	21.6	A	P	H_4	15	—	0 ·25	6 ·99957	6146 ·92	1 ·01829$_0$	26*	Pot, Akron Cruc. Co.
79*b*	21.6	B	R	H_4	15	—	0 ·25	950	6146 ·92	1 ·01829$_0$	25*	
79*c*	21.6	C	P	H_4	15	—	0 ·25	980	6146 ·92	1 ·01829$_0$	30*	Pot, W. & J. George.
79*d*	21.6	D	,,	H_4	15	—	0 ·25	951	6146 ·92	1 ·01829$_0$	25*	
80*a*	22.6	A	R	H_4	15	—	0 ·50	634	6147	1 ·0 variable	27	
80*b*	22.6	B	,,	LR	15	Chloride	0	759	6147	1 ·0 ,,	47	
80*c*	22.6	C	,,	LR	15	Oxide	0	729	6147	1 ·0 ,,	42	
80*d*	22.6	N and O	,,	H_4	15	—	0 ·25	651	6147	1 ·0 ,,	30	
81*a*	1.7	A	,,	H_4	15	—	0	6 ·98542	6147	1 ·0 ,,	30	
81*b*	1.7	B	,,	H_4	3	—	0	521	6147	1 ·0 ,,	27	
81*c*	1.7	C	,,	—	5	—	0	534	6147	1 ·0 ,,	29	Chlorate solution.
81*d*	1.7	D	,,	—	5	—	0	727	6147	1 ·0 ,,	60	Perchlorate solution.
82*a*	3.7	A	S	H_4	15	—	0	7 ·00342	15000	0 ·4 ,,	34	Temperature = 92° C.
82*b*	3.7	B	,,	H_4	15	—	0	301	15000	0 ·4 ,,	27	,, = 15° C.
82*c*	3.7	L	EL. K.	H_4	15	—	0	281	15000	0 ·4 ,,	24	
83*a*	5.7	A	R	H_4	15	—	0 ·50	785	6147	1 ·0 ,,	27	
83*b*	5.7	B	,,	—	10	—	0	867	6147	1 ·0 ,,	40	Perchlorate 150 cub. centims.
84*a*	8.7	A + D	,,	H_4	15	—	0	20 ·49181	8998 ·1 × 2	1 ·01826$_8$	25*	
84*b*	8.7	B + C	,,	H_4	15	—	0	242	8998 ·1 × 2	1 ·01826$_8$	28*	
85*a*	10.7	A	,,	H_4	15	—	0	7 ·00104	6147	1 ·0 variable	27	
85*b*	10.7	B	,,	H_4	15	H_2S	0	118	6147	1 ·0 ,,	29	
85*c*	10.7	C	,,	H_4	15	H_2S	0	110	6147	1 ·0 ,,	28	
86*a*	13.7	A	,,	H_5	15	—	0	10 ·00208	8784 ·00	1 ·01825$_5$	26*	
86*b*	13.7	B	,,	H_5	15	—	0	213	8784 ·00	1 ·01825$_5$	26*	
86*c*	13.7	C	,,	H_5	15	H_2S	0	228	8784 ·00	1 ·01825$_5$	28*	
87*a*	15.7	A	,,	H_5	15	—	0 ·5	7 ·10582	6147	1 ·0 variable	27	Loose deposit.
87*b*	15.7	B	,,	LR	15	H_2S	0	89	6147	1 ·0 ,,	28	Very firm deposit.
88*a*	17.7	A	,,	H_5	15	—	0 ·5	6 ·10634	5000	1 ·0 ,,	27	
88*b*	17.7	B	,,	LR	15	Hyponitrite	0	884	5000	1 ·0 ,,	73	Very striated.
88*c*	17.7	C	,,	LR	15	—	0	6 ·11424	5000	1 ·0 ,,	1 ·11972	Overheated; very striated.

Discussion of the Results.

Observations 1 to 13 were made with solutions which are now known to have been impure. Apart from the electrolytes, the observations are also very unsatisfactory, for in these early experiments the silver deposits were partly removed with the aid of a platinum spatula, and the remainder with warm nitric acid; the bowls were much scratched in consequence, and many of the deposits were very loose. In addition, we were not so expert in the manipulation of the voltameters as in the later experiments, although the errors introduced on this account are regarded as very much smaller than the differences in the electrochemical equivalent which we found from day to day. As the electrolytes were not pure we have deferred the discussion of the first 13 sets of observations to Part II. (pp. 582, 595).

The Rayleigh Form of Voltameter.

Table II. summarises the results obtained with the Rayleigh form. In all, there are 52 independent observations; the mean value of the electrochemical equivalent is

TABLE II.—Rayleigh Form. Absolute Determinations.

No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.	Difference from mean.
14*a*	1·11827	0	22*c*	1·11825	−2	43*a*	$1\cdot11826_9$	0
14*b*	25	− 2	23*d*	32	+5	43*b*	26_4	− 1
15*a*	26	− 1	24*a*	27	0	43*c*	25_3	− 2
15*b*	22	− 5	24*b*	25	−2	43*d*	27_5	0
16*a*	25	− 2	25*d*	28	+1	44*a*	27	0
16*b*	22	− 5	27*a*	28	+1	44*b*	26	− 1
17*a*	22	− 5	27*c*	28	+1	44*c*	16	−11
17*b*	33	+ 6	27*d*	30	+3	46*b*	32	+ 5
17*c*	27	0	28*a*	33	+6	46*c*	30	+ 3
17*d*	25	− 2	28*b*	28	+1	47*a*	25	− 2
18*a*	38	+11	28*c*	26	−1	51*a*	23	− 4
18*b*	40	+13	29*a*	27	0	79*b*	25	− 2
18*c*	26	− 1	29*b*	29	+2	84*a*	25	− 2
19	29	+ 2	30*a*	27	0	84*b*	28	+ 1
20	25	− 2	30*b*	27	0	86*a*	26	− 1
21*a*	34	+ 7	30*d*	23	−4	86*b*	26	− 1
21*b*	29	+ 2	31*a*	28	+1			
21*c*	30	+ 3	34*b*	28	+1			

Mean = $1\cdot11827_3$ milligrammes per coulomb.

$1\cdot11827_3$ milligrammes per coulomb, and the mean observational error is 2·4 parts in 100,000. The greatest differences from the mean occur with 18*a*, 18*b*, and 44*c*, and it is possible that the solution used on the occasions 18*a* and 18*b* was impure owing to its prolonged contact with the atmosphere. If we exclude these results the mean is $1 \cdot 11826_8$. The mean difference of 2·4 parts in 100,000 must not be taken as the figure indicating the reproducibility of the Rayleigh form, for the errors of time, of current determination, of weighing, and of manipulation, are factors in this, as well as the possible changes which ensue due to slight variations in anode, kathode and electrolyte, and which jointly constitute the error associated with the voltameter. If we exclude all of the errors except those due to the voltameter and faulty manipulation, the mean difference is very small; this is well illustrated in observations 43*a*, *b*, *c*, *d*, the results of which are given to 1 part in 1,000,000. The mean of these four results is $1 \cdot 11826_5$, and the mean difference is only 7 parts in 1,000,000, which is probably much lower than the usual error of manipulation. We feel justified, therefore, in regarding the Rayleigh form of voltameter, as employed by us, to be reproducible within 1 part in 100,000.

The Richards Form of Voltameter.

The results obtained with the Richards form were at first more variable and always lower than when the Rayleigh form and the syphon form were employed. For some time we were at a loss to understand why the Richards value should be lower than that of the syphon, for both forms do, to a considerable extent, exclude the anode liquid from the kathode vessel, and the changes in concentration of the kathode liquids are also comparable. We eventually found the discrepancy to be due to the porous pots, of which we had three kinds :—(1) From the Akron Insulator and Marble Company of the United States of America; (2) from PUKAL of Berlin; (3) from an unknown source. Dr. GUTHE kindly obtained the pots (1) for us, and they are similar to those used by him in his research on the Silver Voltameter at the National Bureau of Standards.* The second type of pot is larger, but presumably of the same kind of ware as the pots used by RICHARDS. The third class of pot is from an unknown source; they were made from large porous pots obtained through the agency of Messrs. W. & J. GEORGE, Ltd.

We cleaned the pots with aqua regia, potassium cyanide, nitric acid, and hot distilled water before using in the voltameter. After a few runs they became stained, and further cleaning with potassium cyanide, nitric acid, and water was necessary. In our earlier experiments the pots were soaked in several lots of distilled water for 24 hours before using, and in neutral silver nitrate solution for 3 or more hours before the erection of the voltameter. The water in which the pots were finally soaked was invariably free from acid sufficient to redden very sensitive blue litmus paper, but we were forced to conclude that the pots were not acid-free, for on electrolysis of silver nitrate with a pot interposed between anode and kathode the solution in contact with the kathode became sufficiently acid to affect litmus. An

---

* GUTHE, 'Phys. Rev.,' 19, p. 138, 1904; 'Bull. Bureau of Stands.,' vol. 1, No. 1, pp. 28 and 349, 1904.

acid solution usually gives a lower deposit of silver than a neutral one (p. 595), and in consequence the results with the porous pot form were at first more variable and lower than with the Rayleigh form. In addition, some cyanide may have been present in solution. More consistent results were obtained on prolonged soaking, but we found the most satisfactory treatment was to place the pot in an electric furnace for a few hours. This procedure was adopted in our later observations, and the mean of the values resulting from these is given separately (Tables III. and IV.). The final result, 1·11828, is practically the same as that obtained for the Rayleigh form, and we conclude that the porous pot in our form of voltameter is of no advantage.

TABLE III.—Richards Form. Absolute Determinations.

No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.	Difference from mean.
22*a*	1·11797†	− 8	46*d*	1·11831*	+3
34*c*	809†	+ 4	79*a*	26*	−2
34*d*	05†	0	79*c*	30*	+2
44*d*	00†	− 5	79*d*	25*	−3
46*a*	16†	+11			

Mean of * observations = 1·11828 milligrammes per coulomb.
Mean of † „ = 1·11805 „ „ „

* Porous pots baked in electric furnace after soaking in water.

† Porous pots soaked in acid and afterwards in water for several days.

TABLE IV.—Comparison of the Richards Form with the Rayleigh Form. The latter is taken as the Standard (1 Coulomb deposits 1·11827 Milligrammes of Silver).

No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.	Difference from mean.
32*a*	1·11813†	−7	49*c*	1·11827*	−1
39*b*	20†	0	57*b*	27*	−1
41*a*	20†	0	64*c*	30*	+2
41*d*	20†	0	69*b*	28*	0
42*a*	22†	+2	69*c*	28*	0
42*c*	22†	+2			
45*b*	21†	+1			
45*c*	20†	0			

Mean of * observations = 1·11828 milligrammes per coulomb.
Mean of † „ = 1·11820 „ „ „

* Porous pots baked in electric furnace after soaking in water.

† Porous pots soaked in acid and afterwards in water for several days.

That the porous pots were sufficiently close-grained to keep the anode and kathode liquids apart is shown on p. 566. The results obtained with pots soaked in nitric acid, and afterwards in several lots of distilled water for about 2 to 4 days, are given in 22*a*, 34*c*, 34*d*, 44*d*, 46*a*, 32*a*, 39*b*, 41*a*, 41*d*, 42*a*, 42*c*, 45*b*, and 45*c*. These values are in fairly good agreement with one another, but all are lower than the figure obtained for the Rayleigh form.

The Syphon, Pot-Syphon-Bowl (P.S.B.), and Syphon-Pot-Bowl (S.P.B.) Forms (Table V.).

The results for the syphon form and for the P.S.B. and S.P.B. types are mainly comparative, the Rayleigh form being taken as the standard. The P.S.B. and S.P.B. types give the effect of the porous pot and clearly indicate that the low results of the early experiments with the Richards form were due to contamination of the solution by the liquid included in the pot. The result of observation 51*c* is not comparative (see Table I.), the very large syphon being used on this occasion. The mean value of the electrochemical equivalent is practically the same for the three forms, and agrees also with the values obtained with the Rayleigh and Richards types of voltameter.

Table V.—Comparison of the Syphon, Pot-Syphon-Bowl, and Syphon-Pot-Bowl Voltameters with the Rayleigh Form. The latter is taken as the Standard (1 Coulomb deposits 1·11827 Milligrammes of Silver).

Syphon.			P.S.B.			S.P.B.	
No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.
32*c*	1·11825	−2	33*b*	1·11825	−3	35*a*†	1·11819
39*c*	28	+1	35*b*	31	+3	36*a*†	01
42*d*	29	+2	36*b*	31	+3	37*a**	25
49*d*	29	+2	37*b*	27	−1	40*b**	28
51*c*‡	25	−2	40*c*	24	−4		
55*c*	31	+4	45*d*	30	+2		
57*c*	25	−2					
58*b*	28	+1					
69*d*	27	0					
Mean = 1·11827			Mean = 1·11828			Mean of * = $1\cdot11826_5$ Mean of † = 1·11810	

* Porous pots baked in electric furnace after soaking in water.

† Porous pots soaked in acid and afterwards in water for several days.

‡ Absolute determination.

Elevated Kathode Type.

The results are given below (Table VI.) and call for no comment. No difference from the usual type was anticipated, for the Rayleigh and syphon forms had been found to agree before the first of the observations in Table VI. had been made.

TABLE VI.—Comparison of the Elevated Kathode Voltameter with the Rayleigh Voltameter (1·11827).

No.	Milligrammes per coulomb.	Difference from mean.
51*b**	1·11829	+3
51*d**	26	0
82*c*	24	−2
Mean = 1·11826 * Absolute determinations.		

Efficiency of Porous Pots and of Syphons.

Nearly all previous researches have led to the conclusion that a source of trouble exists at the anode, and the porous pot voltameter was designed by RICHARDS to prevent the anode liquid having access to the kathode. NOVAK[*] was the first to suggest the possible existence of a complex silver salt in the electrolyte; RODGER and WATSON[†] independently made the same suggestion; RICHARDS'[‡] experiments strengthened the view, and the work of KAHLE,[§] GUTHE,[||] VAN DIJK[¶] and others supports the theory of anode complications. When the very excellent work of these observers is reviewed the results of our observations are astonishing, and we deem it necessary to give evidence of the reliability of our porous pots and syphons.

When the porous pots of classes (1) and (2) were filled with water and allowed to stand for 12 hours, about 40 per cent. of the liquid appeared to pass through their walls. When pots of class (3) were similarly treated, less than 5 per cent. of the liquid passed through the pots. In one of the pots of class (3) 50 cub. centims. of the electrolyte used in observation 30*c*, which gave a deposit of 1·12055 milligrammes per coulomb, were used for the anode liquid in observation 49*c*, the kathode liquid being normal $AgNO_3$ solution. The result is 1·11827, showing that very little of the

---

[*] NOVAK, 'Proc. Roy. Bohemian Ac. Sci. Prague,' 1, pp. 387–432, 1892.

[†] RODGER and WATSON, 'Phil. Trans.,' A, 186, p. 631, 1895.

[‡] RICHARDS, COLLINS and HEIMROD, 'Proc. Am. Ac.,' 35, p. 123, 1899.

[§] KAHLE, 'Zeitschr. Inst.,' 18, pp. 229–267, 1898.

[||] GUTHE, 'Phys. Rev.,' 19, p. 138, 1904; 'Bull. Bureau of Stands.,' vol. 1, pp. 28 and 349, 1904.

[¶] VAN DIJK and KUNST, 'Ann. der Phys.,' 14, p. 569, 1904; VAN DIJK, 'Ann. der Phys.,' 19, p. 249, 1906.

abnormal liquid could have diffused through the walls of the pot. An analysis of the strength of the anode and kathode solutions before and after electrolysis was made in other experiments and led to the conclusion that the pots were efficient. The syphon was tested by placing the electrolyte used in observation 30*c* in the anode bowl and a normal solution in the syphon limb and kathode bowl; the result, 1·11829 (49*d*), shows that no appreciable quantity of the anode liquid could have diffused into the kathode vessel.

Deposit on Platinum and on Silver.

Table VII. gives the results when silver bowls were employed as kathodes. Our successful employment of these bowls is in a large measure due to the use of an electric oven for drying purposes.

TABLE VII.—Comparison of Results with Platinum and Silver Kathodes. The Mean Value of the Results with Platinum Bowls is 1·11827 Milligrammes of Silver per Coulomb.

Results with Silver Bowls as Kathodes.

No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.	Difference from mean.	No.	Milligrammes per coulomb.	Difference from mean.
14*b*	1·11825	− 3	22*c*	1·11825	− 3	30*a*	1·11827	− 1
15*a*	26	− 2	23*d*	32	+ 4	30*b*	27	− 1
16*a*	25	− 3	25*d*	28	0	31*a*	28	0
17*a*	22	− 6	26*a*	30	+ 2	32*c*	25	− 3
17*b*	33	+ 5	26*b*	27	− 1	34*b*	28	0
18*b*	40	+ 12	27*a*	28	0	64*d*	28	0
21*c*	30	+ 2	28*a*	33	+ 5			
Mean = 1·11828								

It is apparent that the deposit on a clean platinum surface is the same as that on a silver surface. This result is in agreement with VAN DIJK'S* observations.

GORE, KAHLE,† and RICHARDS and HEIMROD‡ found a somewhat larger deposit when the kathode of the Rayleigh form was of platinum with silver deposited on it than when the kathode at the commencement of the observation was platinum only. RICHARDS found that the deposit on a silver kathode was 1 part in 10,000 heavier

---

* VAN DIJK, 'Ann. der Phys.,' 19, p. 282, 1906.

† KAHLE, 'Zeitschr. Inst.,' 18, pp. 229–267, 1898.

‡ RICHARDS and HEIMROD, 'Proc. Am. Ac.,' 37, p. 418, 1902.

than that on one of platinum when the Rayleigh form of voltameter was used, but that the masses were equal for the porous pot form. GUTHE[*] confirmed the latter result.

Influence of Pressure.

In testing for a pressure effect, one of the voltameters was placed under a glass bell jar in which the gaseous pressure could be varied from 2·5 centims. of mercury to atmospheric pressure. The voltameter was supported on a cast-iron plate through which the leads passed, the latter being well insulated from the plate by ebonite and rubber, and tests made before and after each experiment proved the efficiency of the insulation. In two cases the solution under diminished pressure was made with silver nitrate and distilled water which was boiled a few minutes before setting up the voltameter; in the remaining cases the solution was prepared in the ordinary way. For obtaining a continuous low pressure a large filter pump was used and proved satisfactory. The mass of silver deposited per coulomb is practically the same as before and there is, therefore, no pressure effect in the Rayleigh form of voltameter if set up and used in the manner specified in this communication. SCHUSTER and CROSSLEY[†] found that the amount of silver deposited, when their voltameter was subjected to a gaseous pressure of about 2·8 centims. of mercury, was 4 parts in 10,000 greater than when in air, and Dr. KAHLE[‡] verified this result. MYERS,[§] who repeated these experiments, found the difference between deposits in air and *in vacuo* to be as much as 1 part in 1000, and also found an excess of 5 parts in 10,000 if the deposit was made in an

TABLE VIII.—Pressure Effect. Rayleigh form of Voltameter used.

No.	Pressure in centimetres of mercury.	Milligrammes per coulomb.	Difference from mean.
19	8	1·11829††	+3
20	8	25††	−1
21*b*	2·5	29††	+3
70*b*	2·4	28‡‡	+2
75*b*	2·4	20‡‡	−6
Mean = 1·11826			

†† Absolute determinations.

‡‡ Rayleigh voltameter at atmospheric pressure taken as the standard (1·11827).

---

[*] GUTHE, 'Phys. Rev.,' 19, p. 138, 1904; 'Bull. Bureau of Stands.,' vol. 1, p. 34, 1904.

[†] SCHUSTER and CROSSLEY, 'Roy. Soc. Proc.,' 50, p. 344, 1892.

[‡] KAHLE, 'Brit. Assoc. Report,' Section A, 1892.

[§] MYERS, 'WIED. Ann.,' 55, p. 288, 1895.

atmosphere of nitrogen. RICHARDS and HEIMROD* verified these results. MERRILL† varied the pressure from 1 to 103 atmospheres and found no pressure effect for this range—he did not make observations at less than atmospheric pressure.

Temperature Coefficient.

In order to investigate the effect (if any) of temperature upon the silver deposits, we first compared the deposit in two Rayleigh forms maintained at different temperatures, but in the same circuit. The lower temperature was that of the room in which the observations were made and averaged about 16° C. The higher temperature was that of an electric oven and was varied from 40° C. to 95° C. Sufficient distilled water was taken to fill the voltameters and was warmed until its temperature was comparable with that of the electric oven. The solution was made and divided into two parts, that portion for the voltameter at the normal temperature being cooled to 16° C. and the other portion inserted in the kathode vessel of a voltameter and the whole placed in an electric oven. The results were as follows :—

grammes.	° C.		grammes.	° C.		$\alpha =$
7·00401	15	(70*a*)	7·00483	65	(70*c*)	$+2_4\times10^{-6}$,
7·01085	16	(71*a*)	7·01210	92	(71*b*)	$+2_4\times10^{-6}$,
7·05431	16	(72*a*)	7·05500	46	(72*b*)	$+3_3\times10^{-6}$.

The values are fairly consistent, but we were not satisfied. The mean temperature coefficient appears to be positive and about 2 or 3 parts in 1,000,000 per degree, but it appeared to us that there were sufficient disturbing influences at work to account for the higher deposits at the higher temperatures. The filter paper cup, the folds of which were secured with platinum wire and not with wax, turned a very dark brown colour on exposure to the atmosphere of the electric oven, and we felt that we were not justified in using filter paper at temperatures much higher than that of the room. The same thing happened to the exposed portions of a porous cup, and we resolved, therefore, to use a syphon at both high and low temperatures. In addition, we placed sheets of glass over the kathode bowl, so that, together with the limb of the syphon which entered the vessel, they shielded the electrolyte from currents of air. The following results were obtained :—

grammes.	° C.		grammes.	° C.		$\alpha =$
6·98703	16	(77*b*)	6·98754	90	(77*a*)	$+1_0\times10^{-6}$,
7·00301	15	(82*b*)	7·00342	92	(82*a*)	$+0_8\times10^{-6}$.

These indicate that the temperature coefficient over the range 15° C. to 92° C. is either *nil* or negligibly small. Unfortunately, we could not pass a current of 1 ampere

---

* RICHARDS and HEIMROD, 'Proc. Am. Ac.,' 37, p. 430, 1902.

† MERRILL, 'Phys. Rev.,' 10, p. 170, 1900.

through the electrolyte in the syphon at high temperatures. The heat produced by the passage of such a current raised the temperature of the liquid sufficiently to vaporise a portion of it and so break the circuit at the bend of the tube.

Our results are not in agreement with those of most other observers. Lord RAYLEIGH[*] found a higher deposit at 50° C. than at 15° C., and a higher deposit at 15° C. than at 4° C. The temperature coefficient was therefore positive and averaged about 0·001 per cent. per 1° C. for the range 4° C. to 50° C. LEDUC found a negative coefficient. RICHARDS, COLLINS, and HEIMROD obtained at 60° C. and also at 0° C. a larger deposit than at 20° C. They state, however, that the apparent gain at 0° C. was undoubtedly due to the difficulty in washing the deposited silver. The temperature coefficient obtained from their results is about 0·0017 per cent. per 1° C. for the range 20° C. to 60° C.

MERRILL,[†] who experimented with fused silver nitrate and solutions at normal temperatures, concluded that temperature has no effect on the mass of the deposit.

Liquid Inclusions in the Deposit.

The appearance of the deposits in the platinum bowls varied with the solutions used, but with pure solutions they were generally of very open texture. The deposits were usually dried in an electric oven at 160° C., but in eight cases we reheated at 240° C. without observing any loss in weight, and on three other occasions some deposits in silver bowls were heated to over 400° C. In no case was there a diminution in weight, but in two of the latter experiments a gain of 3 parts in 100,000 was recorded. This was possibly due to the formation of silver sulphide.

Lord RAYLEIGH and Mrs. SIDGWICK[*] sometimes found no loss on a second heating, but more often a slight decrease. RICHARDS[‡] found a mean loss of 18 parts in 100,000 when the deposits were reheated over an alcohol flame to constant weight. The most extensive observations have been made, however, by VAN DIJK,[§] who after washing and drying at 150° C. reheated in an electric furnace to 500° C., and in some cases to 600° C. No loss in weight was observed. VAN DIJK used smaller bowls and crucibles than RICHARDS, but the amounts of silver deposited by him are comparable with those deposited by RICHARDS; it is apparent, therefore, that the texture of the deposits must have been different or that something in addition to silver was deposited in RICHARDS' experiments.

Size of Kathodes.

In general the area of the kathode surface in our experiments was 200 sq. centims., but in observation 58*d* the bowl L of 100 sq. centims. kathode surface was used, and

---

[*] RAYLEIGH and SIDGWICK, 'Phil. Trans.,' 175, p. 411, 1884.

[†] MERRILL, 'Phys. Rev.,' 10, p. 170, 1900.

[‡] RICHARDS, COLLINS and HEIMROD, 'Proc. Am. Ac.,' 35, p. 145, 1899.

[§] VAN DIJK, 'Ann. der Phys.,' 19, p. 266, 1906.

in 58*e* one of the bowls (N) belonging to Professor VAN DIJK was employed. The area of the kathode surface of this last bowl was 40 sq. centims. only, and this is the smallest kathode area employed by us for currents of nominal value 1 ampere. The results of observations 58*a*, *b*, *d*, and *e* are in remarkable agreement (1·11827, 1·11828, 1·11827, and 1·11827), and it appears that within the limits stated above the area of the kathode has no influence on the deposit, conditionally, of course, that the concentration of the electrolyte is within certain limits, and that the current density is not too great. In some of our earlier experiments we used rotating kathodes; the large platinum bowls were rotated about 40 times per minute and stationary glass vanes were inserted in the kathode liquid to prevent its uniform rotation. The steadiness of the current was not appreciably affected by this motion, and had more satisfactory deposits been obtained in the rotating bowls than in the stationary ones we should have no hesitation in recommending the method. The deposits were much the same in texture, however, and there was no difference in their masses. As an example we may refer to 38*a*, *b*, and *c*. 38*a* and 38*b* were rotated; 38*c* was not. The masses of the deposits were 7·03110, 7·03096 and 7·03108 grammes respectively.

Size of Anodes.

In most of our experiments it was impossible to estimate the extent of the anode surface owing to the outer coating of the electrically deposited silver. The silver plates generally used as anodes were about 5 × 5 × 0·4 centims., and the current density at an anode was therefore comparatively small. In observations 25*a*, 26*c* and 41*b* the anodes were very small silver discs, having a total area of about 2·5 sq. centims. at the commencement of the deposit, and about 1 sq. centim. at the conclusion; they were not coated with electrolytic silver. On one occasion the mass of the anode disc at the commencement was 12 grammes only, and 7 grammes of silver were deposited. This is an extreme case. The results of the "small anodes" observations are as follows:—

25*a*	1·11825.
26*c*	37.
41*b*	27.

According to SCHUSTER and CROSSLEY,[*] a small anode may give a deposit which is too small. LEDUC[†] states the opposite of this, and MERRILL[‡] observed no difference due to variation in the size of the anode. In the porous cup form GUTHE[§] found the size of the anode to be immaterial, but states that the drop of potential

---

[*] SCHUSTER and CROSSLEY, 'Roy. Soc. Proc.,' 50, p. 344, 1892.

[†] LEDUC, 'J. de Phys.,' 1, p. 561, 1902.

[‡] MERRILL, 'Phys. Rev.,' 10, p. 172, 1900.

[§] GUTHE, 'Bull. Bureau of Stands.,' vol. 1, p. 361, 1904.

from anode to kathode should not be large enough to allow of a decomposition of water. We have made experiments to test this, and give the results obtained when the potential difference was varied from 0·03 volt to 30 volts. The effect of using a platinum anode is discussed in Part II., p. 588.

Effect of Potential Difference between Anode and Kathode (56*a* and 56*b*).

When a syphon form of voltameter and a Rayleigh form were placed in series and a current of 1·02 ampere passed through them, the drop in potential on the syphon form (small syphon) was of the order of 30 volts and on the Rayleigh form about 1 volt. It has already been shown that the mass of silver deposited on these occasions is the same. Comparison observations were also made with a very high resistance Rayleigh voltameter and one of the usual type. The voltameters were placed in series and the kathode bowls of each contained 350 cub. centims. of a 15 per cent. solution of silver nitrate. The high-resistance voltameter was one in which the filter paper was enclosed in a glass funnel perforated with small holes, and the funnel was enclosed in a second similarly perforated. With a current of 0·03 ampere the difference of potential on the high-resistance voltameter was 3·0 volts, and that on the usual form was 0·03 volt. The deposits were very loose and markedly striated. The mass of silver deposited in 50 hours in the usual form was 7·10382 grammes (56*a*), and in the high-resistance form 7·10411 grammes (56*b*). These results are interpreted as indicating that in all ordinary cases the potential difference produces no disturbing effect.

Variable Concentration of Electrolyte.

The extreme range in the concentration of the electrolyte has been from 1·5 parts to 50 parts of silver nitrate in 100 parts of the solution, the intermediate values being 5, 10, and 15 parts in the same quantity of solution. The chief difference in the deposits was that of texture, the solutions of higher concentration giving less adherent and more striated deposits than the weak solutions when the current employed was between 0·1 and 1·0 ampere, but from 1·0 ampere upwards the striæ were faint even for the concentrated solutions. When the 1·5 per cent. solution was used, only 3·3 grammes of silver were present in the electrolyte, and the degree of the electrolysis at the end of this experiment was therefore 7·1/3·3 = 2·15.

The masses of silver in milligrammes per coulomb recorded as deposited from the various solutions are as follows :—

1·5 per cent. solution	=	1·11823 (64*b*).
5·0 ,, ,,	=	$1{\cdot}11825_5$ (40*a*, 40*c*).
10·0 ,, ,,	=	1·11827 (33*a*, *b*, *c*).
15·0 ,, ,,	=	1·11827 (large number of observations).
50·0 ,, ,,	=	1·11827 (30*b*).

The differences from the mean value are within the limits of error, and there is, therefore, no certain change in the mass of silver deposited per coulomb from electrolytes containing from 1·5 to 50 parts of silver nitrate in 100 parts of solution.

We think it necessary, however, to point out that a current of 0·1 ampere was used to electrolyse the 1·5 per cent. solution; when strong currents were used the silver was deposited as long, needle-shaped crystals, and on one occasion it was precipitated in a spongy form. It is insufficient, therefore, to state the range in the concentrations of the electrolyte without also specifying the quantity of the electrolyte, the extent of the kathode surface, and the current to be used.

Variation of Current Density.

We believe that one of the objections to the silver voltameter is that the ordinary size of voltameter possibly allows only of currents of the magnitude of 1 ampere to be measured. It was of some importance, therefore, to decide whether or not currents of the order of half an ampere and others of the order of 10 amperes deposited exactly the same mass of silver per coulomb in our form of the Rayleigh voltameter. This might have been tested by evaluating the currents, noting the times, and determining the masses, but a much simpler and more accurate way was a comparison of the masses of silver deposited, similar to the calibration of a box of weights. This latter method was adopted by us. In our first experiment we compared the masses of the bowls A and B and of C and D. B and C were then placed in parallel and A in series with them, and a current of 1 ampere passed through A for 2·4 hours. A mass of silver, weighing about 10 grammes, was thus deposited in A. The bowl D was then substituted for A and the same current passed through it for the same time. At the conclusion of the experiment there were about 10 grammes of silver in each bowl, but the silver in A and D had been deposited with a current of 1 ampere, and that in B and C with a current of half an ampere. A was again compared with B, and C with D. The difference (A−B)−(C−D) should be the same as before if the change in current had no effect. Similar observations were made for currents in the main circuit of 2, 4, and 8 amperes. The masses of silver deposited and the difference (A−B)−(C−D) before and after the depositions are given in Table IX., p. 574.

We conclude from these results that the voltameter employed by us can be used for the determination of currents as great as 8 amperes and as small as 0·5 ampere, and that these currents will deposit the same mass of silver per coulomb. With a current of 4 amperes the electrolyte was warm to the hand after the experiment, and with 8 amperes the temperature rose from 18° C. to 35° C. The deposits with high current densities are firm and of a matt surface, while with very low current densities the silver is loose and the deposit striated.

We have made one observation which connects the deposits obtained with 1 ampere

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

TABLE IX.—Rayleigh Form of Voltameter.

Current through bowls A and D.	Current through bowls B and C.	Difference in mass of bowls (A − B) − (C − D).	Difference in mass of bowls plus about 10 grammes of silver in each (A − B) − (C − D).	Deposit in A + D greater than in B + C by
amperes.	amperes.	grammes.	grammes.	per cent.
1	0·5	3·13707	3·13647	$-0{\cdot}003_0$
2	1·0	3·13710	3·13676	$-0{\cdot}001_7$
4	2·0	3·13722	3·13788	$+0{\cdot}003_3$
8	4·0	3·13720	3·13720	$0{\cdot}000_0$

with those obtained with 0·75 and 0·25 ampere. In this case a resistance was added to that portion of the branch circuit containing C for one-half of the time of the experiment and to B for the other half. A current of 1 ampere was passed through A and D, and through B and C currents of 0·75 and 0·25 ampere passed. The total mass of silver deposited in A and D was 14·02215 grammes and in B and C it was 14·02246 grammes, a difference of $0{\cdot}002_2$ per cent. (62*a*, *b*, *c*, *d*).

Effects of Electrolysis on the Concentration of the Electrolyte.

When the current first leaves the anode it spreads out in the approximately homogeneous electrolyte which surrounds it, and, if the normal distance from the anode to the kathode is everywhere the same, the current density over the anode surface is uniform, and the same is true for the kathode surface. Immediately, the layers of liquid in contact with each electrode become changed in concentration and density: around the silver anode a film of dense liquid of high concentration is formed and about the kathode a film results the density of which approximates to that of water and is of very small concentration. In the Rayleigh form of voltameter the heavy anode liquid descends, and since it constitutes a path of high conductivity, more silver per unit area is deposited on the base of the bowl than on the sides if the anode surface is everywhere at the same normal distance from the kathode surface. This descending column of heavy anode liquid gives rise to the star-shaped deposit on the base of the bowl which has been so frequently noticed by other observers and by ourselves (fig. 8, Plate 9). If the distance of the anode from the base of the bowl is appreciably greater than the distance from the sides, the path of least resistance is not necessarily that of the descending column, and the deposit per unit area on the base is less than on portions of the sides. This latter condition holds for the Rayleigh voltameter as we have generally used it.

It follows that the lowest point of the anode is in contact with a thin layer of electrolyte of greater concentration than the solution at the surface. A concentration cell is thus produced and normally a current would flow through the electrolyte from the highest point of the anode to the lowest. This, however, only holds good for a few seconds after the cessation of the current in the main circuit. The superposition of the effect on the main current effect results in the current density being greatest at the point where the anode enters the electrolyte, and this is, in general, the first portion of the anode which becomes noticeably thin. If the current is very feeble, diffusion tends to keep the liquid more homogeneous. Observations show that when silver rods are used as anodes there are other effects of electrolysis which produce vertical grooves in them.

If the concentration of the electrolyte is diminished, the ratio of the concentration of the anode film to that of the main electrolyte is increased and that of the kathode film to the liquid is probably diminished. There is, however, a similarity with respect to the action of the current on the surfaces of separation of these films and the electrolyte. In both cases the current in its passage through the voltameter flows from a liquid of high concentration into a mass of liquid of lower concentration, and hence, if there is a marked surface of separation of anode liquid and electrolyte, and kathode liquid and electrolyte, any effect of the current on these surfaces will be similar. GORE[*] has shown that when a solution of small concentration rests on one of high concentration and a current is passed downwards, the surface of separation of the liquids becomes indistinct, but if the current is reversed the surface of separation becomes more marked. By using silver anodes and kathodes of platinum foil in electrolytes contained in glass vessels we were able to see the heavy anode liquid in its descent from the anode and the light liquid in its ascent from the kathode. Even when at a distance of a few millimetres from the electrode these liquids appeared to be quite distinct from the main body of the electrolyte, and we are justified therefore in assuming the existence of even more distinct surfaces of separation around the anode and kathode when the current is flowing.

An interesting question is whether the properties of these films of liquids are very different from the main portion of the electrolyte. Observation shows that as they leave the electrodes they break up into cylindrical columns, but whether or not they are in the form of uniform thin films when in contact with the electrodes direct observation does not show, but a number of experiments with currents of different intensities and electrolytes of different concentrations enable an opinion to be formed. When weak electrolytes are used (*e.g.*, $1\frac{1}{2}$ per cent. solutions) a current of 0·1 ampere produces a deposit having a matt surface, but with a 15 per cent. solution the deposit is markedly striated (figs. 9[†] and 10, Plate 9). We interpret these results in the following manner. The film of liquid in contact with the kathode has a greater mean thickness in the $1\frac{1}{2}$ per cent. solution than in the 15 per cent. solution. This follows because the rate of deposition of silver is the same in each voltameter. If the film is very thin, it is unstable and breaks up into cylindrical columns of liquid. Hence in

---

[*] GORE, 'Roy. Soc. Proc.,' No. 203, p. 332, 1880, and No. 212, p. 56, 1881.

[†] Fig. 9 represents a portion of a deposit which was stripped from the side of a platinum bowl.

contact with the kathode surface there are columns of liquid of low concentration, and in between these the electrolyte is of approximately normal concentration. The latter has the higher conductivity, and since in addition there is an E.M.F. acting from the columns of low concentration towards the main body of the electrolyte, the current will pass into the kathode through the liquid in between the columns. Immediately the concentration falls and possibly the resultant liquid of small density is pulled into the columns of low concentration. If our assumptions are correct, an increase in the current should result in the kathode film becoming thicker and more stable, and when it is sufficiently stable to remain as a film a striated deposit should not be formed. This was tested by experiment and found to be so.

The following table indicates the results. All the solutions were pure, and the same volume of electrolyte (350 cub. centims.) was taken in each case.

No. of experiment.	Electrolyte.	Current.	Character of deposit.
	per cent.	amperes	
1	1·5	0·1	No striæ.
2	3·0	0·7	" "
3	2·0	1·0	" "
4	15·0	0·1	Marked striæ.
5	15·0	0·3	" "
6	15·0	0·7	Striæ, but not so marked as in (4).
7	15·0	1·0	Very faint striæ at bend of bowl.
8	15·0	2·0	No striæ.
9	15·0	4·0	" "
10	15·0	8·0	" " fine matt surface.
11	50	1·0	Striæ.

It appears that for solutions of all concentrations striated deposits are obtained for small current densities at the kathode, and matt deposits for very large current densities.

We may now compare the changes in the Rayleigh and Richards forms of voltameter. In the latter case there is no descending anode liquid, and there will be, therefore, less tendency for a star-like deposit to be formed on the base of the bowl. In our own form of RICHARDS' voltameter the volume of kathode liquid was in general about 250 cub. centims., and during electrolysis the mean concentration of the solution must have diminished from 15 to 10·6 per cent. The mean concentration of the electrolyte in the Rayleigh form remains constant and, in consequence, for the same current density striæ were produced in the Rayleigh form when they were absent in the Richards form. This effect has also been observed by GUTHE[*] and by VAN DIJK[†]. In the Richards form, as employed by the latter observer, the kathode

---

[*] GUTHE, 'Phys. Rev.,' 19, p. 147, 1904.

[†] VAN DIJK, 'Ann. der Phys.,' 19, p. 271, 1906.

liquid consisted of about 30 cub. centims. of a 20 per cent. solution, and at times nearly 3 grammes of silver were deposited, the concentration being thus reduced to about 4·3 per cent. Professor van Dijk observed little or no striæ in the Richards form, but marked striæ in the Rayleigh form.

In the Rayleigh form the process of intermixing of the anode and kathode liquids is considerably accelerated by their ascent and descent respectively. We have made observations on the currents of liquid thus produced and find that they may be approximately represented by fig. 11. The electrolyte which is above the horizontal plane containing the sheet of silver which forms the anode is certainly of lower concentration than that below this plane when electrolysis has proceeded for a short time. It therefore appears that the kathode film may be stable in the upper portion of the electrolyte when it is unstable in the lower portion. In other words, it should be possible to produce striæ at the base and bend of the bowl when the upper portion of the deposit presents a matt surface (see fig. 9). Probably this has been observed by other workers besides ourselves, but we have found no reference to the phenomenon. Our own deposits at low current densities were often markedly striated at the bend of the bowl and gradually merged into the matt surface which existed above the point A. The portion B of the electrolyte, which is partly enclosed by the curved surface of the liquid, is in a most unfavourable position for the renewal of its original concentration, and it is probably of smaller density than any other part of the solution. Because of this the conductivity is small, and an appreciable E.M.F. acts from B towards the main body of the electrolyte; in consequence, the quantity of silver precipitated by the passage of electricity through B is very small. In most of our experiments we have closely observed the deposit and the electrolyte, and in about six instances have found a distinct gap between the line of contact of electrolyte and platinum and the edge of the deposited silver. In these cases a few crystals of silver were sometimes

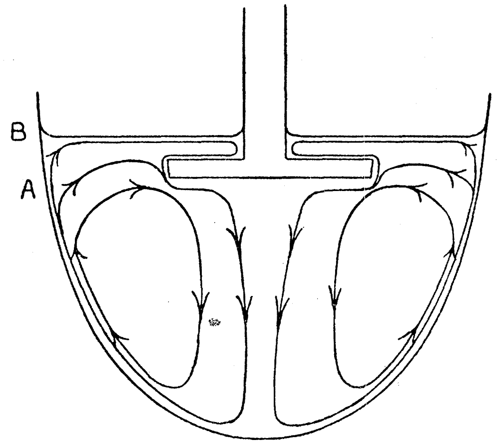

Fig. 11.

deposited in the form of a thin ring where the electrolyte was at its highest point, and one or two millimetres below this ring the edge of the main deposit was formed. A photograph of such a ring deposit is given in fig. 13 (Plate 9).

Another interesting question is whether the kathode and anode films can be easily scattered by agitation of the liquid. We have made experiments with the kathode only, for there were no means of detecting whether the anode film was disturbed or not. Our solutions were such (solutions used in Observations 1 to 13) that striæ were readily produced, and the method of investigation was to rotate the kathode and insert stationary glass vanes in the electrolyte to prevent a uniform motion. We were astonished to find the striæ as distinct as ever, but instead of being vertical they were in the form of a spiral. This is well shown in figs. 12 and 13, which are from photographs. Examination of the inclination shows (1) that the kathode liquid moved upwards; (2) that on the assumption that the kathode alone rotated and the whole of the electrolyte remained stationary, the vertical velocity was 21 centims. per second.* The electrolyte was not stationary, however, and we judged the kathode film to rotate at very nearly the same rate as the kathode; had it been at exactly the same rate the striæ would have been vertical. It is evident, therefore, that the vertical velocity of the kathode film was not very great; it was possibly of the order of 1 centim. per second. The stability of the liquid columns is, however, astonishing.

It is well to point out that the Richards voltameter is a concentration cell after electrolysis commences. The anode liquid within the porous pot is of higher concentration than the kathode liquid, and in consequence any short-circuiting of the voltameter after the main circuit has been broken will diminish the mass of silver on the kathode bowl. A steady current may thus be produced for some time, and is easily measured by an ammeter.

Another point investigated by us was the possibility of silver being deposited from a concentrated solution of silver nitrate at the bottom of a platinum bowl when a second solution of much lower concentration rests on it. We employed solutions containing 50 per cent. and 1 per cent. of silver nitrate, but neither in platinum bowls nor in silver ones was any increase observed.

Other effects have been observed, but it is not easy to suggest an explanation of them. The most remarkable occurs when a kathode bowl is half filled with an electrolyte, left for an interval of about 10 minutes, and the remaining portion of the electrolyte added just prior to the completion of the electric circuit. If about 5 grammes (or less) of silver are deposited, the level of the electrolyte when the bowl was half filled is clearly indicated in the deposit, the density of the latter being appreciably greater below the original level of the solution, and the change in the density is marked by a clear line running round the bowl.

---

* The bowl rotated clockwise at the rate of 40 turns per minute: its maximum diameter was 10 centims., and the inclination of the striæ was almost exactly 45° C.

The Electrochemical Equivalent of Silver.

The mean of the values for the mass of silver deposited by the passage of 1 coulomb of electricity through any of the normal voltameters described in this communication is

1·11827 milligrammes.

The quantity of electricity which passed through a voltameter in any experiment was determined by a measurement of time, to which measure no appreciable error can be attached, and by an evaluation of a current in absolute measure through the medium of the Ayrton-Jones ampere balance. It is shown elsewhere* that the error in such a determination of current is of the order of 2 parts in 100,000, and this also is the probable error of the value stated above for the mass of silver deposited per coulomb.

The value has been obtained not from one solution, nor with one voltameter, but with many solutions and many forms, as well as many voltameters. It has, moreover, been shown that the value is the same whether a current of half an ampere is passed through a voltameter, or a current of 8 amperes; whether the pressure is atmospheric or equivalent to that of a few centimetres of mercury; and if the temperature is 90° C. instead of 15° C., it is probable that the value is still the same.

The remarkable consistency of our results is probably due to the large kathode bowls, the purity of our anodes, the small mass of filter paper in the Rayleigh form, and most of all to the purity of the electrolyte. With very small bowls, a small quantity of electrolyte, a small anode, a relatively large mass of filter paper, and current densities which are very high or very low, the estimated mass of silver deposited in the passage of 1 coulomb may be different from the value given by us. Secondary reactions may then occur which never happened in our experiments, or if they did the large volume of electrolyte masked their effects and rendered their detection impossible by any means tried by us.

Comparison of Results with those of other Observers.

Professor VAN DIJK very kindly forwarded to Dr. GLAZEBROOK two of his voltameters together with a considerable quantity of silver nitrate which he had recrystallised, and which was comparable with that employed in his investigations. We here express our hearty thanks to Professor VAN DIJK. Solutions were prepared from the salt which was sent, and they were found to be abnormal. In one case the value found for the electrochemical equivalent was 1·11847 (52*b*), and in a second experiment 1·11860 (76*b*) resulted. The solutions, as originally prepared, were slightly turbid and had to be filtered, and the deposits with a current of 1 ampere were noticeably striated. If different quantities of an abnormal electrolyte are contained in

---

* AYRTON, MATHER, and SMITH, 'Phil. Trans.,' A, vol. 207, p. 534, 1908.

two similar voltameters in series, the one containing the least quantity of solution does in general give the smaller deposit. This is well illustrated in 77*c* and *d*. In one of these, 450 cub. centims. of an abnormal electrolyte gave 1·12007 as the value of the electrochemical equivalent, while the other, which contained 150 cub. centims., gave 1·11923. With an abnormal electrolyte a large bowl will therefore give a heavier deposit than a small one, but although there is an appreciable difference in the size of the Rayleigh bowl and the Richards crucible which Professor VAN DIJK used, we do not think that the differences which he observed are to be entirely attributed to this cause.

Professor WATSON also sent a silver nitrate solution used by him in 1895. This gave 1·11872 (23*a*) for the electrochemical equivalent, and when diluted to a 7½ per cent. solution it gave 1·11850 (60*a*) with a current of 2·3 amperes, and 1·11837 (61*a*) on a second electrolysis with a current of 0·1 ampere.

In view of these facts and the great difference in the size of the voltameters, &c., used by other observers, it appears that no very useful purpose would be served by an attempt to explain the results of other experimenters without first reproducing as nearly as possible the conditions under which they worked. This we shall endeavour to do.

It is of some interest, however, to compare the results obtained by absolute methods, since a form of voltameter practically identical with that used by Lord

TABLE X.

Observer.	Year.	Value.
		milligrammes per coulomb
MASCART[*]	1884	1·1156
FR. and W. KOHLRAUSCH[†]	1884	1·1183
RAYLEIGH and SIDGWICK[‡]	1884	1·1179
PELLAT and POTIER[§]	1890	1·1192
KAHLE[‖]	1899	1·1183
PATTERSON and GUTHE[¶]	1898	1·1192
PELLAT and LEDUC[**]	1903	1·1195
VAN DIJK and KUNST[††]	1904	1·1182
GUTHE[‡‡]	1906	1·1182

---

[*] MASCART, 'J. de Phys.,' 3, p. 283, 1884.

[†] FR. and W. KOHLRAUSCH, 'WIED. Ann.,' 27, p. 1, 1886.

[‡] RAYLEIGH and SIDGWICK, 'Phil. Trans.,' 175, p. 411, 1884.

[§] PELLAT and POTIER, 'J. de Phys.,' 9, p. 381, 1890.

[‖] KAHLE, 'Zeitschr. Inst.,' 18, pp. 229–267, 1898.

[¶] PATTERSON and GUTHE, 'Phys. Rev.,' 7, p. 257, 1898.

[**] PELLAT and LEDUC, 'C. R.,' 136, 1649, 1903.

[††] VAN DIJK and KUNST, 'Ann. der Phys.,' 14, p. 569, 1904. VAN DIJK, 'Ann. der Phys.,' 19, p. 249, 1906.

[‡‡] GUTHE, 'Bull. Bureau of Stands.,' vol. 1, No. 1, p. 36, 1904, and vol. 2, p. 70, 1906.

Rayleigh has been employed on most occasions. We are unaware of the exact conditions of the experiments, but it will be seen that the differences between the values and the mean value are not appreciably greater than the probable errors of many of the current determinations. It must be remembered that in the very early observations great precision was not claimed.

Patterson and Guthe used a type of voltameter in which the electrolyte was saturated with silver oxide, and their result is not therefore comparable with the others. Guthe and van Dijk employed the Richards and the Rayleigh forms; the values given in Table X. are those obtained by them for the Rayleigh pattern.

Conclusions.

(1) The Rayleigh, the Richards, the Syphon, the Pot-Syphon-Bowl, the Syphon-Pot-Bowl, and the Elevated Kathode forms of voltameter give identical values within 1 or 2 parts in 100,000 for the electrochemical equivalent of silver, subject to easily attained conditions with respect to the size of the voltameter and the purity of the electrolyte. (The purity of the electrolyte is dealt with in Part II.)

(2) The mass of silver deposited is independent of the pressure to which the voltameter is subjected, and also independent of the temperature, except that at high temperatures the filter paper of the Rayleigh form may interact with the silver nitrate solution, and give rise to a very slightly abnormal value for the electrochemical equivalent of silver.

(3) The current through the Rayleigh form ot voltameter* may vary from 0·5 ampere to 8 amperes, and possibly beyond these limits without producing any appreciable disturbing effect.

(4) The electrochemical equivalent of silver is

1·11827 *milligrammes of silver per coulomb* (10^{-1} C.G.S.).

This value is subject to a probable error of about 0·002 per cent.

PART II.

The Chemistry of the Silver Voltameter;

by F. E. Smith, *A.R.C.Sc., and* T. M. Lowry, *D.Sc.*

A. *Preparation of Pure Silver Nitrate.*

In the earlier experiments (1 to 13) on the electrochemical equivalent of silver considerable difficulty was experienced in obtaining concordant figures when different samples of silver nitrate were electrolysed under apparently identical conditions. Many

---

* The size of the voltameter is assumed to be the same as that described in this communication.

of the solutions used had been prepared from silver nitrate recovered from previous electrolyses, purified by adding nitric acid, boiling down to dryness, and fusing in a platinum basin; the fused mass was dissolved in water, filtered from the black residue which was always left after fusion, and was often used for electrolyses without further purification. On a few occasions silver nitrate was crystallised from the filtrate and a 15 per cent. solution made from this recovered salt. The values for the electrochemical equivalent of silver varied from 1·11832 to 1·11886 milligrammes per coulomb (mean of 14 determinations = 1·11857) when the Rayleigh voltameter was used, and from 1·11786 to 1·11854 (mean of 21 determinations = 1·11825) when the porous pot voltameter was used.

Before a definite figure could be established for either form of voltameter it was necessary first to demonstrate the possibility of preparing again and again from silver nitrate of different origins solutions which should give identical weights of silver when electrolysed under identical conditions. The following experiments were therefore made in order to test the constancy of the electrochemical equivalent of a range of silver nitrate samples of different origins.

I. *Silver Nitrate from Electrolytic Silver.*—185 grammes of electrolytic silver recovered from previous electrolyses were dissolved in a mixture of equal volumes of "commercial pure" nitric acid and water. The resulting solution was filtered, by means of a small Gooch crucible, from a small residue of insoluble matter,* and evaporated on a water-bath (since it was not thought to be desirable to fuse the product) during 50 hours, water being added from time to time. A crop of crystals was then drained off and dried overnight in the oven. When recrystallised the product was found to be neutral, but yellow in colour. After three further recrystallisations the electrochemical equivalent of the sample was tested. The solution for electrolysis was prepared by dissolving 90 grammes of the purified salt in 600 cub. centims. of water of low conductivity, and when electrolysed in a Rayleigh voltameter gave a deposit of 1·11825 milligrammes per coulomb (24*b*).

II. *From Recovered Silver Nitrate.*—850 grammes of strongly acid crystals, recovered from previous electrolyses by acidifying and concentrating the solutions, were purified by *repeated crystallisation only*, without any attempt to remove the acid by evaporating on the water-bath, by drying in an oven, or by fusing. After four crystallisations the nitrate was found to be neutral to litmus, and after one further crystallisation it was dissolved in water (113 grammes $AgNO_3$ in 750 cub. centims. of water of low conductivity) and electrolysed. The electrochemical equivalent of the sample was found to be 1·11827 milligrammes per coulomb (24*a*).

---

* The insoluble residue referred to was suspended in very minute particles in the liquid, to which it imparted a red colour suggestive of a colloidal metal. It was found to be platinum, and 0·0136 gramme was obtained from 185 grammes of electrolytic silver. The impurity, therefore, was probably not a product of electrolysis, but may have been derived from the platinum bowls or from the platinum spatula which was used to remove the electrolytic silver.

III. The strongly acid mother-liquors from II. were evaporated on the water-bath and dried in the oven until free from acid. The dry salt was further heated until the blue colour of the copper nitrate had disappeared, and was then dissolved in water, filtered, and recrystallised until colourless. After one further crystallisation a solution was prepared as before, and the electrochemical equivalent determined. Three determinations gave the values

III.	1·11827	(26*b*)
	1·11830	(27*d*)
	1·11827	(29*a*)

Mean 1·11828 milligrammes per coulomb.

Other samples of recovered silver nitrate purified by this method gave the values

IV.	1·11826	(28*c*)
V.	1·11831	(35*b*)
	1·11827	(35*c*)
VI.	1·11816 (?)	(44*c*)
	1·11830	(46*c*)
VII.	1·11830	(65*b*)

whilst a 50 per cent. solution prepared by dissolving recovered silver nitrate (purified as above) in its own weight of water gave the value

VIII. 1·11827 (30*b*).

IV. *Silver Nitrate from Commercial Samples.*—As a further test of the possibility of preparing silver nitrate of constant properties, two commercial samples were procured, one from an English and one from a German firm, and these were purified by recrystallising two or three times from water. One of these samples was of especial interest, as it gave initially a lower value for the electrochemical equivalent than any of the samples I. to VIII. which we had purified for ourselves, and we were uncertain at first whether a higher standard of purity might not perhaps be attained by a works-recrystallisation on a large scale than when smaller quantities were dealt with. The recrystallised samples gave, however, entirely normal values, and the low value of one of the commercial samples was therefore due to an impurity which could be removed by recrystallising (see later p. 595). The values obtained for the electrochemical equivalent were :—

IX.	1·11830	(26*a*)
	1·11828	(27*c*)
	1·11828	(28*b*)
X.	1·11827	(44*a*)
XI.	1·11826	(44*b*)

It will be seen that with one exception all the eleven solutions gave, when electrolysed under similar conditions, values for the electrochemical equivalent lying between 1·11826 and 1·11831, the mean value being 1·11828 milligrammes per coulomb. The average error for the nine concordant solutions is 0·00001, and is of about the same magnitude as that observed in the case of duplicate determinations with the same sample of nitrate.

The only discordant value in the above series (No. VI.) gave on a first electrolysis the figure 1·11816, but this may possibly have been due to some accident of manipulation, *e.g.*, to the loss of a trace of loose silver from the bowl; a redetermination of the electrochemical equivalent gave the value 1·11830, a figure which differs only by 0·00003 from the mean. One solution prepared subsequently for use in a comparative test gave the value 1·11836 (52*c*), but the nitrate used for making the solution had been exposed to the air for a long time and was considered not to be sufficiently pure for an absolute determination.

B. *Tests of Commercial Silver Nitrate.*

Having established a definite figure for the weight of deposit obtained from highly purified samples of silver nitrate when electrolysed under standard conditions, it was desirable to ascertain how far commercial "pure" silver nitrate could be relied upon to give a correct weight of deposit. The result was encouraging in so far as with one exception all the samples examined gave figures agreeing with those obtained in the preceding section A. The values for the different samples were as follows:—

H_1	1·11827	Very large number of observations (see Table I.).
H_2	1·11827	
H_3	1·11827	
W_1	1·11819	(22*b*, 23*b*, 25*a*, 25*b*, 31*b*).
G_1	1·11827	(30*a*).
M	1·11829	(30*d*).
G_2	1·11827	(38*a*).
W_2	1·11826	(48*a*).

The abnormal specimen W_1 gave a normal deposit (IX.) when recrystallised and was therefore considered to contain a removable impurity. When the 15 per cent. solution was tested with neutral litmus paper it did not show any acid reaction; but a more concentrated solution tested with blue litmus showed a marked acidity which was absent from the solutions which gave normal deposits. The acidity of the specimen was further established by precipitating the solution with neutral sodium chloride and testing with methyl orange. The makers subsequently stated that the nitrate had been crystallised from a slightly acid liquid in order to secure the formation of clear crystals, and there can be little doubt that a trace of acid mother-liquor had been retained, and that this was the cause of the abnormal character of the deposit. The makers forwarded a second sample which was crystallised from a neutral liquid, and normal results (W_2) were obtained with this.

C. *Standard Method of Preparing Silver Nitrate Solutions for Electrolysis.*

It is now possible to state the conditions that should be complied with in preparing silver nitrate solutions for use in the voltameter.

(1) If commercial "pure" silver nitrate is used, a part of it should be purified by recrystallising twice from water and the deposit compared with that from the original sample. If the values agree, this can be used without purification; if not, the whole of the sample should be twice recrystallised. For rough work in which an error less than 0·1 per cent. may be neglected the commercial nitrate may be used directly without testing or purifying.

(2) If recovered silver nitrate is used it should be freed from acid by evaporating to dryness and heating in the oven at 140° C. until the blue colour of the copper nitrate (if present) is destroyed, then dissolved, filtered and recrystallised until the mother-liquor drained from the crystals is colourless, then once again recrystallised before being used for electrolysis.

(3) In crystallising the nitrate it is desirable to effect the dissolution of the crystals by heating on a water-bath, rather than over a bare flame, so as to avoid all risk of overheating the solution, and to dissolve in a conical flask of Jena glass rather than in a beaker, so as to reduce the risk of contamination by exposure to the air.

(4) For filtering the hot solution we prefer to use a Hirsch porcelain funnel, the perforated plate of which is covered by two discs of filter paper. The funnel is attached to a filter pump and warmed by pouring boiling distilled water through it; there is then but little risk that the hot solution will crystallise in the filter. The filtered solution is allowed to crystallise in the pump-flask, so as to avoid unnecessary exposure to the air. If the flask is cautiously cooled and shaken it is generally possible to secure the separation of the nitrate in small crystals; these can subsequently be drained much more effectively than the larger crystals, which separate when the solution is allowed to cool slowly and without disturbance. As an alternative the filtered solution may be left to deposit large crystals from which the mother-liquor can be poured off, but in this case the separation of the mother-liquor is much less complete and a larger number of crystallisations is required. Towards the end of the crystallisation the flask may be cooled in ice, so as to reduce the amount of material left behind in the mother-liquors.* A porcelain filter funnel may be used without filter paper for collecting and draining the crystals; when these are well pressed down in the funnel, most of the mother-liquor can be removed by means of a

---

* 100 grammes of water dissolve 115 grammes $AgNO_3$ at 0°, 160 grammes at 10°, and 215 grammes at 20° C.

filter pump, but if the liquors contain much impurity it is advisable to rinse the crystals cautiously with a few cubic centimetres of iced distilled water.

(5) If it is desired to dry the crystals, the best method is to make use of a HEMPEL'S vacuum desiccator charged with stick potash, and cautiously heated over a water-bath to accelerate the drying. As a rule, however, it is best to use the moist crystals for preparing solutions, the exact strength of which can, if necessary, be determined by evaporating a known weight of the solution.

(6) The water used in the earlier experiments for the final crystallisation of the nitrate and for the preparation of the solutions was a specially pure sample prepared at Hendon by Mr. W. R. BOUSFIELD, by a process of continuous fractional distillation, and stored in a large Welsbach bottle. Its electrical conductivity had been measured and found to be only 1 reciprocal megohm per centimetre cube. Subsequent experiments showed that commercial distilled water could generally be used without introducing any error.

D. *Effects produced by Repeated Electrolysis.*

That an increase in the value obtained for the electrochemical equivalent of silver may result from repeated electrolysis of a silver nitrate solution was first observed by NOVAK,* and later by RODGER and WATSON,† KAHLE,‡ VAN DIJK§ and GUTHE.‖ RODGER and WATSON record as successive relative values the numbers

9983, 9987, 9990, 9999, 9995, 9993, 9995, 10002, 10005, 10006, 10002.

In an attempt to confirm these observations we repeatedly electrolysed two solutions of silver nitrate, the one being contained in a platinum bowl and the other in a silver bowl. The resulting values of the electrochemical equivalent were,

when the platinum kathode was used :—	and when a silver kathode was used :—
1·11827 (14*a*)	1·11825 (14*b*)
1·11822 (15*b*)	1·11826 (15*a*)
1·11822 (16*b*)	1·11825 (16*a*)
1·11827 (17*c*)	1·11833 (17*b*)
1·11838 (18*a*)	1·11840 (18*b*)
1·11834 (21*a*)	1·11830 (21*c*)

It thus appears that there may be a small increase, but nothing comparable with that observed by RODGER and WATSON.

---

* NOVAK, 'Proc. Roy. Bohemian Ac. Sci. Prague,' 1, pp. 387–432, 1892.

† RODGER and WATSON, 'Phil. Trans.,' A, 186, p. 631, 1895.

‡ KAHLE, 'Zeitschr. Inst.,' 18, pp. 229–267, 1898.

§ VAN DIJK and KUNST, 'Ann. der Phys.,' 14, p. 569, 1904. VAN DIJK, 'Ann. der Phys.,' 19, p. 249, 1906.

‖ GUTHE, 'Phys. Rev.,' 19, p. 138, 1904; 'Bull. Bureau of Stands.,' vol. 1, p. 355, 1904.

In a final experiment a current of 1 ampere was passed through a solution during 200 hours until the solution was blue with copper from the "pure" silver anode. During this interval the mass of silver transferred through the solution amounted to no less than 820 grammes, or more than 100 times as much as in a normal electrolysis. The values obtained for the electrochemical equivalent were :—

Before electrolysis	1·11827	(solution H_1)
After 100 hours	1·11822	(17*a*)
After 200 hours	1·11832	(23*d*)

We were therefore driven to the conclusion that the mere act of electrolysis is not sufficient to produce the effects recorded by RODGER and WATSON and others.

The only change which we have been able to detect in the properties of the solution after repeated electrolysis is that it gives somewhat more coherent and very slightly striated deposits. KAHLE[*] has pointed out that the filter paper may have an effect on the electrolyte, and this view is adopted by VAN DIJK[†] in explanation of the increase which he observed. In our experiments the volume of the electrolyte was exceptionally large, and the mass of filter paper[‡] immersed was small ; contamination of the solution by the paper would therefore not be likely to produce any marked effect in the course of a few electrolyses at ordinary temperatures ; at higher temperatures we have reason to think that important effects may be produced by the action of the filter paper on the electrolyte. No filter paper was used in the 200-hour electrolysis except during the actual determination of the electrochemical equivalent.

E. *The Question of Anodic Impurities.*

It has been generally assumed that the high values obtained on repeated electrolysis were due to the introduction of impurities at the anode during electrolysis. It was to overcome the supposed effects of such impurities that the porous pot voltameter was introduced by RICHARDS. We were at first inclined to agree with this view ; it is well known that when silver nitrate is electrolysed with a platinum anode, crystals are formed of a "peroxynitrate," Ag_7NO_{11}. This substance was discovered by RITTER[§] in 1804 ; its composition has been established by repeated analysis,[||] and it is known to be decomposed when warmed with water at temperatures from 25° upwards according to the equation

$$Ag_7NO_{11} = AgNO_3+3Ag_2O_2+O_2,$$

---

[*] KAHLE, 'Zeitschr. Instr.,' 22, p. 155, 1902.

[†] VAN DIJK, 'Ann. der Phys.,' 19, p. 249, 1906.

[‡] SCHLEICHER and SCHULL, No. 595.

[§] RITTER, 'GERLEUS Neues J.,' 3, p. 561, 1804. SULC, 'Zeitschr. Anorg. Chem.,' 12, p. 90, 1896.

[||] MULDER and HERINGA, 'Verh. Kon. Ak. Wet.,' 3, p. 37, 1896. TANATAR, 'Zeitschr. Anorg. Chem.,' 28, p. 331, 1901 WATSON, 'Trans. Chem. Soc.,' 89, p. 578, 1906.

and this affords the only general method of preparing silver peroxide. It was possible that whilst this compound does not crystallise out when a silver anode is used, and does not occur in the anode slime, it might be produced in small quantities and pass into solution, especially if high current densities are used at the anode. It was found, however, that no increase in the electrochemical equivalent resulted when the area of the silver anode of the Rayleigh voltameter was made very small and when high current densities were employed (pp. 571 and 573, Part I.).

In further experiments it was shown that this action at the anode, which is accompanied by a liberation of acid, actually lowers the value of the electrochemical equivalent instead of raising it. An apparatus was arranged with a platinum crucible as an anode, and between it and the cathode a large filter paper cup was suspended to prevent any crystals of Ag_7NO_{11} falling on the platinum bowl. The solution was very acid after electrolysis, and the resulting values of the electro-chemical equivalent were 1·11779 (34*a*) and 1·11811 (55*b*). The abnormally high equivalents are therefore not due to the formation of peroxynitrate at the anode.

RICHARDS* found that the anode liquid was so changed during electrolysis that it deposited silver on prolonged contact with silver crystals. We have been unable to confirm this in our voltameters.

The following experiment was performed so that the anode liquid should come into contact with the silver surface a few seconds after its formation. The anode and kathode liquids were contained in two silver bowls (fig. 14) connected by a syphon, and the anode was a silver plate which dipped into a glass funnel fitted with a filter paper. On electrolysis, the dense liquid descended to the bottom of the bowl and thus came into contact with silver. The anode bowl was weighed both before and after electrolysis, but no gain in weight was recorded in any of the experiments, even though on one occasion 20 grammes of silver were deposited on the kathode bowl. In the first experiment the silver plate was surrounded with filter paper only, but this led to complications, owing to part of the current entering and leaving the

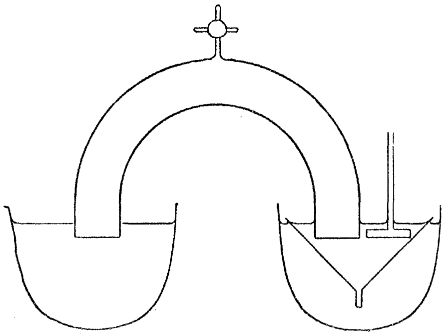

Fig. 14.

---

* RICHARDS and HEIMROD, 'Proc. Am. Ac.,' 37, p. 431, 1902.

bowl surrounding it. The glass funnel largely prevented such a distribution of current.

The experiments recorded in Part I. indicate further that, under normal conditions of working, the exclusion from the kathode vessel of the anode liquid by means of a porous pot is without influence on the deposit, and we therefore conclude that the cause of the abnormal values in our voltameter (Observations 1 to 13) is to be sought in the contamination of the solution, but that this is not due to any change which is inseparably connected with the conditions of electrolysis.

F. *Examination of the Mother-Liquors from Recovered Silver Nitrate.*

Although it was not found possible to obtain appreciably higher values for the electrochemical equivalent by repeated or prolonged electrolysis, or by bringing the anode liquid into contact with the kathode, it was known that high values could readily be obtained by using recovered silver nitrate that had been cleared with acid and rendered neutral by fusion, but not otherwise purified. It was therefore thought to be desirable to investigate these solutions in order to determine the nature of the impurity which they contained. For this purpose the mother-liquors left behind during the purification of the recovered nitrate, as described in § A II. and III., were collected and examined. After recovering in a pure state the greater part of the 850 grammes of nitrate there remained a yellowish liquid containing about half its weight of silver nitrate. On dilution with water the liquid became turbid and a thick brown cloud was formed which ultimately settled down as a black precipitate.* The diluted solution, which contained 14·4 per cent. $AgNO_3$, was then electrolysed and gave the extraordinary value

1·12141 milligrammes per coulomb (27*b*)

for the electrochemical equivalent. A second electrolysis gave the value

1·12055 (30*c*),

and a third electrolysis, after the addition of 1 gramme of crystallised ferric nitrate to about 400 cub. centims. of the mother-liquor, gave the value

1·12171 (74*d*).

As it appeared that the impurities were largely precipitated by diluting to 15 per cent., an electrolysis was carried out with a more concentrated mother-liquor containing 43 per cent. $AgNO_3$. The value obtained for the electrochemical equivalent was 1·12252 (47*b*), which is no less than 0·00425, or 0·36 per cent., higher than the normal, and is possibly the highest yet recorded.

---

* A slight cloudiness had already been noticed when the fused nitrate referred to at the beginning of the section was dissolved in water and diluted after filtration instead of before.

The impurity present in the mother-liquor evidently consists, then, to a considerable extent of substances which are insoluble in water, but soluble in silver nitrate solutions of moderate concentration. These impurities are partially precipitated on diluting the solutions, but a certain amount remains in solution. The property of dissolving in silver nitrate appears to be possessed by a large range of silver salts which are insoluble in water, and many of these possess the property of increasing the weight of the deposit obtained on electrolysing the solution. The removal of silver at the kathode leads, as is well known, to the formation of a film of dilute solution which (owing to its small density) flows upwards towards the surface of the solution. The film immediately in contact with the kathode may be regarded as almost pure water, and the dilution from 15 per cent. to nearly 0 per cent. (by removal of silver nitrate instead of by addition of water) probably causes a precipitation of impurity similar to that which results from the dilution from 50 per cent. to 15 per cent. In this direction we believe an explanation may be sought of the abnormally high equivalents obtained from impure silver nitrate solutions.

In the course of the later work several centigrammes of the precipitate formed on diluting the silver nitrate mother-liquors were collected and fractionated as follows:—

	gramme.
Soluble in dilute nitric acid (Ag_2O, &c.) . .	0·0231
,, ammonia ($AgCl$, &c.)	0·0664
Undissolved (Ag_2S, &c.)	0·0274
	0·1169

From the first fraction there was recovered 0·0113 gramme $AgCl$, equivalent to 0·0091 Ag_2O; from the second fraction 0·0567 gramme $AgCl$. It appears, therefore, that about half the residue consisted of silver chloride, whilst the remaining part contained sufficient oxide and sulphide to give the precipitate a black colour, and so disguise to a large extent the chloride which was its chief constituent.

G. *Striation of the Deposit.*

It was noticed very early in the investigation that high values for the electrochemical equivalent were almost invariably accompanied by a characteristic striation of the deposit, whilst normal equivalents were almost always obtained from unstriated deposits with currents of 1 ampere; it was in fact possible to guess roughly what the weight of the deposit would be by noting the appearance of the silver deposited in the bowl. The impurity which causes the high values is evidently characterised by the property of producing marked striations, and this property was for some time the only qualitative test for the presence or absence of the substance in the silver solutions. It was also considered to be of importance in seeking to determine the nature of the impurity; thus if high values could be obtained with a variety of added impurities, that one which most readily gave striated deposits was the most likely to be the characteristic impurity of the actual solutions used for electrolysis.

The deposits from the mother-liquors showed an exceedingly marked striation, although the silver was dull in appearance.

H. *Influence of Oxide, Carbonate and Chloride.*

The influence of silver oxide on the silver voltameter has been investigated by PATTERSON and GUTHE,* GUTHE,† RICHARDS,‡ and KAHLE§. PATTERSON and GUTHE used a solution saturated with silver oxide, and GUTHE's comparison of it with the Rayleigh type showed the two to agree. RICHARDS, however, found his form of voltameter to give a deposit lower by 0·1 per cent. when compared with PATTERSON and GUTHE's type, and KAHLE§ found the effect of silver oxide was to increase the deposit by 0·05 per cent. From the point of view to which we have referred it was probable that any silver salt which was insoluble in water would, if dissolved in the nitrate solution, give an abnormally heavy deposit. Two experiments made with solutions containing silver oxide gave confirmation to this view. Pure sodium hydroxide was prepared by the action of water-vapour on metallic sodium and was added to a 50 per cent. solution of silver nitrate; the filtered solution gave a slight brown precipitate on diluting to 400 cub. centims., and on electrolysis it gave for the electrochemical equivalent the value

1·11852 (50*d*),

0·021 per cent. higher than the normal figure. A later experiment carried out in the same way gave the value

1·11842 (80*c*).

These results are not directly comparable with those of other observers owing to the difference in the size of the voltameters, but may be regarded as substantially in agreement with that of KAHLE.

Very similar results were obtained on adding sodium carbonate, which raised the electrochemical equivalent by about two parts in 10,000 (Observation 53*b*).

Addition of potassium chloride gave the values

1·11840 (50*c*), 1·11847 (80*b*).

The chloride is freely soluble in concentrated silver nitrate solutions, especially when hot, and is copiously precipitated on dilution; its effect on the electrochemical

---

* PATTERSON and GUTHE, 'Phys. Rev.,' 7, p. 257, 1898.

† GUTHE, 'Phys. Rev.,' 19, p. 145, 1904.

‡ RICHARDS and HEIMROD, 'Proc. Am. Ac.,' 37, p. 426, 1902.

§ KAHLE, 'Brit. Assoc. Report,' Section A, 1892.

equivalent is, however, unimportant, possibly because a sufficient weight is not retained by the 15 per cent. solution.

The above results go far to justify the view that the majority of silver salts which are insoluble in water dissolve to a slight extent in concentrated silver nitrate solutions, and that the increase in the electrochemical equivalent which usually results may be related to this difference in solubility, which probably acts by causing a precipitation of the sparingly soluble salt from the impoverished solution at the kathode.

I. *Influence of Sulphide.*

In view of the readiness with which metallic silver blackens on exposure to air, it was evident that silver sulphide was likely to be a frequent impurity in the nitrate solutions. The blackening of the bottles in which silver nitrate solutions are kept is a universal experience in the laboratory, and in voltameter work the blackening of the porous pots has constantly proved a source of trouble. The sediment from the silver nitrate mother-liquors undoubtedly contained sulphide, and it was therefore very important to determine the influence of this substance on the electrochemical equivalent.

(1) A solution of 60 grammes of silver nitrate in an equal weight of water was prepared in a wide test-tube, and a small volume of hydrogen sulphide gas was delivered into the tube above the surface of the solution. The first effect of the sulphuretted hydrogen was to produce on the surface of the solution a yellow film which turned black where the gas was present in largest quantities. On shaking the solution a granular precipitate of a canary-yellow colour became distributed throughout the solution, and the black sulphide disappeared. It was evident that where the nitrate was in excess the precipitate was stable in a yellow form, and became black only when the proportion of sulphuretted hydrogen to nitrate was increased. When a considerable quantity of the yellow precipitate had been formed the solution was filtered. On diluting with distilled water to 400 cub. centims., a brown cloud appeared which slowly settled to a black precipitate at the bottom of the colourless solution. The behaviour of the sulphide solution was thus essentially similar to that of the silver nitrate mother-liquors. The diluted solution was filtered and transferred to a voltameter. It gave a normal electrochemical equivalent

1·11828 milligrammes per coulomb (87*b*).

Three other solutions (85*b*, 85*c*, 86*c*), prepared by somewhat similar methods, also gave normal values,

1·11829, 1·11828, 1·11828.

We are therefore driven to the conclusion that although many of the heavy deposits were obtained from solutions which were undoubtedly contaminated with sulphide (mother-liquors 27*b*, 47*b*), the presence of this substance alone is not sufficient to account for the production of these abnormally high values.

Our experiments have shown that the abnormally heavy deposits cannot be explained as due to sulphide acting in presence of copper or of iron.

Two solutions were prepared by dissolving 60 grammes of silver nitrate in 60 grammes of water, and to each of these was added 0·12 gramme of commercial pure copper foil; this was left in contact with the solution until the copper had dissolved as nitrate by displacing an equivalent quantity of metallic silver. Hydrogen sulphide was then added and the solution filtered and diluted as before; very little sulphide was precipitated by diluting, and the electrochemical equivalent was found to be in the case of the first solution

1·11850 (67*c*);

in the case of the second solution, to which hydrogen sulphide had been lavishly added, a nearly normal value was obtained,

1·11824* (74*a*).

Similar experiments were made with iron. This could not be introduced in the same way as the copper, for the metal appeared to become passive in contact with the strong nitrate solution and refused to dissolve. Two solutions were prepared by adding 1 gramme of crystallised ferric nitrate to 60 grammes of silver and adding sulphuretted hydrogen as before. The first solution gave the perfectly normal electrochemical equivalent

1·11825 (67*d*),

and the second, to which much more hydrogen sulphide was added, gave the value

1·11834 (74*c*),

also substantially normal. The ferric nitrate was strongly acid, and this fact must be taken into account in discussing the above result, but it is clear that the extraordinarily high electrochemical equivalent of the mother-liquors cannot be attributed to the presence either of iron or of copper. Addition of ferric nitrate to the mother-liquor produced no marked change in the electrochemical equivalent, the value obtained being 1·12141 (27*b*) and 1·12055 (30*c*) before and 1·12171 (74*d*) after the addition of 1 gramme of ferric nitrate to about 400 cub. centims. of 15 per cent. mother-liquor.

J. *Influence of Nitrite and Hyponitrite.*

The abnormally high deposits obtained with the silver voltameter have usually been attributed to anodic impurities. Such impurities would normally be oxidised substances comparable with the persulphuric acids, with lead peroxide, or with silver peroxynitrate. Richards has, however, made the suggestion that reduction may

---

* The fact that this figure is somewhat lower than the normal may be due to the trace of acid which is liberated by the sulphide $2AgNO_3 + SH_2 = Ag_2S + 2HNO_3$. The solution did not, however, appear acid to litmus.

take place at the anode with formation of silver nitrite. It was therefore of interest to determine the effect of this substance on the electrochemical equivalent.

RICHARDS* prepared silver nitrite by boiling silver nitrate solution with finely divided silver, and obtained with a nitrate solution saturated with it a value identical within 1 part in 200,000 with that found with a pure nitrate solution. He also prepared nitrite from pure potassium nitrite and silver nitrate and concluded, from voltameter experiments made with a nitrate solution saturated with the salt so prepared, that the nitrite caused an increase in the deposit of between 30 and 80 parts in 100,000.

A first experiment, in which a solution of pure silver nitrate was saturated with silver nitrite (purchased as pure) by making a saturated solution of the latter and dissolving the requisite quantity of silver nitrate in it, gave 1·11832 (24*d*) as the equivalent. That the solution was saturated with nitrite was evident from the copious precipitate of this salt which resulted when the silver nitrate crystals were dissolved in it.

A second experiment, in which a 50 per cent. solution of silver nitrate was saturated with nitrite by the addition of KNO_2 and then diluted and filtered, gave the value 1·11837 (52*d*) for the electrochemical equivalent. In this case the saturation of the solution was evidenced by the fact that needles of silver nitrite actually crystallised out from the solution on standing in a cool place.

The above experiments show clearly that silver nitrite even when present in considerable quantity does not raise the electrochemical equivalent by more than one part in 10,000 and can only be an unimportant impurity. In view of the yellow tint of the nitrite crystals, which should be colourless when pure, we are by no means certain that the slight increase which we have observed may not be due to hyponitrite (*vide infra*) and not to the nitrite itself.

The influence of hyponitrite on the deposit does not appear to have been determined. The salt was prepared by reducing sodium nitrite with sodium amalgam, neutralising with acetic acid and precipitating with dilute silver nitrate solution. The yellow precipitate of silver hyponitrite was drained on a filter, thoroughly washed with water and shaken up with 120 grammes of a 50 per cent. solution of silver nitrate. The strong saturated solution was then filtered and diluted to 400 cub. centims. with water. A slight cloud was produced which was removed by filtration and the solution was then electrolysed. The deposit was strongly striated and gave the value 1·11873 (88*b*). An earlier preparation gave a higher figure, 1·11930 (47*c*), but we do not wish to lay stress on this.

K. *Influence of Acids.*

It has been shown that there are a considerable number of impurities which raise the electrochemical equivalent of a silver nitrate solution—oxide, carbonate, chloride

---

* RICHARDS and HEIMROD, 'Proc. Am. Ac.,' 37, p. 423, 1902.

and nitrite increasing the value by about one part in 10,000 and hyponitrite by about one part in 2000. Occasionally, however, abnormally low values are obtained, as, for instance, in the case of the commercial sample W_1, which gave the mean value 1·11818, and in a large number of the earlier porous pot experiments 1·11786 (4*a*), 1·11810 (5*a*), 1·11818 (6*a*), 1·11815 (7*b*), &c.*

These low values we were able to associate in most cases with the presence of acid, but if acid was responsible for the low values the quantity required to lower the electrochemical equivalent by one part in 10,000 appeared to be very small and could not easily be detected by litmus and other indicators. The commercial sample W_1 had admittedly been crystallised from an acid solution and showed a trace of acid when carefully tested with blue litmus paper. Finally it was found that the porous pots which had been cleaned with nitric acid but soaked in water for a fortnight until all the acid had apparently been removed, gave up acid to the solutions when a current was passed through them, and this in sufficient quantity to be detected by litmus. It was thought, however, to be desirable to make direct experiments on the influence of acids.

Our own experiments have shown that the addition of nitric acid to silver nitrate solutions produces very irregular results. The normal effect appears to be a small decrease in the electrochemical equivalent, but this never exceeds about two parts in 10,000, and there is very little difference in the effect produced by a mere trace of acid which can only be detected with difficulty by means of litmus and that produced by the addition of acid corresponding to 1 per cent. *of the silver nitrate present in the solution.* On the other hand we have found that addition of diluted nitric acid may produce an increase in the electrochemical equivalent; this we attribute to the presence in the nitric acid of oxides of nitrogen or other substances which, like the hyponitrite, may raise the electrochemical equivalent to such an extent as to mask completely the small decrease due to the acid.

The irregular effects obtained may be seen from the following summary† :

I.	Normal solution	1·11830 (65*b*).	II.	Normal solution	1·11826 (66*b*).
	0·1 per cent. HNO_3	1·11841 (65*c*).		0·1 per cent. HNO_3	1·11860 (66*c*).
	1·0 per cent. HNO_3	1·11836 (65*d*).		1·0 per cent. HNO_3	1·11840 (66*d*).
III.	Normal solution	1·11830 (46*c*).	IV.	Normal solution	1·11827.
	0·2 per cent. HNO_3	1·11812 (73*b*).		1·0 per cent. HNO_3	1·11814(58*c*).
	1·0 per cent. HNO_3	1·11814 (73*c*).		1·0 per cent. HNO_3	1·11810 (75*c*).
III*a*.	1·0 per cent. HNO_3	1·11829 (73*d*).		1·0 per cent. HNO_3	1·11819 (78*b*).
				0·1 per cent. HNO_3	1·11822 (78*c*).

---

* There was, however, a considerable quantity of loose silver in most of the early determinations.

† One series, No. 53, has been omitted, as the unacidified solution (53*c*) gave a high value and the nitrate was therefore not pure.

In all cases but IV. the nitric acid was purified by distillation from silver nitrate; in series III. and III*a*. the acid was added in a concentrated form, in the others it was diluted and titrated. LEDUC found a diminution in the mass of the deposits of 2 parts in 10,000 when free acid was present.

We conclude, therefore, that whilst the abnormally low values which are observed from time to time can only be explained by the presence of acid, it may be very difficult in practice to add nitric acid without at the same time introducing other impurities which may more than counterbalance the effects produced by the acid itself.

L. *Effect of Heating Silver Nitrate.*

It has been shown above that the mere act of electrolysis does not cause any increase in the electrochemical equivalent of a silver nitrate solution, and that in our experiments no contamination appears to be produced by the changes which take place at the anode. For a considerable time we were of opinion that atmospheric contamination with sulphide might in some way produce an alteration in the electrical behaviour of the solution, but finally we were unable to uphold this explanation of the heavy deposits. We believe, however, that a clue to the origin of the abnormal deposits may be found in the behaviour of the nitrate when heated, and, on the other hand, in the action of the nitrate on the filter paper, to which we have referred above, but which in our own experiments we have only been able to detect at high temperatures.

Very early in the course of the investigation we noticed that the fusion of the nitrate caused an increase in the weight of the deposit. A perfectly normal salt (H_1) was fused, dissolved in water, and its electrochemical equivalent was found to be 1·11838 (24*c*), an increase of 1 part in 10,000. A second similar experiment with a slightly acid salt (W_1) showed an increase in the electrochemical equivalent from 1·11819 (mean of several) to 1·11835 (25*c*), the latter value being again 1 part in 10,000 higher than the normal. It was further noticed that the mother-liquors which gave such high deposits were all obtained from samples of nitrate which had been fused or strongly heated at some stage of their treatment.

In order to test the effect of heat alone on the nitrate a quantity of the purified salt was heated to incipient fusion for several hours, and the greater part of the nitrate was removed by crystallisation. The colourless mother-liquor was electrolysed, and gave for the electrochemical equivalent the value of 1·11972 (88*c*). We therefore feel justified in suggesting that whilst other causes (action of light, action of filter paper, &c.) may contribute to the production of heavy deposits, the heating of the nitrate appears to be one of the most effective ways of producing this effect. It is possible that traces of hyponitrite may be formed both by the action of heat and by the reducing action of filter paper, but we do not wish to commit ourselves to the view that the hyponitrite is the only, or even the main, source of the disturbances which have been noticed by ourselves and others. We hope at some future date to enquire more closely into the nature of the impurities which affect so strongly the weight of the deposit from the silver nitrate mother-liquors.

M. *Other Electrolytes.*

(1) *Silver Acetate.*—Lord RAYLEIGH* found that the addition of a small quantity of silver acetate to a solution greatly improved the texture of the deposit, but that the mass of silver deposited per coulomb was considerably increased thereby. We prepared a saturated solution of silver acetate and electrolysed in the usual manner; the deposit was of very fine texture, and the resulting electrochemical equivalent was 1·12154 (31*c*) or 0·3 per cent. higher than the normal. There was evidence, however, that the deposit was not silver alone, for on stripping a portion of it from the platinum bowl a yellowish-white film was plainly visible on both silver and platinum where they had been in contact.†

(2) *Silver Chlorate.*—Lord RAYLEIGH* also employed silver chlorate as an electrolyte, independent of the nitrate, and obtained very satisfactory results from it, and if the mean value of the electrochemical equivalent is deduced from the chlorate observations alone, it is higher than the value obtained with the nitrate solutions by only 6 parts in 100,000. In our first attempt to use silver chlorate as an electrolyte we used a 10 per cent. solution and obtained 1·11839 (49*a*) for the electrochemical equivalent. It was apparent, however, that the electrolyte also contained silver chloride, for a white precipitate had to be filtered from the original solution, and the effect of silver chloride in solutions of silver chlorate is possibly the same as in nitrate solutions. The chlorate was recrystallised to free from chloride and a 5 per cent. solution used to minimise the effect of any remaining impurity. The resulting deposit had a matt surface and its mass was 2 parts in 100,000 greater than that from a 3 per cent. solution of the nitrate, but less by 1 part in 100,000 than that from a 15 per cent. solution (81*a*, *b*, *c*). The electrochemical equivalent may therefore be taken as 1·11827, and confirms Lord RAYLEIGH's view that a solution of silver chlorate gives the same mass per coulomb as one of silver nitrate.

(3) *Silver Perchlorate.*—CARHART, WILLARD and HENDERSON‡ have suggested the use of silver perchlorate as an electrolyte. They found the deposits from such a solution to be striated and firmly attached to the bowl, but heavier than the deposits from the nitrate by about 0·007 per cent. It appears, however, that silver chloride may also have been present in the perchlorate, as instructions are given by them for this to be filtered out. A small quantity of perchlorate was prepared for us by some

---

* RAYLEIGH and SIDGWICK, 'Phil. Trans.,' 175, p. 411, 1884.

† VAN DIJK found a diminution in the mass of a silver deposit from an acetate solution when it was heated to a high temperature in an electric oven.

‡ CARHART, WILLARD and HENDERSON, 'Amer. Electrochem. Soc.,' 1906.

manufacturing chemists, but it was far from pure, and our results are not therefore comparable with those of CARHART. The chloride was filtered out, and when a 5 per cent. solution was used, the value 1·11860 (81*d*) milligrammes per coulomb resulted; subsequently we used a 10 per cent. solution and obtained 1·11840 (83*b*). We infer that pure perchlorate of silver will give the same value as pure nitrate, but it is much more difficult to prepare.

(4) Acting on a suggestion of Mr. W. C. D. WHETHAM, we prepared an electrolyte by dissolving silver nitrate in pyridine. Considerable heat was evolved during dissolution, but the liquid was quite clear. On electrolysis the deposited silver was of a brownish-red tint, but when washed with very hot water the intensity of the colour was considerably reduced. It was apparent, however, that the mass was not pure silver, and the result (1·11890) (67*b*) is not of very great interest.

(5) *Fused Silver Nitrate.*—MERRILL* was successful in obtaining coherent deposits from fused silver nitrate, and compared them with deposits obtained from solutions of the same salt. He concluded that the masses were identical. We have on several occasions deposited about 7 grammes of silver on platinum bowls and obtained very coherent deposits, but errors introduced in the manipulation have so far prevented us from making a satisfactory comparison with deposits obtained in the usual way.

Summary.

1. It is possible to prepare again and again samples of silver nitrate which give in the voltameters described in Part I. of this communication values for the electrochemical equivalent which do not vary by more than 3 parts in 100,000 on either side of the mean figure.

2. A standard method of purification is described. Commercial samples are usually pure, but cannot be absolutely relied on.

3. High values are obtained for the electrochemical equivalent if the solution contains oxide, carbonate, chloride, nitrite or hyponitrite. Low values are caused by the presence of acid.

4. Impurities which increase the mass of the deposit per coulomb are usually substances which are insoluble in water, but soluble in silver nitrate solutions; they are therefore precipitated from the impoverished solution at the kathode.

5. Silver chlorate and silver perchlorate appear to give normal deposits, but are more troublesome in use and have no advantage over the nitrate.

6. There may be slight changes in the electrolyte due to its interaction with filter paper, but the mass of the deposit is not seriously affected thereby in our size of voltameter in the course of one electrolysis at ordinary temperatures. It is inadvisable, however, in measurements of precision, to use an electrolyte more than once.

---

* MERRILL, 'Phys. Rev.,' 10, p. 170, 1900.

We desire to thank the Committee of the British Association for grants of money for the purchase of materials; Messrs. JOHNSON, MATTHEY and Co. for the loan of several platinum vessels; Mr. L. OERTLING and Dr. SCOTT for the loan of sensitive balances; and Professor G. VAN DIJK for the loan of apparatus used by him in his researches. Our thanks are also due to Lord RAYLEIGH and Dr. GLAZEBROOK for much advice during the progress of the investigation.

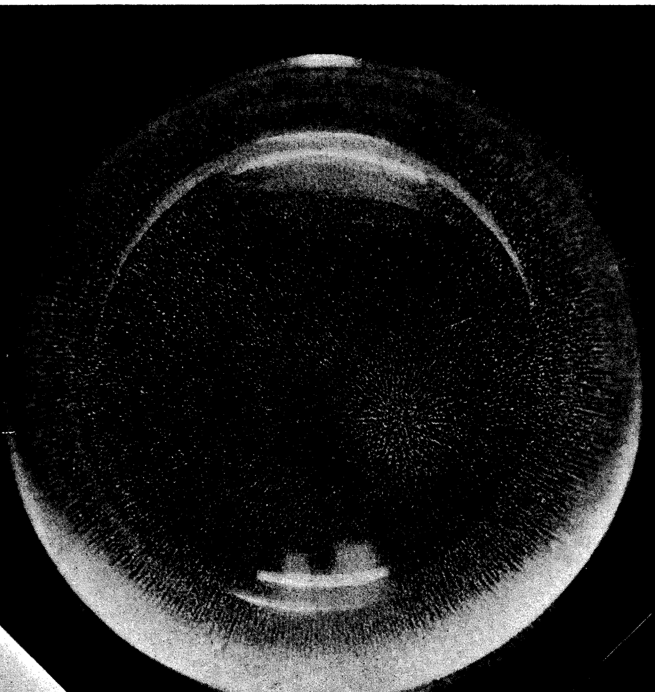

FIG. 8.

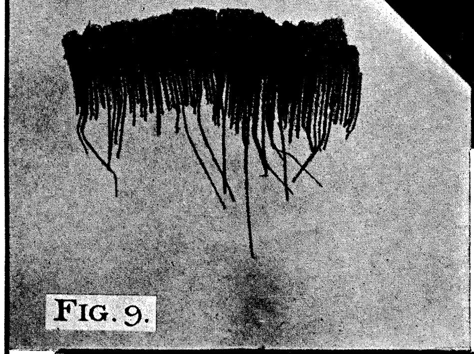

FIG. 9.

FIG. 10.

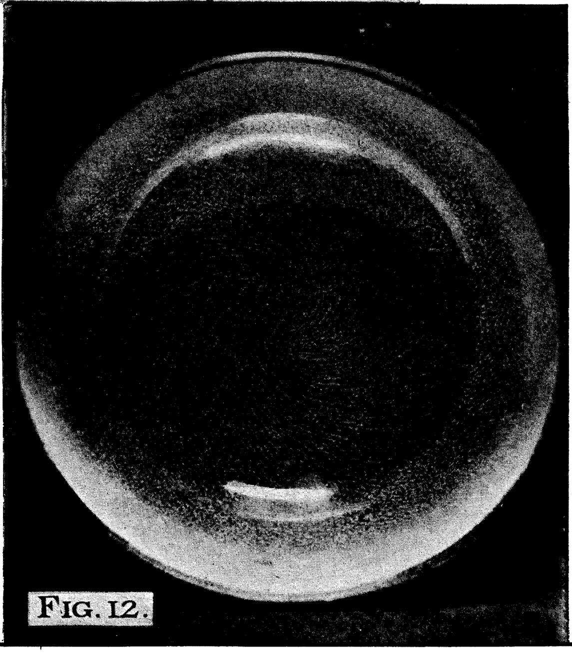

FIG. 12.

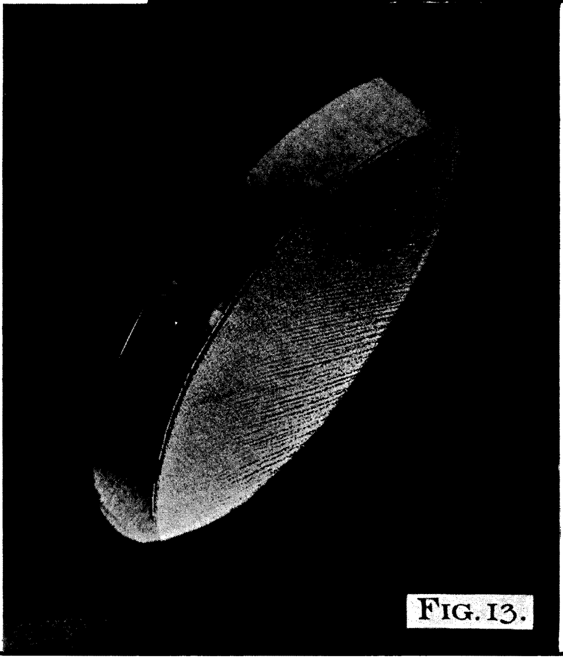

FIG. 13.

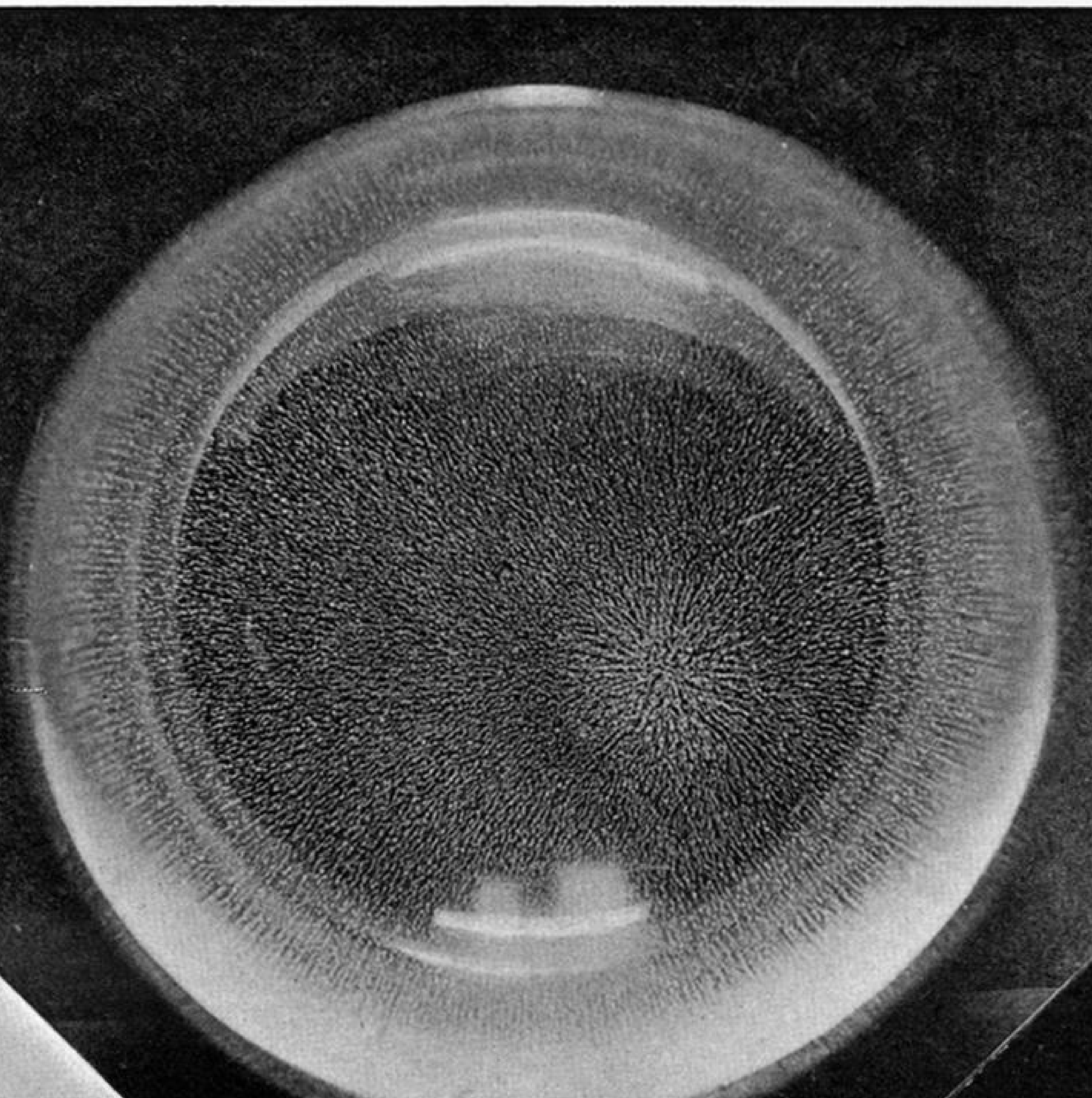

FIG. 8.

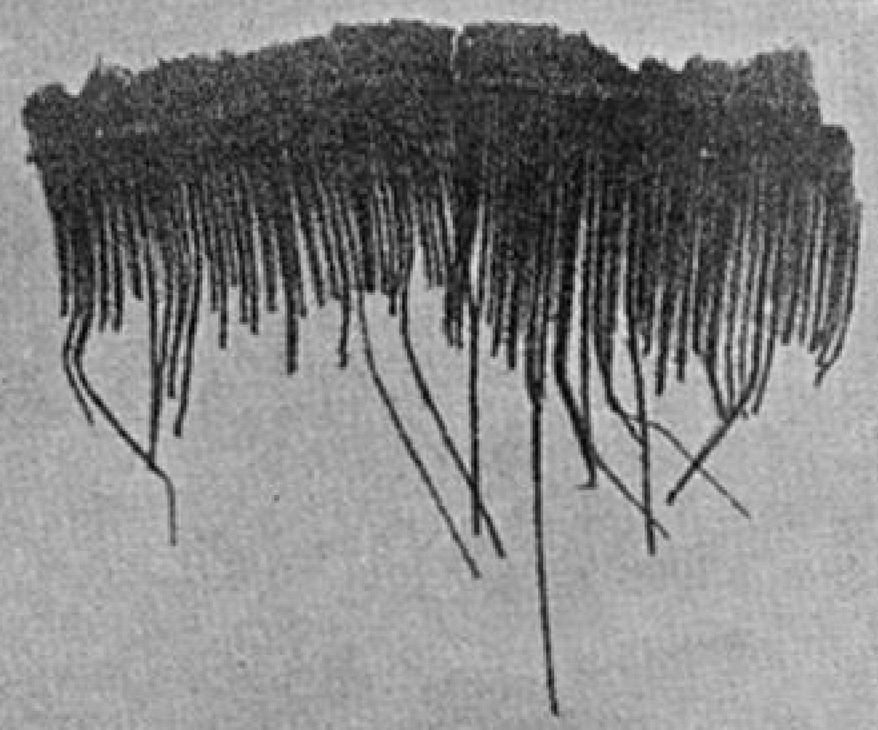

FIG. 9.

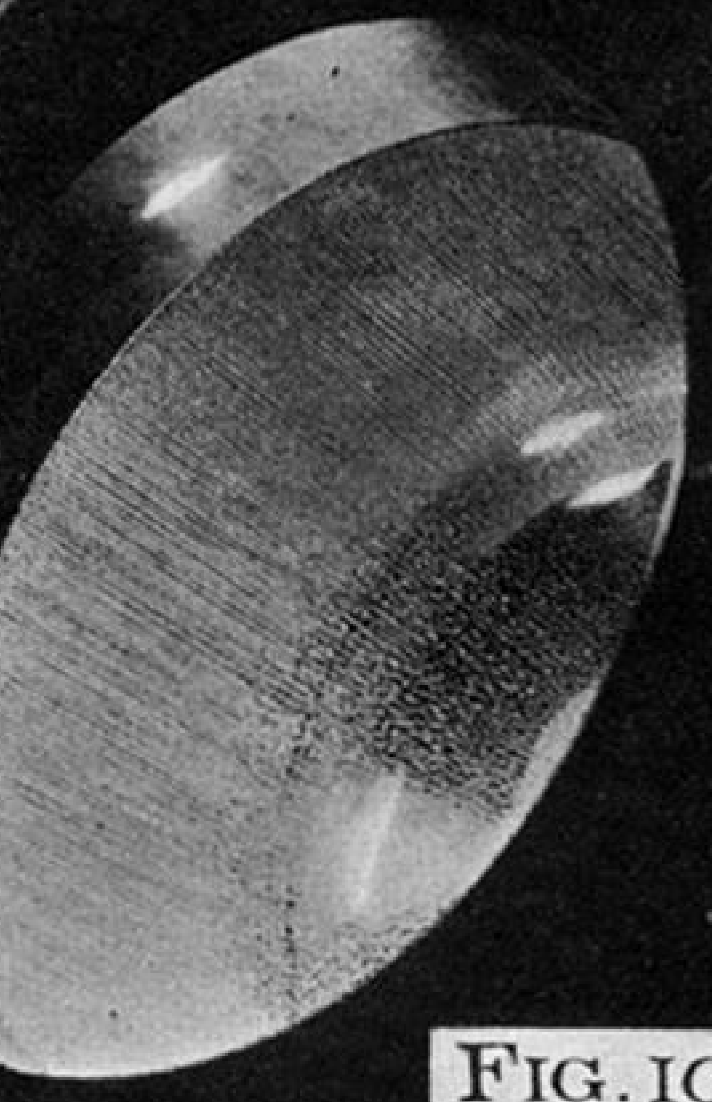

FIG. 10.

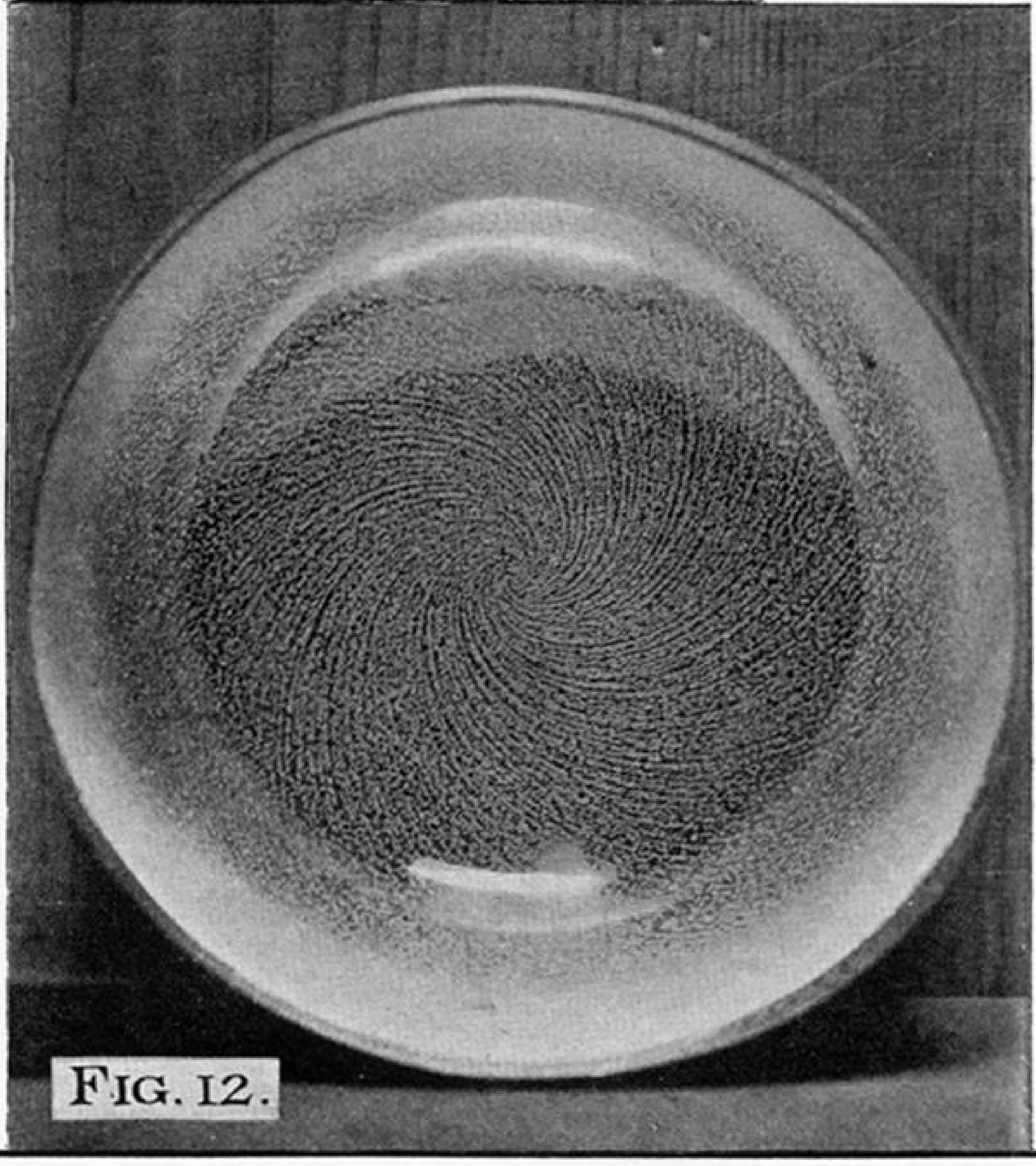

FIG. 12.

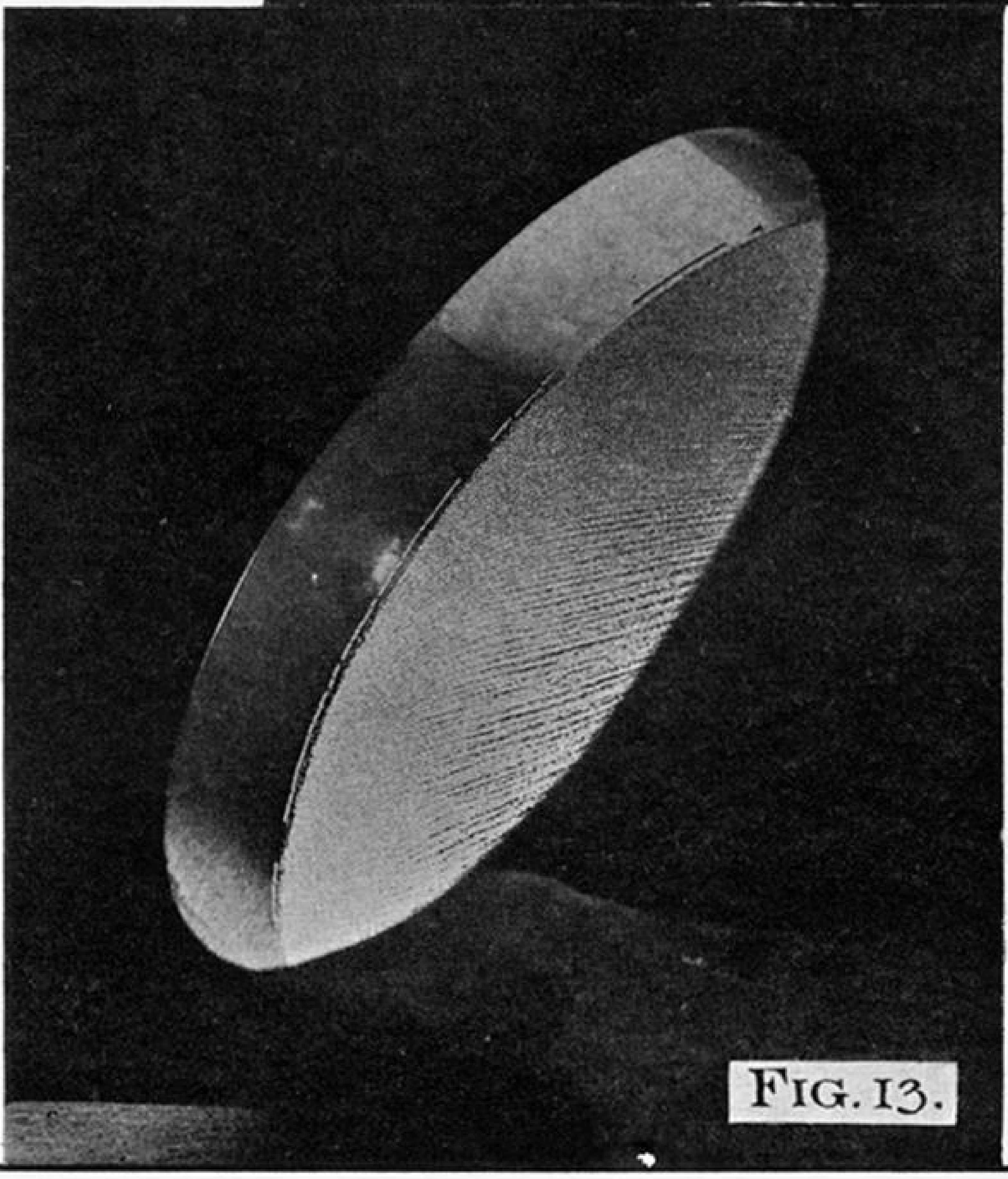

FIG. 13.