ERRATUM.

Page 339, line 25: *for* "indicating a decomposition of 1 gramme electrochemical equivalent in 30,000 years," *read* "indicating the separation, by decomposition, of 1 gramme of Hydrogen or of its electrochemical equivalent in 3,000,000 years."

VII. *Galvanic Cells Produced by the Action of Light.—The Chemical Statics and Dynamics of Reversible and Irreversible Systems under the Influence of Light.* (*Second Communication.*)

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[PLATES 1–8.]

INTRODUCTION.

IN this communication we devote all our attention to constant reversible galvanic cells created by light. Having first shown in § 1 that the E.M.F.'s created by light in the combinations of BECQUEREL and MINCHIN, or any others, are not surface phenomena on the plates of the electrodes, but galvanic, we shall have next to establish in § 2 that the E.M.F. created by light represents a new phenomenon, and is not an ordinary thermo E.M.F. Having further shown in § 3 that all wave-lengths act as actinic rays, we shall then proceed, after the account given of the method employed to secure accurate results, to a very detailed study of constant cells reversible in respect of the cation (§ 6) and reversible in respect of the anion (§ 7) carried out with the total light of acetylene or arc, or with the total light passing coloured screens. A study (in § 5) of the chemical statics and dynamics in constant reversible cells created by light, which at the same time enables us to fix any chemical combination of cell into its proper class, must evidently proceed to the research given in § 6 and § 7. In § 8 we shall collect from the results given in § 6 and § 7 the experimental evidence in support of the physico-mathematical theory of galvanic cells given by the author in 'Roy. Soc. Proc.,' November, 1904, vol. 74. Finally, in § 9, a short outline will be given of the general laws obtained for chemical statics and dynamics under the action of light, of which galvanic cells form only a part.

§ 1. *The Experiments of* Becquerel *and* Minchin. *The Phenomena Observed by* Becquerel *and* Minchin *are not Surface Phenomena, but their Combinations form Inconstant Galvanic Cells under the Action of Light. Polarisation.*

Becquerel was the first to show that when two metallic plates are immersed in a liquid, and one is exposed to light while the other is kept in the dark, an E.M.F. is created.

Which now is the nature of this E.M.F. ? Becquerel's and Minchin's (more especially the latter's) experiments brought to our knowledge peculiar facts, which all seemed to indicate that the above phenomena are surface phenomena, and strongly to oppose the author's conception of such systems as galvanic cells. What were now these observations of Becquerel and Minchin? According to Becquerel: "by depositing on one of the Ag plates a thin layer of iodide, obtained by the action of the vapour of iodine at the ordinary temperature and then exposing this plate to light, it was found that it took positive electricity from the liquid. With a thick layer of iodine on the surface of the Ag, there is on the contrary a current the inverse of the proceeding, *i.e.*, the plate exposed to light took negative electricity"; further, "whilst with precipitated chloride and bromide of silver placed on plates of platinum there is always produced a current of the same sense, the exposed plate being positive; with a layer deposited on Ag there is an effect depending upon the thickness of this layer." "These two inverse facts indicate that there should necessarily be a thickness of layer for which the electric effect is almost nothing" ('La Lumière,' vol. II., p. 129). Minchin again observes ('Phil. Mag.,' 1891, XXXI., p. 207) with AgCl, AgBr in collodion an E.M.F. in the opposite direction to that of AgI in gelatine (p. 200).

The observations of Minchin with metallic plates seem to be still more inexplicable. He tells us of "a very curious case on inversion of the current produced by light observed with silver plates immersed in water containing eosine in solution (p. 211), or in alcohol containing naphthalene red (p. 212); the E.M.F. is sometime in one, at others in the opposite direction." He made the same observation with "bismuth in water" (p. 213). In "nearly every cell used with tin plates the exposed plate was positive to the unexposed; but after a time, varying from a few minutes to a few hours, it was found that this positive current died out and was replaced by an apparently stronger current, in which the exposed plate was negative, &c." The results were similar with the "sensitive" cells which he obtained by exposing a compound of tin deposited on tin plates (obtained by acting on tin plates (alloys) with nitric acid and nitrate of ammonia and afterwards heating them till a white precipitate—the greater part evidently SnO_2—was formed on them) to light, while another tin plate without deposit is kept in the dark, both plates being immersed in methyl alcohol. He draws the conclusion that "if the deposit is not uniform, some parts of the plate give on exposure to light positive, others negative E.M.F.'s," and "such has actually been found to be the case in many experiments" (p. 222); on the whole, just as many mysterious results were obtained as there were experiments made.

The E.M.F.'s obtained changed also in their value. The "tin plates, *e.g.*, placed in alcohol, gave large deflections, but almost none, if any, chloride was introduced into the alcohol, &c.," though this ought to increase the conductivity (p. 216), &c.

Now what is more characteristic of a galvanic combination than the direction of the current in it? No galvanic combination we know of gives a current sometimes in one direction and at others in the opposite, the anode and cathode exchanging their *rôles*. At the hands of two such excellent investigators as BECQUEREL and MINCHIN only one conclusion would seem possible, a conclusion which MINCHIN, and apparently also BECQUEREL, draw all along, that the action of light upon AgCl, AgBr, AgI, and especially metal plates, leads to some special kind of surface phenomena, depending in some unknown way upon the thickness of the layer or films, and which for still unknown reasons are of a varied and complicated character.

From the first it was clear to the author that, to make substantial progress, the research must be carried out on quite different lines. It is not sufficient to notice the direction of the current; the total curve in all its complexity from beginning to end, including the deduction and induction periods, must be studied and photographed so as to get a complete, objective, and not only a partial, knowledge of the total phenomenon. The investigation must be carried out with much greater detail than hitherto, and be of quantitative, not of qualitative character, and the results so obtained be studied in connection with the chemical composition of the whole heterogeneous system and with those reactions which must take place in it under the action of light. These problems, which BECQUEREL and MINCHIN did not attempt to study, confining all their attention to the plates only, alone can lead to a satisfactory knowledge of this region.

After a long and detailed study of the method adopted, necessarily spent in obviating thermo-effects in the metallic circuit and in the cells and other sources of error, the phenomena under consideration were isolated, all complications caused by the variation of the intensity and composition of the light and other interfering phenomena being removed from the curves. The numerous varieties of curves were thus finally reduced to two special kinds only. It was only from this point that serious attention could be given to the meaning of the special course of the curves, and real advance made.

The curves of a great many of the systems studied (Ag plates, Sn plates, Pt plates, Au plates in NaCl solution) had a peculiar course. On exposing to light, a deflection, say to the right, is first obtained (the E.M.F. is positive), which gradually decreases till it becomes stationary in light, the E.M.F. still remaining positive; or it continues to decrease until it becomes "zero" and then becomes negative, and this deflection in the opposite direction goes on for some time till it becomes stationary in light. On removal of the light from the system a similar though not identical curve is obtained, which is the reversal of the first. It should be added that it has been established beyond doubt, in four different ways, that the peculiar form of the curves was not due to the inertia of the moving galvanometer mirror, but represented the true nature of the phenomena.

When we look away from the line which gives in the above-mentioned kind of curve zero deflection in the dark, we are struck by the fact that all these curves seem to have one characteristic course, as if under the action of light two opposite E.M.F.'s of two different values and with two different rates of increase were simultaneously produced, each of them ultimately reaching a maximum value, and on removal of the light the two E.M.F.'s disappear with different speeds. According as one or the other is more rapidly produced, the total E.M.F. starts by moving in one or other direction; as long as one E.M.F. preponderates over the other, the total E.M.F. continues in the same direction; when the preponderating E.M.F. reaches, or almost reaches, its maximum, while the opposite, owing to its being produced with a smaller speed, is still increasing, the total E.M.F. begins again to decrease, the mirror begins to move in the opposite direction, and the total E.M.F. goes on diminishing, until the opposite E.M.F. reaches its maximum; then the total E.M.F., which is equal to the difference of both constant E.M.F.'s, will remain constant in light, *i.e.*, will give a line parallel to that in the dark. If now light is removed from the system, exactly the reverse must take place. The E.M.F. which was first more rapidly created will now more rapidly disappear, the galvanometer mirror will now move in a direction opposite to that in which it started on exposure to light; when the preponderating E.M.F. has almost or completely disappeared, the other, losing its value more slowly, will still be present, and continue to diminish, and the galvanometer mirror will move back in the opposite direction. As both the E.M.F.'s disappear, the deflection of the galvanometer will approach the line giving the zero deflection in the dark, *i.e.*, the line obtained before the system was exposed to light. What can these opposite E.M.F.'s be? There seems only one logical answer possible: as an E.M.F. in those combinations is produced by light, an E.M.F. of *polarisation* is created also at the same time.

This now showed clearly that by placing two Ag plates into, say, a solution of NaCl, we get a real galvanic cell, because a consideration of the reactions going on in the above systems shows that they ought to show polarisation. There would thus only be so far a difference between the ordinary galvanic cell and our light cell, as in our case both the E.M.F. of the cell and the E.M.F. of polarisation are gradually and simultaneously produced by exposure to light, or disappear when light is removed, so that we cannot have as in ordinary galvanic cells one E.M.F. without the other.

The first important result obtained from the above explanation of the peculiar course of the curves was thus the discovery of *galvanic polarisation sui generis* created by the action of light. In the course of the induction and deduction periods we have at the same time the most efficient and reliable method of distinguishing between constant cells showing no polarisation and combinations showing polarisation. If a system shows no polarisation, and the above conception of the curve be true, there ought to be, during the induction period, only a gradual increase of the E.M.F. till the maximum is reached, and no drop, and similarly only a gradual diminution of the E.M.F. should be observed when light is removed and the system returns to its state in the dark. This is now the second kind of curves we actually obtain with a series of other systems giving constant reversible cells. A careful consideration of the reactions going on in these systems, under the action of light, shows also why they must be reversible constants.

As a result of this varied and very complicated research, which took over three years, we find that under the action of light we have a region of galvanic cells which is just as wide, just as varied, though often inaccessible to measurement, but regulated by just as solid principles, as ordinary galvanic cells. As in the case of ordinary galvanic cells, we have, under the action of light, reversible and irreversible cells, constant and inconstant cells; constant cells, the electrodes of which are "reversible in respect of the anion," constant cells, the electrodes of which are "reversible in respect of the cation"; we have cells showing polarisation owing to the gases separating on the electrodes, and cells showing polarisation owing to the electrodes changing the nature of their surfaces, &c. The chemical reactions (and chemical equilibrium) occurring in these systems and their individual nature are now perfectly clear to us and can be measured quantitatively, though the amounts of the transformations, as will be seen later on, are so exceedingly small that there is not the remotest possibility of even detecting the products of reaction by any chemical means, 10^{-9} ampère indicating a decomposition of 1 gramme electrochemical equivalent in 30,000 years.

The true meaning of the observations of BECQUEREL and MINCHIN is now apparent. "The very curious inversion of the current" observed by MINCHIN with "Ag plates immersed in water containing eosine in solution" (p. 211), "Ag plates immersed into alcohol containing naphthalene red" (p. 212), with "bismuth in water" (p. 213), with "tin plates in alcohol" (p. 216), with his "sensitive" cell, consisting of a tin plate acted upon by nitric acid, and a tin plate in methyl alcohol (p. 222), is evidently in each case due to the fact that all these systems, as now clearly appears from their composition, must form inconstant cells exhibiting polarisation.

The reason why BECQUEREL with Ag, BrAg and IAg plates found a current sometimes in one direction, sometimes in another, is not "the thickness of the layer," but the kind of combination of the heterogeneous system, of which the given plate forms only a part. An Ag-AgCl plate in NaCl solution gives a constant cell, reversible in respect of the anion; its current must, as will be shown later on, flow from the plate in the dark to the plate in the light. If, however, the layer of AgCl is very thin, such a system will soon transform under the action of light into the system (Ag in light, NaCl solution, Ag-AgCl in dark) which is inconstant, showing polarisation; Ag-AgCl plates in water form inconstant cells which exhibit polarisation and will give a current in one direction or the other. An Ag-AgCl plate placed in water containing SO_4H_2 is, in the first instance, an inconstant cell, showing polarisation; subsequently Ag_2SO_4 is formed in solution by the acid acting upon the silver plates, the system transforming into Ag plates in an Ag_2SO_4 solution, which is a constant cell reversible in respect of the cation, and its current must flow, as will be seen later on, from the plate in light to the plate in the dark. This, however, will not be the last possible transformation of such a system (Ag-AgCl in SO_4H_2 solution). Since Ag_2SO_4 is not easily soluble in water, and under the action of light the current will pass first from the plate in light to the plate in the dark, SO_4 ions will separate on the Ag-AgCl plate in light, forming Ag_2SO_4 on the same; the system (Ag-Ag_2SO_4 in light, Ag_2SO_4 solution, Ag-AgCl in the dark) will thus gradually be formed, which is reversible in respect of the anion in which the current must flow from the plate in the dark to the plate in the light. This now is exactly the combination BECQUEREL used for his actinometer, employing AgCl, AgBr, and AgI, deposited upon Ag plates immersed in a solution of "2 grammes of sulphuric acid monohydrate in 100 grammes of water," by no means a weak acid.

Again, in his experiments with AgCl, AgBr, AgI precipitated on platinum or gold plates, he puts them into pure water. Such systems must form inconstant cells, showing polarisation.

§ 2. *What is the Nature of the E.M.F. Created by Light?*

Before entering upon a study of the effect of light upon different combinations, the very first question to be clearly settled was: Are the phenomena produced by light new phenomena, or are they ordinary heat phenomena (since one plate is heated by light, the other not)?

A calculation on the basis of the quantitative measurements made for the purpose showed that if light should heat up the electrodes of different systems to the same degree as it heats up the Rubens thermopile, the total deflections which ought to be obtained under the action of light with different systems ought to be even greater than those actually observed, and the conclusion would become inevitable that the E.M.F. created by light may be nothing else but a thermo E.M.F. We take the two principal systems: Ag plates in $AgNO_3$ solution (June 6, 1903) and Ag-BrAg plates in NaBr solution (July 29, 1903).

The first system gave, with the arc at a distance = 27 centims., 5·5 centims. deflection; at the same distance the Rubens thermopile gave 101·6 centims. deflection = 1°·466 C. The thermo E.M.F. of the system in the dark being 0·0011 volt per 1° C., we ought to have got 16·35 centims. deflection, if the system were also heated by the light 1°·466 C. Similarly with the second system: the deflection observed with acetylene light at a distance = 116 centims. was 8·16 centims.; the same light heated Rubens thermopile at 116 centims. distance 0°·1208 C. The thermo E.M.F.

of the system in the dark being 0·00079 volt per 1° C., we ought to have got 8·56 centims. deflection, if the system were also heated by light 0°·1208 C.

Now the same light passing a liquid column of a bath has evidently a very much smaller heating effect than when it passes air only; the rise of the temperature of the same thermopile would have been very much smaller if it could be immersed into water instead of being in the air; it would have been smaller if, instead of very thin plates, thicker plates were used as in our experiments, &c. The first problem of all thus became to determine in each case quantitatively and by correct methods whether the observed E.M.F.'s were not entirely a thermo E.M.F.; or, if not, which part in the total phenomena was due to one effect and which part to the other.

We shall now illustrate the method used for this investigation: Let the system of two silver plates in a 0·1 normal $AgNO_3$ solution be investigated. First, the thermo E.M.F. of this combination (Ag wires in 0·1 normal $AgNO_3$) was determined (as will be described in a future publication in a section dealing with thermo-galvanic cells) and found to be, per 1° C., about 0·00011 volt. Next the rise of temperature in the quartz vessel for the same system (Ag_{pl} 0·1 normal $AgNO_3$ solution) under the action of light, under the given experimental conditions, was determined. For this a thermopile with four junctions of very thin iron-nickel wires was made and covered with shellac; 1° C. difference of temperature was found to give 65·2 millims. deflection on Nalder N1. The same thermopile was then placed in the quartz vessel containing the same two silver plates immersed in a 0·1 normal $AgNO_3$ solution (which at one time were connected with 850 ohms to a circuit, and the other time left in open circuit); two junctions of the thermopile were placed in front of the plate exposed to light, the other two near the plate kept in the dark. The deflection of Nalder N1, connected with the thermopile, on the same scale (when the arc of intensity 12·7 centims. was removed 27 centims. from quartz vessel), was in open and closed circuit between 2 and 3 millims. The heating effect upon the exposed plate under these conditions of experiments was therefore between 0°·03 and 0°·045 C., and the thermo E.M.F. for Ag in $AgNO_3$ solution, under the action of the light, thus was between $4·8 \times 10^{-6}$ and $3·2 \times 10^{-6}$ volt.

The total deflection produced by the arc upon the silver plates, immersed in the 0·1 normal $AgNO_3$ solution was next measured under the same experimental conditions (distance of the arc from quartz vessel, 26 centims., the same intensity of light, sensitiveness of Nalder N1, &c.) (see Table I., June 6, 1903). The total deflection obtained was 55 millims. Since the resistance of the solution in the quartz vessel was 13·4 ohms, of the galvanometer 834·4 ohms, the deflection caused by the thermo E.M.F. of $3·2 \times 10^{-6}$ volt was 3·2 millims., *i.e.*, about 5·8 per cent. of the total deflection observed (the total E.M.F. at 37 centims. distance from arc, this being 55×10^{-6} volt).

We thus got direct proof that under the action of light upon metallic plates two E.M.F.'s are produced: one is due to the heating of one of the plates by light and is a *thermo E.M.F.*, the chemical potential of one of the two plates becoming, owing to its rise of temperature, greater; the other is *an E.M.F. due to light at a constant temperature*, the chemical potential of the exposed plate becoming greater under the action of light.

Similar results are obtained with the constant arc, and the still more constant acetylene light, for systems (Ag-BrAg, NaBr solution, Ag-BrAg), (Ag-ClAg, NaCl solution, Ag-ClAg), (Ag-IAg, KI solution, AgI-Ag), &c.

In the experiments carried out with the system Ag-BrAg plates in a 0·1 normal NaBr solution, *e.g.*, on July 29, 1903 (*a*), acetylene light was used at a distance of 116 centims. from the quartz vessel. We get: total E.M.F. observed = 81·6 millims. or 77×10^{-6} volt; the thermo E.M.F. = $0·8 \times 10^{-6}$ to $1·2 \times 10^{-6}$ volt; the thermo E.M.F. = 1·0 per cent. to 1·5 per cent. of the total E.M.F.

§ 3. *The Rays of all Wave-lengths act both "Chemically" and as "Heat Rays," only in different Degrees.*

The next question was: Is the E.M.F. produced by the red part of the spectrum solely due to its heating action, or does it act "chemically" in the same manner as blue, violet, &c., rays—the so-called "actinic rays" of light? For this the same combinations (Ag, $AgNO_3$ solution, Ag, Ag-BrAg, NaBr solution, Ag-BrAg, &c.) were exposed to light passing different coloured screens, and the total E.M.F. so obtained compared with the thermo E.M.F. corresponding to the heating effect of the coloured light. For the first system the arc, and for the second, as before, the arc and the acetylene lights were used.

The relative values of the thermo E.M.F.'s of the total light and of the total light, passing the different screens was first determined from the heating effect of the same. A specially made thermopile with 40 iron-nickel junctions (made dead black) was introduced into the air space of the quartz vessel, placed in the bath 8 centims. behind the quartz window (as in all our subsequent experiments with the different galvanic cells) and connected with the dead-beat galvanometer (Nalder N1), used for photographing all the curves in this investigation.

The deflections of the galvanometer for the total light without screens and the total light passing a series of screens (without dye, red, green, yellow and blue) prepared for me from thin gelatine by Mr. Hilger, and placed before the quartz window of the bath, were photographed. The thickness of each screen was also measured so as to be able to introduce the correction for the absorption by gelatine; the photographed deflections so obtained gave the following results:—

With the same source of light (arc, $v = 6·6$, $A = 60$, distance from quartz vessel = 36 centims.) we got: total light, without screen, gave 89·5 centims. deflection; the same light passing the gelatine screen (0·125 millim. thick), 62·9 centims.; the red gelatine screen (0·08 millim. thick), 65·5 centims.; the yellow-green gelatine screen (0·11 millim. thick), 41·0 centims.; the blue gelatine screen (0·10 millim. thick), 49·0 centims. deflection.

A spectroscopic investigation of the light passing through the different screens showed that only the red light was perfectly pure, while the light passing through the blue and green-yellow screens contained very much red, the thickness of the gelatine having been far insufficient for its total absorption. This explains the above data with the thermopile. A pure red light, comparable with the total whole light was, however, all that was required for the present purpose.

Table A, p. 344, gives the E.M.F.'s obtained in the course of this research for different combinations with the total light and with the same light passing first through the red screen in each system expressed in the same units (millims.) taken from the photographed curves, one of the plates having been exposed to light, the other kept in the dark (under identical experimental conditions).

The table shows that while the heating effect of the light passing the red screen upon the thermopile (Column VI.) is still 73·2 per cent. of the heating effect of the total light, the deflections caused in the different systems by the total light passing the red screen are only a fraction, mostly a small fraction (Columns IV. and V.) of the deflections caused by the total light without screen (Column III.).

Thus the total deflection caused by the total light could not be due to the heating effect of light alone. In Column VII., the exact values of the thermo E.M.F.'s caused by the total light are given, as they follow from direct measurements of the rise of temperature at the illuminated front plate, and of the thermo E.M.F.'s per 1° C. of the given system. Column VIII. gives the same values for the total light passing first the red gelatine screen. The difference between Columns III. (100 per cent.) and VII. gives the deflections caused by the total light at a constant temperature in per cent. of the total deflection observed in Column III. This difference shows that almost the total deflection is under our conditions of experiment created by light at a constant temperature, and only a small part principally in systems (1), (3), and (5) is due to a thermo E.M.F. created by light. Column X. gives the difference between Columns V. and VIII., *i.e.*, the deflection at a constant temperature caused by the total light passing the red gelatine screen. This Column X. shows that in both cases of the systems (2) and in (3) the light passing the red screen gives pretty considerable deflections at a constant temperature, *i.e.*, the red light is also "actinic." In case of the other systems, *e.g.* (5) or (7), the total deflection caused by red light is very small, and it is difficult to show experimentally how much of this value is a thermo E.M.F., and how much an E.M.F. at a constant temperature.

Table B, p. 345, gives the relative deflections observed for each of the systems given in the previous table with the total light, and the same light passing through the red, yellow, green and blue screens; the same values at a constant temperature are given in the last three columns.

TABLE A.

The system consists of—	Date of table.	Deflection caused by total light. A.	Deflection caused by total passing the red screen. B.	B in per cent. of A. B′.	B in per cent. of A when measured with Rubens thermopile.	The thermo E.M.F. of the total light at the distance D in per cent. of A′. $\frac{d\pi}{d\tau}$.	The thermo E.M.F. of the total light passing the red screen of the distance D_1 in per cent. of A. $\frac{d\pi'}{d\tau}$.	Deflection of the total light at a constant temperature in per cent. of A′.	Deflection of the total light passing the red screen at a constant temperature in per cent. of A′.	Distance of the light from quartz vessel. D.	Kind of cell.	Kind of light.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
		millims.	millims.							centims.		
(1) Ag-ClAg plates in NaCl solution	June 30, 1903	54·5 (55·5)	3·5	6·4	$\frac{65\cdot5}{89\cdot5} = 73\cdot2$	6·2–9·3	4·6–6·9	93·1–95·4	about 0–1·8	37	constant	arc
(2) Ag-BrAg plates in NaBr solution	July 29, 1903	70·2 (40 ohms shunt)	5·0	7·1	73·2	0·74–1·1	0·54–0·8	98·9–99·3	6·3–6·6	118	constant	arc
		80·0	28·5	35·6	73·2	1·0–1·5	0·7–1·1	98·5–99·0	34·5–34·9	116	constant	acetylene
(3) Ag-BrAg plate in light, NaBr solution, Ag in dark	July 20, 1903	86·5	11·9	13·76	73·2	4·7–7·1	3·4–5·2	92·9–95·3	8·56–10·4	50	constant	arc
(4) Ag plate in light, NaBr solution, Ag-BrAg in dark	July 18, 1903	75·0	2·0	2·7	73·2	—	—	—	—	67	inconstant	arc
(5) Ag plates in $AgNO_3$ solution	June 11, 1903	32·0	circa 2·0	6·2	73·2	6–9	4·4–6·6	91–94	circa 0	36(7)	constant	arc
(6) Ag plates in $AgSO_4$ solution	June 25, 1903	62·0	2·0	3·2	73·2	—	—	—	—	26	compound constant	arc
(7) Ag-IAg plates in KI solution	Feb. 17, 1904	217·0 (40 ohms shunt)	perhaps 0·5	3·2	73·2	—	—	—	circa 0	92	constant	arc

TABLE B.

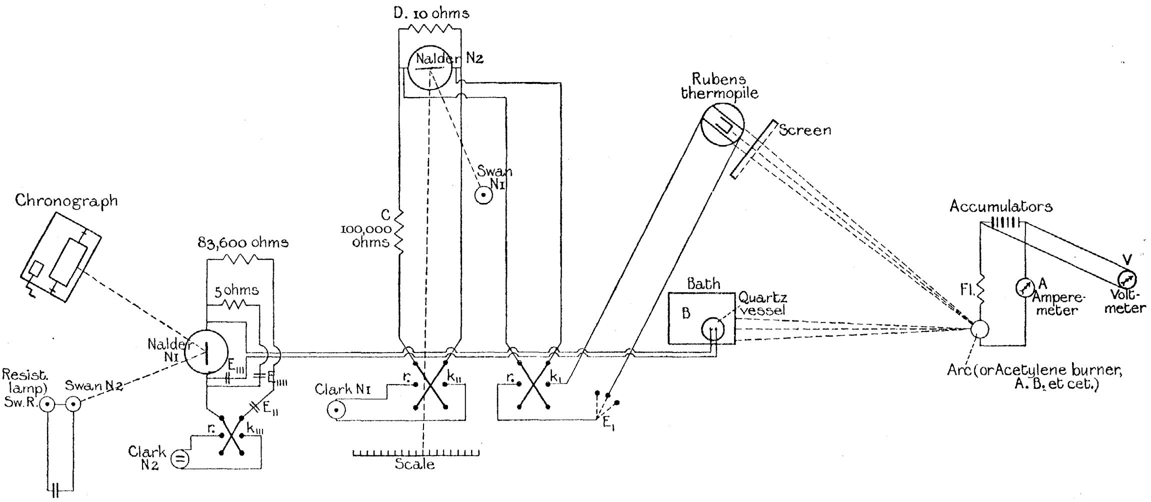
The system consists of—	Date of plate or table.	Deflection of total light. A.	Deflection of total light passing the red screen. B.	Deflection of total light passing the yellow-green screen. C.	Deflection of total light passing the blue screen. D.	B in per cent. of A = B′, red screen.	C in per cent. of A = C′, yellow-green screen.	D in per cent. of A = D′, blue screen.	B′ at a constant temperature in per cent. of A, red screen.	C′ at a constant temperature in per cent. of A, yellow-green screen.	D′ at a constant temperature in per cent. of A, blue screen.
		millims.	millims.	millims.	millims.						
(1) Ag-ClAg plates in NaCl solution	June 30, 1903	54·5 corr. 55·5	3·5	5·5	13·0	6·4	10·1	23·8	0–1·8	3·4–5·6	16·9–19·2
(2) Ag-BrAg plates in NaBr solution	July 29, 1903	70·2* (40 ohms shunt)	5·0*	3·5*	23·0*	7·1	5·0	32·8	6·3–6·6	4·25–4·5	32·0–32·3
		168†	60·0	41·0	48·5	35·6	24·4	28·9	34·5–34·9	23·4–23·7	27·9–28·2
(3) Ag-BrAg plate in light, NaBr solution; Ag plate in dark	July 20, 1903	86·5	11·9	6·3	10·6	13·76	7·3	12·3	8·5–10·4	2·5–4·1	7·3–9·0
(4) Ag plate in light, NaBr solution; Ag-BrAg plate in dark	July 18, 1903	75·0	2·0	1·75	29·0	2·7	2·3	38·7	—	—	>38·7–2·7 = >36·0
(5) Ag plates in $AgNO_3$ solution	June 11, 1903	32·0	circa 2·0	2·0–2·5	15·0	6·2	6·2–7·8	46·9	circa 0	circa 1·7–2·2	40·6–42·7
(6) Ag plates in $AgSO_4$ solution	June 25, 1903	62·0	2·0	—	15·5	3·2	—	25·0	—	—	>25·0–3·2 = >21·8
(7) Ag-IAg plates in KI solution	Feb. 17, 1904	217	<1·0	circa 1·0	78	<0·5	circa 0·5	36·0	circa 0	—	>36·0–0·5 = >35·5

* Arc; shunt of Nalder N1 = 40 ohms; observed.

† Acetylene; calculated for 80 centims. distance.

§ 4. *The Method of Investigation. General Arrangements of the Experiments.*

The general arrangements of the experiments are given in the following diagram :—



On the right are the arrangements for a constant source of light : acetylene or the arc was used. AB is the acetylene burner. Acetylene from the generator passes through a balance governor, regulating tap, water manometer, drying apparatus to the specially constructed burner, as described in my previous publications.

The arrangement of the arc light is as follows :—The current from the accumulators (Acc) passes through a resistance Fl (Fleming) of 3 ohms, the arc (Ar), and the ampèremeter (A) ; the voltmeter (V) is connected either with the terminals of the Dubosc arc, or, since the resistance is kept constant, at the terminals of the accumulators where the voltage was much higher (67 volts instead of 42), to get more sensitive reading.

The light passes to a Rubens thermopile (RTh). The wooden screen (Scr) is placed between the Rubens thermopile and the source of light. The leads from the Rubens thermopile pass to the interrupter ($E_{\prime}$) and reversing key ($rk_{\prime}$), thence to a Nalder galvanometer N2. The incandescent Swan lamp (SwN1) throws a spot of light upon Nalder N2, which falls upon a transparent celluloid scale (Sc). When the screen is closed, the spot of light gives zero deflection and the reversing key gives the E.M.F. of the thermopile in the dark, if any ; when the screen is opened, the deflection of the galvanometer read on the scale gives the intensity of light.

This deflection was then calibrated in standard units. The Clark N1 is connected with the reversing key ($rk_{\prime\prime}$), then with a standard 100,000 ohms manganin resistance (C), and the Nalder N2 is provided with a shunt D (10 ohms). The arrangements of the photometer are described in the former paper. The light also falls on the quartz window of the bath (B) (only one of the six quartz windows is open) and passes to the quartz vessel (QV) placed behind it at a distance of about 10 centims. The source of light is during the experiments placed at a suitable or desirable distance from it. A description of the bath has also been given. A few alterations have been made in it. The quartz vessel was placed in an ebonite holder and kept in the position by the iron stand placed on the bath. The leads from the plates in the quartz vessel were passing in the air behind thick asbestos screens fixed to the bath, and were connected with two thick flexible copper leads, one being red, the other blue, to know the direction of the current. The copper leads were connected with the Nalder galvanometer N1.

On the left of the diagram are the arrangements for photographing the deflections of the Nalder N1, caused by exposing one of the plates in the quartz vessel to light, as well as for calibrating these deflections in standard units, and for measuring the resistance of the liquid between the two plates in the quartz vessel.

The incandescent Swan lamp (SwN2) was connected with another incandescent lamp enclosed in a box and serving as an additional resistance (SwR). The spot of light, made more brilliant by the use of an increased voltage, was thrown upon the galvanometer mirror (Nalder N1) and reflected as a vertical line upon the horizontal slit of the chronograph (Ch) containing a revolving drum on which extra-sensitive bromide paper was fixed. The deflection due to the E.M.F. produced under the action of light upon the plates was photographed.

The results obtained were calibrated in standard units A Clark N2 was connected with the key ($E_{//}$), reversing key ($rk_{///}$), the manganin resistances (83,600 ohms), and the galvanometer Nalder N1 (resistance 834·4 ohms) with a shunt (5 ohms). The deflection of the galvanometer was also measured on a wooden millimetre scale placed on the drum during the time of this measurement (the measurement of the E.M.F. in the dark).

After the effect of light upon the plates was photographed and standardised, the resistance of the liquid between the plates in the quartz vessel, including the thick copper leads up to the terminals of the galvanometer, was measured by the method of Kohlrausch. Arrangements were made ($E_{///}$, $E_{////}$) not to disturb during this measurement the connection at the terminals of the galvanometer. The blue lead could be disconnected from a small part of it connected with the galvanometer, and the red lead was connected at the terminal of the galvanometer with another lead of a negligible resistance which could be connected to one end of the bridge. The arrangements for these measurements can be clearly seen in the diagram.

The Constant Source of Light (Acetylene and Arc). The Measurement and Adjustment of its Intensity.

Acetylene.—In his paper "On Chemical Statics and Dynamics under the Action of Light," 'Phil. Trans.,' A, 1902, vol. 199, pp. 351–363, the author gave a detailed account of how to arrange a constant acetylene light of 250 candles and more, and how to measure the intensity of light (by means of thermopile, galvanometer, &c., &c.) with an accuracy of 0·1 per cent. (see photographic curves, plate N1; lines C_1–C_1,

C_2–C_2, giving the maximum deflection in light, are perfectly straight and parallel to a_1–b_1, a_2–b_2, which give zero deflection in the dark).

The Arc.—We had to investigate some reactions in which more actinic light than acetylene was urgently required and the use of the arc became there unavoidable. Of several arcs tried, that of KÖRTING and MATHIESEN seemed to be the best, but even it gave 15 to 20 per cent. variation, as may be seen from its photographed curves of the same plate N1.

The arc which I found most useful, and with which I succeeded in getting better results, is a Dubosc lent me by the Royal Institution. It has the disadvantage of requiring to be wound up every 5 or 10 minutes, in order that the same part of the spring may be used, but it served well our special purpose, where short exposures were required. It allows a very sensitive continuous adjustment for very small variations in the distance between the carbons. The variations on the ampèremeter show then continuous rapid oscillations of the ampères, within the narrow limits of 1 millim. or more, exceptionally 2 millims., when the total value equals 31 millims. (6·2 ampères); while the volts almost remain stationary, their variations amount to about $\frac{1}{4}$ a division out of the total of 65 to 67. Those continuous oscillations of the ampères about one mean value counteract one another, so that the integral intensity of light remains the same within very narrow limits, and this is just what we require, because a constant light is in reality only a light whose oscillations about the mean value are rapid and very small; the great regularity of the numerous curves given in this communication and the straight lines obtained for the maximum E.M.F. in light give solid evidence that I succeeded in getting a constant light with the Dubosc.

The conditions found necessary to obtain the above result are:—(1) The voltage at the terminals of the arc should be 42, at the terminals of the accumulators 65 to 67. The ampères in the circuit should be between 6·0 and 6·2. The Fleming resistances (3 ohms) inserted into the circuit should never be changed. Unless the voltage and ampères at the given resistance of circuit were exactly those given here, constant results could not be obtained with the arc. (2) The carbons were never allowed to burn down more than 1 to 2 centims., the incandescent surfaces must be kept as uniform as possible, and must be trimmed from time to time with a file. (3) There is a special distance between the carbons (between 3 and 4 millims.) which gives the best result with the arc. It is difficult to give the exact distance, which has to be determined experimentally, using a Rubens thermopile and following the indications of the ampèremeter. It is got by changing the resistance (Fl) till the desired effect is got, when the resistance (Fl) is always kept constant. (4) There is a special distance of the armature from the electromagnet, and a special tension of the spring of the arc, at which alone it gives the best result. (5) Great care must be taken in the choice of the carbons. This is a difficult point. The hard, short "Imperial Crown carbons" of the London Electric Company proved the best and most steady of all, but the author had also good results with a somewhat softer kind. The "Imperial

Crown carbons" used were 8 millims. thick on the top, 14 millims. thick below. The carbons should not be placed one at the side of the other to throw more light in the horizontal direction, as this leads to a rapid deformation of the incandescent surface of the lower carbon, but should be placed one over the other, so that the crater should come into the centre of the carbon, with only a small inclination to the side which we wish to illuminate; less light for the purpose, but more constant and for longer periods, is thus obtained, and trimming is required only at longer intervals. New carbons should never be used at once for the experiments, but only after some time, when the Rubens thermopile indicates that their intensity has come already to rest, *i.e.*, that the carbons have reached their permanent shape.

Direct measurements with the Rubens thermopile show that the intensity of the light sent by the arc horizontally in different directions differs as far as 30 to 50 per cent. according to the position of the crater with respect to the thermopile (and therefore also the quartz vessel). Similar measurements show that a variation of the voltage may lead to an essential increase of the space between the carbons, considerably change the brilliancy and intensity of the crater, and not change, or only very immaterially change, the ampères in the circuit. It is for this reason evident that at all times the intensity of the arc light cannot be indicated by the ampèremeter, but must be directly measured with the Rubens thermopile (or bolometer), care being taken that exactly the same most advantageous side of the arc which was turned to the quartz vessel should be also turned to the thermopile. For the reasons given above it is possible to get constant light for shorter periods, but it is very difficult to get every time anew the same constant intensity, as the variation in the shape and quality of carbons and the movement of the crater alone are more than enough to frustrate all attempts to get a constant light with the arc for longer periods.

The Quartz Vessel.—In this the plates and solutions of the different combinations were exposed to light. The front and back plates (45 millims. by 45 millims. and removed 13 to 15 millims. from one another), which were exposed to light, were made of quartz, all other parts were of glass, cut to the correct shape and ground at their edges. The quartz plates were cut perpendicularly to the optical axis and were optically pure. The different parts of the vessel were stuck together by means of Crookes cement and the seams covered with asphaltum. An ebonite piece fitted well into the upper part of the quartz vessel, and had two holes drilled through it to allow two copper or glass rods, to which the plates were fixed, to pass through them. The copper or glass tubes were held on the top by means of screws or shellac. In the wider part of the ebonite piece below two thin parallel slots were cut to receive the plates and keep them always in position; the front plate was about 1 millim. apart from the front quartz window.

The Plates.—They were all taken 30 millims. wide, 42 millims. long; at the top the plates had strips about 3 to 4 centims. long, both, plates and their strips, having been cut out of one and the same metal sheet. To the lower end of the thin strips of the plates wires drawn of the same piece of metal from which the plates were made, about ½ meter long, were fused to serve as leads. I am indebted to Messrs. MATTHEY and JOHNSON for having kindly prepared the plates for me, and for having supplied me with the purest metals it is possible to procure. This is necessary to avoid local action between the different metals of the same plates in a solution. The Ag was 1000/1000, the platinum was of the purest kind, as used for platinum thermometers, &c. Special care was taken to avoid thermoelectric currents in the metallic part of the circuit. The copper rods or glass tubes to which the plates were fixed serve only as supports of the plates, while the current from the plate passes along the thin insulated wires drawn of the same piece of metal as the plates, which, coming from the ebonite piece, pass in the air behind the asbestos screens of the bath. Thus the first contact of two metals in the circuit was removed half a meter from the heated plate. These junctions of the two leads in contact with copper were wrapped up in ribbons of indiarubber, both then put together and wrapped up with thick ribbons of asbestos cloth (subsequently the wires and junctions covered with several towels). The terminals of the galvanometer were also wrapped up in indiarubber, and then in very thick ribbons of asbestos, and a thick asbestos screen was besides placed in front of it, so as to ensure that the incandescent lamp used for photographing the results should have no effect upon the thermo-couple here.

Still more interfering in the present research is the thermo E.M.F. created by one of the two metal plates in contact with the liquid being heated by light, while the other is remaining in the dark, as shown in § 2. This effect can, in the nature of the case, never be completely avoided, but it may be very much reduced by the use of a bath and stirrer. The quartz vessel was placed into the large bath containing about 70 litres of water described in my previous communication, its front side being 8 to 10 centims. away from the quartz window of the bath, so that the light had first to pass through a sufficient layer of water.

Even under these conditions it was found that the rise of temperature was still for the arc about 0°·03 to 0°·045 C., when the arc was removed about 27 centims. from the quartz vessel. This, as shown before, is in our investigation enough to change the obtained results in some cases very essentially. That the effect must be much greater when the vessel containing the plates is simply held in the air is self-evident.

The Preparation of the Plates for the Experiments.

As already mentioned, the currents obtained with the metal plates were exceedingly small, the deflections on Nalder N1 ranging from several millimetres to several centimeters. Now 0·000001 of an ampère gives, with my galvanometer Nalder N1, about 85 centims. deflection; these 85-centim. deflections are therefore got with about 0·001 of a volt, the resistance of my galvanometer being 837·4 ohms, *i.e.*, 1 centim. deflection of my galvanometer is caused by about 0·000012 of a volt. Now, although the plates were prepared of one piece, underwent absolutely the same treatment, and were polished with the greatest possible care, it is found that their E.M.F. in the dark on immersing them in a liquid is, in comparison with the above values, enormous. Moreover, the E.M.F. of the plates is unceasingly varying, the mirror of the galvanometer is continuously in movement. It is only on account of the observations of BECQUEREL that the E.M.F. of AgCl, AgBr, AgI plates in the dark, in a closed circuit, gradually diminishes and becomes stationary, that research in this region becomes at all possible. But it is only with exceedingly well polished plates that the constant very small values of the E.M.F. finally obtained in the dark can be of real use. This is one of the very first conditions for getting good, reliable results in this region of research.

After the plates were polished, they were annealed by heating them gradually to about 120° to 140° C., and gradually cooling for several hours, repeating the operation. The plates were then polished again, to remove the thin film of oxide, and uniformly covered on one side with shellac and over this with paraffin, or with paraffin only, so that the current should pass between the two surfaces of the two plates only. The plates so prepared are then placed in the liquid of the quartz vessel for the investigation, the circuit is left closed until the E.M.F. in the dark not only ceases to vary, but gradually diminishes till it reaches the smallest possible value (in case of many plates it can be brought to about 1 centim. or less on my galvanometer, *i.e.*, to 0·00001 volt and less), which remained quite stationary for longer periods, so as no more to interfere with the research. This takes hours, sometimes 24 hours, 48 hours, sometimes much longer. Once the plates have been further finally polished by the current (this is what actually happens here) they give no more trouble. They require very little time for reaching their zero deflection on exposure to and on removal of the light, or on opening and closing of the circuit.

Photographing the Effect of Light upon the Plates.

The reactions which take place under the action of light are of so great speed, and the curves themselves are of such a complicated course, that there can be no correct and complete study of the phenomena, unless they are put on record by photography.

The nature of the phenomena with the plates is such that it became necessary to take more than one curve on the same sheet. Special arrangements were made so as to know with absolute certainty the meaning of each of the curves from their position on the plate obtained, and not to mix them up with one another, and also not to fog the very sensitive bromide paper while there was light in the room and the different measurements made. When inconstant cells, showing polarisation, will be dealt with, proof will be given in several ways that the special course of the parts of curves giving the induction and deduction periods is not due to the inertia of the moving galvanometer mirror, but represents a true phenomenon. The curves (Plates 1–8) give the originals reduced to half their size. All the details which were written down on each plate at the time of the experiment can only now be read with the help of a lens. All the data given on the plates are contained in the accounts of the experiments.

§ 5. *On the Nature of the Chemical Processes in Galvanic Cells created by Light. Light, Heat, and Pressure—Galvanic Cells.*

Becquerel and others assume that "a current is created, because a chemical reaction of decomposition goes on on the plate exposed to light," but he at once falls into difficulties when he has to explain the nature of the action of light upon metallic plates, where no "chemical reaction" can be assumed. Under the action of light in a galvanic combination a reaction takes place, *not on the exposed plate only, but on the plate in the dark as well*, that is, a reaction takes place between both plates, and the kind of reaction depends upon the composition of the system. A reaction in open circuit is not necessarily the same in closed circuit.

The general cause and condition for the creation of a galvanic cell is, that the chemical potential of the two electrodes should be different. *Since under the action of light, temperature, or pressure, the chemical potential of a substance becomes different, we must therefore get galvanic cells created by light, thermogalvanic cells, galvanic cells created by pressure*, when two plates are exposed to light of different intensity, or different temperatures or pressures. Direct observations of the direction of the current, as far as they go to the present, show that under the action of light, and with the rise of temperature, the chemical potential changes in the same manner. By this *an important analogy between the action of light and heat* is established.

Since the point of equilibrium of a system depends upon the values of the chemical potentials of its components, it is evident that a variation in the potentials under the action of light makes the system strive towards a new point of equilibrium, *i.e.*, a reaction takes place in it tending to bring it to this point. *As to the direction in which the equilibrium will be shifted by light*, this is given by my generalisation: "Each kind of equilibrium between two states of matter is, at a constant volume, on exposure to light, shifted in the direction accompanied by greater absorption of light," a principle analogous to that put up by van 't Hoff for heat (see 'Zeitschr. für Physik. Chemie,' 1902, p. 332).

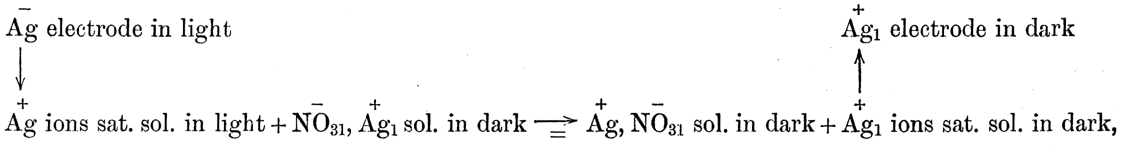
Velocity of Reaction and Equilibrium.

Let us take the system: M in light, solution MA (a salt of metal M, where A is the acid radical), M in the dark, *e.g.*, Ag plate in light, $AgNO_3$ in light and in the dark, Ag plate in the dark. Here the two electrodes consist of the same metal, one is exposed to light, the other is in the dark. Both are immersed in a solution of a salt of the metal forming the electrodes. This system is reversible in light in respect of the cation and is constant.

The chemical system taken in all details consists of:—

$$\begin{array}{lcr}
\overset{-}{\text{Ag}}\text{ electrode in light} & & \overset{+}{\text{Ag}}\text{ electrode in dark} \\
| & & | \\
\overset{+}{\text{Ag}}\text{ ions sat. sol.} + \overset{-}{\text{NO}_3},\ \overset{+}{\text{Ag}}\text{ sol. in light} \ldots & + & \overset{-}{\text{NO}_3},\ \overset{+}{\text{Ag}}\text{ sol. in dark} + \overset{+}{\text{Ag}}\text{ ions sat. sol. in dark.}
\end{array}$$

When the current passes in the normal direction the reaction in such a system evidently consists of the following:—



$$\overset{-}{Ag}\text{ electrode in light}\ \downarrow \qquad\qquad \overset{+}{Ag_1}\text{ electrode in dark}\ \uparrow$$

$$\overset{+}{Ag}\text{ ions sat. sol. in light} + \overset{-}{NO_{31}}, \overset{+}{Ag_1}\text{ sol. in dark} \underset{=}{\rightarrow} \overset{+}{Ag}, \overset{-}{NO_{31}}\text{ sol. in dark} + \overset{+}{Ag_1}\text{ ions sat. sol. in dark,}$$

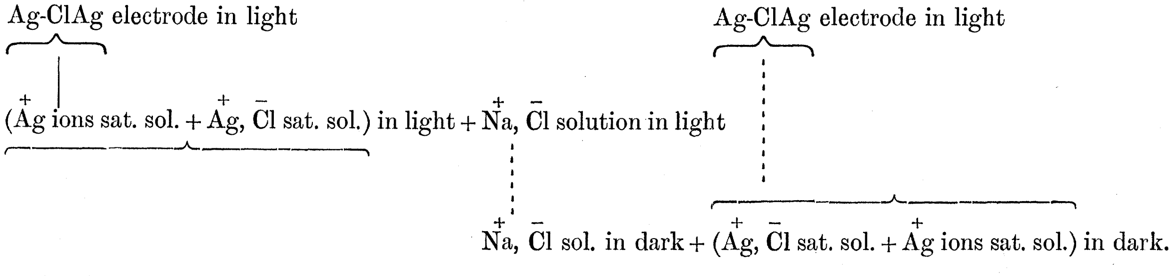
i.e., under the action of light there is a movement of the Ag ions from the plate in light to the plate in the dark. This disturbs the equilibrium, and a reaction takes place under the action of light, consisting of: (1) the transformation of 1 gram-atom of Ag in light into $\overset{+}{Ag}$ ions of the higher chemical potential in light; (2) the separation of 1 gram-atom of $\overset{+}{Ag_1}$ ions of the lower chemical potential in the dark upon the Ag_1 plate in the dark; (3) the transformation in the dark of 1 gram-atom of $\overset{+}{Ag}$ ions of higher potential into 1 gram-atom of $\overset{+}{Ag_1}$ ions of lower potential passing a *deduction* period. The first two reactions take place between the different parts of the heterogeneous systems, *i.e.*, between the electrodes and their ions in solution, as in all galvanic cells. The last takes place in the homogeneous liquid part.

If now we *send a current* through the system *in the direction opposite* to that of the current produced by light, while one of the plates is exposed to light and the other is kept in the dark as before, the same reaction in the opposite direction takes place. If the opposite E.M.F. is equal to the E.M.F. produced by light, no current will pass through the system; if it is greater we shall be able to reverse the reaction which previously went on in the light.

The system is therefore a *reversible* one in respect of the *cation.*

Similar is the case with the system M (metal) covered with the solid salt MA in light, M′A solution (salt of the same anion as MA) in light and in the dark, M covered with the solid MA in the dark, *e.g.*, Ag-AgCl in light, NaCl solution in light, NaCl solution in the dark, Ag-ClAg in the dark, &c., &c. These are reversible in light in respect of the *anion* and are constant.

The chemical system taken in all detail consists of—



$$\overbrace{\text{Ag-ClAg electrode in light}} \qquad\qquad \overbrace{\text{Ag-ClAg electrode in light}}$$

$$\underbrace{(\overset{+}{Ag}\text{ ions sat. sol.} + \overset{+}{Ag}, \overset{-}{Cl}\text{ sat. sol.})}\text{ in light} + \overset{+}{Na}, \overset{-}{Cl}\text{ solution in light}$$

$$\overset{+}{Na}, \overset{-}{Cl}\text{ sol. in dark} + \overbrace{(\overset{+}{Ag}, \overset{-}{Cl}\text{ sat. sol.} + \overset{+}{Ag}\text{ ions sat. sol.})}\text{ in dark.}$$

Such a system is reversible in light.

When the current is passing in the normal direction:—

(1) 1 gram-atom of Cl passes from the Ag-ClAg plate in light into the solution in light as $\overset{-}{Cl}$ ions of the higher chemical potential.

(2) The gram-atom of $\bar{Cl}$ ions passes from the solution in light to the solution in the dark, falling from the higher chemical potential to the lower, through a deduction period.

(3) The gram-atom of $\bar{Cl}_{\prime}$ ions of the lower chemical potential separates from the solution in the dark upon the Ag-ClAg plate in the dark.

And, conversely, *if the current is sent in the opposite direction*, the opposite reaction takes place, the system returning to its initial state. The mechanism of the reaction is here similar to that observed for the first system, with the only difference that the anions play here the same part as the cation in the first.

We have next to see whether such reversible heterogeneous systems are also constant cells. In a paper "On Chemical Statics and Dynamics of Galvanic Cells," which will soon be sent for publication, the author puts forward *the following generalisation* as a condition for a galvanic cell to be "truly reversible and constant": "That a galvanic cell should be reversibly constant, the chemical composition of the heterogeneous system constituting the same must, while the current is passing through it, remain constant; for this all substances in solution taking part in the chemical reaction under the action of the current (whether passing in the normal direction or in the opposite) and those which result from this reaction must not be allowed either to increase or decrease while the current is passing." This, it is shown, "can be achieved in ordinary galvanic cells if the substances taking part in and resulting from the reaction are all taken in a saturated solution in contact with their solids so as to keep the concentrations of the substances in solution each at the constant point of saturation, preventing thus the formation under the action of the current of an over-saturated or unsaturated solution of any of them. The nature and composition of an heterogeneous system being independent of the amount of the solid present in the same, all we require is evidently to keep the composition of the solution constant." The same principle, which is more of an axiomatic nature, must evidently be applied here: "That a galvanic cell should under the action of light be reversibly constant, the composition of the heterogeneous system, while the current is passing through it or is sent in the opposite direction, must remain constant."

In the first combination, the Ag plate in light and the Ag_1 plate in dark remain under the action of the current the same, whether more or less Ag ions pass from a plate into the solution or separate on it from the solution. When one gram-atom of Ag passes from one electrode into the solution, a gram-atom of Ag separates on the other electrode. Thus the total amount of nitrate of silver in solution, whether saturated or not, also remains the same. A little reflection shows also that the above system must soon reach in light a state when the ratio of Ag_1 ions to Ag and of NO_{31} to NO_3 ions will remain constant. The composition of the homogeneous liquid part, and with it of the whole of the heterogeneous systems, will thus remain under the action of the current constant. Similar is evidently the case with the *second* type of cell, reversible in respect of the anion.

The cells produced by the action of light differ from ordinary constant reversible cells as follows:—

(1) The cell is a galvanic combination only so long as it is exposed to light, so long as the chemical potentials at the two electrodes are kept different by light, while an ordinary galvanic cell is a permanent galvanic combination depending upon the permanent differences of the chemical potential at the two electrodes.

(2) We have here periods of induction before the constant maximum E.M.F. is reached, and also a period of deduction, on removal of light.

(3) The reactions under the action of the current are always accompanied by the phenomena of induction and deduction also when the maximum E.M.F. is reached.

(4) The "sensitiveness" of the electrodes to light does not always remain the same (see § 7).

(5) The E.M.F. of such a combination, and the value of the solution tension and of the chemical potential, are functions of the intensity, composition of light, of the amount of light absorbed under different physical conditions by the electrode, &c.

It remains now to consider whether there is a connection between the constancy of the above reversible systems in light and GIBBS' *rule of phases.* If we take the system reversible in respect of the anion, p. 353,

$$N = \text{Ag, Cl, Na, } H_2O = 4,\ m = \text{Ag, ClAg, and solution} = 3,$$

if AgCl and solution in light and in the dark are regarded each as one phase, but $m = 5$ if AgCl and the solution in light and in the dark are regarded as in two different phases. In this case $m = n+1$, the system is one of complete equilibrium, and such combinations ought to be constant.

Similar is the case with the cells reversible in respect of the cation (p. 352) $n = (Ag, NO_3, H_2O) = 3$, while $m = 2$ if the same substance in light and in the dark is regarded as one phase; but $m = 4 = n+1$ if it is regarded as two phases.

Before passing to the account of the experiments made, I should like to state that all curves obtained during the first year and a-half were rejected, and that when it was thought that all possible errors in the methods, &c., were removed to justify complete confidence in the results obtained, all previous experiments were repeated again. Some of the more important results were investigated, after this a second time, after an interval of a year or more, for greater security.

§ 6. *Experimental Results obtained with Constant Cells reversible in respect of the Cation.*

(*a*) *The system* Ag *plate in light,* $AgNO_3$ *solution in light,* $AgNO_3$ *solution in the the dark,* Ag *plate in dark.*—Plates of the 3rd and 4th, 5th, 6th, 8th, 11th, (18th), 19th (*a*), 19th (*b*), 19th (*c*) of June, 1903, under N1, 2, 3, 4, 5, 6, 7, 8, 9, and Table I., pp. 390–391, give the investigation of the different problems, connected with constant cells, reversible in respect of the cation, carried out on the system Ag in light, $AgNO_3$ solution, Ag in the dark. Each of the plates contains a series of curves. All of them have exactly the same course, showing that the curves are characteristic of this type of cell. The part of the curves *a–b*, representing a straight line, gives the position of the spot of light from the galvanometer Nalder N1, when both Ag plates are in the dark in a closed circuit (the E.M.F. in the dark having reached in the different plates constant and very small values); the part of curve *b–c* is of a logarithmic shape and gives the gradually increasing deflection of the galvanometer, when one of the Ag plates is exposed to light (at *b*); the part of the curve *c–d* is again a straight line, and gives the maximum deflection of the galvanometer ultimately reached in light; the straight line *c–d* is running parallel to line *a–b*, indicating that the system (Ag plate in light, $AgNO_3$ solution in light, $AgNO_3$ solution in the dark, Ag plate in the dark) acquires after a time (after the period given by *b–c*) a constant new state in light, given by *c–d* as characteristic of it, as is its constant state in the dark, given by *a–b*; the further part of the curve *d–e* gives the gradual diminution of the deflection of the galvanometer, when light is removed from the system (at *d*), *i.e.*, the gradual drop of the E.M.F. of the system, when the system gradually passes in the dark from its constant state in light to its constant state in the dark. When this return is complete, we must evidently get again a straight line, a continuation of *a-b*; before then it only gradually approximates to its constant state in the dark.

We note that the system passes in light from the state *a–b* to the state *c–d* only gradually (not suddenly) and so also on removal of the light the system passes in the dark from the state *c–d* to the state *a–b* only gradually (not suddenly). It follows from this that *b–c* and *d–e* represent truly gradual transformations in the state of the system, passing from one constant state in the dark to another constant state in light and *vice versâ*. We shall call *b–c* the *induction* period, *d–e* the *deduction* period, since the phenomena here are similar to the phenomena of "induction" and "deduction," observed for chemical reactions (such as CO and Cl_2) in light and dealt with in the author's papers on "Chemical Statics and Dynamics in Light," 'Phil. Trans. Royal Society,' 1903, 'Zeit. Physik. Chemie,' June, December, 1902, &c., &c.

We notice the course of the induction and deduction periods; *b–c*, as well as *d–e*, change their curvature, have a point of inflection, changing sign from positive to negative or *vice versâ*, and the curves approximate asymptotically either to *c–d* or *a–b*. Their equations, meaning and content are given in the "Preliminary Communication of Galvanic Cells produced by Light," 'Roy. Soc. Proc.,' Nov., 1904, and will be specially dealt with later on.

Plate of June 3 *and* 4, 1903 (16 *Curves*), *N*2, *Table I.*

The Ag plates, prepared as described in § 4, and polished before by the current, were immersed in a 0·25 normal $AgNO_3$ solution. To know the direction of the current in the solution, the red and blue thick leads from the quartz vessel were always connected in the same way to the galvanometer (Nalder N1), the red lead with the plate exposed to light. On replacing the light cell by a Daniell, it was found that the plate in light behaves to the plate in the dark as Zn to Cu in the Daniell, *i.e.*, under the action of light the current passes in the solution from the Ag plate in light to the Ag plate in the dark.

After an hour the E.M.F. in the dark was = 2·7 centims. to the right, and next day (June 4) = 1·5 centims. to the right = $17{\cdot}6 \times 10^{-9}$ ampère = $15{\cdot}0 \times 10^{-6}$ volt. The arc (Dubosc) was at 65 volts, 6 ampères. The intensity of light (measured by the Rubens thermopile on Nalder N2) = 11·6 centims. (right and left), while the calibration with the Clark and 100,000 ohms resistance and 10 ohms shunt of galvanometer gave a deflection (right and left) 19·8 centims. The quartz vessel was removed from the quartz window 8 centims. There are 16 curves on this plate, numbered in the order they were taken. After the curves were taken, the sensitiveness of the galvanometer (Nalder N1) was measured in standard units (Clark, 83,600 ohms in circuit; 5 ohms in shunt of galvanometer); the same was (right and left) = 17·4 centims. The resistance of the solution in the quartz vessel between the plates 13·4 ohms.

Curve N1 shows that, after the first exposure to light, the system passes on removal to the light, in the dark, through a deduction period, back to its former state in the dark before illumination, approaching it however very slowly and asymptotically.

Curves N2, 3, 4, 5, 6 (distance of the arc from the quartz vessel 37 centims.) show that after the first exposure we get the same curves on repetition of the experiment, at the same distance of the arc from the quartz vessel. The return to the state in the dark on removal of the light is complete in (2), (3), (4), (5), (6), after curve (1), when the small residue of energy created by the heating effect of light, which leaves the system only very slowly, is allowed to remain in it (2 millims. deflection). The deflections are in (1) 20 millims., in (2) 19 millims. (corr. 21 millims.), in (3) 17 millims. (corr. 19 millims.), in (4) 18 millims. (corr. 20 millims.), in (5) 18 millims. (corr. 20 millims.), in (6) 16 millims. (corr. 18 millims.), *i.e.*, if not corrected, 20, 19, 17, 18, 18, 16, average = 18 millims. = $21{\cdot}1 \times 10^{-9}$ ampère = $18{\cdot}0 \times 10^{-6}$ volt; if corrected, 20, 21, 19, 20, 20, 18 millims. = average 19·7 millims. = $23{\cdot}1 \times 10^{-9}$ ampère = $19{\cdot}6 \times 10^{-6}$ volt.

This shows beyond dispute that the system is in the dark in one constant state, and in light (of a given intensity) again in another.

The curves N7, 8, 9, 10, 11, 12 test the same point at a distance of 33 centims. After N7, 8, the curves were taken uninterruptedly one after another to see whether the system quickly returns to the same two states in light and in the dark. We find that on every occasion the curves reached, or almost reached, in the dark the same line *a–b*, and again every time it returned in light to the same line *c–d*. The author did not always wait for complete return of the system to the last millimetre, because he had to keep the light of the arc constant during the whole series of experiments.

The deflection in (7) is 24 millims. (removed from zero deflection in the dark 2 millims.); in (8) 24 millims. (corr. 26 millims.); in (9) 26 millims. (corr. not returned 2 millims.); in (10) 24 millims. (corr. 26 millims., not returned 1 millim.); in (11) 23 millims. (corr. + 2 millims. + 1 millim. = 26 millims.); in (12) 23·5 millims. (corr. + 2 millims. + 1 millim. = 26·5 millims). Thus we have for N7, 8, 9, 10, 11, 12, if not corrected, deflections: 24, 24, 26, 24, 23, 23·5, average 24 millims. $= 28{\cdot}1 \times 10^{-9}$ ampère $= 24 \times 10^{-6}$ volt; and if corrected: 24, 26, 26, 26, 26, 26·5 = 25·8 millims. $= 30{\cdot}2 \times 10^{-9}$ ampère $= 25{\cdot}7 \times 10^{-6}$ volt (at a distance of 33 centims. of the arc from quartz vessel). We find $37^2 \times 18 = \mathbf{24{\cdot}6 \times 10^3}$ (not corr.) and $33^2 \times 24 = \mathbf{26{\cdot}1 \times 10^3}$ (not corr.) and $37^2 \times 19{\cdot}7 = \mathbf{27 \times 10^3}$ (corr.) and $33^2 \times 25{\cdot}3 = \mathbf{27{\cdot}5 \times 10^3}$ (corr.), *i.e., the deflection in light, or the E.M.F. created by the light, is directly proportional to the intensity of the light.*

Curve (13) *consists of* 5 *Curves.*—Here the author purposely arranged that the system, after it reached its constant state in light, should in each successive experiment be more and more removed from its state in the dark, passing smaller and smaller parts of the deduction period by every time screening the system from light for shorter and shorter periods. We see that however much or little the system traversed the part of the curve giving the deduction period, it always returns in light to the same line, and this is very clear evidence that the state of the system in light of a given intensity and composition is a strongly defined and a constant one. In the last portion of N13 the system was allowed to completely return to its initial state in the dark, and this shows again that the point in the dark is a perfectly defined and a constant one.

Curves 14, 15, 16 were again taken one after another. We get again three deflections of the same magnitude, 21 millims., 21 millims., 21 millims. (corr. 24 millims., 24 millims., 24 millims. $= 28{\cdot}1 \times 10^{-9}$ ampère $= 24{\cdot}0 \times 10^{-6}$ volt).

The investigation of the above system was then extended for longer periods to observe the influence of time upon the E.M.F. produced.

Plate of June 5, 1903 (9 *Curves*) *N*3, *Table I.*

The same system from June 3 was left short-circuited in the dark. The deflection in the dark was $= 15 \times 10^{-6}$ volt. Experimental data, see Plate N3, Table I.

The deflections obtained at 26 centims. distance are: in (1) 36 millims. in (2) 35 millims. (corr. 37 millims.), in (3) 34 millims. (corr. 37 millims.), in (4) 33 millims. (corr. 36 millims.) = average 34·5 millims. $= 40{\cdot}55 \times 10^{-9}$ ampère $= 34{\cdot}4 \times 10^{-6}$ volt if not corrected, and = average 36·5 millims. $= 42{\cdot}8 \times 10^{-9}$ ampère $= 36{\cdot}4 \times 10^{-6}$ volt if corrected. (Intensity of the arc 12·5 right and left.) The deflections obtained at 36 (7) centims. distance are: in (5) 17 millims., in (6) 15·7 millims., in (7) 17 millims., in (8) 19 millims., in (9) 17 millims., average = 17 millims. = 19×10^{-9} ampère = $16{\cdot}9 \times 10^{-6}$ volt (at intensity of the arc = 11·5 centims.); for light intensity = 12·1 centims., the average deflection = 17·9 millims. The law of intensity:

$$36^2 \times 17{\cdot}9 = \mathbf{23{\cdot}2} \times 10^3 \text{ and } 26^2 \times 34{\cdot}5 = \mathbf{23{\cdot}3} \times 10^3 \text{ if not corrected,}$$

$$37^2 \times 17{\cdot}9 = \mathbf{24{\cdot}5} \times 10^3 \text{ and } 26^2 \times 36{\cdot}5 = \mathbf{24{\cdot}7} \times 10^3 \text{ if corrected.}$$

*Plate N*4 *of June* 6, 1903 (4 *Curves*), *New Carbons* ("*Imperial Crown*"), *Table I.*

The same combination from June 3 was taken. Experimental data, Plate N4, Table I. The deflection obtained at a distance of 26 centims. is: in (1) 55 millims., in (2) 54 millims. = average 54·5 millims. = $63{\cdot}9 \times 10^{-9}$ ampère = $54{\cdot}4 \times 10^{-6}$ volt.

The deflection obtained at a distance of 36 centims. is: in (3) 28 millims., in (4) 28 millims., average = 28 millims. = $32{\cdot}8 \times 10^{-9}$ ampère = $27{\cdot}9 \times 10^{-6}$ volt. We get for the law of intensity: $36^2 \times 28 = \mathbf{36{\cdot}3} \times 10^3$ and $26^2 \times 54{\cdot}5 = \mathbf{36{\cdot}8} \times 10^3$.

Plate of June 8, 1903 (4 *Curves*) (3*rd Curve interrupted, Plate N*5), *Table I.*

The same system from June 3, the same carbons as on June 6; the E.M.F. in the dark = 93×10^{-6} volt. Deflections obtained at 36 centims. distance were: in (1) 29 millims., in (2) 29 millims., in (3) interrupted, in (4) 26 to 27 millims. = average 28·2 millims. = 33×10^{-9} ampère = $28{\cdot}1 \times 10^{-6}$ volt.

Comparing the tables of the 4th and 5th of June with that of the 6th of June, and 8th, 11th, 18th, and 19th of June, which will subsequently be dealt with:—

	Date June, 1903.	Distance of arc from quartz vessel.	Distance of quartz vessel from quartz window.	Deflection of Nalder N1.	Intensity of light in deflections of Nalder N2 = A.	Calibration of Nalder N2, B.	Calibration of Nalder N1.	Intensity of light A/B.	Deflection of Nalder N1 for the intensity of light 0·586 = A/B.
		centims.	centims.	millims.					millims.
	4	37	8	18 19·7 (corr.)	11·6	19·8	17·4	0·586	**18** **19·7** (corr.)
	5	36 (7)	8	17	11·5	19·8	17·4	0·581	**17**
New carbons, "Imperial Crown"	6	36	8·5	28	12·7	19·8	17·4	0·641	**25·6**
	8	36	8·5	28·2	13·5	19·8	17·4	0·682	**24·2**
	11	36 (7)	8·5	32	12·9	19·8	17·4	0·651	**25·2**

This table shows that the different composition of the carbons alone can considerably vary the intensity of their light and influence the value of the E.M.F. produced.

On the 4th and 5th of June we got practically the same deflection (18 and 17 millims.). On the 6th and 8th of June we got with the new carbons 28 millims., and the same result was obtained with the same carbons several days later, on the 11th of June. When corrected for the same intensity of light, A/B = 0·586, we still get for the 6th, 8th, 11th of June the values 25·6, 24·1, 25·2 millims. instead of 18, 17 millims. of the 4th and 5th of June. Thus the composition of light, not only the intensity of the light, changes with different carbons used. It makes also a further investigation necessary, whether a small oxidation of the Ag plates, or change in their brightness which may take place in time, may also influence the values of the E.M.F.'s obtained.

Plate of June 11, 1903 (6 *Curves*), *N*6, *Plate I.*

The same system from June 3. The circuit was always kept closed between the experiments of the different days, and the same plate was always exposed to light. The E.M.F. in the dark = 2·7 centims. = $26·9 \times 10^{-6}$ volt. Experimental data, Plate N6, Table I., pp. 390–391. Distance of the arc from quartz vessel 36 (37) centims. The carbons the same as on the 6th and 8th of June.

Curve N1 obtained with the total white light gave = 32 millims. deflection = $37·5 \times 10^{-9}$ ampère = $31·9 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection at a constant temperature = 32 millims. − (1·9 to 3 millims.) = 29 to 30·1 millims. Curve N2 was obtained with the blue gelatine screen; the deflection in light = 15 millims. = $17·6 \times 10^{-9}$ ampère = $14·5 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection = 15 millims. − (1·3 to 2 millims.) = 13 to 13·7 millims. Curves N3 and N3_1, obtained with the green-yellow gelatine screen, gave 2·5 millims. and 2·5 millims. = average 2·5 millims. deflection = $2·9 \times 10^{-9}$ ampère = $2·4 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection = 2·5 millims. − (1·3 to 1·9 millims.), *i.e.*, no E.M.F. at a constant temperature can be shown to be produced by light. Curves N4 and N4_1, obtained with the red gelatine screen, gave 2 millims. and 1·5 millims. = average 1·75 millims. deflection = $2·1 \times 10^{-9}$ ampère = $1·8 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection = 1·8 millims. − (1·4 to 2·1 millims.), *i.e.*, no E.M.F. at a constant temperature can be shown to be produced by light.

From the above it is to be seen that the E.M.F. produced by light at a constant temperature is principally due to the blue rays of the spectrum and very little to the red or yellow parts of the same. (The results obtained with the gelatine screens contain no correction for the gelatine.)

In § 2 it has been shown that the thermo E.M.F. caused by the total light forms about 6 to 9 per cent. of the total E.M.F.

An application of a correction of 9 per cent. for the heat effect of total light gives the following results for the law of light intensity *at a constant temperature*:—

June 3 and 4 . $37^2 \times 16{\cdot}4 = \mathbf{22{\cdot}5} \times 10^3$ and $33^2 \times 21{\cdot}8 = \mathbf{23{\cdot}7} \times 10^3$ (not corrected).
$37^2 \times 17{\cdot}9 = \mathbf{24{\cdot}5} \times 10^3$ and $33^2 \times 23{\cdot}0 = \mathbf{25{\cdot}0} \times 10^3$ (corrected).
June 5 . . . $36^2 \times 16{\cdot}3 = \mathbf{21{\cdot}1} \times 10^3$ and $26^2 \times 31{\cdot}4 = \mathbf{21{\cdot}2} \times 10^3$ (not corrected).
$37^2 \times 16{\cdot}3 = \mathbf{22{\cdot}3} \times 10^3$ and $26^2 \times 33{\cdot}2 = \mathbf{22{\cdot}5} \times 10^3$ (corrected).
June 6 . . . $36^2 \times 25{\cdot}5 = \mathbf{33{\cdot}0} \times 10^3$ and $26^2 \times 49{\cdot}6 = \mathbf{33{\cdot}5} \times 10^3$,

i.e., since the thermo E.M.F. is directly proportional to the intensity of light, we find, as before, that *the E.M.F. produced by light at a constant temperature is also (as the total E.M.F.) directly proportional to the intensity of light.*

Experiments of June 18, 1903 (2 *Curves*), *Table I.*

The Ag plates of June 3, 1903, were polished again and covered on one side with paraffin, and placed into a 0·0041 normal $AgNO_3$ solution. Resistance of liquid in quartz vessel = 840 ohms. After $1\frac{1}{2}$ hours the E.M.F. in the dark was still 17 centims. to the right, but further diminution became slow. At a distance of the arc of ·27 centims. a deflection = 20 millims. was obtained. (Experimental data, Table I., pp. 390–391.)

A comparison of this result with those subsequently obtained on June 9 shows that the formation of an oxide layer, if any, can take place with pure silver plates only very slowly, and that it is the Ag plate which gives the E.M.F. under the action of light, not a layer of oxide.

Comparing, on the other hand, the above result with those of June 6, and calculating the deflection for the same resistance of the liquid (847·8 instead of 1674), the same intensity of the light $\left(\frac{A}{B} = 0{\cdot}641\right)$, the same distances (37 centims. instead of 27 centims.), we get 20·7 millims. deflection (with the newly polished plates) instead of 28 millims. on June 6 (with plates which were several days in solution). This seems also to indicate either that the problem of getting a light of constant composition with the arc is still awaiting its solution, or that a small diminution in the brightness of the Ag plates still takes place in time, though very slowly.

Plates (*a*), (*b*), (*c*) *of June* 19, 1903 (*Table I.*). *The Influence of the Concentration of the Solution upon the E.M.F. of the System.*

Three different concentrations of $AgNO_3$ were rapidly investigated one after another in the course of about 3 hours, between 11.30 A.M. and 2.20 P.M., passing from the dilute solution to the more concentrated one. The solutions used were 0·0041 normal (Table *a*), 0·025 normal (Plate *b*), and 0·25 normal (Table *c*). Experimental data, see Table I.

Plate (*a*) *contains* 5 *Curves.*—The same solution as used on June 18, but the E.M.F.

in the dark is = 1·9 centim. to the left = $37·4 \times 10^{-6}$ volt (instead of to the right). The deflections obtained in N1, 2, 3, at a distance of the arc = 36 (37) centims., are after the first, 10·5 millims., 10·5 millims. = average 10·5 millims. = $20·6 \times 10^{-6}$ volt, and a distance of 26 (7) centims., 19 and 18 millims. = average 18·5 millims. = $36·3 \times 10^{-5}$ volt. We find again: $37^2 \times 10·5$ = **14·4** $\times 10^3$ and $27^2 \times 18·5$ = **13·5** $\times 10^3$. The resistance of the liquid is, as before, 840 ohms.

Plate (b) contains 5 *Curves.*—The Ag plates are in a 0·025 normal $AgNO_3$ solution. The curves are, for this reason, steadier and better defined. It took an hour for the galvanometer to steady quite down, the deflection in the dark becoming only 1 centim. to the left = $10·3 \times 10^{-6}$ volt. Experimental conditions were the same as in (*a*). Resistance of the liquid in the quartz vessel between the Ag plates was found to be 146 ohms. The deflections obtained at 27 centims. distance were: 40·5 millims. in N1, 30·5 millims. (corr. 34·5 millims.) in N2, 32·5 millims. (corr. 38 millims.) in N3, = average 37·3 millims. corr. = $43·6 \times 10^{-9}$ ampère = $38·4 \times 10^{-6}$ volt. The deflections obtained at 37 centims. distance were 23·5 millims. in N4, and 21·5 millims. (no corr. required) in N5 = average 22·5 millims. = $26·3 \times 10^{-9}$ ampère = $23·2 \times 10^{-6}$ volt. We find again: $37^2 \times 22·5$ = **30·8** $\times 10^3$ and $27^2 \times 37·3$ = **27·2** $\times 10^3$.

Plate (*c*) *contains* 4 *Curves.*—The Ag plates were now in a 0·25 normal $AgNO_3$ solution. The resistance of the solution between the plates in the quartz vessel was found to be 16·5 ohms. The E.M.F. in the dark = 0·9 centim. to the left = $9·0 \times 10^{-6}$ volt. The carbons in (*a*), (*b*), (*c*) were the same, care having been taken to stop the arc at once after the curves of each series were taken and the measurement of the deflection with the Rubens thermopile made (all other measurements were subsequently made). The deflections obtained at a distance of the arc = 27 centims. are: 40 millims. in N1, 38 millims. (corr. 40 millims.) in N2, average 40 millims. = $46·9 \times 10^{-9}$ ampère = $39·8 \times 10^{-6}$ volt. The deflections obtained at a distance 37 centims. are: 26 millims. in N3, 21 millims. in N4 (no corr. was required) = average 23·5 millims. = $27·6 \times 10^{-9}$ ampère = $23·4 \times 10^{-6}$ volt. We get again: $37^2 \times 23·5$ = **32·2** $\times 10^3$ and $27^2 \times 40$ = **29·2** $\times 10^3$.

Let us now compare the results of Tables (*a*), (*b*), (*c*), obtained under exactly the same conditions, except the concentrations of the $AgNO_3$ solution.

The resistance of the Nalder N1 was again measured and found to be 834·4 ohms. Thus the resistance in the circuit was in (*a*) 1674·4 ohms, in (*b*) 980·4 ohms, in (*c*) 851·4 ohms. We get the following table:—

Concentration of the $AgNO_3$ solution.	Resistance in circuit in ohms. W.	Deflection obtained at the distance of light from QV = 27 centims. $D_{,}$.	$D_{,} = (a)$ ampère. A.	The E.M.F. at 27 centims. distance. W.A.	Deflection obtained at the distance of light from QV = 37 centims. $D_{,,}$.	$D_{,,} = (a')$ ampères. A′.	The E.M.F. at 37 centims. distance. W.A′.	Intensity of arc.	Calibration of Nalder N2.	Calibration of Nalder N1.
		millims.			millims.					
in (*a*): **0·0041** n.	1674·4	18·5 (average)	$21·7 \times 10^{-9}$	**36·3** $\times 10^{-6}$ v.	10·5 (average)	$12·3 \times 10^{-9}$	**20·6** $\times 10^{-6}$ v.	11·2	17·2	17·4
in (*b*): **0·025** n.	980·4	37·3 (,,)	$43·6 \times 10^{-9}$	**38·4** $\times 10^{-6}$ v.	22·5 (,,)	$26·3 \times 10^{-9}$	**23·2** $\times 10^{-6}$ v.	11·2	17·2	17·4
in (*c*): **0·25** n.	851·4	40·0 (,,)	$46·9 \times 10^{-9}$	**39·8** $\times 10^{-6}$ v.	23·5 (,,)	$27·6 \times 10^{-9}$	**23·4** $\times 10^{-6}$ v.	11·2	17·2	17·4

Thus we find *that the total E.M.F.* (*i.e.*, the E.M.F. under the action of light at a constant temperature + the E.M.F. due to the heating of the exposed plate and liquid in front of it) *of constant cells reversible in respect of the cation is independent of the concentration* of the $AgNO_3$ solution.

A correction of 9 per cent. for the heating effect gives for the law of intensity and *the volts obtained at a constant temperature* the following data in (*a*), (*b*), (*c*). For the law of intensity we get :—

In (*a*) $37^2 \times 9{\cdot}55 = 13{\cdot}1 \times 10^3$ and $27^2 \times 16{\cdot}83 = 12{\cdot}3 \times 10^3$.
In (*b*) $37^2 \times 20{\cdot}5 = 28{\cdot}1 \times 10^3$ and $27^2 \times 33{\cdot}9 = 24{\cdot}7 \times 10^3$.
In (*c*) $37^2 \times 21{\cdot}4 = 29{\cdot}3 \times 10^3$ and $27^2 \times 36{\cdot}4 = 26{\cdot}5 \times 10^3$.

For the volts obtained we get : *at* 27 *centims. distance* in (*a*) $33{\cdot}0 \times 10^{-6}$ volt, in (*b*) $34{\cdot}9 \times 10^{-6}$ volt, in (*c*) $36{\cdot}3 \times 10^{-6}$ volt. *At* 37 *centims. distance* in (*a*) $18{\cdot}7 \times 10^{-6}$ volt, in (*b*) $21{\cdot}1 \times 10^{-6}$ volt, in (*c*) $21{\cdot}3 \times 10^{-6}$ volt.

§ 7. *Experimental Results obtained with Constant Cells Reversible in Respect of the Anion.*

I. *The System* (Ag-AgCl *in Light, Decinormal* NaCl *Solution in Light, Decinormal* NaCl *Solution in the Dark,* Ag-AgCl *in the Dark*). *Plate N*10 *of June* 30 (10 *Curves were taken*), *Table II.*

The Ag plates of the previous investigation (Ag plates in $AgNO_3$ solution) were covered on one side with shellac and paraffin, and coated on the other with an extraordinarily thin layer of AgCl by immersing them in water containing a merest trace of HCl acid. A decinormal NaCl solution was brought into the quartz vessel, some AgCl was put on the bottom, then the Ag plates were fixed in the quartz vessel. Experimental data see Table II., pp. 392–393.

The curves give a deflection to the left; the course of the induction (*b–c*) and deduction periods (*d–e–f*) show that the system is constant, gives no polarisation. After the induction period has passed, a constant E.M.F. (*c–d*) is obtained (whether the whole light or coloured screens are used). On removing the light from the system it returns, passing the deduction period, to its former state in the dark, as is to be seen from the straight line f'–f'' reached by the system, which is a continuation of the straight line *a–b* before the induction period. The current is flowing in the solution from the plate in the dark to the plate in light. The deflections obtained at a distance of the arc = 37 centims. were : in N1, 56 millims. (did not return 2 millims.) ; in N2, 53 millims. (corr. 55 millims.), average = 55·5 millims. = 59×10^{-9} ampère = $51{\cdot}8 \times 10^{-6}$ volt ; at a distance of 50 centims. : in N3, 31 millims. ; in N4, 34 millims., average = 32·5 millims. = $34{\cdot}6 \times 10^{-9}$ ampère = $30{\cdot}4 \times 10^{-6}$ volt.

The law of intensity: $37^2 \times 55{\cdot}5 = \mathbf{76} \times 10^3$ and $50^2 \times 32{\cdot}5 = \mathbf{81} \times 10^3$, *i.e.*, the E.M.F. is directly proportional to the intensity of light.

Curves N5 and N6 give the deflections obtained with the red screen, curves N7 and N8 with the blue screen, curves N9 and N10 with the yellow-green screen, all at a distance of the arc from quartz vessel = 37 centims. The ratio of the deflections in millimetres of the white light : blue : yellow-green : red = 54·5 (corr. 55·5 millims.) : 13 millims. : 5·5 millims. : 3·5 millims., or in per cent. of the total light without screen = 100 per cent. : 23·4 per cent. : 9·9 per cent. : 6·3 per cent. This shows in the first instance that the so-called "actinic" rays act most. Calculating now the thermo E.M.F. at a distance of 37 centims. we get:—

If $d\pi/d\tau$ is put, according to GOCKEL, = 0·00014 volt, then, since the rise of temperature was

$$\frac{(0^\circ{\cdot}03 \text{ to } 0^\circ{\cdot}045) \times 27^2 \times 19{\cdot}8 \times 15{\cdot}5}{37^2 \times 12{\cdot}7 \times 16{\cdot}7} = 0^\circ{\cdot}023 \text{ to } 0^\circ{\cdot}035 \text{ C.},$$

the thermo E.M.F. = (3·2 to 4·8) . 10^{-6} volt; since the sensitiveness of Nalder N1 was 94·4 centims. per 10^{-6} ampère, we get the thermo E.M.F. on Nalder N1 = 3·5 to 5·2 millims. for the total light, and = 2·5 to 3·8 millims. for the red screen, = 2·6 to 3·7 millims. for the yellow-green screen, = 2·4 to 3·6 for the blue screen. The ratio of the total light : blue : yellow-green : red, at a constant temperature is thus: (93·1 to 95·4 per cent.) : (16·9 to 19·2 per cent.) : (3·4 to 5·6 per cent.) : (0 to 1·8 per cent.). (No correction is made here for the absorption of light by the gelatine of the screens.)

(2) *On July* 1, next day, the cell was no more constant, but showed already a small *polarisation* of 3·6 millims., the above maximum deflection returning back 3·5 millims., remaining only then constant. The maximum constant deflections on the drum at a distance of 37 centims. were: (53·5), 66·1, 68·3, 70·3, 68·3 millims. = average 68·2 millims. = $72{\cdot}5 \times 10^{-9}$ ampère = $63{\cdot}6 \times 10^{-6}$ volt. On shutting the screen, the spot of light first passed the zero deflection in the dark by 3·5 millims., returning to zero deflection, where it remained constant.

It follows from the above: (1) The sensitiveness of the plates remaining in the dark 21 hours increased from about 55 millims. to about 68 millims. (2) The current passing in light from the plate in the dark to the plate in light, the AgCl of the plate in light, or the upper surface of the same, evidently transforms into Ag, while on the plate in the dark new AgCl was formed; the system thus transformed on the previous day into (Ag in light, ClNa solution, Ag-ClAg in dark). A direct investigation of a similar system (Ag in light, BrNa solution, Ag-BrAg in dark) showed that such systems form inconstant cells and show *polarisation.* An analysis of the reactions going on in such systems shows also that this must be the case. By the action of Cl_2 upon this system *the system is reversed* to the original combination, the formed Ag transforming back into AgCl, and the constant cell is again obtained.

II. *The System (*Ag-BrAg *in Light, Decinormal* NaBr *Solution in Light, Decinormal* NaBr *Solution in the Dark,* Ag-BrAg *in the Dark).*

On this system the properties of constant cells reversible in respect of the anion were studied in great detail, the deflections obtained being very large and suitable for quantitative investigation. The AgCl was removed from the Ag plates with a CNK solution, the Ag plates polished again, covered on one side with shellac and paraffin, then immersed into a solution of Br_2 in water for a short time. A very thin layer of AgBr was thus deposited on the same.

These plates were first used on July 25 and 27, 1903, for the investigation of the system (Ag-BrAg plate in light, KNO_3 solution, Ag-BrAg in the dark), which is an *inconstant* cell, and showed polarisation. The same Ag-BrAg plates, carefully washed, were now placed in the quartz vessel containing a decinormal NaBr solution and solid AgBr, and a *constant* cell was obtained. Arc and acetylene light were used; the last, however, almost exclusively on account of its very much greater constancy.

(1) *Plate* N11 *of July* 28, 1903 (3 *Curves*).—Acetylene light used. For experimental data, see Table III., pp. 392–393. Forty-five minutes after the circuit was closed the E.M.F. in the dark was still = 18 centims. to the left = 167×10^{-6} volt. Though it has not yet reached its constant minimum, 3 curves were taken in succession to see the character of the results immediately after the circuit is closed. The curves did not return to zero deflection in the dark. During the time a curve was taken, the E.M.F. in the dark shifted to a new point. The deflections obtained in N1, 2, 3 were 60 millims., 74 to 75 millims., 74 to 75 millims., the distances between *a–b* and *d–d* in N1, 2, 3 were 11 millims., 20 millims., 20 millims. Thus the results corrected for the variation of the E.M.F. in the dark are: 49 millims., 44 to 45 millims., 45 to 46 millims., = average 46·3 millims. = $49{\cdot}2 \times 10^{-9}$ ampère = $43{\cdot}2 \times 10^{-6}$ volt.

(2) *Plate* N12 *of July* 29 (*a*) *contains* 9 *Curves, Table III.*—The plates from July 28 were left short-circuited till the next day: the E.M.F. in the dark found to be = 1·5 centims. = $14{\cdot}2 \times 10^{-6}$ volt to the right (*i.e.*, in an opposite direction to that of the previous day). On opening and shutting the circuit, the spot of light always returned to the same position on the scale. The acetylene light was in all experiments at the same distance of 116 centims. from the quartz vessel; the intensity of light coming from the burner was changed by screening more and more the light with the chimney of the burner and measuring its intensity with the Rubens thermopile. The deflections obtained with N1*, 2, 3, 4, 5, with the intensity of the acetylene = 71 millims. deflection, were 84, 81, 82, 80, 81 millims., average = 81·6 millims. = $86{\cdot}7 \times 10^{-9}$ ampère = $76{\cdot}1 \times 10^{-6}$ volt. The curves return after the deduction period (if we wait sufficient time) to their former position in the dark, as is well illustrated by curves N2 and N4; in N3 and N5 we did not

---

* After the maximum deflection was reached, screen of chronograph fell down, so that the deduction period was not photographed.

photograph the last 3 or 4 millims. of the ends of the deduction period so as to avoid the danger of several lines coinciding on the photographic sheet, but I waited, after the screen of the chronograph was shut, some time till it could be assumed that the deduction was complete.

The deflections obtained with N6 and 7, with the intensity of acetylene = 39 millims., were: 43·5 and 44·5 millims., average = 44 millims. = $46·8 \times 10^{-9}$ ampère = $41·0 \times 10^{-6}$ volt. The curve in N6 was allowed to return to its E.M.F. in the dark, in N7 the last few millimetres of the end of the deduction period were not photographed. The deflections obtained with N8 and 9, with the intensity of acetylene = 28·5 millims., were: 32·5 and 31 millims., average = 31·8 millims. = $33·8 \times 10^{-9}$ ampère = $29·6 \times 10^{-6}$ volt; the last $2\frac{1}{2}$ to 3 millims. were not photographed, but, as before, I waited till the deduction period must have become complete.

From the data given in the above table we get again the law of intensity—81·6 : 71 = **1·15**; 44 : 39 = **1·13**; 31·8 : 28·5 = **1·12.**

The above data obtained for light of the same intensity (and composition) on repetition of the experiment: 84, 81, 82, 80, 81 millims.; 43·5 and 44·5 millims.; 32·5 and 31 millims. give a sufficient illustration that during the time the above curves were taken, and with light of such small intensity, which cannot affect essentially the composition of the electrode exposed to the same, the same deflection is obtained, and this shows that the chemical potential and solution pressure of the same plates remain constant. The cell is reversible, as it follows from the consideration of the reactions going on in it, and from the course of the above curves, the induction and deduction periods of which show no polarisation, while the system always returns to its former state, whenever on removal of the light we allow the deduction period to become complete. It is constant, as is shown by the shape of the parts of the curves giving the induction and deduction periods, from the straight line *c–c*, obtained in light, parallel to the line *a–b* in the dark, and from the fact that on repetition of the experiment the same maximum deflection is obtained.

(3) *Plate* 13 (*b*) *of July* 29, 1903, *contains* 13 *Curves, Table III.*—The same system was investigated a few hours later, first with acetylene, then with the arc.

Acetylene light and coloured screens (*curves N*1, 2, 3, 4, 5, 6, 7), *Experimental data, see Table III., pp.* 392–393.

In curve N1 the total acetylene light as before was used, at a distance = 116 centims.; the deflection was 80 millims. The next curves, M2, 3, 4, 5, were taken with the *red* screen: N2 and 3 at a distance of the acetylene light from the quartz vessel = 116 centims., N4 at a distance of 80 centims., N5 at a distance of 57 centims. The maximum constant deflections obtained for N2 and 3 were 28 and 29 millims. = average 28·5 millims. = $30·3 \times 10^{-9}$ ampère = $26·6 \times 10^{-6}$ volt in N4 = 60 millims. = $63·7 \times 10^{-9}$ ampère = $55·9 \times 10^{-6}$ volt, in N5 it was about 3 millims. greater than could be got on the photographic paper (115 millims.), since the photographed curve shows that the constant maximum was very nearly reached, *i.e.*, the deflection was 118 millims. = $125{\cdot}3 \times 10^{-9}$ ampère = 110×10^{-6} volt. (In all the above curves the deduction period was allowed to become complete.)

We get the law of intensity also with red light (curves N2, 3, 4, 5, taken in about half an hour): $116^2 \times 28{\cdot}5 = \mathbf{383{,}600}$; $80^2 \times 60 = \mathbf{384{,}000}$; $57^2 \times 118 = \mathbf{383{,}500}$.

Curves N6 and 7 were taken with the blue and yellow-green screen at a distance of the light from quartz vessel = 80 centims., and the deflections obtained were 48·5 and 41 millims.

Thus we get for the same 80 centims. distance of light from quartz vessel :—

	Total light (without screen).	Total light passing red screen.	Total light passing blue screen.	Total light passing yellow-green screen.
Deflections observed . . .	168 millims. $= 156{\cdot}6 \times 10^{-6}$ volt	60 millims. $= 55{\cdot}9 \times 10^{-6}$ volt	48·5 millims. $= 45{\cdot}2 \times 10^{-6}$ volt	41 millims. $= 38{\cdot}2 \times 10^{-6}$ volt
In per cent. of total light . .	100	35·7	28·9	24·4

We get the remarkable result that the light of acetylene passing the red screen gives with the above system the greatest deflection, and the yellow-green the smallest, as if two maxima were present, one near the red end of the spectrum, the other near the blue end of the spectrum. (This result compare with the results obtained with the arc.)

The above results change very little when corrected for the thermo E.M.F., which is = 1 to 1·5 per cent. of the total E.M.F. created by light (see § 2).

For the law at intensity at a constant temperature we get (July 29) :—

$$\text{In } (a): 80{\cdot}4 : 71 = \mathbf{1{\cdot}13} \qquad 43{\cdot}3 : 39 = \mathbf{1{\cdot}11} \qquad 31{\cdot}3 : 28{\cdot}5 = \mathbf{1{\cdot}10}$$
$$80{\cdot}8 : 71 = \mathbf{1{\cdot}14} \qquad 43{\cdot}6 : 39 = \mathbf{1{\cdot}12} \qquad 31{\cdot}5 : 28{\cdot}5 = \mathbf{1{\cdot}11}$$

instead of 1·15, 1·13, 1·12.

$$\text{In } (b): 116^2 \times 28{\cdot}1 = \mathbf{378} \times 10^3, \quad 80^2 \times 59{\cdot}1 = \mathbf{378} \times 10^3, \quad 57^2 \times 116{\cdot}2 = \mathbf{378} \times 10^3,$$
$$116^2 \times 28{\cdot}2 = \mathbf{380} \times 10^3, \quad 80^2 \times 59{\cdot}4 = \mathbf{380} \times 10^3, \quad 57^2 \times 116{\cdot}8 = \mathbf{380} \times 10^3,$$

instead of 384×10^3; 384×10^3; 384×10^3; 387×10^3.

Arc (DUBOSCQ) *and Coloured Screens, Plate* 13 *of July* 29, 1903 (*Curves N*3, 9, 10, 11, 12, 13). *Experimental data, see Table III.*

We get for the total light without screen in N8 = 76 millims., in N10 = 69 millims., in N14 = 71·5 millims., for the blue screen in N9 = 23 millims., for the red screen in N11 = 5 millims., for the yellow-green screen in N12 = 3·5 millims. (for the thinner colourless gelatine screen, 0·12 millim. thick), in N13 = 64·5 millims. All the above curves were taken at a distance of the arc from quartz vessel = 118 centims. At the conclusion (after the photographic paper sheet was taken off) I measured also the deflection obtained on the drum with the total light of the arc at a distance of the arc from quartz vessel = 89 centims. and found it to be 120 millims. (we denote this measurement as N14). The deduction period was allowed to become complete or almost complete in most of the curves (N8, 10, 11, 12). We get for the law of intensity :

$$118^2\times\frac{76+69+71\cdot5}{3}=\mathbf{100\cdot5}\times10^4,\ 118^2\times\frac{69+71\cdot5}{2}=\mathbf{97\cdot7}\times10^4 \text{ and } 89^2\times120=\mathbf{95\cdot0}\times10^4.$$

Calculating the thermo E.M.F. created by light, we get: the rise of temperature of the exposed plate $=\frac{(0^\circ\cdot03 \text{ to } 0^\circ\cdot045)\times27^2\times19\cdot8\times9\cdot2}{118^2\times12\cdot7\times17\cdot05}=0^\circ\cdot013$ to $0^\circ\cdot009$ C., $\frac{d\pi}{d\tau}$ = 0·00079 volt, the sensitiveness of Nalder N1 = 93·9 centims. per 10^{-6} ampère, shunt of galvanometer = 40 ohms, the resistance of the solution in quartz vessel = 43 ohms, &c., therefore the thermo E.M.F. = 0·74 to 1·1 per cent. of the total deflection of the total light (without screen).

Thus we get :—

	Total light.	Red gelatine screen.	Blue screen.	Yellow-green screen.
Total E.M.F., in millims .	70·2 (corr. 72·2)	5	23	5
The thermo E.M.F., in millims.	0·54 to 0·8	0·39 to 0·57	0·3 to 0·45	0·25 to 0·4
E.M.F. at a constant temperature, in millims .	69·4 to 69·8	4·4 to 4·6	22·5 to 22·7	4·6 to 4·75
In per cent. of the total light	100	6·3 to 6·6	32·4 to 32·7	6·6 to 6·8

Here we find for the arc: (1) that the light passing the red screen gives a smaller deflection than the light passing the blue gelatine screen, while between the red and yellow-green screens no essential difference is found; (2) that all parts of the spectrum give E.M.F.'s at a constant temperature (*i.e.*, also the red and yellow-green parts of the spectrum). Contrary to this, we found with acetylene that the red screen gave greater deflections than the yellow-green, *i.e.*, that two maxima are existing, one in the red, the other in the blue. It follows from this that the arc is richer in blue, the acetylene in red rays.

I next proceed to the account of comparative experiments, where either the concentrations of the same solutions or the temperature were changed. All these experiments had to be carried out in as short a time as possible, to avoid the effect of time after previous illumination. On the other hand, really good experiments require very small values of the E.M.F. in the dark, which is not possible without waiting with new solutions for a long time. I had therefore to choose the most suitable middle course. I waited only till the diminution of the E.M.F. in the dark became so small that it could but little affect the values of the deflections obtained. The deduction period of only one of the curves taken for every concentration was allowed to become complete, since all we required to know in these experiments was the maximum deflection only. The first deflection in each concentration is for obvious reasons the more reliable one.

III. *Plate N*14 *of July* 30, 31, 1903. *Influence of Concentration, Table IV.*

In all the following experiments the distance of the acetylene from the quartz vessel was 116 centims., the intensity of the acetylene was 67 millims. (right and left), while the calibration of Nalder N2 was = 170 millims. right and left.

(*a*) The system, used on July 29 and consisting of Ag-BrAg plates immersed into a decinormal NaBr solution, is again investigated. The E.M.F. in the dark = 1·3 centims. = $12{\cdot}1 \times 10^{-6}$ volt, to the left. The resistance of the solution = 43·4 ohms. N1 gave 114 millims., N2 113·5 millims. deflection, average = 113·75 millims. = 120×10^{-9} ampère = 106×10^{-6} volt. In Curve N1 the deduction period was photographed to within 3 millims. from *a*–*b*.

(*b*) A great part of the solution was removed and distilled water added. The resistance of the solution in the quartz vessel = 137 ohms. After an hour and an half the E.M.F. in the dark became = 6·0 centims. to the left, and was found almost constant during 15 minutes. N3 gave 114 millims., N4 116 millims. deflection = average 115 millims. = $123{\cdot}3 \times 10^{-9}$ ampère = $118{\cdot}5 \times 10^{-6}$ volt; the deduction period of N3 was photographed to within 6 millims. of its completion.

(*c*) Removed all the solution, added distilled water, so that a very dilute solution was formed. The resistance was found to be 400 ohms. After about 15 minutes the E.M.F. in the dark was still 14 centims. to the right, but seemed almost constant during about 10 minutes. Curves N5 gave 80 millims. and N6 86 millims. deflection = average 83 millims. = $91{\cdot}3 \times 10^{-9}$ ampère = $108{\cdot}8 \times 10^{-6}$ volt. Since N6 was the last curve for the day I allowed its deduction period to become complete. We thus have:—

$$\begin{array}{llll}
\text{In } (a) \text{ in N1}: & E = c \times w = (834{\cdot}4 + 43{\cdot}4)\ 114 & = 100{\cdot}1 \times 10^3 & = \mathbf{106{\cdot}3} \times 10^{-6} \text{ volt.} \\
\quad\text{in N2}: & = (834{\cdot}4 + 43{\cdot}4)\ 113{\cdot}5 & = 99{\cdot}63 \times 10^3 & = \mathbf{105{\cdot}8} \times 10^{-6} \text{ volt.} \\
\text{In } (b) \text{ in N3}: & = (834{\cdot}4 + 137)\ 114 & = 110{\cdot}7 \times 10^3 & = \mathbf{117{\cdot}5} \times 10^{-6} \text{ volt.} \\
\quad\text{in N4}: & = (834{\cdot}4 + 137)\ 116 & = 112{\cdot}7 \times 10^3 & = \mathbf{119{\cdot}7} \times 10^{-6} \text{ volt.} \\
\text{In } (c) \text{ in N5}: & = (834{\cdot}4 + 400)\ 80 & = 98{\cdot}75 \times 10^3 & = \mathbf{104{\cdot}9} \times 10^{-6} \text{ volt.} \\
\quad\text{in N6}: & = (834{\cdot}4 + 400)\ 86 & = 106{\cdot}2 \times 10^3 & = \mathbf{112{\cdot}8} \times 10^{-6} \text{ volt.}
\end{array}$$

Average of N1, 2, 3, 4, 5, 6 $= \mathbf{111{\cdot}3} \times 10^{-6}$ volt.

Average of the more reliable obser. N1, 3, 5 : $\mathbf{109{\cdot}7} \times 10^{-6}$ volt.

The electric conductivities show that the concentrations used were from the decinormal to about centinormal.

Experiments of July 31 (6 *Curves taken*):—

(*a*) A decinormal NaBr solution was used. The resistance of the solution = 50 ohms (distance between the plates a little increased), the E.M.F. in the dark = 3 millims. to the left. Two curves were taken (N7 galvanometer shaken, had to lower screen of chronograph), N8 gave 120 millims. deflection = $127{\cdot}5 \times 10^{-9}$ ampère = $112{\cdot}7 \times 10^{-6}$ volt, the deduction allowed to become complete to within 2 millims.

(*b*) The solution from quartz vessel was removed and a normal NaBr solution added. The resistance was about 5 ohms. The E.M.F. in the dark = 14 centims. to the left. N9 gave 105 millims., N10 gave 106 millims. deflection, average $105{\cdot}5$ millims. = 112×10^{-9} ampère = 94×10^{-6} volt.

(*c*) Removed the greater part of the solution, added water. The resistance found = $163{\cdot}4$ ohms. The E.M.F. in the dark = 7 centims. to the right. Curves N11 gave 92 millims., N12 gave 99 millims. deflection, average $95{\cdot}5$ millims. = $101{\cdot}5 \times 10^{-9}$ ampère = $101{\cdot}2 \times 10^{-6}$ volt. The concentrations of July 31 were therefore between about normal and $0{\cdot}025$ normal NaBr solution. We thus get:—

$$
\begin{array}{lrl}
\text{In } (a') \text{ in N8:} & E = c \times w = (834{\cdot}4 + 50)\ 120 = 106{\cdot}1 \times 10^{3} = & \mathbf{112{\cdot}7} \times 10^{-6} \text{ volt.} \\
\text{In } (b') \text{ in N9:} & = (834{\cdot}4 + 5)\ 105 = 88{\cdot}14 \times 10^{3} = & \mathbf{93{\cdot}6} \times 10^{-6} \text{ volt.} \\
\text{in N10:} & = (834{\cdot}4 + 5)\ 106 = 88{\cdot}97 \times 10^{3} = & \mathbf{94{\cdot}5} \times 10^{-6} \text{ volt.} \\
\text{In } (c') \text{ in N11:} & = (834{\cdot}4 + 163{\cdot}4)\ 92 = 91{\cdot}8 \times 10^{3} = & \mathbf{97{\cdot}5} \times 10^{-6} \text{ volt.} \\
\text{in N12:} & = (834{\cdot}4 + 163{\cdot}4)\ 99 = 98{\cdot}78 \times 10^{3} = & \mathbf{104{\cdot}9} \times 10^{-6} \text{ volt.} \\
\hline
& \text{Average of N8, 9, 10, 11, 12} \quad = & \mathbf{100{\cdot}6} \times 10^{-6} \text{ volt.} \\
\hline
& \text{Average of more reliable obser. N8, 9, 11 :} & \mathbf{101{\cdot}3} \times 10^{-6} \text{ volt.}
\end{array}
$$

The above observations were extended for another day.

On August 1.—The solution of (*c*′) was left in the dark short-circuited for about 18 hours. The resistance was found to be $142{\cdot}9$ ohms (the two plates became a little nearer). The E.M.F. in the dark = $1{\cdot}0$ centim. to the left. On the drum of the chronograph a millimetre scale was placed and the deflection read. Distance, intensity of the acetylene, &c., &c., the same as on the previous day. The deflections obtained were 105 millims., $104{\cdot}5$ millims., 106 millims. = average $105{\cdot}2$ millims. = $111{\cdot}7 \times 10^{-9}$ ampère = $109{\cdot}1 \times 10^{-6}$ volt, the deduction periods having been allowed to become complete. From this it follows:—

$$
\begin{array}{lrl}
\text{N13 } (c''): & E = c \times w = (834{\cdot}4 + 142{\cdot}9)\ 105 = 102{\cdot}6 \times 10^{3} = & \mathbf{109} \times 10^{-6} \text{ volt.} \\
& = (834{\cdot}4 + 142{\cdot}9)\ 104{\cdot}5 = 102{\cdot}1 \times 10^{3} = & \mathbf{108{\cdot}4} \times 10^{-6} \text{ volt.} \\
& = (834{\cdot}4 + 142{\cdot}9)\ 106 = 103{\cdot}6 \times 10^{3} = & \mathbf{110} \times 10^{-6} \text{ volt.} \\
\hline
& \text{Average} = & \mathbf{109} \times 10^{-6} \text{ volt.}
\end{array}
$$

All the above results show that *the E.M.F. of galvanic combinations reversible in respect of the anion is independent of the concentration of the solution.* No correction for the thermo E.M.F.'s was considered necessary to employ, in view of experimental errors here.

IV. *The Effect of Previous Illumination upon the Increase of Sensitiveness of the System in the Dark.*

On July 28 we exposed the Ag-BrAg plate 3 times to the light of the acetylene at the great distance of 116 centims. Remaining then about 16 hours in the dark, the sensitiveness of the plates increased from 61 to 69·2 millims., *i.e.*, by about 0·5 millim. (0·7 per cent.) per hour. It was then exposed 9 times on the 29th (Plate a) to very weak acetylene light at 116 centims. distance. After this it increased in about 4 hours by about 3 millims., *i.e.*, 0·7 millim. (0·9 per cent.) per hour. Then we exposed the plates 7 times on the same day (Plate b) to acetylene, and 8 times to the more powerful arc; during the next 16 hours in the dark the sensitiveness also increased more rapidly, namely, from 83 to 114 millims., *i.e.*, by about 1·5 per cent. per hour (July 30).

The system was then exposed to light 6 times. After the system remained further 22 hours in the dark we found on further exposure to acetylene (on July 31) only a small increase, if any; the maximum of this increase could be from about 113·8 to $\frac{123 \times 885}{878} = 124$ millims., *i.e.*, 10·2 millims. (or 0·47 per cent.) per hour (compare a with a'). The system was then exposed to acetylene 6 times, again at a distance of 116 centims., and left in the dark about 18 hours, till August 1. On exposure to light only a very small increase, if any, was found; the maximum increase was from 96 to 105, *i.e.*, 0·5 millim. (or 0·5 per cent.) per hour (compare c' and c''). If we assume that the E.M.F. is independent of the concentration, (c'') will mean $\frac{105 \times 977{\cdot}3}{877{\cdot}7} = 117$ millims. for the same total resistance in the circuit of 877·7 ohms, *i.e.*, there is a decrease from 124 to 117 millims., *i.e.*, a decrease of 0·4 millim., or 0·4 per cent., per hour. I conclude from this, as well as from numerous other observations to be dealt with later on, that the influence of previous illumination upon the subsequent increase of sensitiveness in the dark is the greatest at the beginning, and is gradually diminishing to small values, when the sensitiveness of the system seems to become constant. It is possible even that after this a decrease in the sensitiveness to light takes place.

The increase of sensitiveness of Ag salts, till they reach a constant maximum, when kept in the dark, after previous illumination, must not be mixed up with the ordinary effect of light upon Ag salts, in darkening them. The last naturally increases to some extent their capacity of absorption of light. The numerous photographic curves obtained on repetition of the same experiment after short time intervals prove, however, conclusively that when, as in our case, a weak source of light is judiciously employed, the variation in the AgBr salts due to this effect is so small that the same deflections are always obtained. But when after the same illumination the two measurements are separated not by short intervals only, but by many hours, a great increase of the E.M.F. obtained is first observed. Similar results were obtained with other systems, also with black Cu-CuO plates in a solution of NaOH, *i.e.*, where no darkening of the electrodes could come into consideration. On the other hand, no such increase of sensitiveness was found with the Ag-AgBr plate of the system which was kept the whole time in the dark. It follows from this that we meet here with a peculiar phenomenon which we may call "*continuous light sensibilisation in the dark.*" The light previously absorbed continues to produce some variation in the plate in the dark: it either continues first to form Ag_2Br, Cu_2O (Ag_2Br gives, according to BECQUEREL, a greater E.M.F. than AgBr), and then continues to form Ag from Ag_2O, Cu from Cu_2O (which give smaller E.M.F.'s), or it produces some other physical variations in the crystals of AgBr or CuO (it is known, *e.g.*, that the process of "ripening" of emulsions in the dark is accompanied by an increase of size of the crystals of BrAg).

We must give our attention to curves N9 and N10, obtained on July 31, with normal NaBr solution: here, on the top (at *b*), we notice for the first time the formation of a very small *polarisation*, though its presence is not yet to be seen at the end of C, when the deduction period begins. This suggests that, as in the case of Ag-ClAg in NaCl solution, under the repeated exposure to light the transformation of AgBr or Ag_2Br into Ag has gone far enough towards the formation of the system (Ag plate in light, NaBr solution, Ag-BrAg plate in the dark) which is in light an inconstant cell.

V. *Influence of Temperature upon the E.M.F. obtained in Cells Reversible in Respect of the Anion (Table V.).*

Some modifications had to be made in the method. It was found impossible to determine the influence of temperature upon the E.M.F. obtained with the above plates up to 40° or 50° C., as before, since the paraffin and the shellac split off from the plates. I covered for this reason the plates on all sides with a (thick) coating of AgBr.

In all the experiments the whole of the front surface of the front plate was always exposed to light, while its back and the two surfaces of the back plate remained always in the dark.

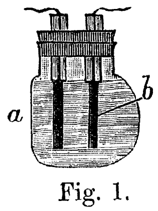


Fig. 1.

Since the quartz vessel, for which Crookes' cement has to be used, could not be well employed for higher temperatures, vessel fig. 1 was used instead. (*a*) represents a very thin and very clear round flat side, about 5 centims. diameter, flattened down with the flame in the thin bulb. The front Ag-BrAg plate was about 5 millims. from the flat side.

The use of ice or hot water and stirrer enabled us to cool or heat up the bath quickly, and the 70 litres water of the same enabled us to keep the temperature constant for longer periods. Experimental data, see Table V.

(α) *The System* Ag-BrAg *Plates in* 0·1 *normal* KBr *Solution* (*8th, 9th, and 13th July,* 1904).

July 8.—The deflections (200 ohms shunt of galvanometer) were :

In N1 = 75·4 millims., in N2 = 75·4 millims. at 38°·1 C. (at 3 P.M.).
In N3 = 81·7 millims., in N4 = 81·7 millims. at 20°·8 C. (at 5 P.M.).

July 9.—The E.M.F.'s in the dark = 6 millims. to the right (no shunt) in N1 and N2, = 5 millims. to the right (no shunt) in N3 and N4. The deflections obtained (200 ohms shunt of galvanometer) were :

In N1 = 107 millims., in N2 = 108 millims. at 2°·8 C. (at 12.30 P.M.).
In N3 = 102 millims., in N4 = 101 millims. at 27°·1 C. (at 1.30 P.M.).

July 13.—The E.M.F.'s in the dark (200 ohms shunt) = 5·5 centims. to the right in N1 and N2, = 1·7 centims. to the right in N3 and N4, = 1·5 centims. to the right in N5 and N6. The deflections obtained (200 ohms shunt of galvanometer) were :

In N1 = 133 millims., in N2 = 133 millims. at 48°·5 C.
In N3 = 136 millims., in N4 = 133 millims. at 33°·5 C. (at 12.30 P.M.).
In N5 = 140 millims., in N6 = 136 millims. at 2°·3 C. (at 3.40 P.M.).

If the results are taken for the intensity of light of the previous experiments = 48·3 to 48·5 millims., 6 per cent. must be added, and we get :

In N1 = 141 millims., in N2 = 141 millims. at 48° C.
In N3 = 144 millims., in N4 = 141 millims. at 33°·5 C.
In N5 = 148 millims., in N6 = 144 millims. at 2°·3 C.

The results obtained with the decinormal KBr solution thus are the following :—

(1) On the 8th, 9th and 13th of July the three series of results differ from one another, the E.M.F. of the combination (with freshly covered plates) becoming again greater when it was left in the dark for longer periods after illumination.

(2) In each series the deflections obtained, differ only by a few millimetres, *i.e., the variation of the E.M.F. created by light with temperature can only be small*

(β) *The System* Ag-BrAg *Plates in* 0·1 *normal* LiBr *Solution* (*July* 20, 1904).

The Ag-BrAg plates used here were those used above, but subjected between the 15th and 19th of July to the action of the solutions of HBr (to be dealt with later on). On the 20th the influence of temperature upon the same Ag-BrAg plates in a decinormal LiBr solution was investigated. Experimental data, see Table V. The E.M.F. in the dark was in N1 and N2 = 1·9 centims. to the right (200 ohms shunt), in N3, N4, N5 = 3 millims. to the left (200 ohms shunt). The deflections obtained (200 ohms shunt of galvanometer) were:

In N1 = 126 millims., in N2 = 119+6 = 125 millims. at **23**° C. (at 1.15 to 1.40 P.M.).

In N3 = 117·5 millims., in N4 = 108+17 = 125 millims., in N5 = 107+17 = 125 millims. at **3**° C. (at 5 P.M.).

These results show again that the variation of the E.M.F. with temperature can only be small.

(γ) *The System* Ag-BrAg *Plates in* 0·1 *normal* NaBr *Solution* (*Plate N*19), *Table V.*

Seven months later, on February 15, 1905, again an experiment was instituted with 0·1 normal NaBr solution, but for a smaller temperature interval, so that one side of each plate could again be covered with shellac and paraffin. The Ag-BrAg plates were not the same as before. The maximum deflections obtained (no shunt used with the galvanometer):

In N1: 85 millims. at **1**° C.; in N2: 87·5 millims. at **21°·5** C.

The results therefore similar to those obtained before with KBr and LiBr solutions.

VI. *On the E.M.F.'s obtained with the same* Ag-BrAg *plates in different Bromides. Influence of the Cation in Cells Reversible in respect of the Anion* (*Table VI.*).

The Ag-BrAg plates covered on all sides with BrAg are those used from July 8, 1904, till July 13 with a decinormal KBr solution, from July 15 till July 19 with solutions of HBr, and on the 20th with the LiBr solutions. In these experiments the same plate was always exposed to light, but now I turned the plates, so that the plate which previously always was in the dark was now exposed to light, while the plate which was always exposed to light was now kept in the dark.

(α) *Experiments of July* 25, 1904:—

(*a*) The decinormal **LiBr** solution from July 20 was now used. The E.M.F. in the dark = 3 millims. (200 ohms shunt) to the right. Intensity of acetylene = 46·5 millims. Calibration of Nalder N2 = 16·0 centims., of Nalder N1 = 16·0 centims.

The deflections obtained (with 1000 ohms shunt of galvanometer) were: In N1 = 116 millims. (deduction not complete 2 millims.), in N2 = 117 millims. (deduction complete), average = 116·5 (at 12°·5 C. and 1.15 P.M.).

(*b*) A decinormal **KBr** solution was now used; intensity of acetylene, calibration of Nalder N2 and N1 the same as in (*a*). The E.M.F. in the dark = 1·5 centims. to the left (1000 ohms shunt). The deflections obtained (with 1000 ohms shunt of galvanometer) were: in N3 = 120 millims., in N4 = 117, average = 118·5 millims. (at 13°·5 C. and at 3.0 P.M.).

(*c*) A decinormal **NaBr** solution was now used: intensity of acetylene = 47 millims., calibration of Nalder N2 and N1 the same as before; the E.M.F. in the dark = 4·7 centims. to the left (1000 ohms shunt of galvanometer). The deflections obtained (1000 ohms shunt of galvanometer) were: in N5 = 136 millims., in N6 = 112 millims., in N7 = 114 millims., in N8 = 114 millims. = average 119 millims (at 13°·5).

It follows from the above (1) that *the E.M.F. of a combination reversible in respect of the anion is independent of the cation of the salt in solution*; (2) comparing the results obtained with the decinormal LiBr solution on July 25 and 20, we find that the Ag-AgBr plate kept the whole time in the dark is less sensitive to light than the plate which had been previously exposed several times to light; (3) we find that the deflections of July 19 and 20 are essentially smaller than those of July 13 instead of being of the same values or even of greater. The reason of this is probably that the Ag-BrAg plates were previously acted upon from the 15th till the 19th of July by BrH *which gradually transformed the* Ag (*or* Ag_2Br) *on the surface previously formed back into* AgBr.

(β) The influence of the cation upon the E.M.F. obtained was again investigated between the 1*st and* 7*th of February*, 1905. Each of the plates was on one side covered again with shellac and paraffin. The plates had a thick coating of BrAg. On February 3 the sensitiveness of the plates reached already such a value that the E.M.F. seemed to change no more on further remaining in the dark, after previous illumination.

February 3, 1905, *Plate* 16:—

0·1 norm. **KBr** sol. gave: in N1, 96·5 millims.; in N2, 96·5 millims. deflection;
0·1 norm. **NaBr** sol. gave: in N3, 85 millims.; in N4, 86 millims. deflection.

Intensity of acetylene = 20·05 right and left, Nalder N2 = 15·75 centims., Nalder N1 = 19·2 centims.

February 6, 1905, *Plate* 17:—

0·1 norm. **NaBr** sol. gave: in N1, 84 millims.; in N2, 77 millims.; in N3, 78 millims. deflection;
0·1 norm. **LiBr** sol. gave: in N4, 91 millims.; in N5, 95 millims.; in N6, 91 millims. deflection.

Intensity of acetylene = 21·5, Nalder N2 = 16·05 centims., Nalder N1 = 19·2 centims.

February 7, 1905, *Plate* 18 :—

0·1 norm. **LiBr** sol. gave : in N1, 92 millims. deflection ;
0·1 norm. **NH_4Br** sol. gave : in N2, 98 millims. ; in N3, 98 millims. deflection.

Intensity of acetylene = 21·5, Nalder N2 = 16·05 centims., Nalder N1 = 21·2 centims. As the distance of the light from the systems was 116 centims., the thermo E.M.F.'s under my conditions of experiment could be neglected.

The results obtained with KBr, NaBr, LiBr, NH_4Br, confirm the results previously found that the E.M.F. created by light is independent of the cation.

VII. *The Effect of Covering the* Ag *Plates with Different Coatings of* AgBr *on the E.M.F. obtained.*

In the course of this research the same Ag plates had many times to be polished again, and covered afresh with AgBr. Surveying the E.M.F.'s obtained with freshly coated Ag-BrAg plates (when one of the two sides of each plate was covered with shellac and paraffin) in the same solutions at different times, there can be no doubt that there is no such thing as getting the same BrAg surface again. However well polished the plate may be, the AgBr surface is a conglomerate of crystals, which, according to the conditions of preparation (such as concentration of Br_2 in BrNa, time of action, temperature, &c.), are of a greater or smaller size, *i.e.*, in the same surface of the Ag plate different surfaces of the AgBr are exposed to light. We may call it "*physical variation of sensitiveness*" of the plates, similar to the phenomena observed with BrAg emulsions in the process of ripening.

VIII. Ag-IAg *Plates in* 0·1 *normal* KI *Solution* (*without solid* IK *on the Bottom of Quartz Vessel*) (*Plate* N20 *of February* 19, 1903), *Table VIII.*

In Table VIII. the investigation of the above system is given carried out with the arc between the 11th and 23rd of February, 1904. The direction of the current in the solution is always from the plate in the dark to the plate in light. The IAg plates were prepared in the dark through immersion of Ag plates (polished, as described before, and covered on one side with the shellac and paraffin) into a solution of iodine in potassium iodide. We find, as in case of Ag-BrAg plates, that the E.M.F. created by light of the same intensity first gradually increases (15th to 19th February), after previous illuminations it then reaches an apparent constant value, or even begins to decrease (18th to 23rd February). For the law of intensity we get (February 17, *with the blue screen*) less good results than with the weak acetylene light: $125^2 \times 45 = \mathbf{70{\cdot}3} \times 10^4$ and $92^2 \times 78 = \mathbf{66} \times 10^4$. The ratio of the deflections of the total light passing no screen to the total light passing the blue screen, the red screen, the yellow-green screen was found on February 15 to be 85·5, 35·4, 0, 0·5 or 100, 41·4, 0, 0·55 ; on February 17 : 117·6, 45, 0, 0·5 or 100, 38·5, 0, 0·045. The E.M.F. created by the total light passing the red screen cannot be measured, and that created by the total light passing the yellow-green screen is also very small, so as not to admit accurate measurement. It follows from this that the above E.M.F.'s given by the total light or the blue screen can be taken as created by light at a constant temperature. Plate of February 19 shows that the system represents a constant reversible cell. The reactions going on in the system are the same as those already discussed in § 5.

IX. *Plate* 15, *Table VII. The Transformation of Constant Reversible Cells into Inconstant Showing Polarisation, and vice versâ.*

The Ag-BrAg plates, which in different solutions of bromide were exposed to light during July, 1904 (see Table V.), began at last to show a very small polarisation. The Ag-BrAg plates were then kept in the dark in a 0·01 normal KBr solution. On November 18, 1904, a small polarisation was already very evident from the course of both the induction and deduction periods (see Plate N15, experimental data in Table VII.).

We remember that similar was the result with Ag-BrAg plates in a 0·1 normal NaBr solution on July 31, 1903 (see curve N9, especially N10 of plate N14), and with Ag-ClAg plates in NaCl solutions on July 1, 1903 (Table II.) after the plates were exposed for sufficient time to light. The differences (the total E.M.F.—E.M.F. of polarisation) were found here at 76 centims. distance: 73, 60 (corr. 71, the Swan a little shaky), 61 (corr. 72), 60 (corr. 75 millims.), *i.e.*, whether corrected or not, the E.M.F. of polarisation seems to be here for a given intensity (and composition) of light always of the same, or nearly the same value, as the principal E.M.F. is.

This transformation of the constant cells, after sufficient exposure to light, into inconstant, follows as a necessity from the kind of reactions going on in these systems and discussed in § 5. Since the current passes in these systems from the plate in the dark to the plate in light, the upper BrAg, ClAg layer of the exposed plate transforms into Ag, and the systems (Ag plate in light, BrNa solution, Ag-BrAg plate in the dark), &c., must be formed. A consideration of the reactions going on in such systems under the action of light, when the Ag plate is exposed to light, and direct experiments instituted with the system (Ag plate in light, BrNa solution, Ag-BrAg plate in the dark), showed that such combinations form inconstant cells, showing polarisation, thus confirming the kind of reactions going on in the system reversible in respect of the anion.

Moreover, a further consideration shows that we must be able to transform back the formed inconstant cell into the former constant cell, if we transform the formed under light Ag surface back into AgBr. This now is actually the case: by immersing the affected Ag-BrAg plate in a solution of Br_2 in water, &c., on several occasions I got back constant cells showing no polarisation.

X. *The Rôle of the Electrode. The System* Ag *Plates as Electrodes in Light and in the Dark,* BrAg *Solid at the Bottom of Cell and* 0·1 *normal* BrNa *Solution in Light and Dark. Polarisation* (*Plate N*24, *of July* 16, 1903. *Table IX.*).

The chemical composition of this system is the same as that of the systems previously dealt with (Ag-BrAg plates in BrNa solution) which is reversibly constant in respect of the anion; but the difference in reality proved to be very great. We find (see Plate N24 of July 16, 1903) that such a system behaves as the inconstant cell (Ag plates in BrNa solution), as is to be seen from the course of the induction and deduction periods, *i.e.*, the presence of the solid BrAg at the bottom of the vessel, without an intimate connection with the Ag plates so as to make it to an electrode does not make it to a constant cell (as if the solid AgBr were an extraneous substance). This puts into special light the rôle of the electrode under the action of light. Under the action of light the solution pressure of the electrode becomes, under given electrostatic conditions, greater, and it is the nature of this that determines the kind and nature of the galvanic cell created and the kind of reactions which can go on in it under the action of light. In one case (Ag-BrAg electrodes) $\overset{-}{\mathrm{Br}}$ ions are passing from the electrode into the solution, in the other case the Ag plate could either send $\overset{+}{\mathrm{Ag}}$ ions into the solution if it contains an Ag salt, forming a constant cell, or in the absence of an Ag salt in solution form, as in our case, an inconstant cell showing polarisation. As to the effect of light upon the chemical potential of the solid BrAg at the bottom of the cell, the same increases under the action of light, the solubility of AgBr may increase in light, though not to a measurable extent, more BrAg molecules may be sent into the solution, but this will be an ordinary and not an electrolytic solution, when $\overset{-}{\mathrm{Br}}$ anions are passing into the solution.

Table IX., giving the experimental data for the above system, and Plate N24 show that the maximum deflection, or the maximum E.M.F.'s produced by light, does not remain constant, but first drops again owing to the further increase of the E.M.F. of polarisation under light. This goes on till a constant value of the E.M.F.'s is obtained, indicated by the lines (*d*) and giving the difference between the E.M.F. which light would have created, if there were no polarisation, and the E.M.F. of polarisation. As both E.M.F.'s are created simultaneously, the absolute values of both E.M.F.'s remain unknown.

For the constant deflections obtained with the light of the arc passing the *blue* screen, we get from N3 and 4: $80^2 \times 25{\cdot}5 = \mathbf{163} \times 10^3$; $42^2 \times 72 = \mathbf{127} \times 10^3$. The value of the E.M.F. of polarisation thus seems to be in comparison with the principal E.M.F. small, since the law of intensity is still only partially obscured. Further we find that the arc (blue screen) gives much greater deflections than (total) acetylene (N4 : N11 or N12 = 72 millims. : 7·5 millims.), that the deflections got with the red and yellow-green screen are very small so as not to admit accurate measurement. It follows from this that in N1, 2, 3 and 4 the thermo E.M.F.'s are very small, so that E.M.F. is created by the total light or blue screen almost exclusively at a constant temperature. (The direction of the current will be discussed when inconstant cells will be dealt with.)

Similar were the results obtained with the system Ag plate in light, Ag-BrAg plate in the dark and BrNa solution. The matter at once becomes different where an intimate contact is established between the two parts which are to form the electrode, *e.g.*, when an insoluble mercury salt is in contact with liquid mercury, as we shall see later on.

XI. *The Systems* (Hg, *Solid* Hg_2Cl_2 *in* 0·1 *normal* NaCl *and* 0·1 *normal* KCl *Solution*), (Hg, *Solid* Hg_2Br_2 *in* 0·1 *normal* KBr *and* 0·1 *normal* NaBr *Solution*). *Plates N*22 *and N*22′, *Table X.*

The E.M.F. of the systems reversible in respect of the cation or anion is composed of the electrical potentials of the electrodes to the liquid in light and in the dark and of the electrical potential of the liquid in light to the liquid in the dark. The system Hg-Hg_2Cl_2 in 0·1 normal ClNa solution in light and in dark was investigated on July 25 and 26, 1904, and the system Hg-Hg_2Cl_2 in 0·1 normal KCl on July 27, 1904, both with acetylene at a distance = 88 centims. from quartz vessel (the light of Hg in the quartz vessel was about 2 centims.). No deflection could be established, at any rate it did not reach a millimetre. Plate N22 gives the photographic curve for ClNa. The system Hg-Hg_2Br_2 in 0·1 normal BrK and 0·1 normal BrNa was investigated with the arc at the distances of 118 and 47 centims. from the quartz vessel. No deflection was obtained (Plate N22′). This proves at the same time that not only does the electrical potential of Hg-Hg_2Cl_2 or Hg-Hg_2Br_2 to the solutions change in light exceedingly little, but *the electrical potential between the* ClNa *or* ClK *solution, or* BrK *or* BrNa *solution in the light and in the dark can only be exceedingly small, if at all measurable.*

Thus the proof is given that in the systems dealt with before, which are reversible in respect of the anion or cation, the variation of the osmotic pressure of the solution in light and resulting from its electrical potential between the solution in light and in the dark can be only very small, and that the last, in comparison with the electrical potentials of the plates to the solution in light and in the dark, is a negligible quantity.

XII. *What is to be understood under the "Electrode Reversible in respect of the Anion."*

In the consideration of the reactions going on in systems reversible in respect of the anion, we assume (with NERNST) that both Ag and ClAg or BrAg of the electrodes take part in the reversible reaction, the result of which is that the anion $\bar{Cl}$, $\bar{Br}$, &c., &c., either passes from the electrode into the solution or separates on the same, "as if" we had an electrode of "Cl," "Br," &c., behaving in a ClNa, BrNa solution as Zn or Cu in a $ZnSO_4$, $CuSO_4$ solution. This "as if" must be only taken as a useful illustration first introduced by NERNST for classification purposes. The electrode is a compound Ag-ClAg, Ag-BrAg and not a "Cl" or "Br" electrode, because otherwise the electrodes of all other combinations reversible in respect of the same anion ought to lead to the same values of the E.M.F. This however is not the case, as we see it from a comparison of the E.M.F.'s obtained with Ag-BrAg and Hg-Hg_2Br_2 in BrNa or BrK solution, obtained with Ag-ClAg and with Hg-Hg_2Cl_2 in the same ClNa solution. Thus we have in one case the compound Ag-ClAg electrode, in the other the compound Hg-Hg_2Cl_2 electrode, which are different, have a different solution pressure, a different electrical potential with the same solution, a different heat of reaction, though the *kind* of reaction going on in the system under the action of the current (transportation of $\bar{Cl}$, $\bar{Br}$ ions from one electrode to the other) is the same, and under the action of light the variation of the solution pressure and of the electrical potential of the different compound electrodes reversible in respect of the same anion to the same solution are different.

XIII. *The System* Hg, *Solid* Hg_2I_2 *in* IK *Solution* (*Table X.*). *The System* Hg, *Solid* SO_4Hg_2 *in Solutions of* SO_4Na_2, SO_4K_2, $SO_4(NH_4)_2$ (*Plate N23, Table XI.*).

The first system could not be investigated, since Hg_2I_2 is decomposed by IK solution already in the dark; the second system could, since the Hg_2SO_4 is not decomposed by sulphates in the dark. The Hg_2SO_4 being very much more affected by light than Hg_2Cl_2, Hg_2Br_2, it was of special interest. In all investigations of the mercury cells the method was the same. The quartz vessel was divided into two compartments by fixing tightly into it an ebonite wall, 1 millim. thick, 2·7 centims. wide, circa 2 centims. high, with Crookes cement and then asphaltum, each compartment serving as an electrode. Mercury was first brought into the two compartments, then the solid SO_4Hg_2 (or Cl_2Hg_2, Br_2-Hg_2) over both mercury surfaces several millims. high, and then the solution on the top a few millims. over the ebonite partition. The mercury, solid salt and solution were mixed at the quartz windows of the vessel and SO_4Hg_2 entangled between the Hg and the quartz windows, so as to get vertical SO_4Hg_2 electrodes (besides SO_4Hg_2 being on the top). Two glass capillary tubes, sealed up at one end with long pieces of platinum wire leading from the closed ends and fixed in the ebonite top piece, were filled with mercury and the ebonite piece cautiously fixed in the quartz vessel. The heating of the HgPt junctions by light was thus as far as was practicable avoided.

It was soon found that the E.M.F. considerably changes with the quantity of mercury. The greater the amount of mercury (the vertical surface of SO_4Hg_2) the smaller the deflection—this is evidently due to the fact that the E.M.F. obtained is principally a thermo E.M.F. The E.M.F. obtained depends upon how the solid

SO_4Hg_2 was mixed up with the mercury. For this reason no comparative experiments with different systems can be made.

In all cases however we get constant cells, showing no polarisation, and the current always passed from the electrode in the dark to the electrode in light, as in all cells reversible in respect of the anion. Plate N23 gives an illustration of this for the system Hg, solid SO_4Hg_2 in 0·1 normal $SO_4(NH_4)_2$.

XIV. *On the Conditions under which a Constant Reversible Galvanic Cell can be realised under the Action of Light.*

It was explained before that according to the composition of the system and the reactions going on in the same, under the action of the current created by light, we get constant cells reversible in respect of the cation or the anion, or inconstant cells. We must however realise the following: the composition of the system and the reactions going on in the same under the action of the current give here, as in ordinary galvanic cells, the conditions of constancy and reversibility *only in general*, but in no galvanic combination we know of does the principal reversible reaction, upon which the constancy of the cell depends, take place alone to the entire exclusion of all other phenomena and reactions simultaneously taking place in the galvanic cell. A constant reversible galvanic cell is in all cases only "practically" reversibly constant. To start with, there are no two electrodes (even when highly polished) made of the same metal, which do not give an E.M.F. in the dark when connected to a circuit. Therefore no two galvanic cells of the same combinations can give the same E.M.F. In the next instance, it is well known that, to keep the E.M.F. of a constant reversible for any length of time practically constant, only small currents must be used. The reason of this is that, besides the principal reaction under the action of the current, subsidiary reactions take place which become more prominent the greater the current density; these reactions also lead to the formation of gas batteries, or attack the electrodes, &c. In the third instance, there are very few metals which can be got chemically pure (absolutely pure perhaps none), and this leads to local currents, local E.M.F., &c. In the fourth instance, there is a variation of concentration at the electrodes. In ordinary constant reversible galvanic cells the principal E.M.F.'s of the principal reversible reaction, due to the composition of the system, happen to be, in comparison with the interfering E.M.F.'s, very great, since the difference in the electrical potentials of the electrodes, consisting of two entirely different metals or combinations, to the solution are great—hence ordinary constant cells can practically be easily realised. When, however, we pass to galvanic cells created by light, where the E.M.F.'s created by light, in connection with the composition of the same, are very small, it is evident that the difficulties for a practical realisation of constant cells must become enormous.

The above fixes the problem and also shows the limit of possible success in this region. Only where the solution pressure of the plate increases in light essentially, so that a comparatively great E.M.F. is created, can we realise, under proper conditions, constant reversible cells, *e.g.*, in case of Ag-ClAg, Ag-BrAg in ClNa, BrNa solution, or Cu-CuO in NaOH solution. As, however, the E.M.F. created by light is always very small, special care will always have to be taken for a corresponding reduction of the other interfering E.M.F.'s, to an extent not known for ordinary galvanic cells: (1) the E.M.F. in the dark must first be reduced by special polishing of the plates, by mechanical means and with the current, to a few hundred thousandths of a volt. On such plates usually, but not always, also very little gas separates while the current is passing between the plates under the action of light. Only very few metals allow such a polishing. The rougher the grain of the metal or the thicker the deposited compound is, the more difficult is the realisation of the same. (2) Only chemically pure metals or compounds should be used as electrodes. This can be realised in case of Ag, Pt, Au, Hg, Ag-ClAg, AgBrAg, Ag-I-Ag, Hg with insoluble Hg salts, and perhaps in one or two more cases, but it is a matter of quite extraordinary difficulty in case of other metals. (3) The currents used should be made, as corresponds to this region, very small by inserting, when possible, resistances into the circuit, and using a very sensitive galvanometer.

In addition to the above conditions, which are common for all galvanic cells, a series of further conditions and possibilities is never to be lost sight of, which are important for this region only, such as the formation of thermo E.M.F.'s in the circuit, the variation of the sensitiveness of the plates to light in the dark, the effect of previous illumination, the character of the induction and deduction periods, the transformation of one system into another, &c., &c., which can be mastered only after a detailed and careful study of each system separately is made.

XV. *On the E.M.F.'s of Constant Reversible Cells and the Intensity of Light.*

Becquerel found with Ag-Ag_2Cl plates in a solution of 2 grammes of SO_4H_2 in 100 grammes water ('La Lumière,' vol. II., p. 145), that the E.M.F. is not directly proportional to the intensity of light, since the product I.H. is not constant. The result obtained by **Minchin** with his sensitised cell, consisting of Sn plates covered (evidently) with SnO_2 in methyl-alcohol, is different. The E.M.F. was "with fair accuracy found to be inversely proportional to the distance" of the candle from the cell, *i.e.*, the intensity is directly proportional to the square root of the intensity of light.

Contrary to these observations, I found that with constant reversible cells (*i.e.*, cells the E.M.F. of which gives the true measure of the maximum work performed under the action of light) the E.M.F. is directly proportional to the intensity of light. The reasons of this discrepancy are:

(1) The system Ag-Ag_2Cl in a solution of SO_4H_2 and the system Sn-SnO_2 in

alcohol are inconstant cells, showing polarisation, *i.e.*, the E.M.F. does not give the maximum work performed under the action of light.

(2) If only strips of the front plate are illuminated (BECQUEREL), local action takes place between the illuminated and non-illuminated parts of the front plate.

(3) In their publications no data are given to show how far the E.M.F.'s in the dark were brought in their experiments not only to constant, but also to sufficiently small values; the thermo E.M.F.'s in the cell, &c., do not seem to have been sufficiently guarded against. They did not possess a constant source of light, nor measure and check the intensity of their source of light, or take into account the induction and deduction periods. We have no evidence as to how far they reached the constant maximum deflections in each case—this is not always easily obtainable—nor how far the E.M.F. in the dark was influenced during their experiments by previous exposure of the system to light, &c., &c.

§ 8. *Experimental Proof of the Physico-Mathematical Theory of "Constant Reversible Cells Created by Light" (given by the Author in 'Roy. Soc. Proc.,' November,* 1904).

In the above paper the same was dealt with by the author in detail. The general equation found was

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860\, T \left(\log_e \frac{Pl}{Pd} - \frac{2v}{u+v} \log_e \frac{pl}{pd}\right) \cdot 10^{-4} \text{ volt}$$

for systems reversible in respect of the cation, and

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860\, T \left(-\log_e \frac{Pl}{Pd} + \frac{2u}{u+v} \log_e \frac{pl}{pd}\right) \cdot 10^{-4} \text{ volt}$$

for systems reversible in respect of the anion.

The present research confirms the conclusions drawn there from the above equations:—

(1) Table IV., Plates 30 of July 31, 1903, August 1, 1903, prove for the cells reversible in respect of the anion; experiments of June 19, 1903, § 6, Plates 7, 8, 9, Table I., prove the cells reversible in respect of the cation, that E.M.F. is independent of concentration.

(2) Experiments, § 7, XI., Table X., Plates N22 and N22′, of the 25th to the 27th of July, 1904, and of February 27, 1905, as well as § 7, XI., Table X., show that both the value

$$0{\cdot}860T \frac{2v}{u+v} \log_e \frac{pl}{pd} \cdot 10^{-4} \text{ volt, or } 0{\cdot}860T \frac{2u}{u+v} \log_e \frac{pl}{pd} \cdot 10^{-4} \text{ volt,}$$

and the electrical potential between the illuminated and non-illuminated parts of the solution can be neglected, so that instead of (I) we can use

$$\Sigma E = 0{\cdot}860T \log_e \frac{Pl}{Pd} \cdot 10^{-4} \text{ volt, and } \Sigma E = 0{\cdot}860T \log_e \frac{Pd}{Pl} \cdot 10^{-4} \text{ volt.}$$

(3) Through this the indirect experimental proof is given that

$$n_e\epsilon_0\Sigma \mathrm{E} = \rho'' + \frac{n_e\epsilon_0\, d\Sigma \mathrm{E}}{d\mathrm{T}} \,.\, \mathrm{T},$$

i.e., a law analogous to that of GIBBS-HELMHOLTZ for ordinary cells holds good for galvanic cells created by light. The experiments (given in § 7) of the 8th till the 13th of July, 20th of July, 1904, and of the 15th of February, 1905, Plate 19, Table V., show, however, that there are enormous difficulties in this region of research to determine the value of

$$\frac{n_e\epsilon_0\, d\Sigma \mathrm{E}}{d\mathrm{T}} \,.\, \mathrm{T},$$

experimentally, the value having proved to be too small for experimental determination in view of other sources of error.

(4) The heat of reaction ρ'', or the difference of the heats of ionisation in light and in the dark can, for the same reason, be determined experimentally only approximately by putting $\rho'' = n_e\epsilon_0\Sigma \mathrm{E}$. *The heat of reactions evidently changes as the E.M.F. does, both with the intensity and composition of light*, which is quite a characteristic feature for galvanic cells created by light. The heats of reaction are always exceedingly small, as the E.M.F.'s are. Thus the heat of reaction for one electrochemical equivalent of $\overline{\mathrm{Br}}$ ions in the system (Ag-BrAg plates in 0·1 norm. NaBr solution) giving, *e.g.*, 106×10^{-6} volt = $23040 \times 106 \times 10^{-6}$ = **2·442 gram. cal.** (see § 7, p. 365). The systems, Ag plates in $\mathrm{NO_3Ag}$ solution, gave E.M.F.'s between $1{\cdot}8 \times 10^{-6}$ volt and $54{\cdot}4 \times 10^{-6}$ volts. The value of ρ'' for 1 electro-chemical equivalent of Ag ions is thus = $23040 \times (1{\cdot}8 \text{ to } 54{\cdot}4) \times 10^{-6}$ = **0·044 to 1·25 gram. cal.** (see § 6, p. 355).

(5) This research (§ 6, § 7, II. and XV.) shows that *the solution pressure of the electrodes in light* is *sui generis*, since it *changes, as well as the E.M.F., with the intensity of light and its composition.* Experiments of § 7, II. and X., show also the effect of the capacity of the plates for absorption of light, the effects of previous illuminations, of physical changes in the dark, upon E.M.F. obtained, and consequently upon the solution pressure and heat of reaction of some systems.

As to the variation of the solution pressure of an electrode on exposition to light, experiments show that it is very small: thus, in case of the system (Ag-BrAg plates in BrNa solution) giving 106×10^{-6} volt, we get

$$\log \frac{\mathrm{P}l}{\mathrm{P}d} = \frac{106 \times 10^{-2}}{0{\cdot}860\mathrm{T} \times 2{\cdot}306}\,; \text{ at } \mathrm{T} = 290^\circ \text{ (17° C.)} : \mathbf{log}\, \frac{\mathrm{P}l}{\mathrm{P}d} = \mathbf{0{\cdot}001846} \text{ and } \mathbf{Pl\ 1{\cdot}0043Pd},$$

i.e., an increase of the solution pressure by 0·43 per cent. For Ag plates in $\mathrm{NO_3Ag}$ solutions, giving (for different intensities) E.M.F.'s from $1{\cdot}8 \times 10^{-6}$ volt to $54{\cdot}4 \times 10^{-6}$ volt, we get for

$$\mathrm{T} = 290^\circ \text{ C.} : \mathbf{log\ Pl/Pd} = \mathbf{0{\cdot}000031 \text{ to } 0{\cdot}00095}, \quad \mathbf{Pl} = \mathbf{1{\cdot}00072 \text{ to } 1{\cdot}0022Pd},$$

an increase by 0·0072 per cent. to 0·22 per cent. If the solution pressure of an electrode in the dark is known, the solution pressure in light, under any given condition, is also known. Putting Pd for Ag = 10^{-15} atmosphere, the solution pressure of Ag plates becomes in light in the investigated systems

$$\mathrm{P}l = (1\cdot00072 \text{ to } 1\cdot0022)\ 10^{-15} \text{ atmosphere.}$$

(6) § 7, I., II., VIII., XV., as well as Table I., § 6, show that in constant reversible cells the E.M.F. created by light, and with it approximately the heat of reaction, are directly proportional to the intensity of light, *i.e.*, $\Sigma\mathrm{E} = \mathrm{CI}$; $\rho'' = \mathrm{C'I}$, and since the same holds good for plates absorbing the total light (CuO in NaOH) and for plates absorbing only a part of it (Ag plates in $\mathrm{NO_3Ag}$), the same law of intensity holds good (at any rate approximately) for the absorbed, as well as for the reflected light. Experiments of July 29, 1903, Plate N13, Table III., carried out with pure red light, and § 7, VIII., with blue light, show that the same law of intensity holds good for monochromatic light as well.

§ 9. *The Results obtained for Chemical Statics and Dynamics under the Action of Light, in General.*

(*a*) *Further Experimental Proof that Velocity of Chemical Reaction in Homogeneous Systems when they are shifted to a New Point of Equilibrium by Light at a Constant Temperature, and Chemical Equilibrium of Homogeneous Systems, follow the Laws of Mass Action as in the Dark.*

The above laws which I found experimentally to regulate, after the induction period has passed, those regions of phenomena under the action of light (see 'Roy. Soc. Proc.,' January, 1902; 'Phil. Trans.,' A, 1902, vol. 199, p. 337; 'Zeitschr. für physik. Chemie,' June and December, 1902; 'Phil. Mag.,' January, 1903) now find further extensive experimental confirmation in the "galvanic cells created by light" as is evident from (*c*).

Having shown here that the chemical potential of the same plate is in light different from that in the dark, the proof is thus given that the thermodynamic deduction of the same laws of mass action (after the induction period) given in the above papers is a mathematical necessity.

Since the publication of the papers above mentioned, a series of efforts have been made by different persons to investigate velocity of reaction, or velocity of reaction and equilibrium under the action of light, but with little success (see GULDBERG, 'Zeitschr. physik. Chemie,' 41, 1902; SLATOR, 'Zeitschr. physik. Chemie,' 45, p. 540, 1903; P. BEVAN, 'Phil. Trans.,' A, 1904; LUTHER and WEIGERT, 'Sitz. K. Preuss. Akad.,' 1904, p. 828).

No reference was made in the above publications to my work. The cause of failure is not far to seek; in all the above researches the reactions used are either of a compound character (Cl_2 and H_2) or they do not admit a quantitative investigation (Anthracen and Dianthracen); the authors possessed no constant source of light and no photometer for measuring its intensity, take no account of the induction (except BEVAN) and deduction periods, nor of the very great number of sources of error one meets in this region.

(b) *Experimental Proof that Chemical Equilibrium in Heterogeneous Systems, when Shifted by Light at a Constant Temperature to a New Point, follows, after the Induction Period has passed, the same Laws as in the Dark.*

Since the E.M.F. of the reversible heterogeneous system forming the galvanic cell gives, after the induction period has passed, the maximum work performed in it under the action of light, and since the equations giving the maximum work under the action of light contain also the constant of chemical equilibrium of the heterogeneous system, as in ordinary galvanic cells, an experimental proof is thus given that chemical equilibrium in heterogeneous systems follows, under the action of light (after the induction period has passed) the same laws as in the dark. In the 'Zeitschr. physik. Chemie' (vol. 30, pp. 371–382, 1899) I showed that the laws of GULDBERG and WAAGE and others, for equilibrium of ordinary heterogeneous systems, must be conceived as the result of a combination of static equilibria between the different parts of the heterogeneous system and of dynamic equilibria in the homogeneous parts, and that it is the form of the last which determines at the same time the form of GULDBERG-WAAGE's laws. The present research, dealing with heterogeneous systems, gives us for this reason at the same time also experimental proof that equilibrium in homogeneous systems, and with it velocity of reaction, follows in light, after the induction period, the laws of mass action.

(c) *The Maximum Work (Constant of Equilibrium) and the Law of Intensity of Light.*

We have found that the E.M.F. or maximum work done under the action of light in the reversible heterogeneous systems forming the galvanic cells is, after the induction has passed, directly proportional to the intensity of light.

This must therefore hold good, after the induction period, also for the maximum work done under the action of light in homogeneous system, *i.e.*,

$$\mathrm{RT}\log_e \frac{C_1^{N_1} C_2^{N_2}}{C_3^{N_3} C_4^{N_4}} = \mathrm{RT}\log_e \frac{K_1}{K_2} = \mathrm{RT}\log_e K = CI_1 \quad . \quad . \quad . \quad . \quad (\alpha),$$

where $C_1, C_2 \ldots C_3, C_4 \ldots$ are the concentrations of the substances taking part in the opposite reactions, K_1, K_2 the velocity constants of the two opposite reactions, K the constant of equilibrium. This law giving the connection between the constant of equilibrium, absolute temperature, and the intensity of light (given first by the author in the 'Zeitschr. für physik. Chemie,' 1902, vol. 42, pp. 319, 333, 'Phil. Mag.,' 1903, (6), pp. 211, 214), is thus amply verified on several systems in this research.

(*d*) *On the Connection between the Velocity of Chemical Reaction produced by the Action of Light, the Intensity of Light and Absolute Temperature.*

From the above equation (α) it follows :—

(a) When both opposite reactions go on under the action of light only :

$$\mathrm{RT}\log_e \mathrm{K}_1 = \mathrm{C}''\mathrm{I} \text{ or } \mathrm{RT}\log_e \mathrm{K}_1 = \mathrm{C}''\mathrm{I}+(\mathrm{K}) \text{ and } \mathrm{RT}\log_e \mathrm{K}_2 = \mathrm{C}'''\mathrm{I}$$
$$\text{or } \mathrm{RT}\log_e \mathrm{K}_2 = \mathrm{C}'''\mathrm{I}+(\mathrm{K}).$$

(b) If only one of the reactions goes on under the action of light, while the other opposite one goes on also in the dark (and its velocity is not influenced essentially by light)

$$\mathrm{RT}\log_e \mathrm{K}_1 = \mathrm{C}''\mathrm{I}+\mathrm{RT}\log_e \mathrm{K}_{11}.$$

At a constant temperature

$$\log_e \mathrm{K}_1 = \mathrm{C}'^{\mathrm{V}}\mathrm{I}+\mathrm{K}_{1\mathrm{V}}.$$

The above gives the true law for the connection between the velocity constant of chemical reactions produced by light, the intensity of light and the absolute temperature (after the induction period has passed).

(e) *The Velocity of Molecular or Physical Reactions between different parts of the Heterogeneous System produced by and going on only under the Action of Light evidently follows the Law found by the Author for these Reactions in the Dark.*

The equations found experimentally by the author for the induction and deduction periods $\frac{d\pi}{d\tau} = c(\pi'_0-\pi)(\pi-\pi_0+\mathrm{K})$ and $-\frac{d\pi}{d\tau} = -c'(\pi_0-\pi)(\pi-\pi'_0+\mathrm{K}')$ (see 'Proc. Roy. Soc.,' vol. 74, 1904, p. 369) give the speed of transformation of a substance (Ag, AgBr, Cu, &c.) from its state of equilibrium with its ions in solution in the dark to its state of equilibrium with its ions in light and *vice versâ.* They correspond both in form and content to the general equation $\frac{dt}{d\tau} = c(t_0-t)(t-t_{0v}+\mathrm{K})$, or $\frac{dt}{d\tau} = c(\Sigma+\mathrm{K})(t_0-t)$, which, as I established experimentally, is giving the speed of all molecular or physical reactions between different parts of the heterogeneous system in the dark.

A full account of my investigations was given in the 'Report of the British Association,' Liverpool, 1896. Since 1896 I often made use of the above results in many of my publications (see 'Report Brit. Ass.,' Liverpool, 1906, the 'Zeitschr. physik. Chemie,' vol. 30, pp. 348–368, 1899, 'Phil. Mag.,' July, 1901, pp. 50–90). The very same equation (and for the same kind of reaction) later on NOYES and WHITNEY ('Zeitschr. physik. Chemie,' vol. 23, p. 689, 1897), and more recently NERNST and BRUNNER ('Zeitschr. physik. Chemie,' vol. 47, pp. 50–102, 1904), confirmed in their investigations of the speed of solution of salts. The equation used by NOYES and WHITNEY (using the same notation) is $\frac{dt}{d\tau} = c' (t_0 - t)$ (they are taking the velocity constant per unit surface); the equation used by NERNST and BRUNNER is $\frac{dt}{d\tau} = \frac{D}{\delta} \Sigma_t (t_0 - t)$ or $= C\Sigma_t(t_0 - t)$, where $\frac{D}{\delta}$ is also a constant as my C is. So far they only confirm the general law which was given and established by me before NOYES and WHITNEY, and long before NERNST and BRUNNER (also for solution and separation of salt, &c., &c.).

As to their attempt to explain the constant C by diffusion, it entails a number of hypotheses, which appear to me to be quite incompatible with experience. As none of their fundamental hypotheses have been, in my opinion, shown to exist by any reliable experiments, they seem to me at present only as arbitrary interpretations of qualitative results. My law has been shown to be general, it gives the velocity of *all* molecular transformations between different parts of the heterogeneous system, including those (such as melting of ice, separation of ice from overcooled water, &c.) where diffusion cannot possibly enter into consideration. It follows, therefore, that a law of such a wide scope cannot be based upon diffusion, and that no more should be read in the content of my equation than it is clearly given by its form.

(*f*) *Velocity of Chemical Reaction in Heterogeneous Systems, produced by and going on only under the Action of Light, evidently follows after the Induction Period has passed, the Laws deduced by the Author for Velocity of Chemical Reaction in Heterogeneous Systems in the Dark.*

We have thus shown, on the one hand, that the velocity of chemical reaction in homogeneous systems under the action of light follows, after the induction period, the law of mass action, as in the dark, and, on the other hand, the equations for the induction and deduction periods in galvanic cells make it highly probable that the speed of molecular or physical transformations between different parts of the heterogeneous system under the action of light must follow the same law as in the dark. It follows from this that the laws governing velocity of chemical reaction in heterogeneous systems under the action of light, must, after the induction period has passed, follow the laws which I deduced for this region in the dark. In 'Zeitschr. physik. Chemie,' 1899, vol. 30, pp. 371–382, and 'Phil. Mag.,' 1902 (6) 4, pp. 468–489, I showed that the laws for velocity of chemical reaction in heterogeneous systems follow (in the dark), as a mathematical necessity, from two well-established laws—one governing the speed of reaction in homogeneous parts of the system (the law of mass action) and the other the speed of molecular reactions (speed of solution or evaporation and of separation or condensation of solids or liquids in the system) between the different parts in the system (a law established by myself). After the work of HELMHOLTZ and PLANCK, and others who find themselves constrained to assume that every substance has a solution pressure or vapour pressure, in order to explain the phenomena of formation of electrical potential in a galvanic combination, &c., the above treatment of the subject becomes an unavoidable necessity.

Messrs. NERNST and BRUNNER therefore should not have applied a law which I established for molecular reactions between the same substance in different parts of the heterogeneous system to the velocity of chemical reaction in heterogeneous systems, which is a conglomerate of reactions. The reactions investigated by NERNST and BRUNNER are only particular instances of my laws and equations for chemical reactions in heterogeneous systems, and any conceivable values may be taken for each member of the equations without impairing in the least degree their validity. If the numerous assumptions of NERNST and BRUNNER be true, they must therefore follow as a particular case of my equations; but, as I will show at another place, both their assumptions and experiments are arbitrary.

In conclusion I wish to express my thanks to the Managers of the Royal Institution for enabling me to make use of the resources of the Davy-Faraday Laboratory, and especially to Dr. LUDWIG MOND, who by his kind assistance and interest in my work enabled me to undertake and to carry out the above research.

TABLE I.—Ag Plate in Light, $AgNO_3$ Solution in

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
2	Ag in light and in dark	0·25 normal $AgNO_3$	June 3 and 4, 1903	1·5 centims. to right	15·0	1, 2, 3, 4, 5, 6	20, 19, 17, 18, 18, 16 = average 18 corr. 20, 21, 19, 20, 20, 18 = average 19·7	13·4 13·4	847·8 847·8
	ditto	ditto	June 3 and 4, 1903	ditto	15·0	7, 8, 9, 10, 11, 12	24, 24, 26, 24, 23, 23·5 = average 24 corr. 24, 26, 26, 26, 26, 26·5 = average 25·8	13·4 13·4	847·8 847·8
	ditto	ditto	June 3 and 4, 1903	ditto	15·0	13	compound curve	13·4	847·8
	ditto	ditto	June 3 and 4, 1903	ditto	15·0	14, 15, 16	21, 21, 21 = average 21 corr. 24, 24, 24 = average 24	13·4 13·4	847·8 847·8
3	ditto	ditto	June 5, 1903	ditto	15·0	1, 2, 3, 4	36, 35, 34, 33 = average 34·5 corr. 36, 37, 37, 36 = average 36·5	13·4 13·4	847·8 847·8
	ditto	ditto	June 5, 1903	ditto	15·0	5, 6, 7, 8, 9	17, 15·7, 17, 19, 17 = average 17	13·4	847·8
4	ditto	ditto	June 6, 1903	8·5 centims. to right	84·8	1, 2	55, 54 = average 54·5	13·4	847·8
	ditto	ditto	June 6, 1903	ditto	84·8	3, 4	28, 28 = average 28	13·4	847·8
5	ditto	ditto	June 8, 1903	9·5 centims. to right	94·8	1, 2, —, 4	29, 29, —, 26 (7) = average 28·2	13·4	847·8
6	ditto	ditto	June 11, 1903	2·7 centims. to right	27·0	1	32	13·4	847·8
	ditto	ditto	June 11, 1903	ditto	27·0	2	15	13·4	847·8
	ditto	ditto	June 11, 1903	ditto	27·0	3, 3′	2·5	13·4	847·8
	ditto	ditto	June 11, 1903	ditto	27·0	4, 4′	1·75	13·4	847·8
—	ditto	0·0041 normal $AgNO_3$	June 18, 1903	17 centims. to right	27·0	1	20·5	840	1674
7	ditto	0·0041 normal $AgNO_3$	June 19, 1903 (*a*)	1·9 centims. to left	38·2	(1), 2, 3	10·5, 10 = average 10·25	840	1674
	ditto	ditto	June 19, 1903 (*a*)	ditto	38·2	4, 5	19, 18 = average 18·5	840	1674
8	ditto	0·025 normal $AgNO_3$	June 19, 1903 (*b*)	1·0 centim. to left	10·3	1, 2, 3	40·5, 34·5, 38 = average 37·3	146	980·4
	ditto	ditto	June 19, 1903 (*b*)	ditto	10·3	4, 5	23·5, 21·5 = average 22·5	146	980·4
9	ditto	0·25 normal $AgNO_3$	June 19, 1903 (*c*)	0·9 centim. to left	9·0	1, 2	40, 40 = average 40	16·5	851·9
	ditto	ditto	June 19, 1903 (*c*)	ditto	9·0	3, 4	26, 21 = average 23·5	16·5	851·9

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* The temperature *of the bath and of the room* were those of the

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
Light, $AgNO_3$ Solution in Dark, Ag in the Dark.												
21·1	18·0	17·4	19·8	37	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	2
23·1	19·6	—	—	—	—	—	—	—	—	—	—	
28·1	24·0	17·4	19·8	33	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	
30·2	25·7	—	—	—	—	—	—	—	—	—	—	
—	—	17·4	19·8	33	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	
28·1	24·0	17·4	19·8	33	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	
32·1	27·4	—	—	—	—	—	—	—	—	—	—	
40·5	34·4	17·4	19·8	26	110	121	ordinary temperature*		constant	total light	arc: 65 volts, 6 ampères	3
42·8	36·4	—	—	—	—	—	—		—	—	—	
19·0	16·9	17·4	19·8	36 (7)	110	115	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	
63·9	54·4	17·4	19·8	26	110	127	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	4
32·8	27·9	17·4	19·8	36	110	127	ordinary temperature		constant	total light	—	
33·0	28·1	17·4	19·8	36	110	135	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	5
37·5	31·9	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	6
17·6	15·0	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	blue screen	arc: 65 volts, 6 ampères	
2·9	2·4	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	yellow green screen	arc: 65 volts, 6 ampères	
2·1	1·8	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	red screen	arc: 65 volts, 6 ampères	
—	—	—	17·2	27	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	—
12·3	20·6	17·4	17·2	36 (7)	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	7
21·7	36·3	17·4	17·2	26 (7)	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	
43·6	38·4	17·4	17·2	27	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	8
26·3	23·2	17·4	17·2	37	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	
46·9	39·8	17·4	17·2	27	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	9
27·6	23·4	17·4	17·2	37	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	

ordinary temperature of the room, *i.e.*, between 17°·5 and 20° C.

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volt.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
TABLE II.—Ag-ClAg Plates in									
10	Ag-ClAg in light and in dark	0·1 normal NaCl	June 30, 1903	5·0 centims. to right	46·2	1, 2	56, 53 (corr. 55) = average 55·5	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	3, 4	31, 34 = average 32·5	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	5, 6	3·5, 3·5	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	7, 8	13, 13	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	10	5·5	44·5	878·9
	ditto	ditto	July 1, 1903	0·13 centim.	12·1	1, 2, 3, 4, 5	(53·5), 66·1, 68·3, 68·3, 70 = average 68·2	44·5	878·9
TABLE III.—Ag-BrAg Plates in									
11	Ag-BrAg in light and in dark	0·1 normal NaBr	July 28, 1903	18 centims. to left	16·7	1, 2, 3	49, 44–45, 45–46 = average 46·3	43	877·4
12	ditto	ditto	July 29, 1903	1·5 centims. to right	14·2	1, 2 3, 4, 5	84, 88, 82, 80, 81 = average 81·6	43	877·4
	ditto	ditto	July 29 1903	ditto	14·2	6, 7	43·5, 44·5 = average 44	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	8, 9	32·5, 31·0 = average 31·8	43	877·4
13	ditto	ditto	July 29, 1903	ditto	14·2	1	80	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	2, 3	28, 29, = average 28·5	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	4	60	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	5	118	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	6	48·5	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	7	41	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	8, 10, 14	76, 69, 71·5	43	Resistance of galvanometer = 834·4 ohms; shunt of galvanometer = 40 ohms
	ditto	ditto	July 29, 1903	ditto	14·2	15	120	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	9	23	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	11	5	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	12	3·5	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	13	64·5	43	ditto

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* Formation of the system Ag in the light NaCl solution, Ag-ClAg

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI, in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
0·1 Normal NaCl Solution.												
59	51·8	19·2	16·7	37	110	155	20	20	constant	total light	arc: 65 volts, 6·0 ampères	10
34·6	30·4	19·2	16·7	50	110	155	20	20	constant	total light	arc: 65 volts, 6·0 ampères	
3·7	3·3	19·2	16·7	37	110	155	20	20	constant	red screen	arc: 65 volts, 6·0 ampères	
13·8	12·1	19·2	16·7	37	110	155	20	20	constant	blue screen	arc: 65 volts, 6·0 ampères	
5·8	5·1	19·2	16·7	37	110	155	20	20	constant	yellow-green screen	arc: 65 volts, 6·0 ampères	
72·5	63·6	19·2	16·7	37	110	155	20	20	beginning of polarisation*	total light	arc: 65 volts, 6·0 ampères	
0·1 Normal NaBr Solution.												
49·2	43·4	19·2	17·0	116	110	61	ordinary temperature†		constant	total light	acetylene	11
86·7	76·1	19·1	17·05	116	110	71	ordinary temperature		constant	total light	acetylene	12
46·8	41·0	19·1	17·05	116	110	39	ordinary temperature		constant	total light	acetylene	
33·8	29·6	19·1	17·05	116	110	28·5	ordinary temperature		constant	total light	acetylene	
85·0	74·7	19·1	17·05	116	110	64·6	ordinary temperature		constant	total light	acetylene	13
30·3	26·6	19·1	17·05	116	110	64·6	ordinary temperature		constant	red screen	acetylene	
63·7	55·9	19·1	17·05	80	110	64·6	ordinary temperature		constant	red screen	acetylene	
125·3 to 126·4	110 to 111	19·1	17·05	57	110	64·6	ordinary temperature		constant	red screen	acetylene	
51·6	45·3	19·1	17·05	80	110	64·6	ordinary temperature		constant	blue screen	acetylene	
43·6	38·3	19·1	17·05	80	110	64·6	ordinary temperature		constant	yellow-green screen	acetylene	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	total light	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	89	92	64·6	ordinary temperature		constant	total light	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	blue screen	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	red screen	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	yellow-green screen	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	colourless gelatine	arc: 70 volts, 6·2 ampères	

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in the dark.

† Temperature of bath and of room, 17°·5 C. to 20° C.

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.

TABLE IV.—Ag-BrAg Plates in NaBr

14	Ag-BrAg electrode in light and in dark	from **0·1** normal to circa **0·01** normal NaBr	July 30, 1903	1·3 centims. to left	12·1	1, 2 (*a*)	114, 113·5	43·4	877·4
	ditto	ditto	July 30, 1903	6·0 centims. to left	61·8	3, 4 (*b*)	114, 116	137	971·4
	ditto	ditto	July 30, 1903	14 centims. to right	183·5	5, 6 (*c*)	80, 86	400	1234·4
	ditto	from circa **0·1** normal to circa **0·025** normal NaBr	July 31, 1903	0·3 centim. to left	2·8	(7), 8 (*a′*)	(123), 120	50	884·4
	ditto	ditto	July 31, 1903	14 centims. to left	125·0	9, 10 (*b′*)	105, 106	5	839·4
	ditto	ditto	July 31, 1903	7 centims. to right	74·2	11, 12 (*c′*)	92, 99	163·4	950·8
Scale on the drum of chronograph.	ditto	**0·025** normal NaBr	August 1, 1903	1 centim. to left in 13, 14, 6·5 centims. to left in 15	10·4 in 13, 14, 5·2 in 15	13, 14, 15	105, 104·5, 106	142·9	977·3

TABLE V.—Ag-BrAg Plates in Decinormal KBr Solution and LiBr Solution. Influence of Tempe

	Ag-BrAg plates in light and in dark	0·1 normal KBr	July 8, 1904	0·5 centim. to right (no shunt)	—	1, 2	75·4, 75·4	17·9	Resistance of galvanometer =834·4; the galvanometer is shunted with 200 ohms
	ditto	ditto	July 8, 1904	ditto	—	3, 4	81·7, 81·7	17·9	ditto
	ditto	ditto	July 9, 1904	0·6 centim. to right (no shunt)	—	1, 2	107, 108	17·9	ditto
	ditto	ditto	July 9, 1904	ditto	—	3, 4	102, 101	17·9	ditto
	ditto	ditto	July 13, 1904	5·5 centims. to right	—	1, 2	133, 133	17·9	ditto
	ditto	ditto	July 13, 1904	1·7 centims. to right	—	3, 4	136, 133	17·9	ditto
	ditto	ditto	July 13, 1904	1·5 centims. to right (200 ohms shunt)	—	5, 6	140, 136	17·9	ditto

From the 15th till the 19th of July the Ag-BrAg plates were in HBr solutions. This made the deflections gradually smaller :
temperature on these plates was again tested. A 0·1 normal

	Ag-BrAg in light and in dark	0·1 normal LiBr	July 20, 1904	1·9 centims. to right	—	1, 2	126, 125	—	ditto
	ditto	ditto	July 20, 1904	0·3 centim. to left	—	3, 4, 5	117·5, 125 corr., 125 corr.	—	ditto

On the 15th of February, 1905, the influence of temperature again tested with plates newly covered; one side of

19	Ag-BrAg	0·1 normal NaBr	February 15, 1905	18·3 centims. to left	—	1	85	17·70	852·1
	ditto	ditto	February 15, 1905	ditto	—	2	87·5	17·70	852·1

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
Solutions. Influence of Concentration.												
120	106	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	14
122	106	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
88	106	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
127·5	112·7	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
112	94	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
101·5	101·2	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
111·7	109·1	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	Scale on the drum of chronograph.
rature. (Both sides of the Ag Plates covered with AgBr; Glass Vessel instead of Quartz Vesssel.)												
—	—	17·0	16·0	89	123	48·5	**38·1**	ordinary temperature	constant	total light	acetylene	
—	—	17·0	16·0	89	123	48·5	**20·8**	ditto	constant	total light	acetylene	
—	—	17·2	16·05	89	123	48·8	**2·8**	ditto	constant	total light	acetylene	
—	—	17·2	16·05	89	123	48·8	**27·1**	ditto	constant	total light	acetylene	
—	—	17·2	16·03	89	123	45·5	**48·5**	ditto	constant	total light	acetylene	
—	—	17·2	16·03	89	123	45·5	**33·5**	ditto	constant	total light	acetylene	
—	—	17·2	16·03	89	123	45·5	**2·3**	ditto	constant	total light	acetylene	
from 140, 136 millims. to 65 millims., for reasons to be explained in another place. On the 20th July the influence of LiBr solution (with 200 ohms. shunt of galvanometer) gave :—												
—	—	16·0	16·2	89	123	46·5	**23**	ditto	constant	total light	acetylene	
—	—	16·0	16·2	89	123	46·5	**3**	ditto	constant	total light	acetylene	
each electrode was covered with shellac and paraffin. NaBr solution was taken. No shunt with galvanometer :—												
—	—	17·7	16·0	115–116	146	21·5	**1**	ordinary temperature	constant	total light	acetylene	19
—	—	17·7	16·0	115–116	146	21·5	**21·5**	ditto	constant	total light	acetylene	

<table>
<tr><th>Photographic plate number.</th><th>Electrodes.</th><th>Solution.</th><th>Date of experiment.</th><th>The E.M.F. in the dark, in centimetres on Nalder N1.</th><th>The E.M.F. in the dark, in units of 10^{-6} volts.</th><th>Number of experiment (curve) when the system was exposed to light.</th><th>Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.</th><th>Resistance of the solution in cell, in ohms.</th><th>Total resistance of circuit, in ohms.</th></tr>
<tr><th>I.</th><th>II.</th><th>III.</th><th>IV.</th><th>V.</th><th>VI.</th><th>VII.</th><th>VIII.</th><th>IX.</th><th>X.</th></tr>
<tr><td colspan="10">TABLE VI.—Ag-BrAg Plates in LiBr, KBr, NaBr Solutions. Influence of the Cation.</td></tr>
<tr><td></td><td>Ag-BrAg in light and in dark</td><td>0·1 normal LiBr</td><td>July 25, 1904</td><td>0·3 centim. to right (200 ohms shunt)</td><td>—</td><td>1, 2</td><td>116, 117</td><td>—</td><td>Resistance of galvanometer = 834·4 ohms, shunt of galvanometer = 1000 ohms</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal KBr</td><td>July 25, 1904</td><td>1·5 centims. to left (1000 ohms shunt)</td><td>—</td><td>3, 4</td><td>120, 117</td><td>—</td><td>ditto</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal NaBr</td><td>July 25, 1904</td><td>4·7 centims. to left (1000 ohms shunt)</td><td>—</td><td>5, 6, 7, 8</td><td>136, 112, 114, 114</td><td>—</td><td>ditto</td></tr>
<tr><td colspan="10">The experiments again instituted on February 3 to 7, 1905, with KBr, NaBr, LiBr, NH_4Br solution (with</td></tr>
<tr><td>16</td><td>Ag-BrAg in light and in dark</td><td>0·1 normal KBr</td><td>February 3, 1905</td><td>17 centims. to left</td><td>—</td><td>1, 2</td><td>96·5, 96·5</td><td>12·2</td><td>846·6</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal NaBr</td><td>February 3, 1905</td><td>6·1 centims. to left</td><td>—</td><td>3, 4</td><td>85, 86</td><td>17·7</td><td>852·1</td></tr>
<tr><td>17</td><td>ditto</td><td>0·1 normal NaBr</td><td>February 6, 1905</td><td>14 centims. to left</td><td>—</td><td>1, 2, 3</td><td>84, 77, 78</td><td>—</td><td>—</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal LiBr</td><td>February 6, 1905</td><td>13·6 centims. to left</td><td>—</td><td>4, 5, 6</td><td>91, 95, 91</td><td>14·7</td><td>849·1</td></tr>
<tr><td>18</td><td>ditto</td><td>0·1 normal LiBr</td><td>February 7, 1905</td><td>18·5 centims. to left</td><td>—</td><td>1</td><td>92</td><td>—</td><td>—</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal NH_4Br</td><td>February 7, 1905</td><td>9·5 centims. to left</td><td>—</td><td>2, 3</td><td>98, 98</td><td>11·4</td><td>845·8</td></tr>
<tr><td colspan="10">TABLE VII.—Transformation of the Constant Cell (Ag-BrAg Plates in KBr Solution)</td></tr>
<tr><td>15</td><td>Ag-(BrAg) in light and in dark</td><td>0·1 normal KBr</td><td>November 18, 1904</td><td>8·8 centims. to left (200 ohms shunt)</td><td>—</td><td>1, 2, 3, 4</td><td>73, 60 (corr. 71), 61 (corr. 72), 60 (corr. 75)</td><td>—</td><td>galvanometer shunted with 200 ohms</td></tr>
</table>

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
(Both sides of each Plate covered with AgBr; Glass Vessel instead of Quartz Vessel used.)												
—	—	16·0	16·0	89	123	46·5	12·5	—	constant	total light	acetylene	
—	—	16·0	16·0	89	123	46·5	13·5	—	constant	total light	acetylene	
—	—	16·0	16·0	89	123	47·0	13·5	—	constant	total light	acetylene	
plates cleaned and freshly covered with AgBr on December 17, 1904; one side covered with paraffin):—												
—	—	19·2	15·75	115–116	146	20·05	16	—	constant	total light	acetylene	16
—	—	19·2	15·75	115–116	146	20·05	16	—	constant	total light	acetylene	
—	—	19·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	17
—	—	19·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	
—	—	21·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	18
—	—	21·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	
into an Inconstant Cell (Ag in Light, KBr Solution, Ag-BrAg in the Dark).												
—	—	16·3	16·2	76	—	58·5	ordinary temperature		inconstant (polarisation)	total light	acetylene	15

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
TABLE VIII.—Ag-IAg Plates in 0·1 Normal									
	Ag-IAg in light and in dark	0·1 normal KI	February 11, 1904	9·5* centims. to right	—	—	—	—	—
	ditto	ditto	February 12, 1904	5·0* centims. to right	—	1, 2, 3	86, 85	15·7	Resistance of galvanometer = 834·4 ohms; shunt of galvanometer = 40 ohms
	ditto	ditto	February 15, 1904	4·5 centims. to right	—	4	35·4	15·7	ditto
	ditto	ditto	February 15, 1904	ditto	—	5	no change	15·7	ditto
	ditto	ditto	February 15, 1904	ditto	—	6	circa 0·5	15·7	ditto
	ditto	ditto	February 17, 1904	5·3* centims. to right	—	(1), 2, 3, 4	112, 118, 123 = average 117·7	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	{ 5	{ 45	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	6	78	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	7	no change	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	8	circa 0·5	15·7	ditto
20	ditto	ditto	February 19, 1904	5·0* centims.	—	{ 1	{ too large to be photographed: over 135	15·7	{ ditto
	ditto	ditto	February 19, 1904	5·0* centims.	—	2, 3	96, 95	15·7	Resistance of galvanometer = 834·4 ohms; shunt of galvanometer = 20 ohms
	ditto	ditto	February 23, 1904	2·2* centims. to right	—	1, 2	95, 94	15·7	ditto
TABLE IX.—Ag Plates in Decinormal NaBr Solution									
24	Ag plates in light and in dark	**0·1 normal NaBr and solid AgBr**	July 16, 1903	2 9 centims. to right	—	1, 2	64·5, 67·2	—	—
	ditto	ditto	July 16, 1903	ditto	—	3 and 4	25·5 and 72	—	—
	ditto	ditto	July 16, 1903	ditto	—	5 and 6	circa 1 and 9	—	—
	ditto	ditto	July 16, 1903	ditto	—	7 and 8	? and ?	—	—
	ditto	ditto	July 16, 1903	ditto	—	9, 10	12·5, 12·5	—	—
	ditto	ditto	July 16, 1903	ditto	—	11, 12	7·5, 7·5	—	—

* With shunt of

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
IK Solution (no Solid IAg added).												
—	—	—	—	—	—	—	—	—	—	—		
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	blue screen	arc : 66 volts, 6·2 ampères	
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	red screen	arc : 66 volts, 6·2 ampères	
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	green-yellow screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	125	—	118	ordinary temperature		constant	blue screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	92	—	118	ordinary temperature		constant	blue screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	92	—	118	ordinary temperature		constant	red screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	92	—	118	ordinary temperature		constant	yellow-green screen	arc : 66 volts, 6·2 ampères	
—	—	18·0	16·8	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	20
—	—	18·0	16·8	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
—	—	18·0	16·8	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
and Solid AgBr. *Rôle* of the Electrode.												
—		17·3	16·8	82	—	98	—	—	inconstant	total light	arc : 66 volts, 6·2 ampères	24
—	—	17·3	16·8	30 and 42	—	98	—	—	inconstant	blue screen	arc : 66 volts, 6·2 ampères	
—	—	17·3	16·8	82 and 30	—	98	—	—	inconstant	red screen	arc : 66 volts, 6·2 ampères	
—	—	17·3	16·8	82 and 30	—	98	—	—	inconstant	yellow-green screen	arc : 66 volts, 6·2 ampères	
—	—	17·3	16·8	32	—	59	ordinary temperature		inconstant	total light	acetylene	
—	—	17·3	16·8	42	—	59	ordinary temperature		inconstant	total light	acetylene	

galvanometer = 40 ohms.

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
TABLE X.—The Electrical Potential between the Hg, solid Hg_2Cl_2 in Decinormal NaCl and HCl Solutions,									
22	Hg, Hg_2Cl_2 in light and in dark	0·1 normal NaCl	July 25, 1904	10·0 centims.* to left	—		no deflection, perhaps ½	83	Resistance of galvanometer =834·4 ohms; shunt of galvanometer =1000 ohms
	ditto	ditto	July 26, 1904	4·3 centims.* to left	—		no deflection, perhaps ½	83	ditto
	ditto	0·1 normal HCl	July 26, 1904	7·2 centims.* to right	—		no deflection, perhaps ½	83	ditto
	ditto	ditto	July 27, 1904	23·3 centims.* to right	—		no deflection, perhaps ½	83	ditto
21	Hg, Hg_2Br_2 in light and in dark	0·1 normal KBr	February 27, 1904	compensated by opposite E.M.F. 1 centim. to left	—	1 and 2	no deflection	—	no shunt
	ditto	0·1 normal NaBr	February 27, 1904	ditto	—	3	perhaps ½ to 1	—	no shunt
TABLE XI.—Hg, solid Hg_2I_2 in KI Solution, and Hg, solid Hg_2I_2 in Solution of KI could not be investigated,									
23	$Hg_1SO_4Hg_2$ in light and in dark	0·1 normal $SO_4(NH_4)_2$	December 9, 1904	17·8 centims. to left	—	1, 2, 3	44·5, 51·5, 42·5†	—	—
	ditto	ditto	December 9, 1904	ditto	—	4, 5	21, 20·5	—	—
To all the above investigations the intensity of light measured with the Rubens thermopile (Column XVII.) gives the Column XVI., and when the sensitiveness of Nalder No. 2 was that given by									

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* With 1000 ohms

† Did not return to zero deflection 12, 6, 5½ millims.; no shunt used with the galvanometer. Height of Hg = circa

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given to Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
Illuminated and not Illuminated parts of the Solution.												
Hg, solid Hg_2Br_2 in Decinormal NaBr and KBr Solutions.												
—	—	16·0	16·0	88	123	46, 7	18·7	ordinary temperature	—	total light	acetylene	22
—	—	16·0	16·0	88	123	46, 7	18·7	ditto	—	total light	acetylene	
—	—	16·0	16·2	88	123	46, 7	18·7	ditto	—	total light	acetylene	
—	—	16·0	16·2	88	123	46, 7	18·7	ditto	—	total light	acetylene	
—	—	16·0	16·8	118 and 47	—	98	ordinary temperature		—	total light	arc	21
—	—	16·0	16·8	47	—	98	ordinary temperature		—	total light	arc	
Hg, solid SO_4Hg_2 in Soluble Sulphates, $SO_4(NH_4)_2$, &c.												
since Hg_2I_2 is Decomposed by KI already in the Dark.												
—	—	16·0	16·85	30	98	98	ordinary temperature		constant	total light	arc: 65 volts, 6·1 ampères	23
—	—	16·0	16·85	30	98	98	ordinary temperature		constant	red screen	arc: 65 volts, 6·1 ampères	
deflections obtained with Nalder N2, when the light was removed from Rubens thermopile, by the distance given in Column XIV. (with a Clark, 100,000 ohms. inserted, and shunt of galv. = 10 ohms.).												

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shunt of galvanometer.

1 centim. Different heights of mercury give different values. The E.M.F. is principally a thermo E.M.F.

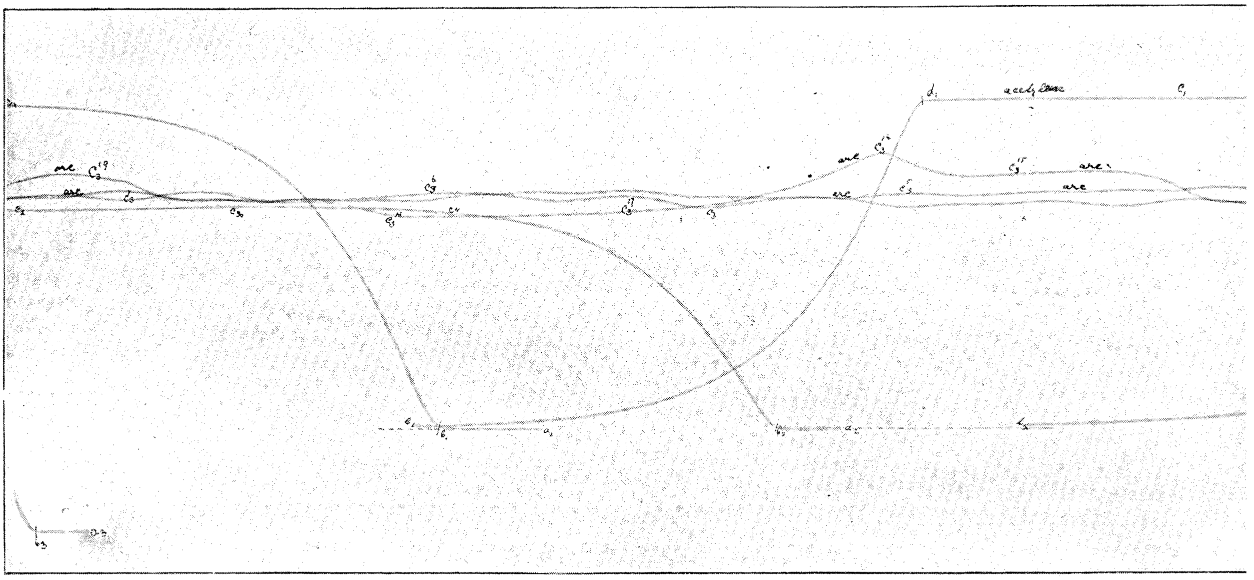


Plate N1.

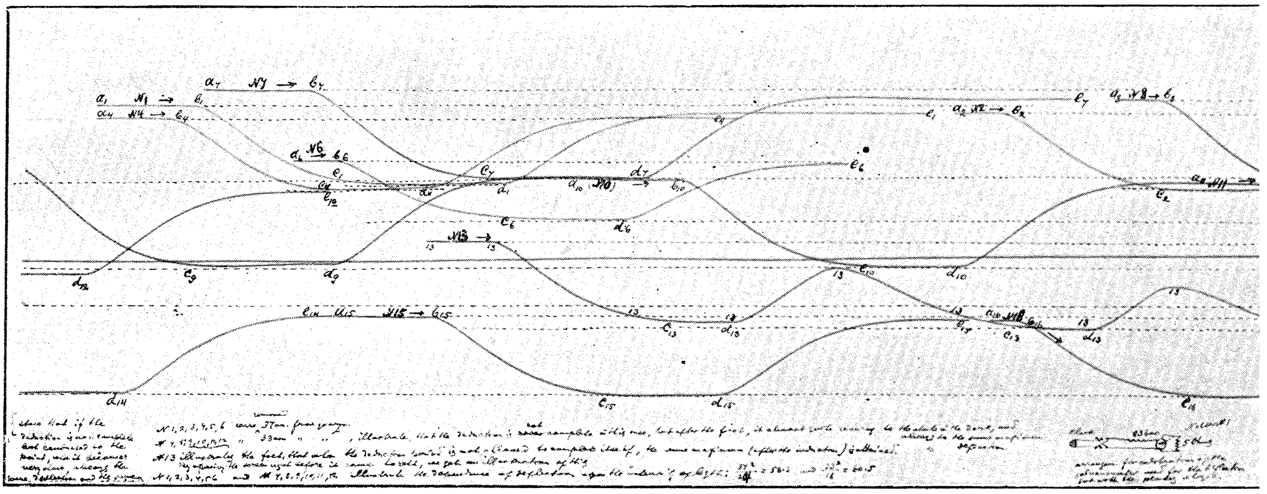
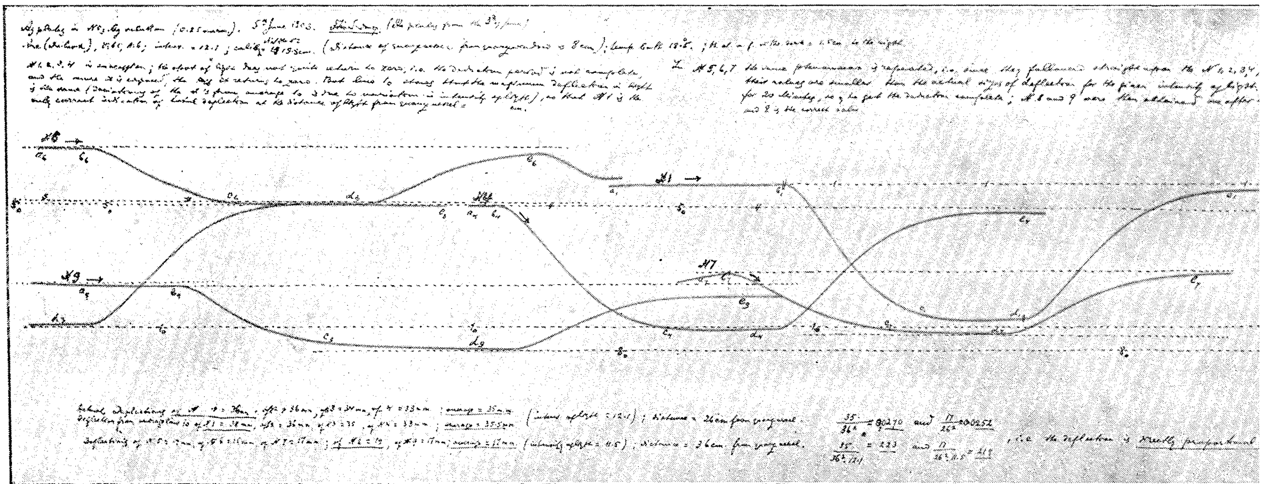
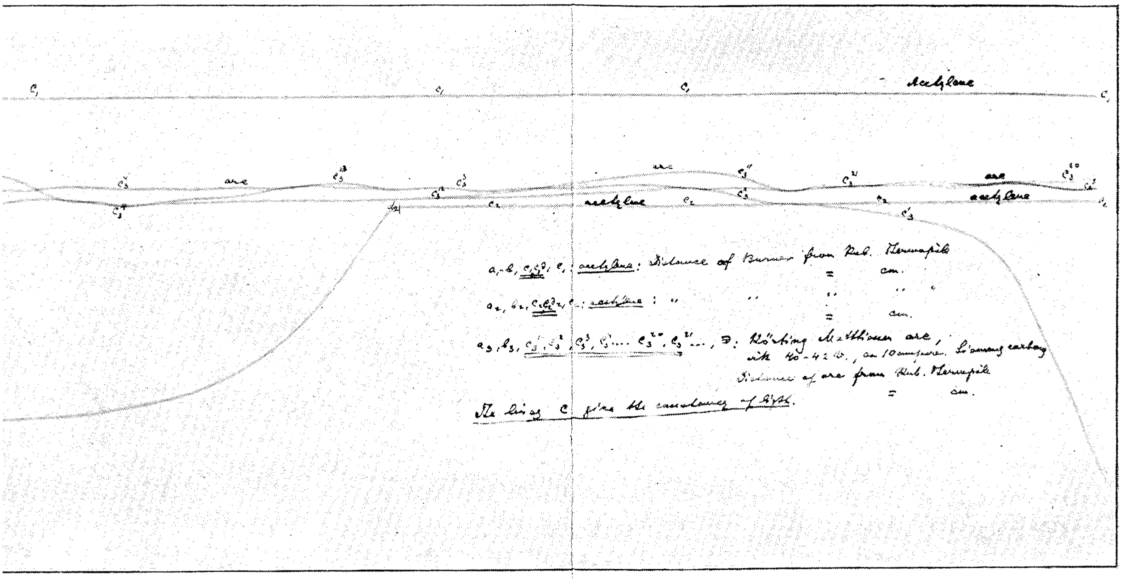
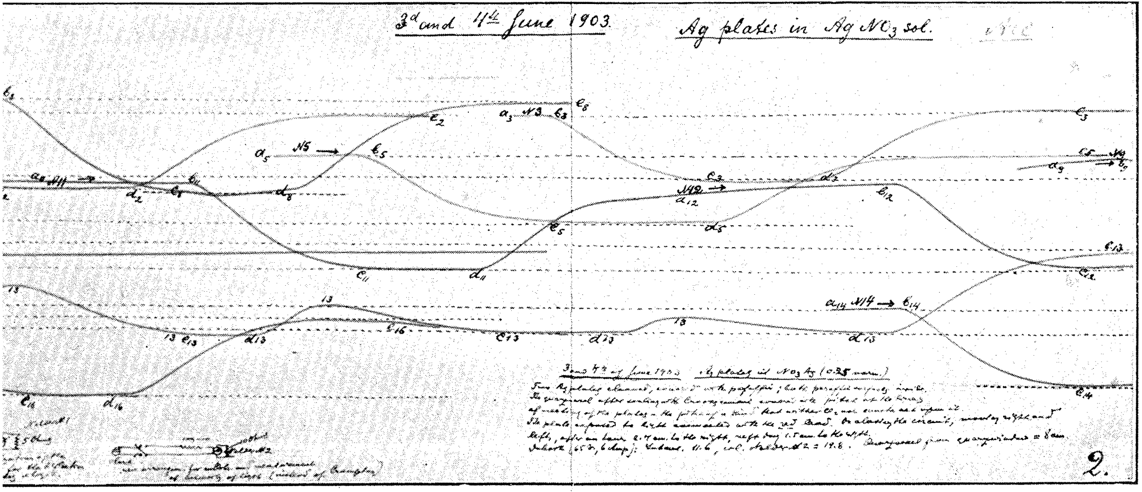


Plate N2.

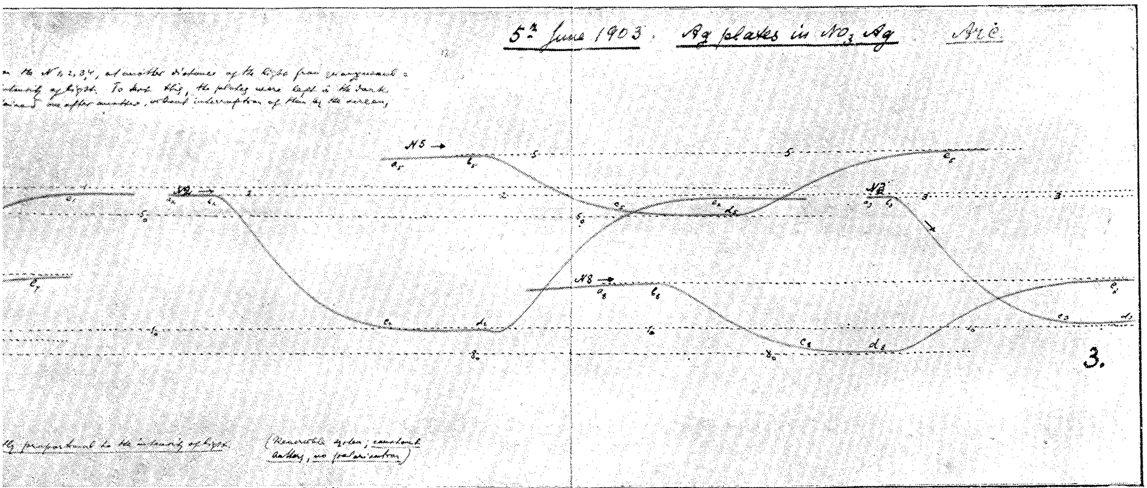



Acetylene
arc
acetylene
c_1
c_2
c_3
Distance of Burner from Rub. Thermopile = cm.
Körting Matthiesen arc, with 40-42 V., or 10 ampere.
Distance of arc from Rub. Thermopile = cm.
The lines c give the constancy of light.

N1.


3d and 4th June 1903.
Ag plates in Ag NO3 sol.
Arc
N3
N5
N11
N12
N14
3d and 4th of June 1903. Ag plates in NO3 Ag (0.25 norm.)
2.

N2.


5th June 1903.
Ag plates in NO3 Ag
Arc
N2
N3
N5
N8
3.

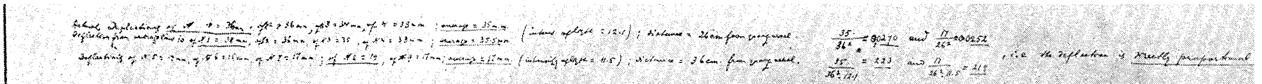
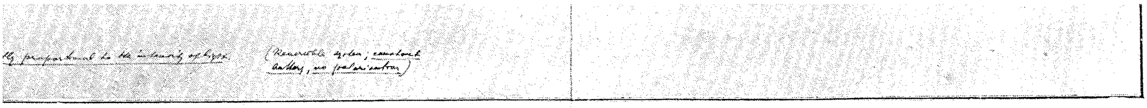


Plate N3.



lly proportional to the intensity of light.

(Reversible system; constant battery, no polarisation)

N3.

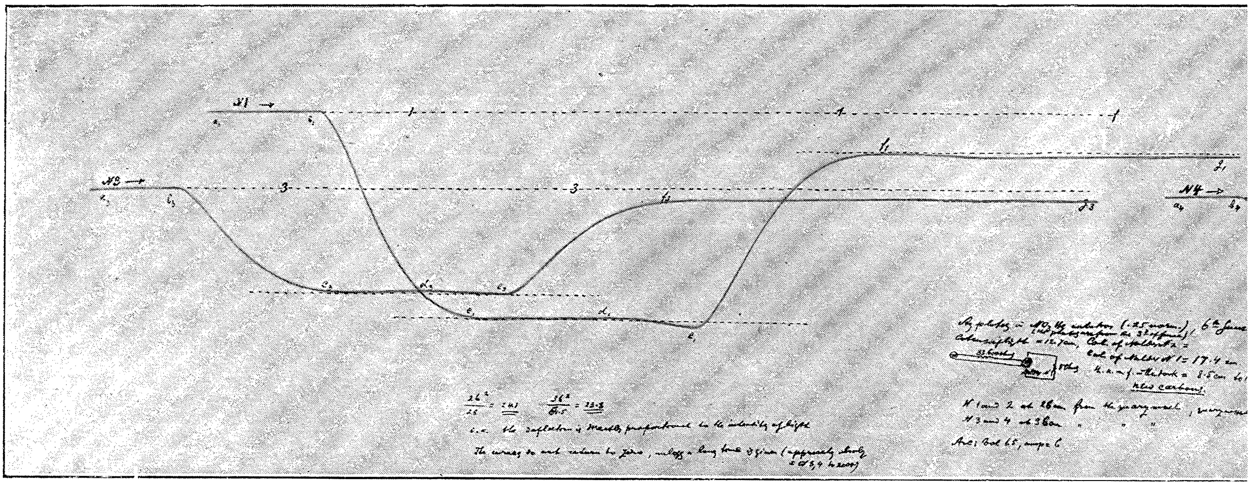


Plate N4.

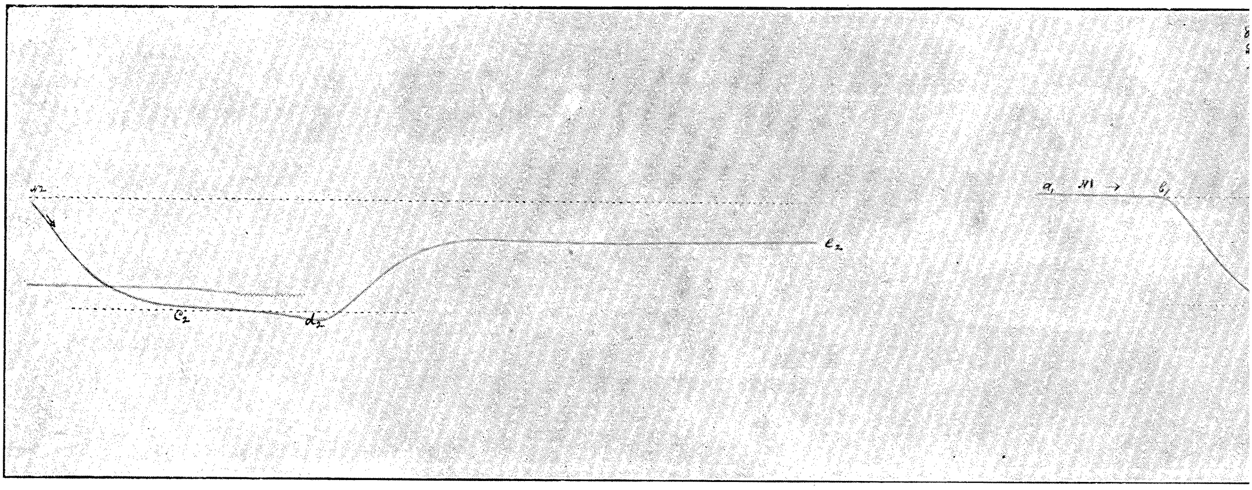


Plate N5.

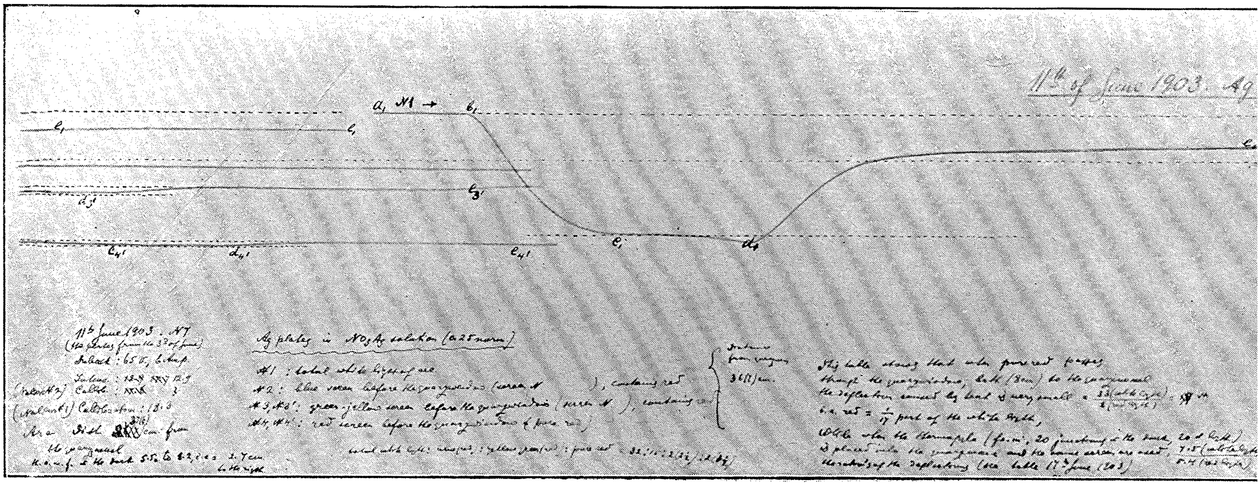
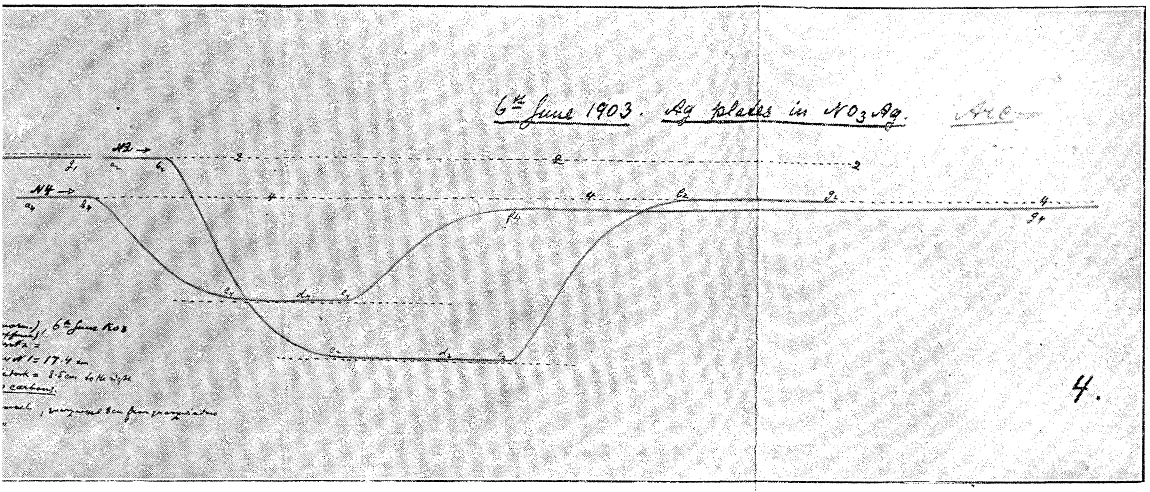
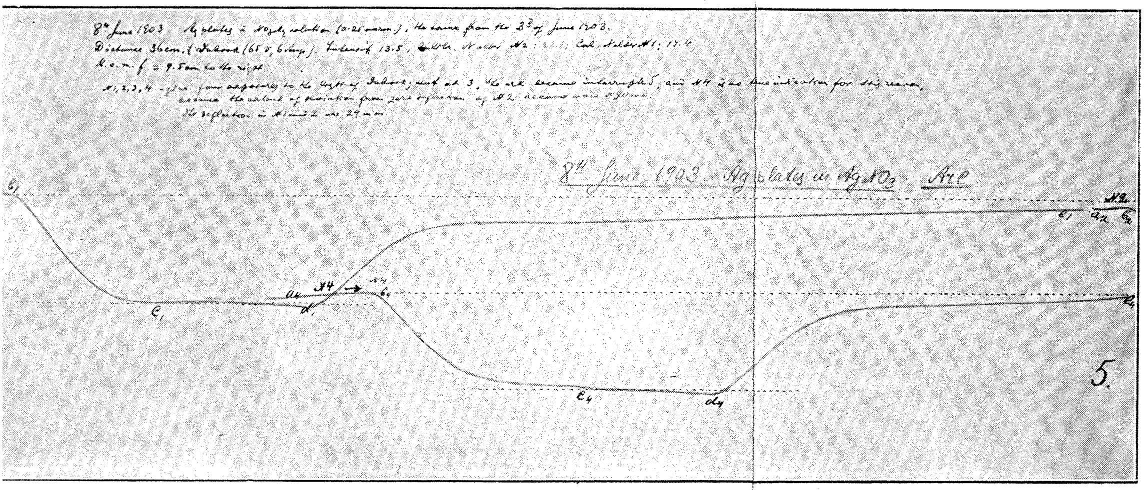


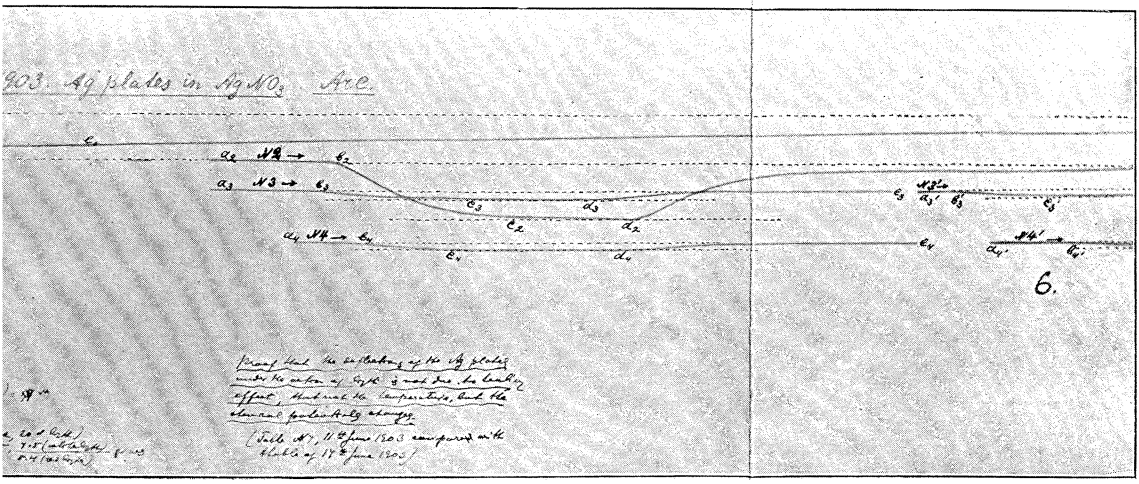
Plate N6.


6th June 1903. Ag plates in NO$_3$Ag. Arc
N2 →
N4 →
a$_2$
b$_2$
c$_2$
d$_2$
e$_2$
a$_4$
b$_4$
c$_4$
d$_4$
e$_4$
f$_4$
g$_2$
g$_4$
2
4
6th June K03
N1 = 17.4
4.

N4.


8th June 1903 Ag plates in NO$_3$Ag solution (0·21 norm.), the same from the 3rd of June 1903.
Distance 36 cm. Col. N1: 17.4
8th June 1903. Ag plates in AgNO$_3$. Arc
N2
N4 →
a$_2$
b$_2$
a$_4$
b$_4$
c$_1$
d$_1$
e$_1$
c$_4$
d$_4$
e$_4$
5.

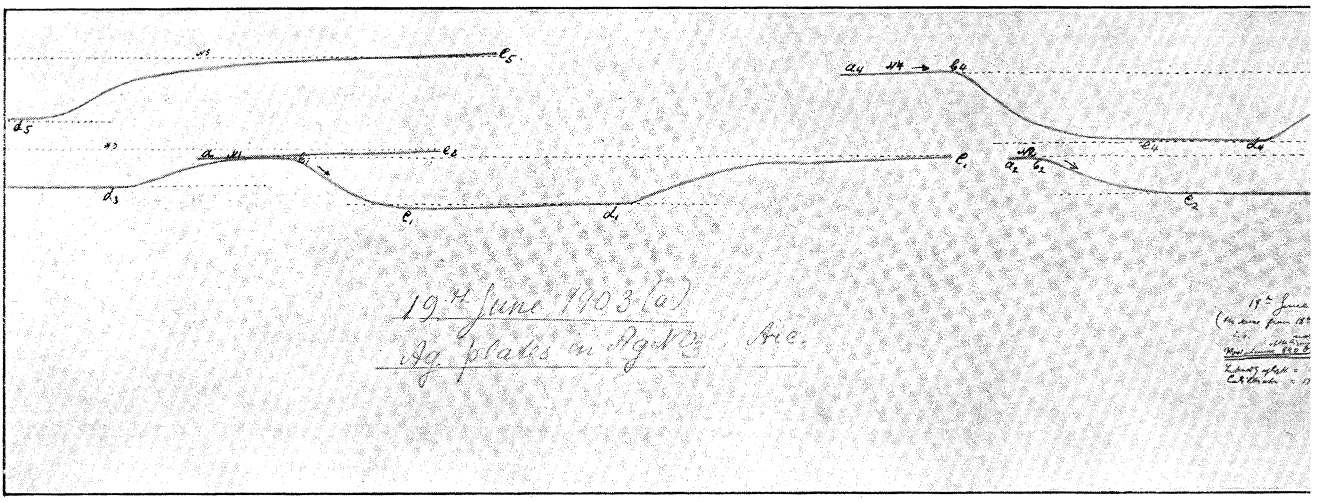
N5.


1903. Ag plates in AgNO$_3$. Arc
N2 →
N3 →
N4 →
N3′
N4′
a$_2$
b$_2$
a$_3$
b$_3$
c$_3$
d$_3$
e$_3$
c$_2$
d$_2$
e$_2$
a$_4$
b$_4$
c$_4$
d$_4$
e$_4$
a$_3$′
b$_3$′
c$_3$′
a$_4$′
b$_4$′
6.
(Table N7, 11th June 1903 compared with those of 17th June 1903)

N6.

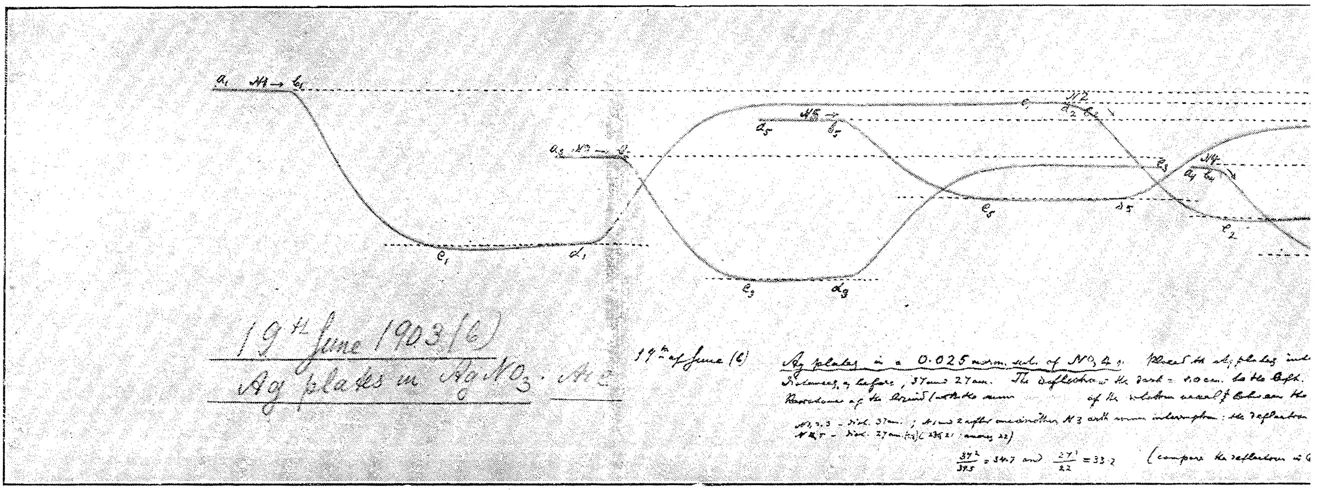
Plate N6.

N6.



19th June 1903 (a)
Ag plates in AgNO3 Arc.

Plate N7.



19th June 1903 (b)
Ag plates in AgNO3 Arc.

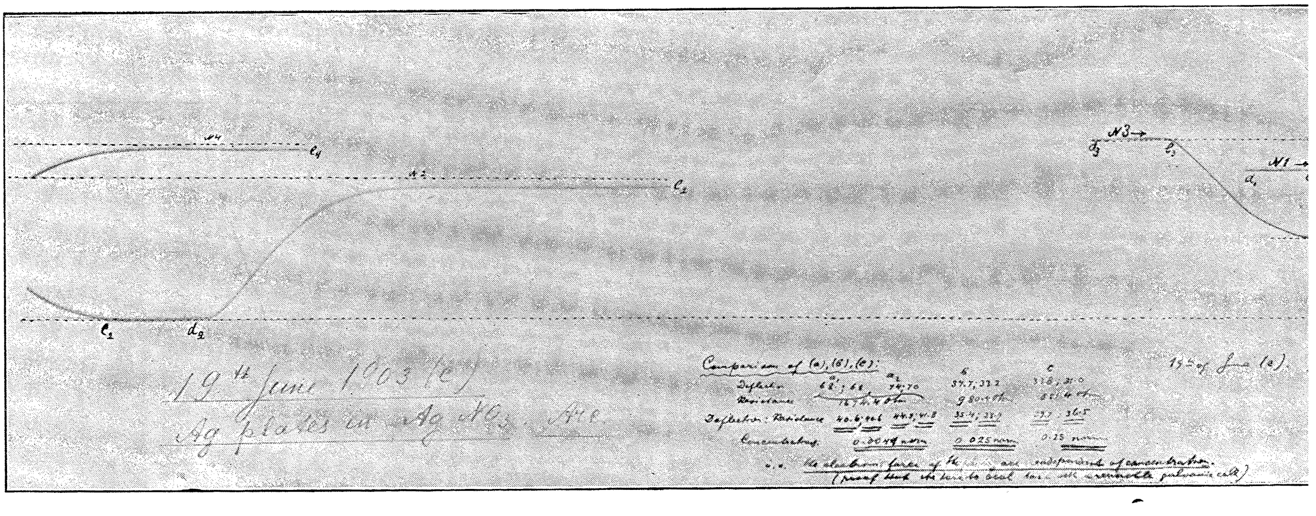
19th of June (b)

Ag plates in a 0.025 norm. sol. of NO3 Ag. Placed the ag. plates [illegible]
Distances, as before, 37 and 27 cm. The deflection w. the dark = 1.0 cm. to the left.
Resistance of the circuit [illegible] of the solution [illegible]

N1, 2, 3 – dist. 37 cm.; 1 and 2 after one another, N3 with [illegible] interruption: the deflection
N4, 5 – dist. 27 cm. (22) (23, 21 average 22)

$\frac{37^2}{39.5} = 34.7$ and $\frac{27^2}{22} = 33.2$ (compare the deflection in

Plate N8.



19th June 1903 (c)
Ag plates in AgNO3 Arc.

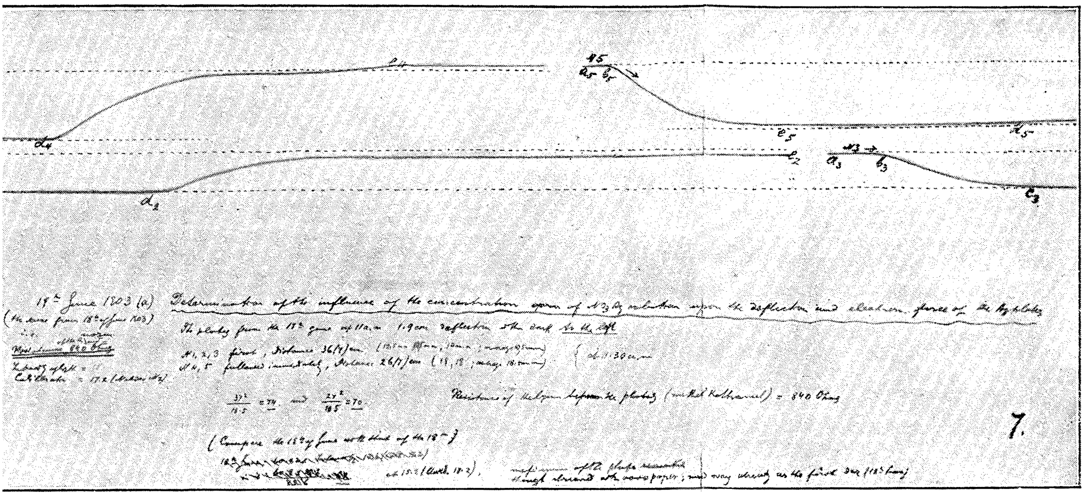
Comparison of (a), (b), (c):

19th of June (c).

	a1	a2	b	c
Deflection	62; 64	74; 70	34.7; 33.2	33.8; 31.0
Resistance	1574.4 Ohm		980.4 Ohm	851.4 Ohm
Deflection : Resistance	40.6; 40.6	44.3; 44.8	35.4; 33.9	39.7; 36.5
Concentration	0.0044 norm		0.025 norm	0.25 norm

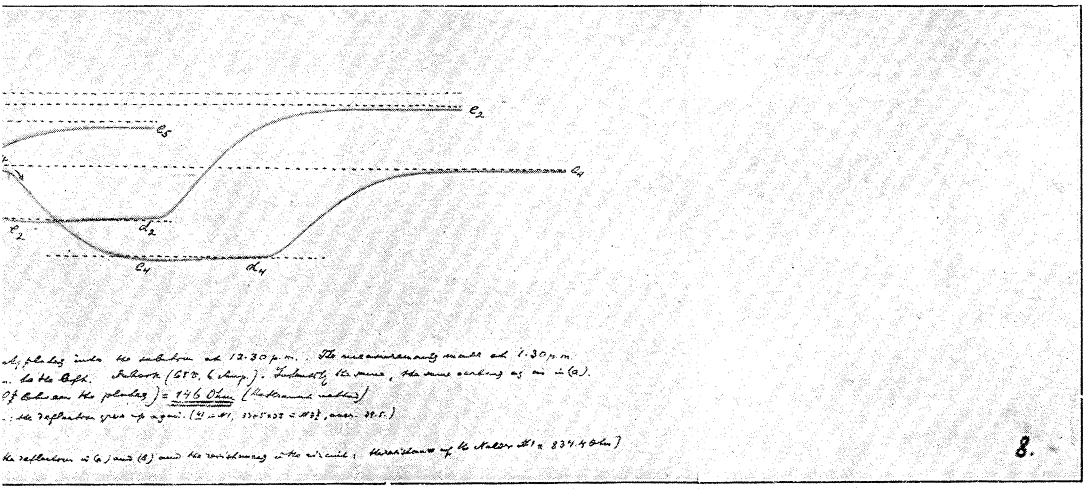
∴ the electromotive forces of the [illegible] are independent of concentration.
(proof that [illegible] real [illegible] reversible galvanic cells)

Plate N9.



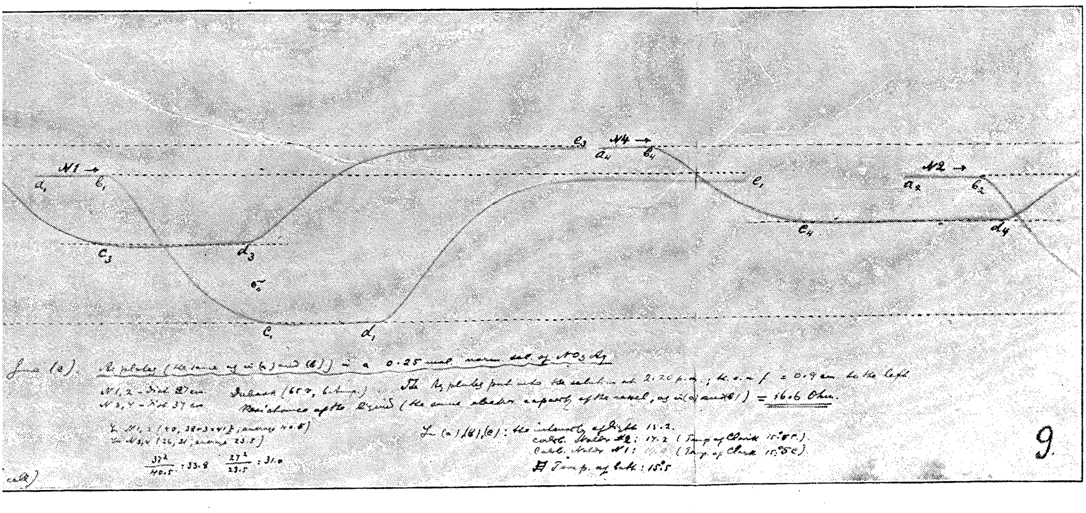
d_4
c_4
$N5$
a_5 b_5
c_5
d_5
c_2
d_2
$N3$
a_3 b_3
c_3

7.



c_5
c_2
d_2
c_4
d_4
e_2
e_4

8.



$N1$
a_1 b_1
c_3
d_3
c_1
d_1
c_3
$N4$
a_4 b_4
e_1
c_4
$N2$
a_2 b_2
d_4

9.

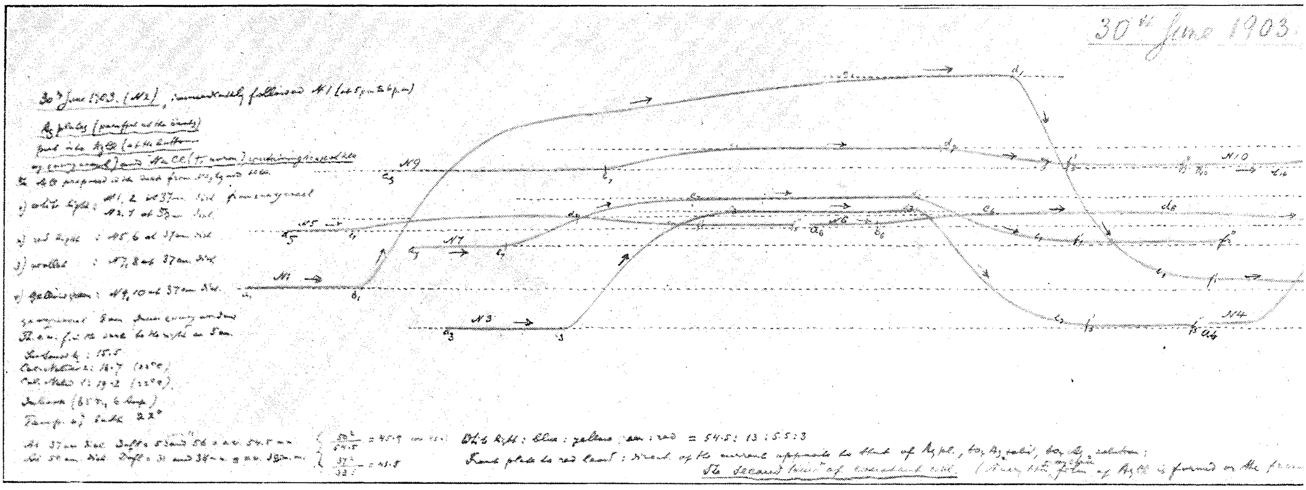


Plate N10.

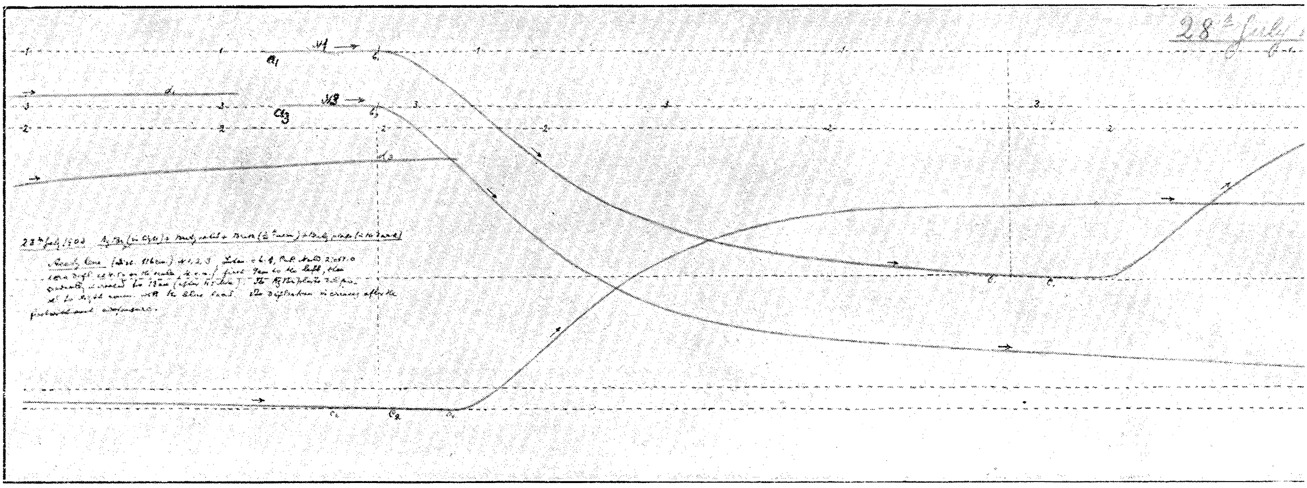


Plate N11.

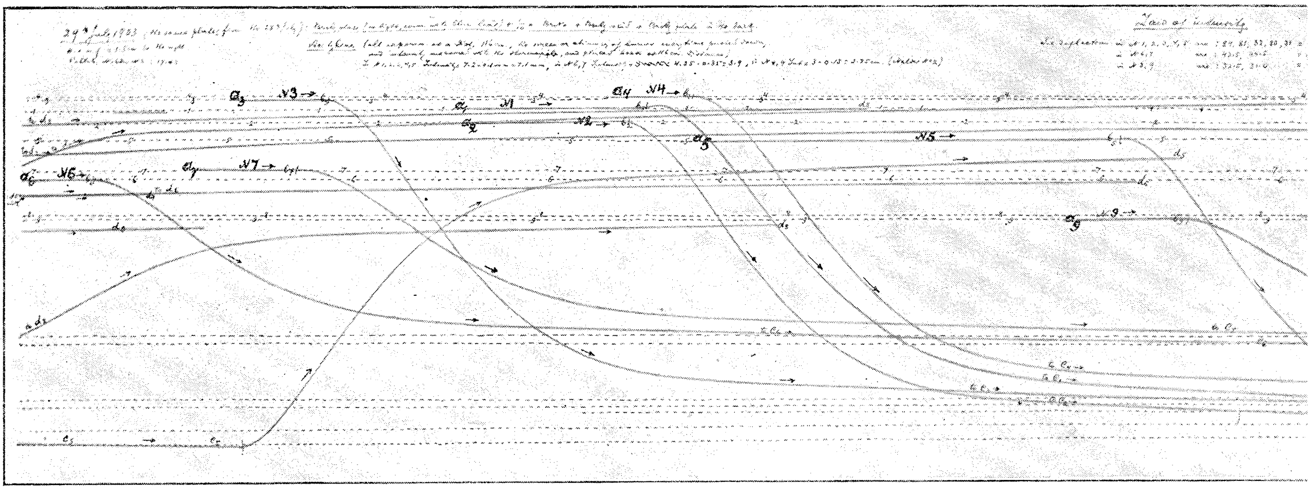
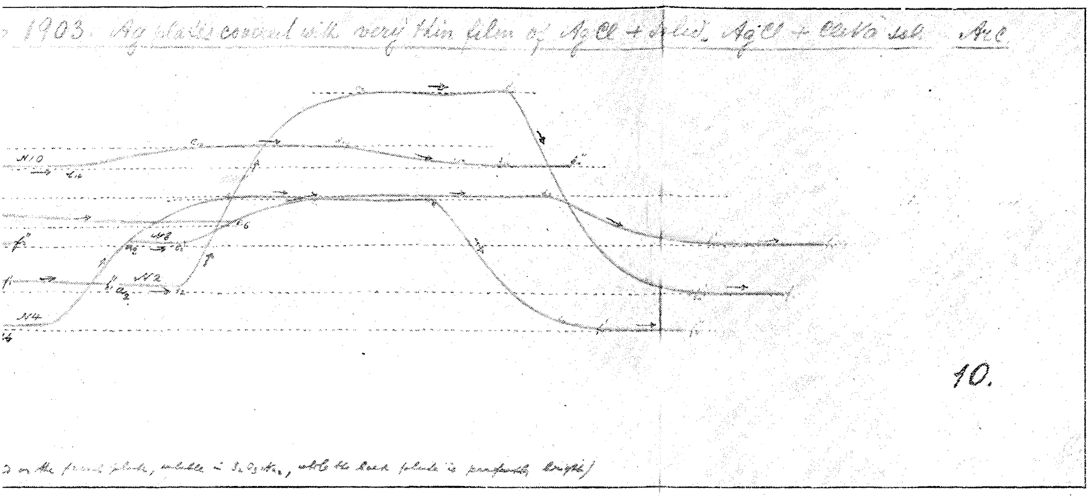
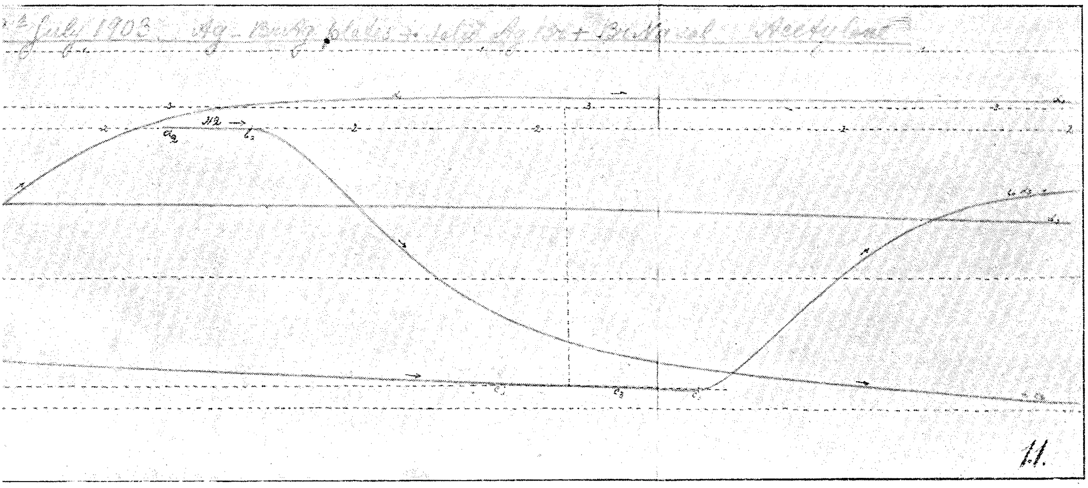


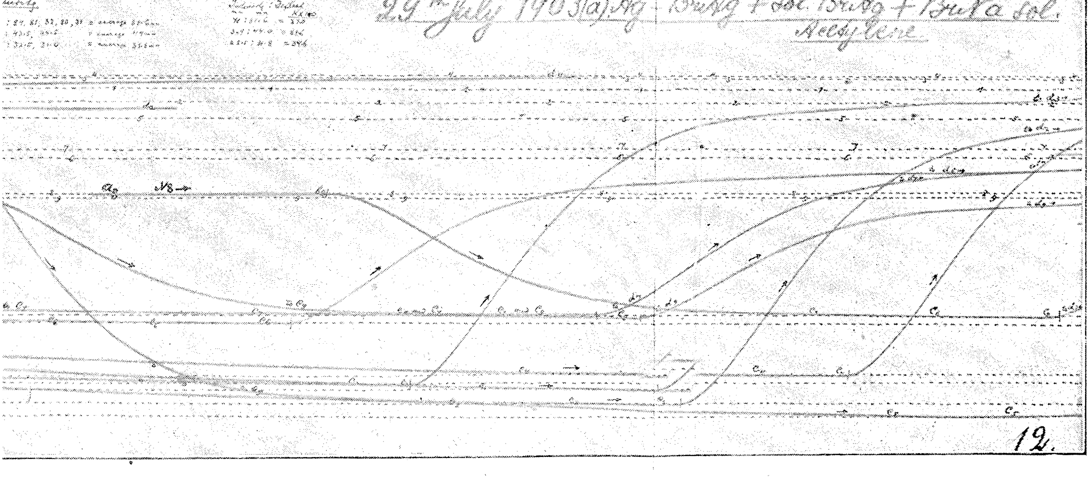
Plate N12.


1903. Ag plates covered with very thin film of AgCl + solid AgCl + ClNa sol. Arc
N10
N8
N2
N4
on the front plate, soluble in $S_2O_3Na_2$, while the back plate is perfectly bright)

10.


July 1903. Ag – BrAg plates + solid AgBr + BrNa sol. Acetylene
N2

11.


29th July 1903 (a) Ag BrAg + Sol. BrAg + BrNa sol.
Acetylene
N8

12.

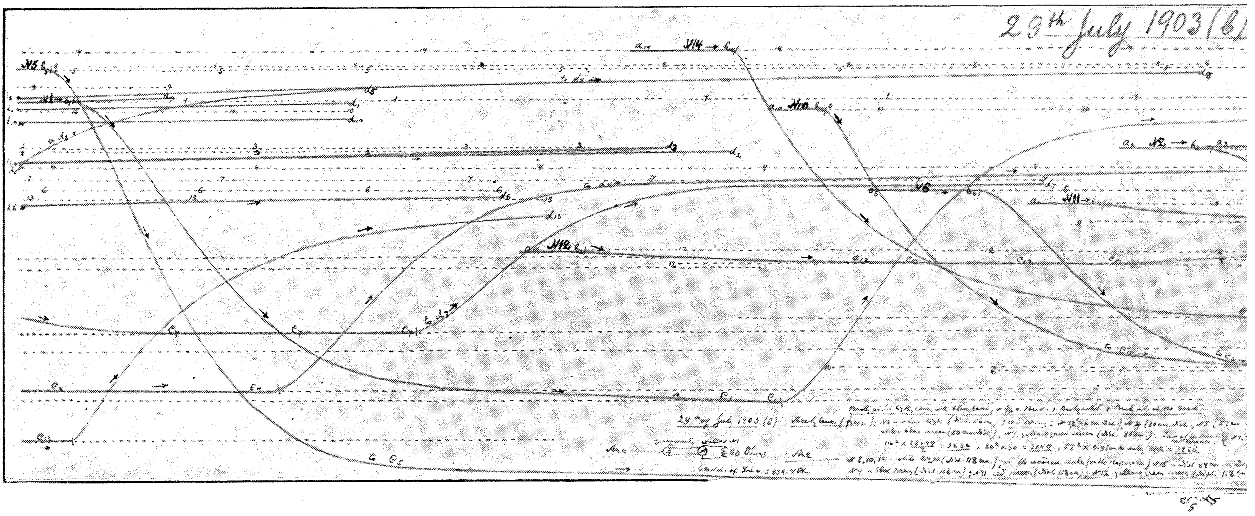


Plate N13.

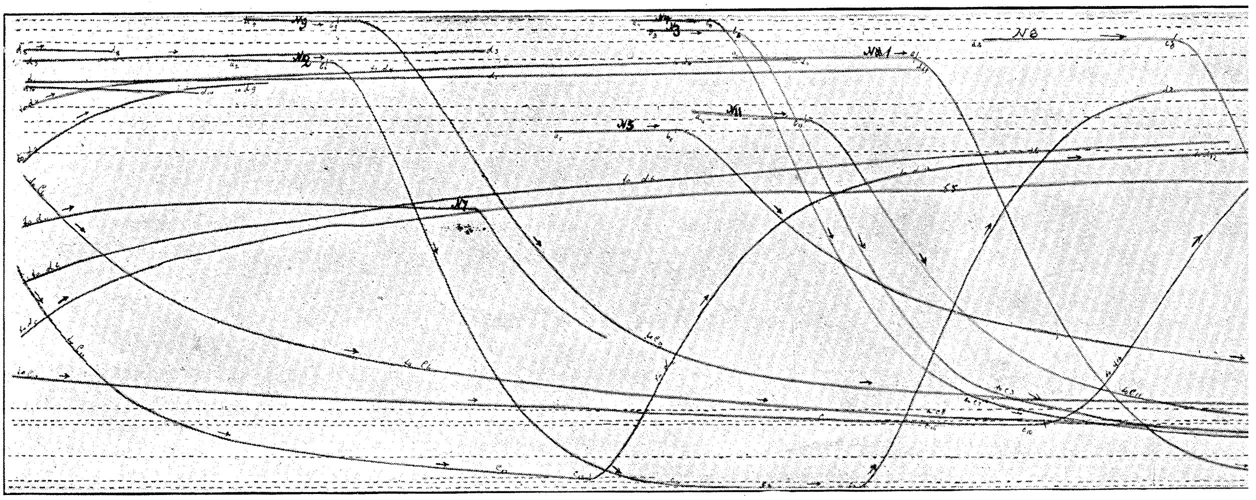
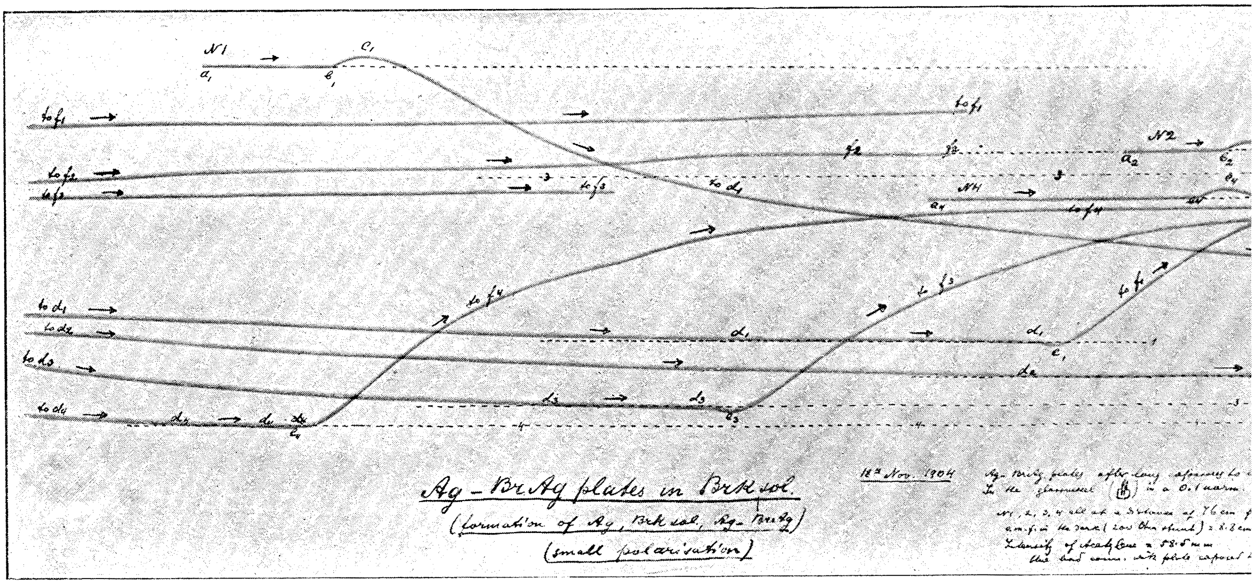
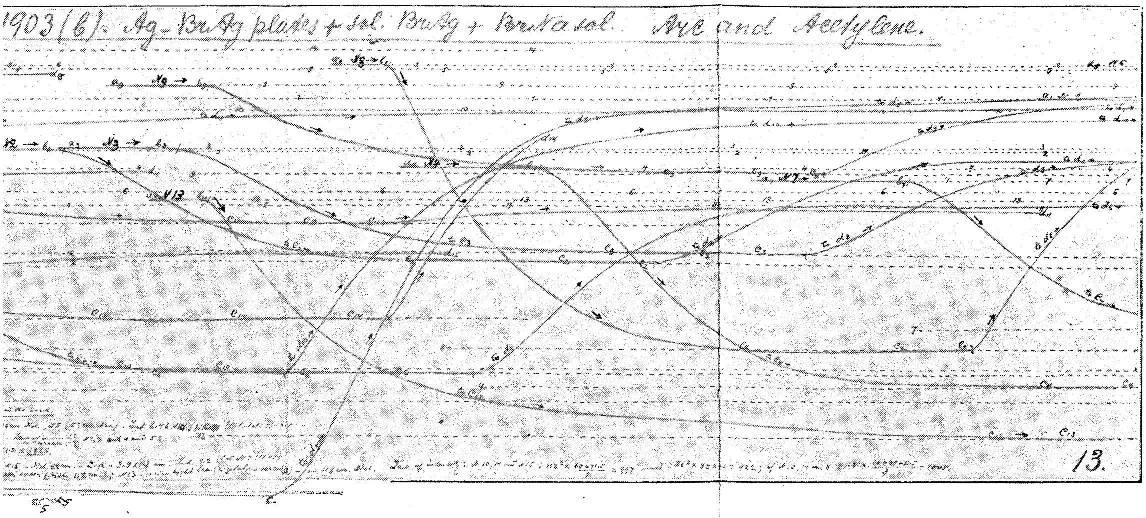
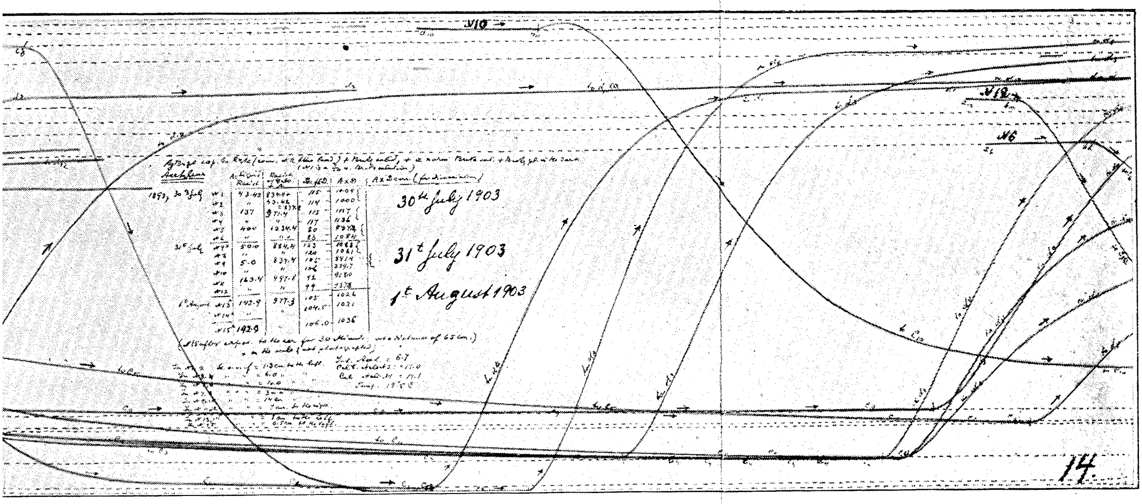


Plate N14.

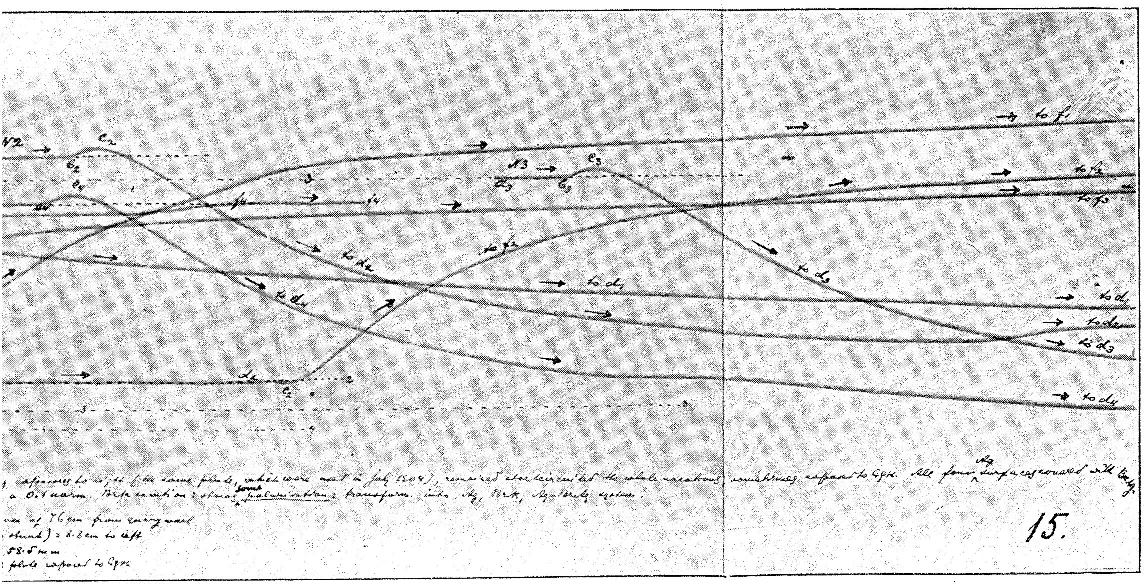


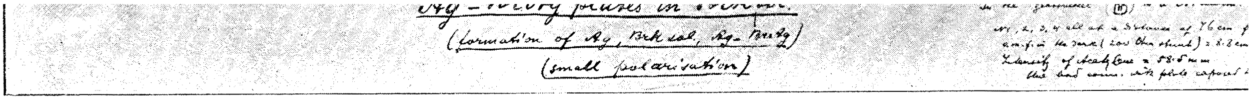

1903(b). Ag-BrAg plates + sol. BrAg + BrNa sol. Arc and Acetylene.
N8
N9
N2
N3
N4
N7
N13
N15
13.

N13.


N10
N12
N6
30th July 1903
31st July 1903
1st August 1903
14.

N14.


N2
N3
to f1
to f2
to f3
to d1
to d2
to d3
to d4
15.



(formation of Ag, BrK sol, Ag-Br+Ag)

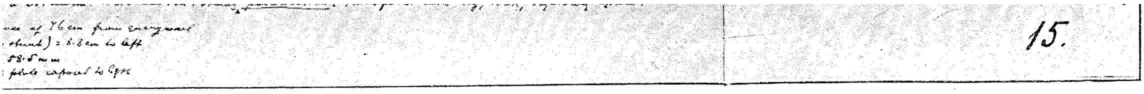
(small polarisation)

Nr. 1, 2, 3, 4 all at a distance of 76 cm

e.m.f. in the dark (200 Ohm shunt) = 8.8 cm

Intensity of Acetylene = 58.5 mm

Plate N15.



…ae of 76 cm from emergent
…stand) = 8.8 cm to left
58.5 mm
plate exposed to Cpx

15.

N15.

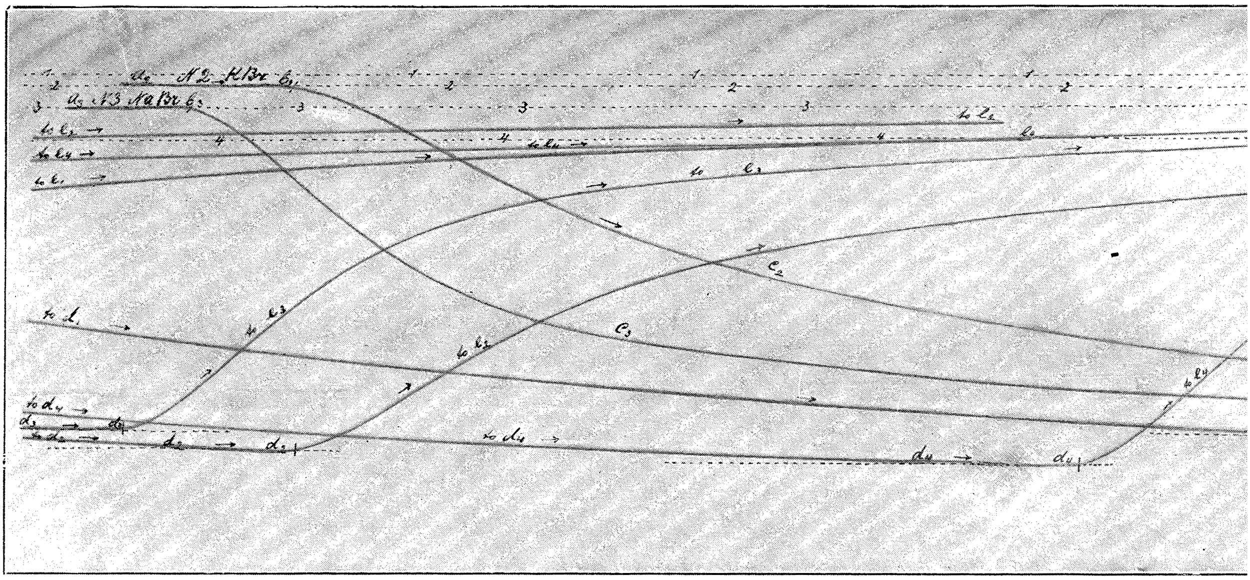
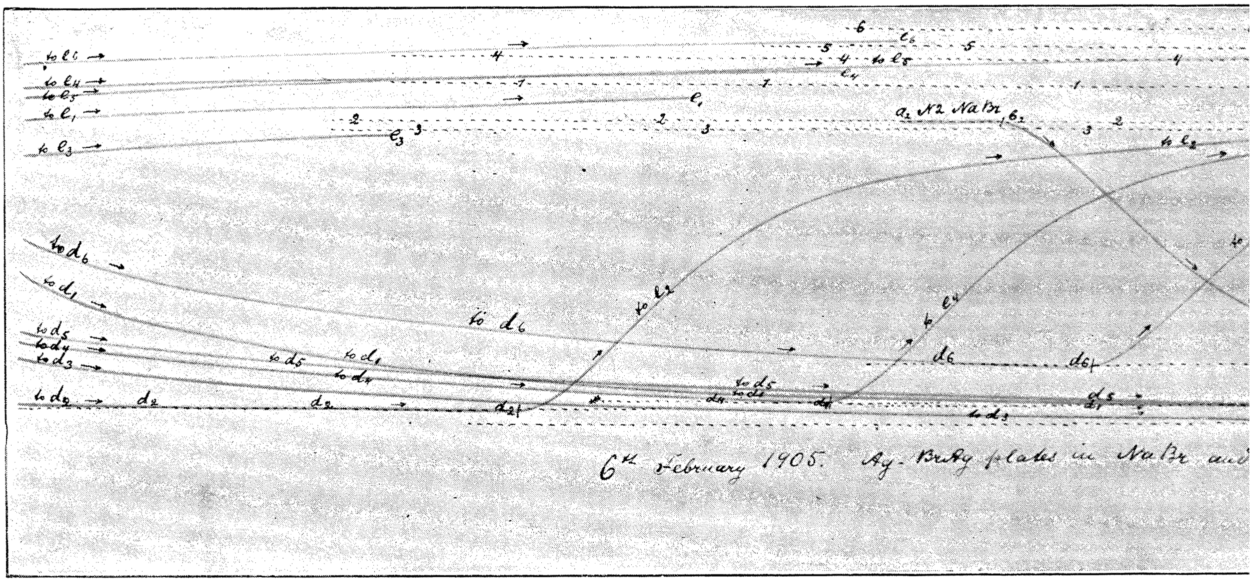
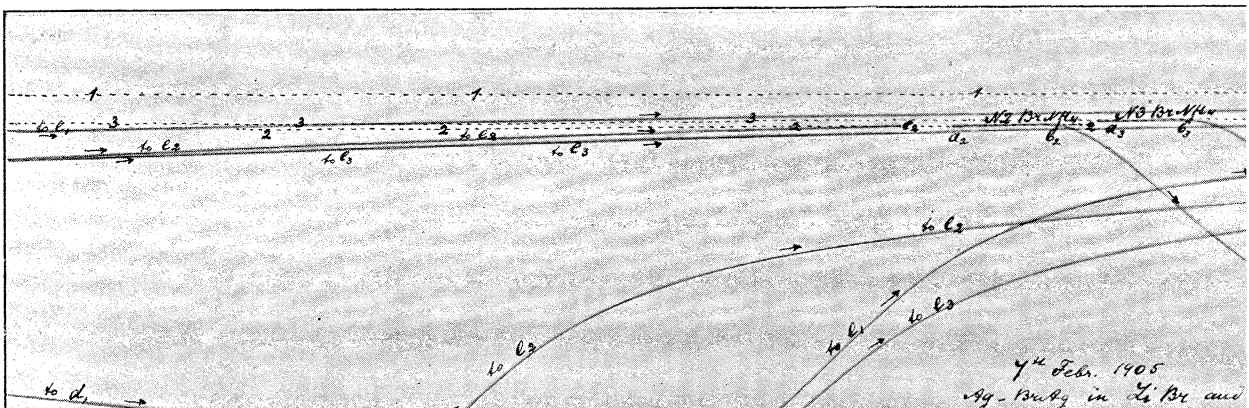


Plate N16.

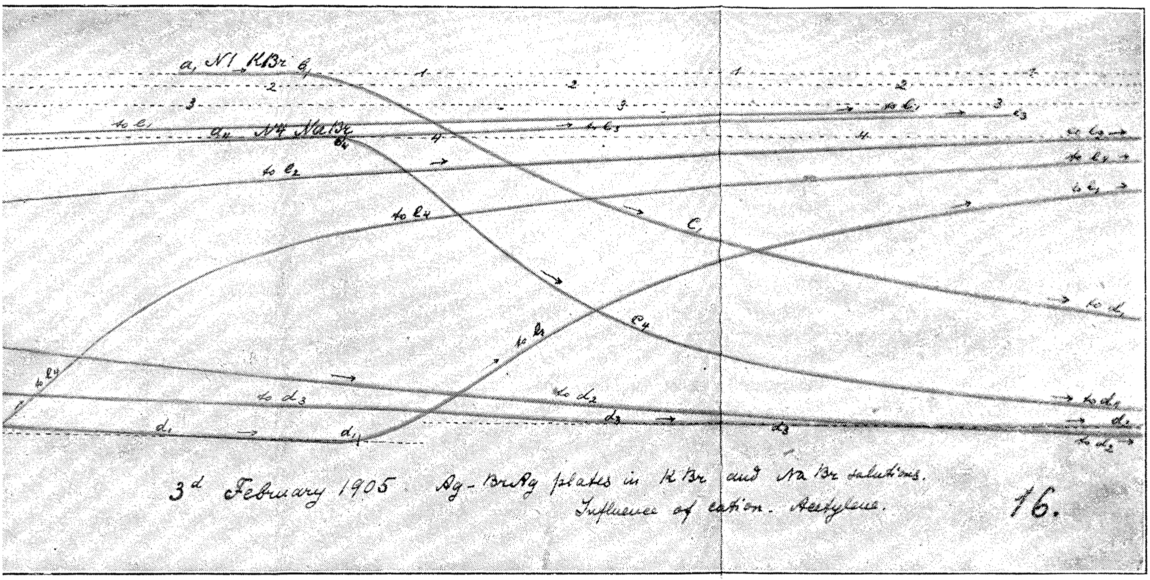


6th February 1905. Ag-BrAg plates in NaBr and

Plate N17.

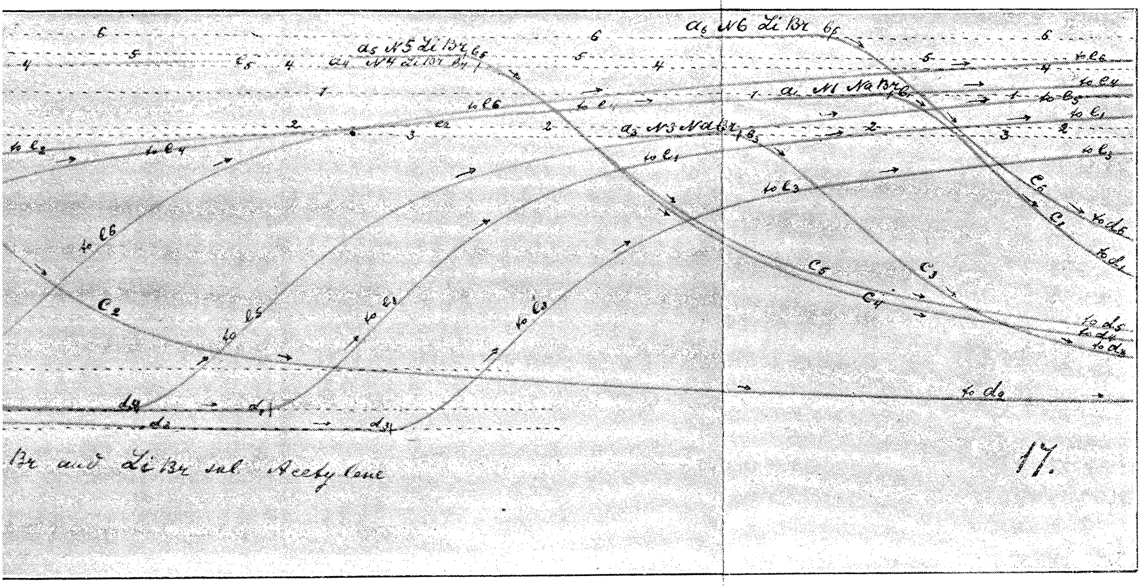


7th Febr. 1905
Ag-BrAg in LiBr and



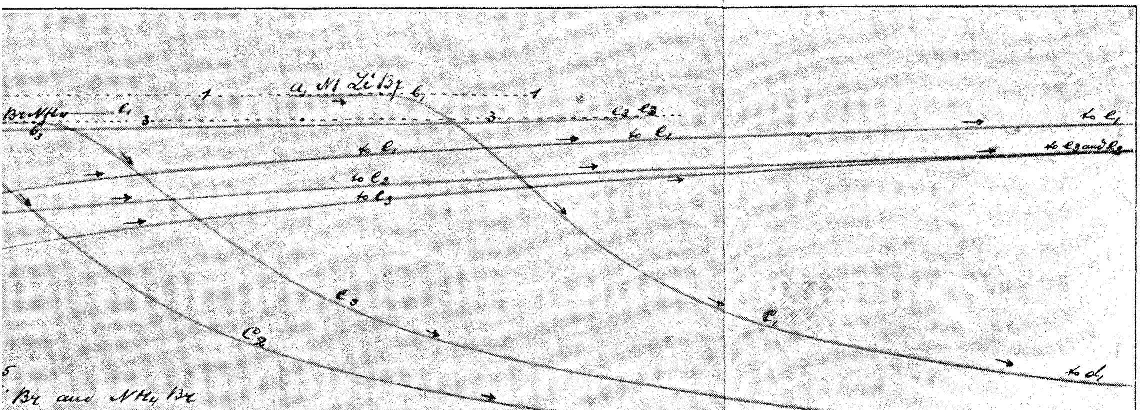
3d February 1905 Ag-BrAg plates in KBr and NaBr solutions. Influence of cation. Acetylene.

N16.



Br and LiBr sol. Acetylene

N17.



Br and NH4 Br

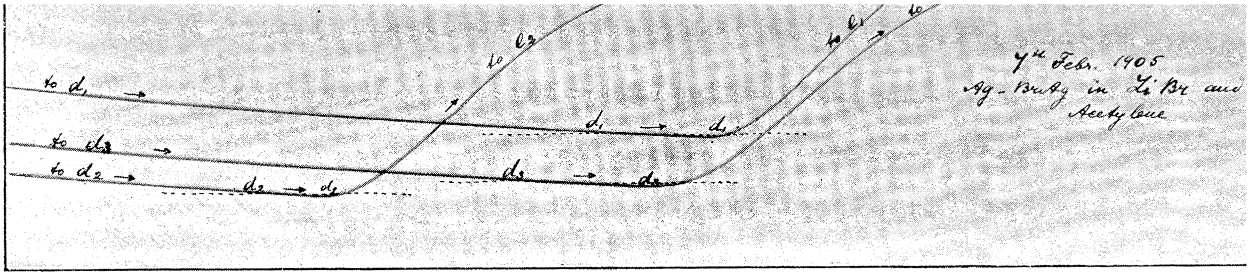
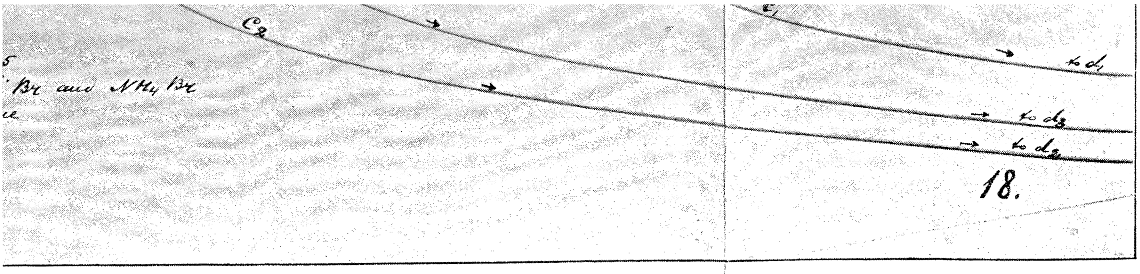

to d₁ →
to d₃ →
to d₂ →
d₂ → d₂
to d₃
d₁ → d₁
d₃ → d₃
to d₁
to
7th Febr. 1905
Ag-BrAg in LiBr and
Acetylene

Plate N18.



N18.

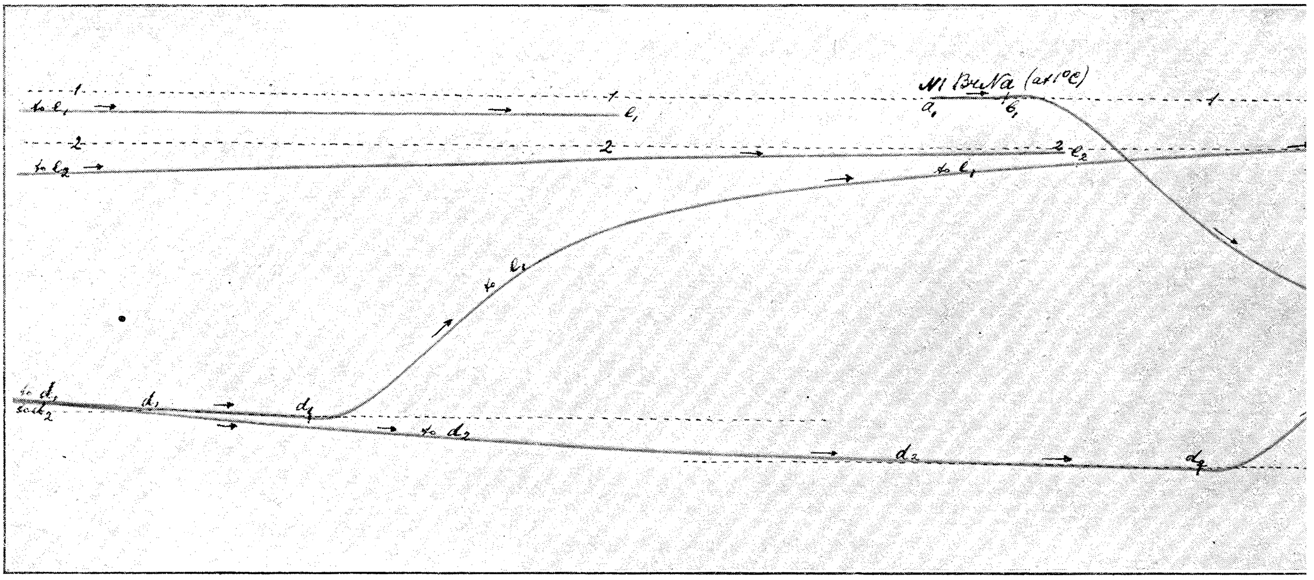


Plate N19.

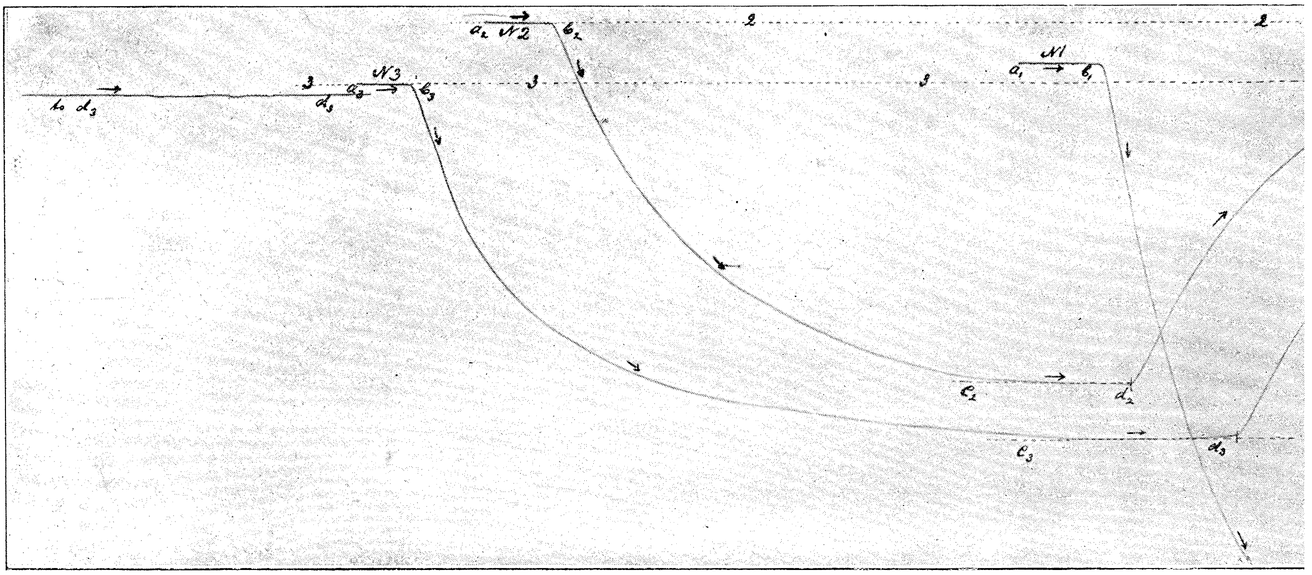
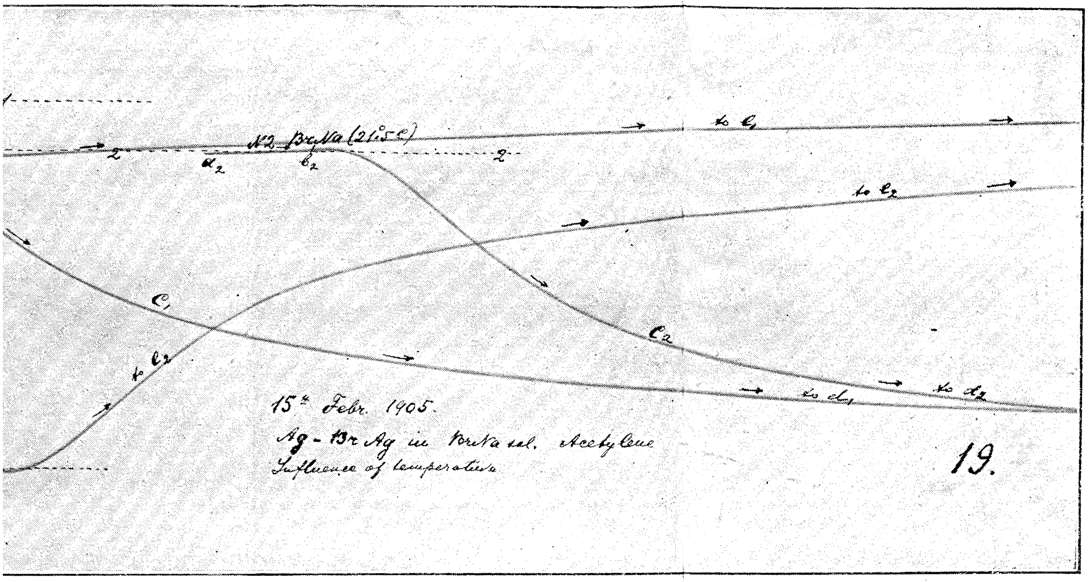


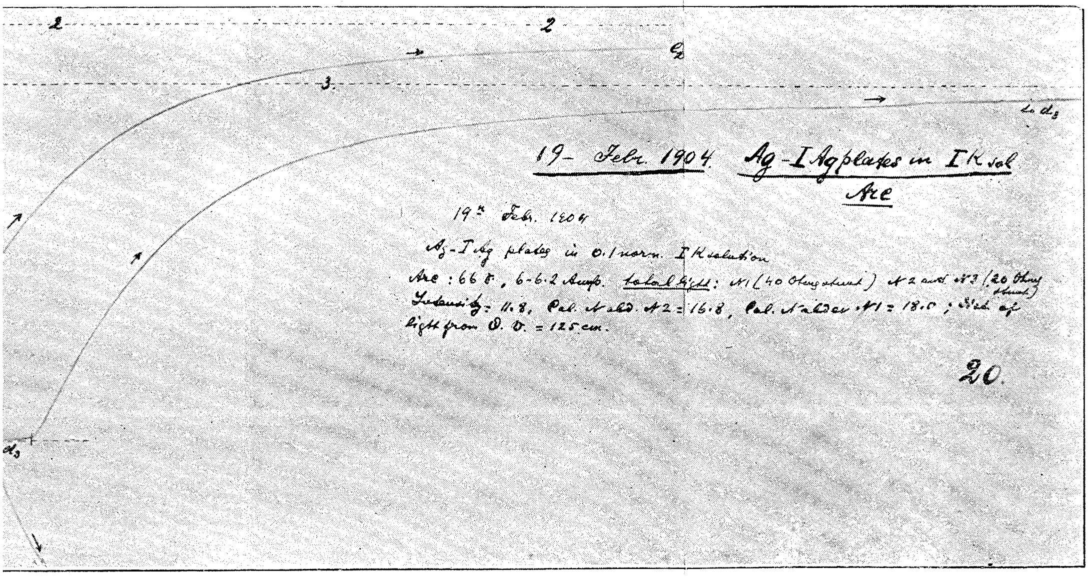
Plate N20.

Plate N21.



15th Febr. 1905.
Ag - Br Ag in BrNa sol. Acetylene
Influence of temperature

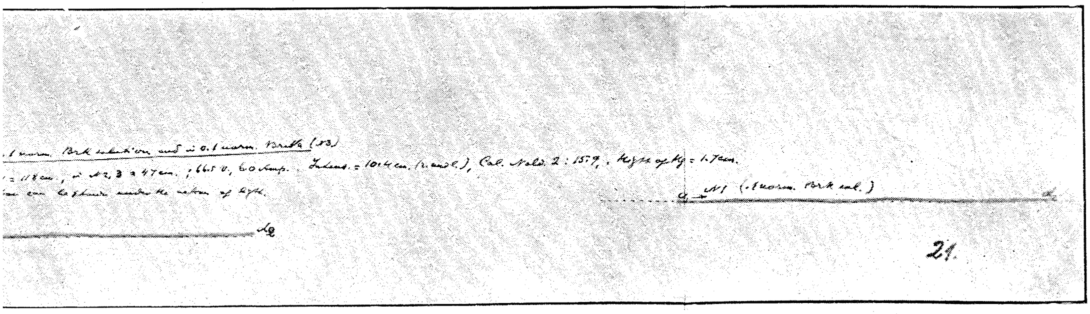
19.



19 - Febr. 1904. Ag - I Agplates in I K sol
Arc

19th Febr. 1904
Ag - I Ag plates in 0.1 norm. I K solution
Arc : 66.8, 6-6.2 Amp. total light: N1 (40 Ohm shunt) N2 and N3 (20 Ohm shunt)
Intensity: 11.8, Cal. Nald. N2 = 16.8, Cal. Nalder N1 = 18.0; dist. of light from O. V. = 125 cm.

20.



.1 norm. BrK solution and in 0.1 norm. BrNa (N3)
= 118 cm., in N2, 3 = 47 cm. ; 66.5 V, 6.0 Amp. Intens. = 10.4 cm. (...), Cal. Nald. 2 : 15.9, Height of Hg = 1.7 cm.
can be shown under the action of light.

21.

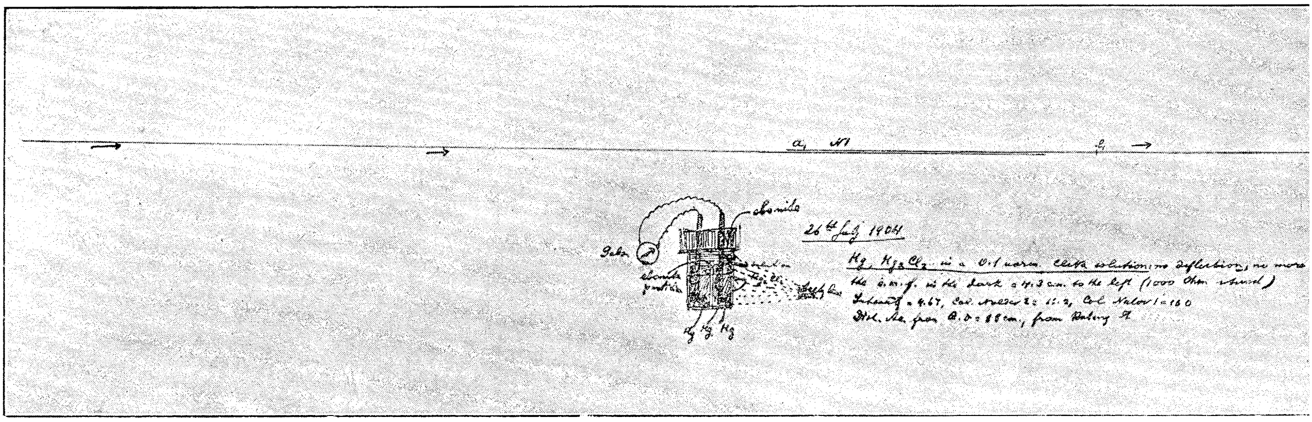


Plate N22.

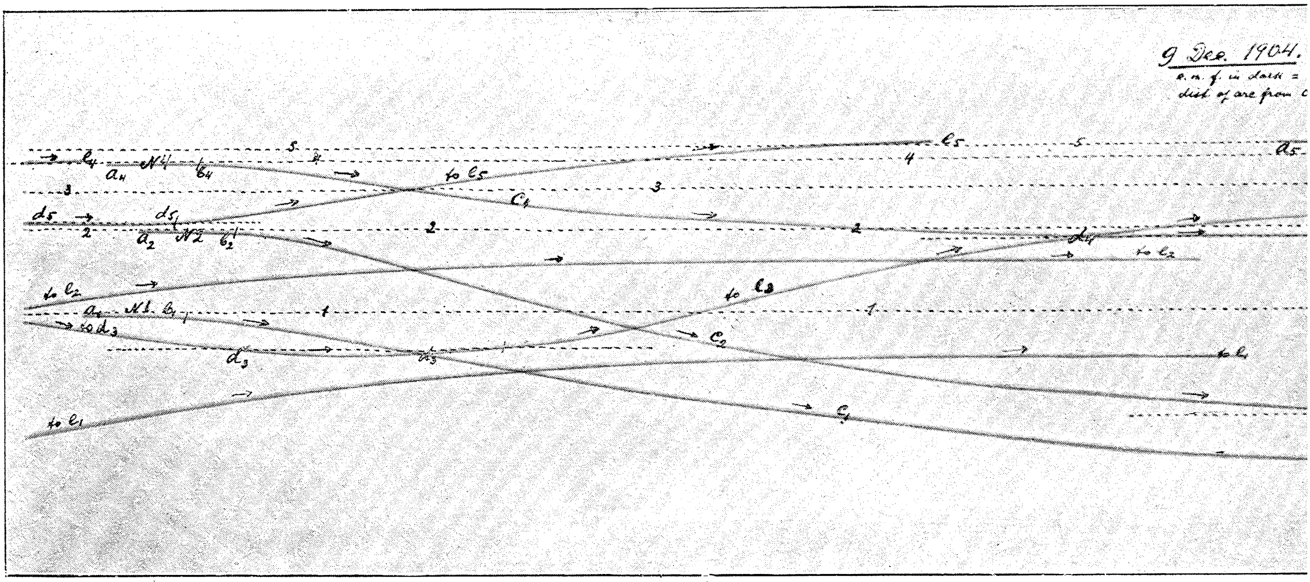


Plate N23.

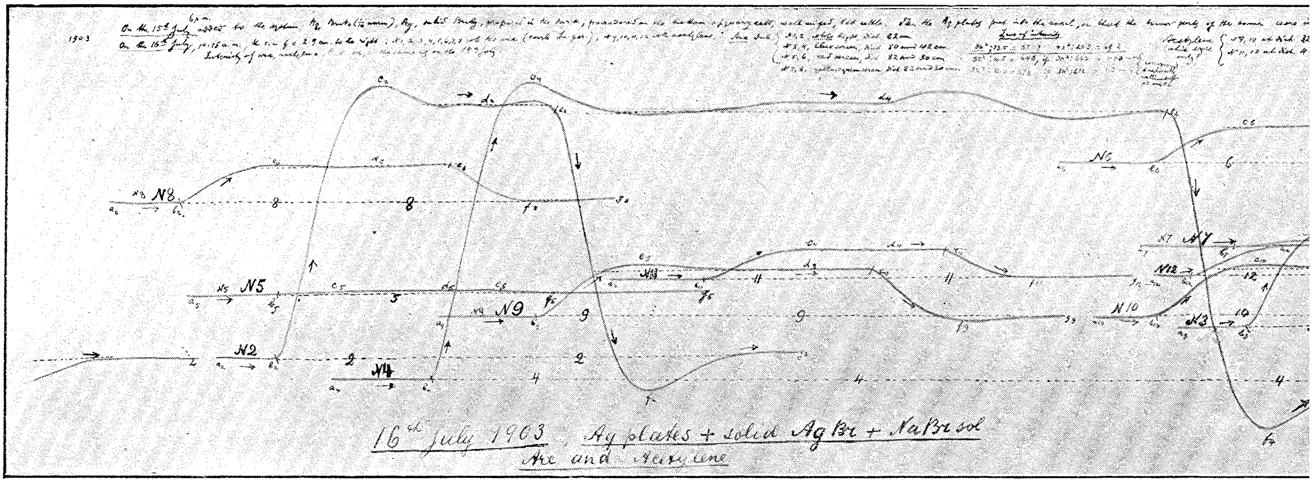
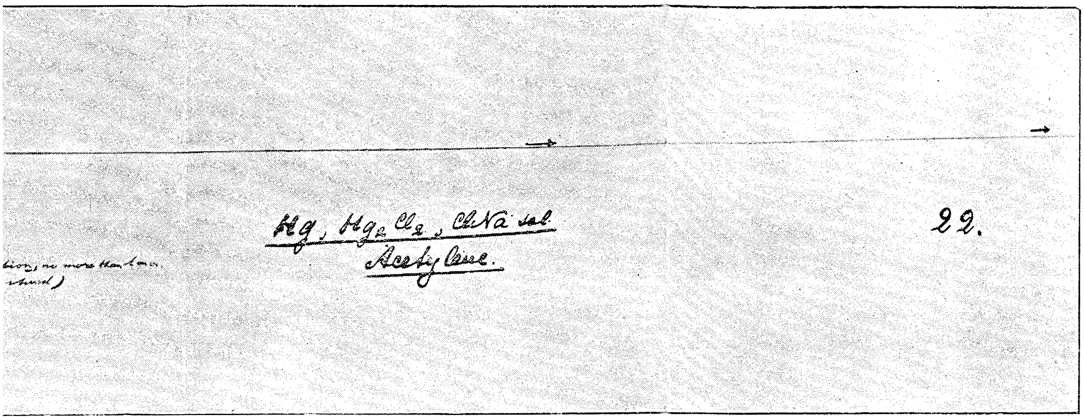
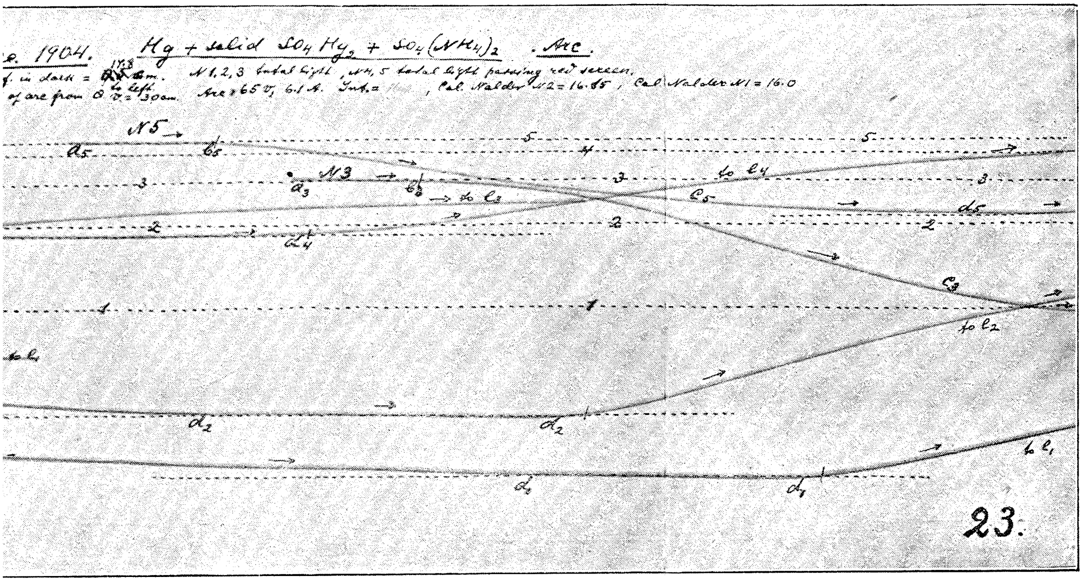
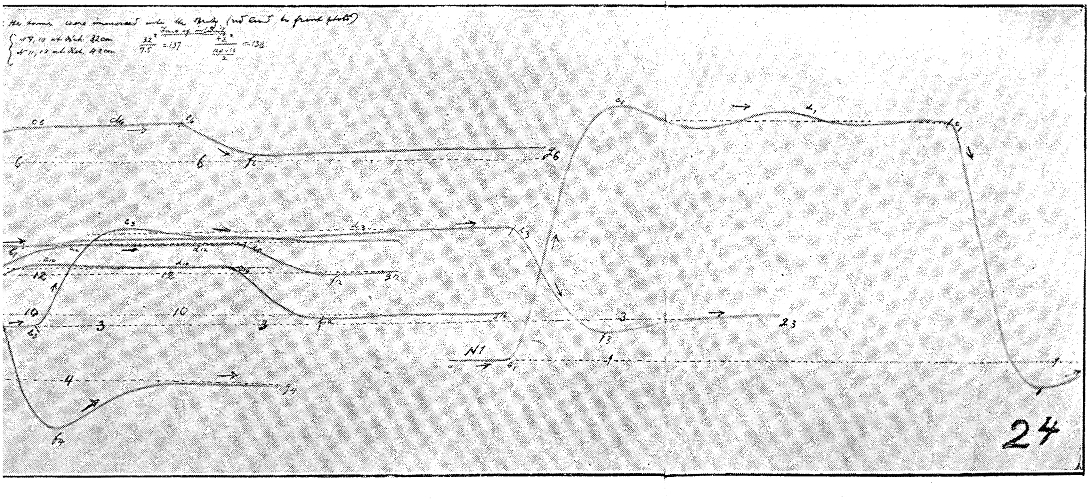


Plate N24.


Hg, Hg2Cl2, ClNa sol.
Acetylene.
22.


1904. Hg + solid SO4Hg2 + SO4(NH4)2 . Arc.
N1, 2, 3 total light, N4, 5 total light passing red screen.
Arc 65 V, 6.1 A. Cal. Nalder N2 = 16.85, Cal. Nalder N1 = 16.0
N5
a5
b5
N3
a3
to e3
to e4
c5
d5
c3
to e2
d2
d1
to e1
23.


32²/7.5 = 137
= 138
N1
24

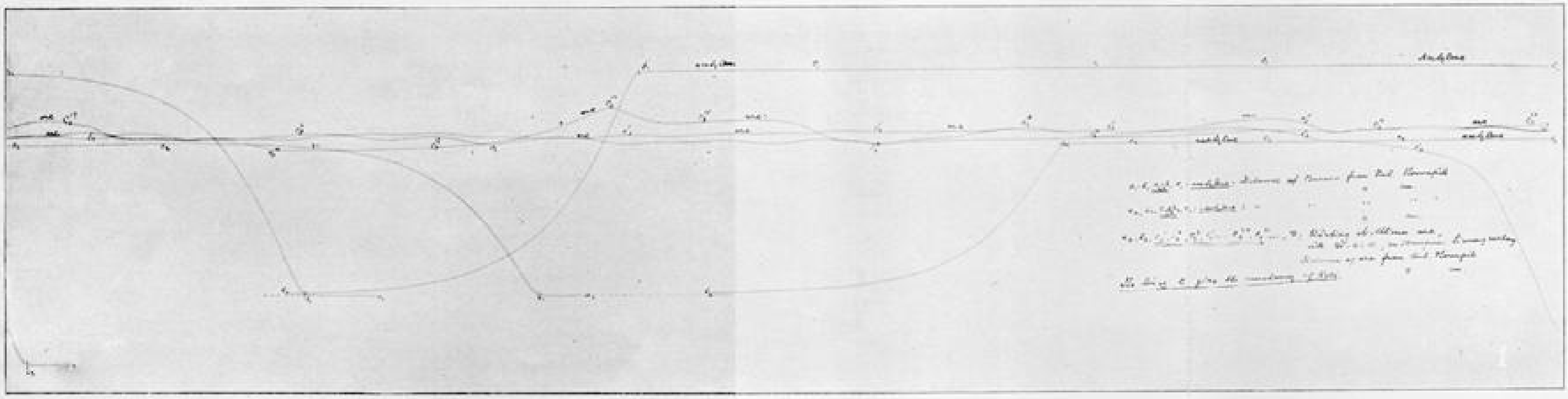


Plate N1.

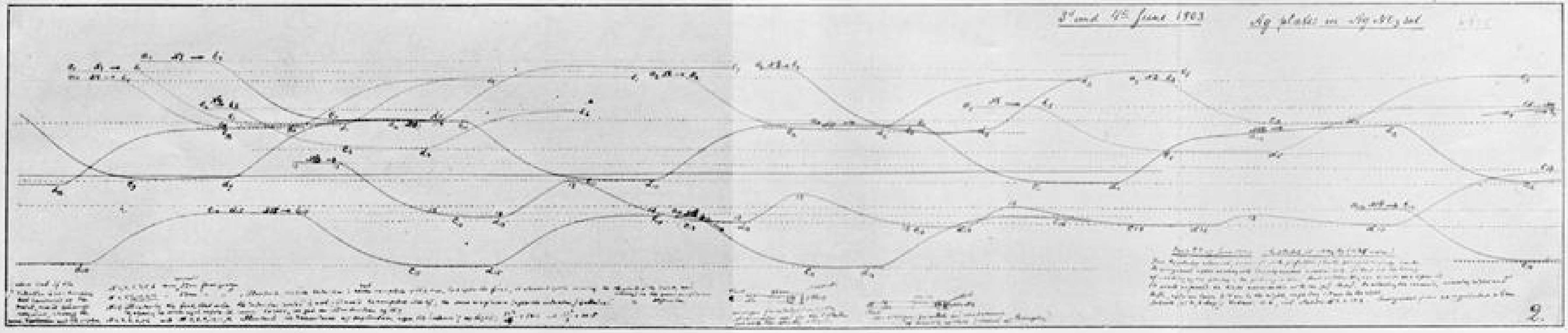


Plate N2.

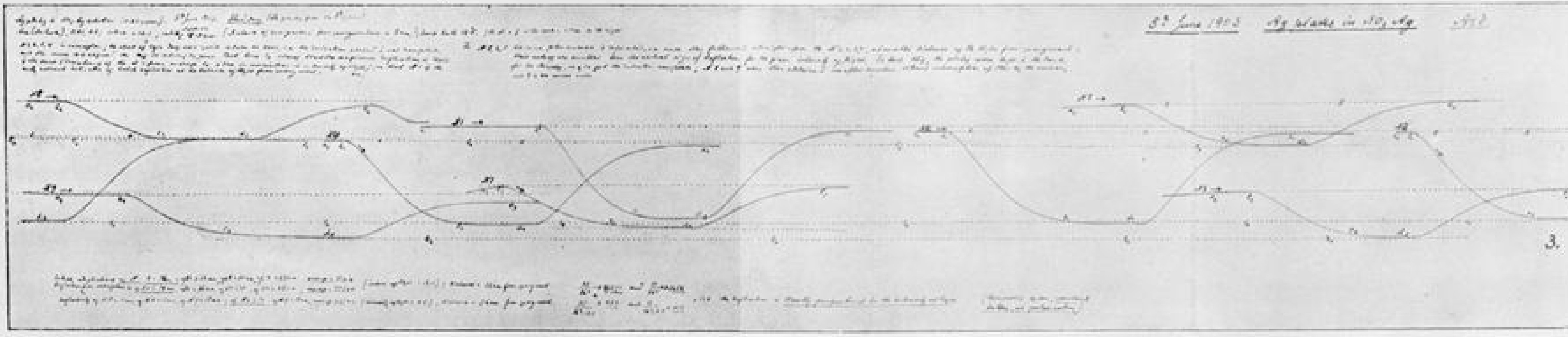


Plate N3.

Meyer Wilderman.

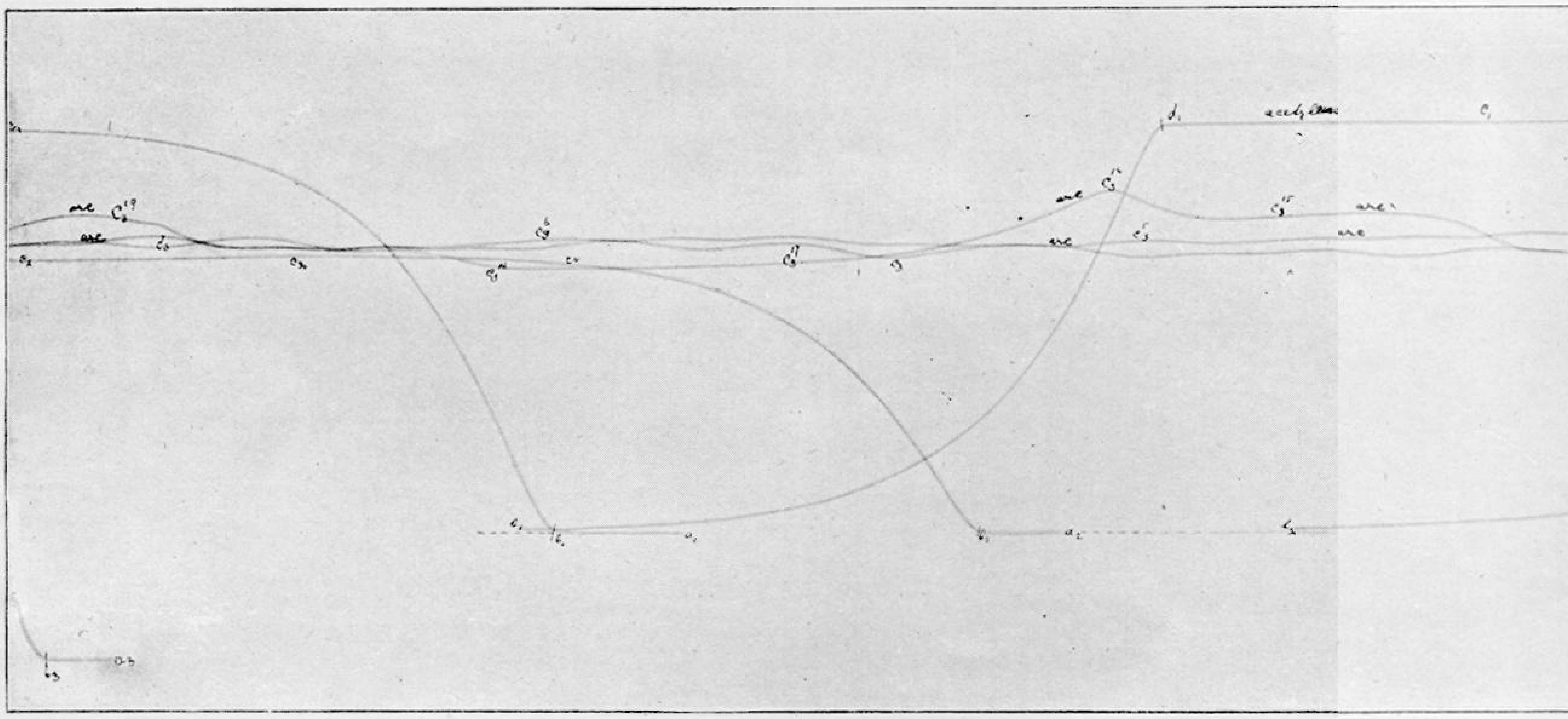


Plate N1.

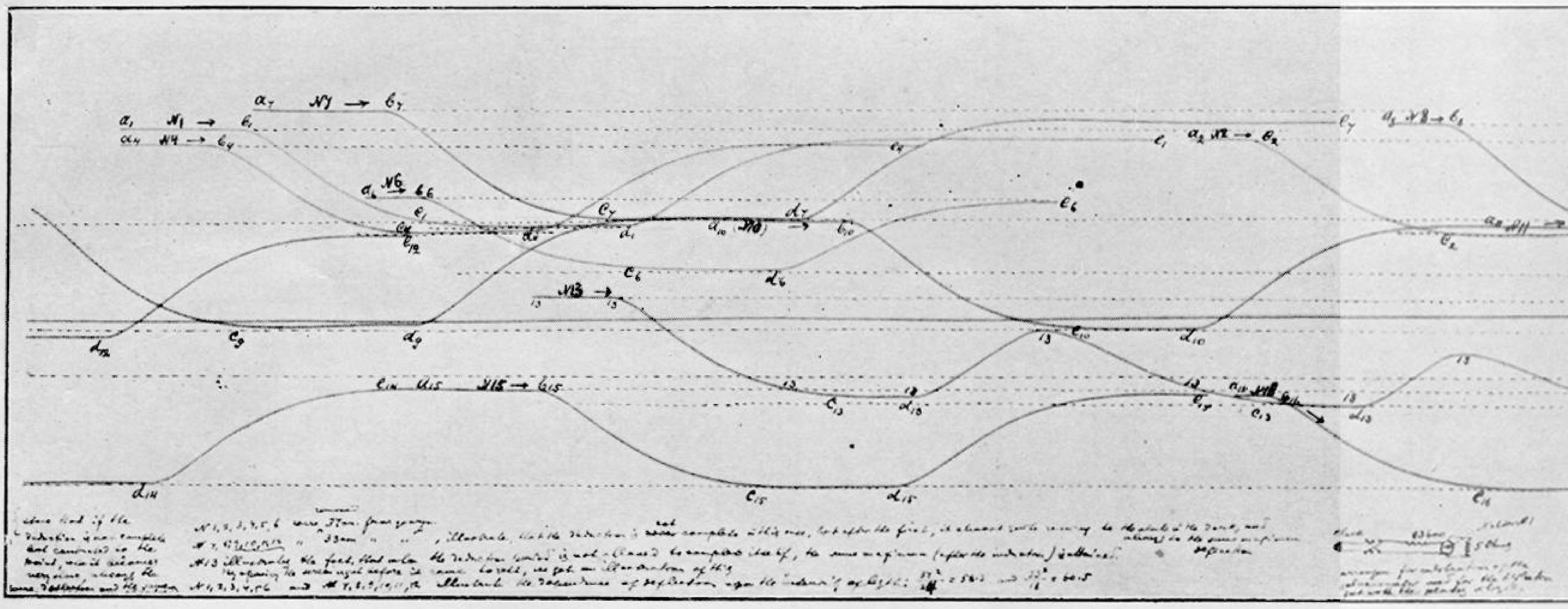
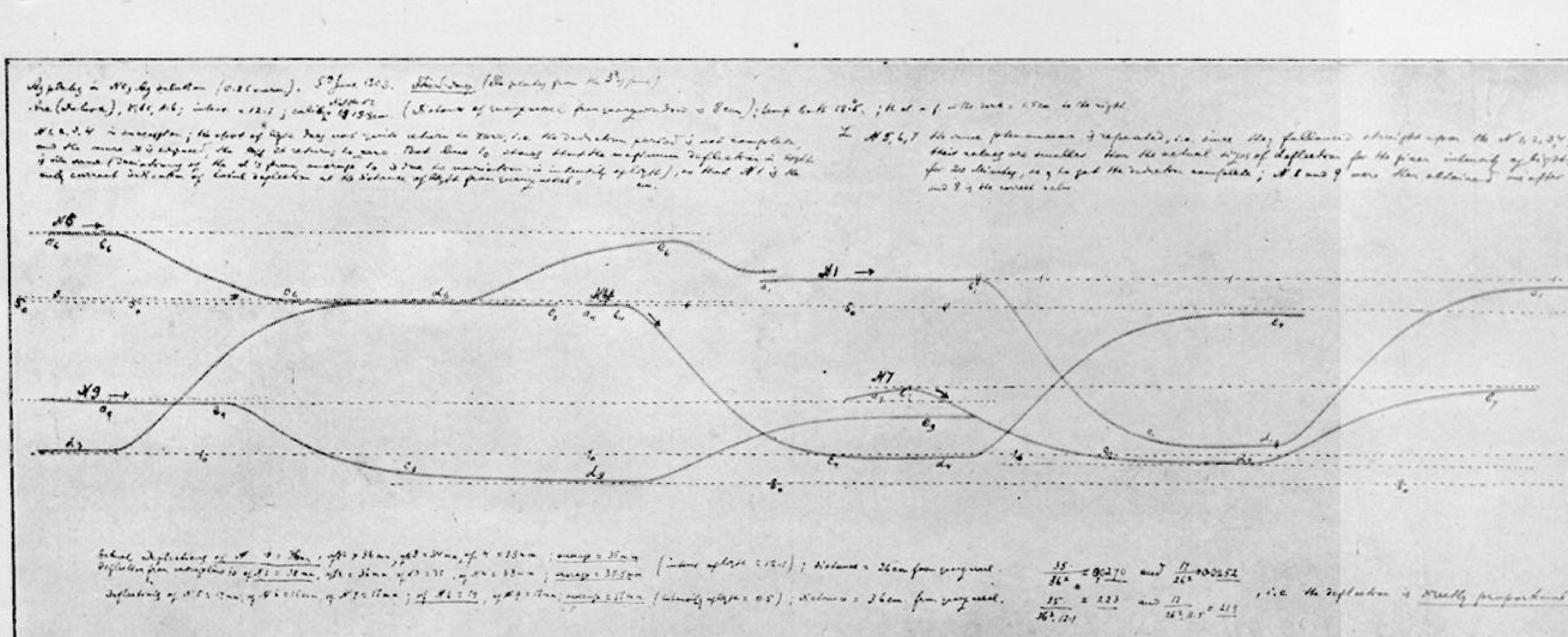
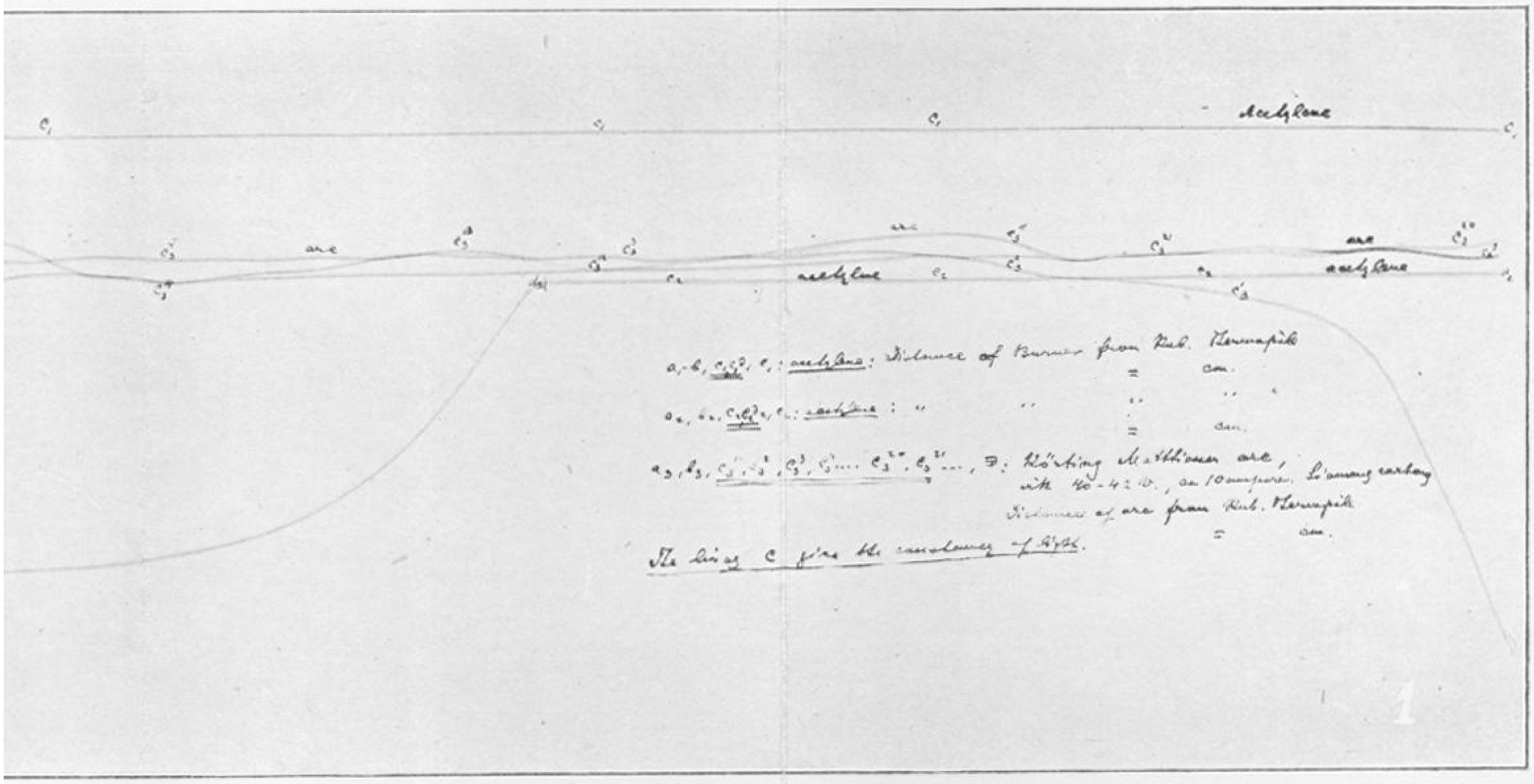
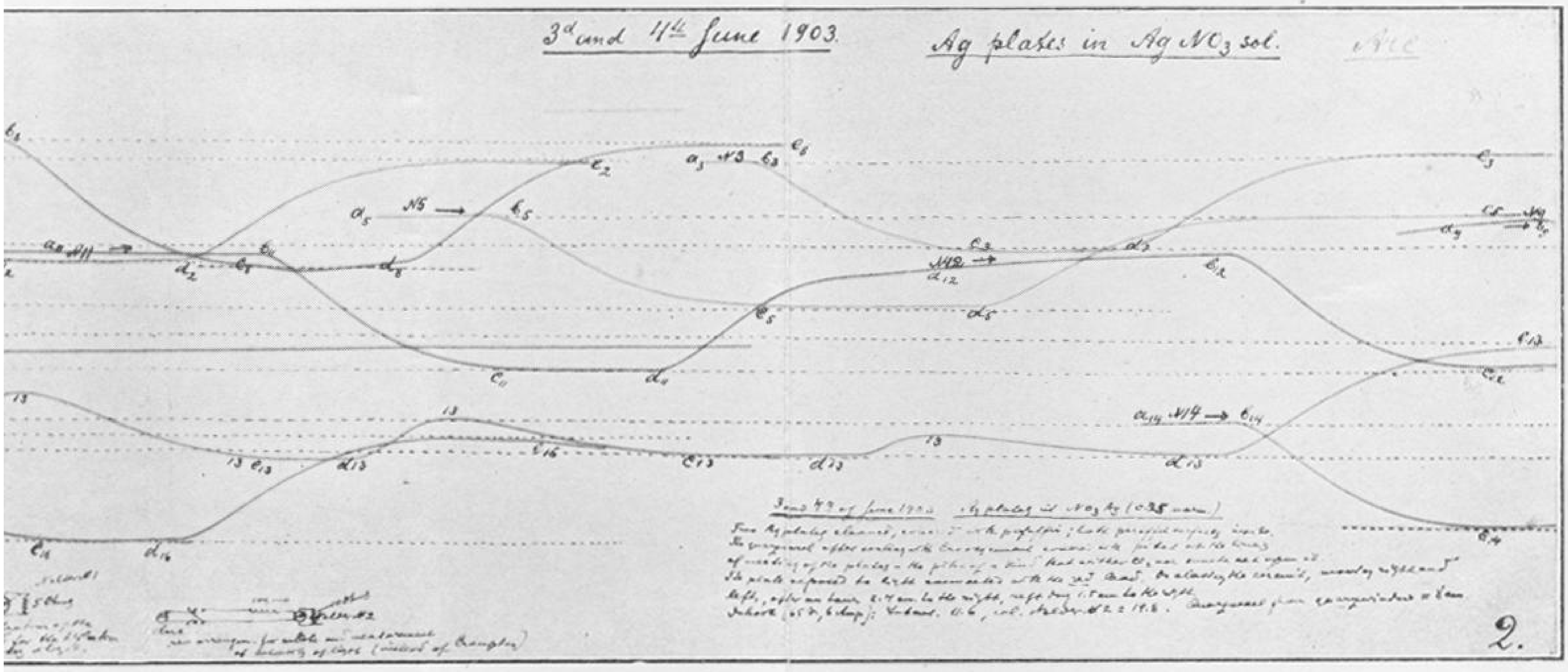


Plate N2.

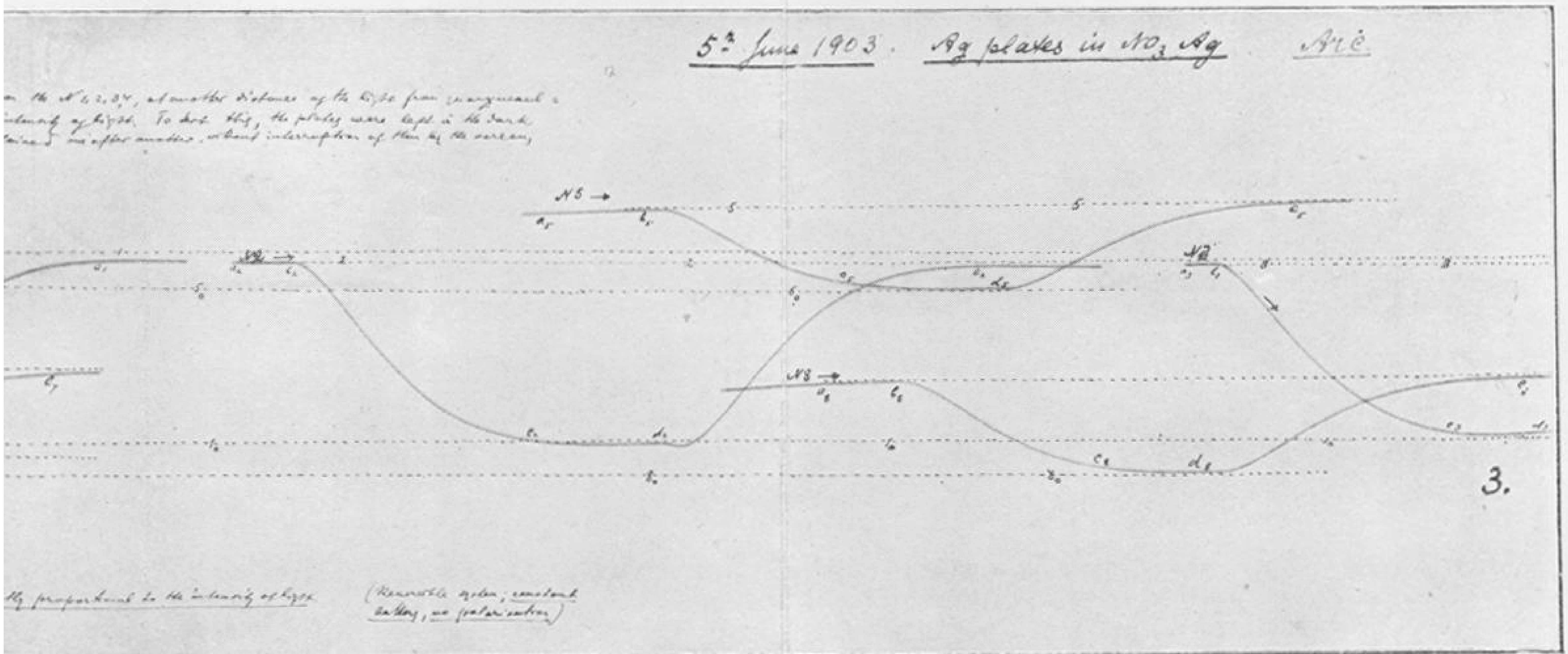


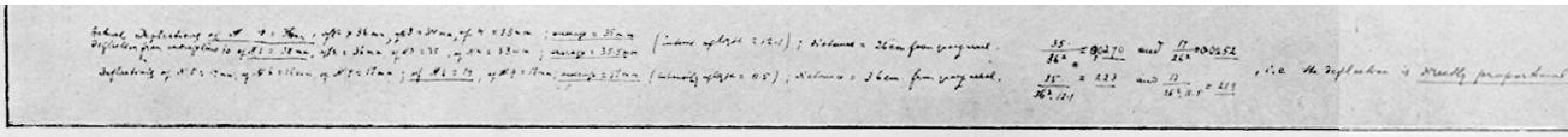

Acetylene
arc
acetylene
Distance of Burner from Rub. Thermopile
Körting Matthiessen arc, with 40-42 V., ca 10 amperes. Siemens carbons
Distance of arc from Rub. Thermopile
The lines c give the constancy of light.
1

N1.


3d and 4th June 1903.
Ag plates in Ag NO3 sol.
Arc
2.

N2.


5th June 1903.
Ag plates in NO3 Ag
Arc
3.



Actual deflections of [illegible] = 35mm; of [illegible] = 36mm, of [illegible] = 34mm, of [illegible] = 33mm; average = 35mm (intensity of light = 12.1); distance = 26cm from zero-point. $\frac{35}{26^2} = 0.0270$ and $\frac{17}{26^2} = 0.0252$

Deflection from [illegible] = 38mm, of [illegible] = 36mm, of [illegible] = 35, of [illegible] = 33mm; average = 35.5mm

Deflections of [illegible] = 17mm, of [illegible] = 17mm; of [illegible] = 19, of [illegible] = 17mm; average = 17mm (intensity of light = 5.5); distance = 26cm from zero-point. $\frac{35}{26^2 \cdot 12.1} = 223$ and $\frac{17}{26^2 \cdot 5.5} = 219$, i.e. the deflection is directly proportional

Plate N3.

ly proportional to the intensity of light

(Reversible system; constant battery, no polarisation)

N3.

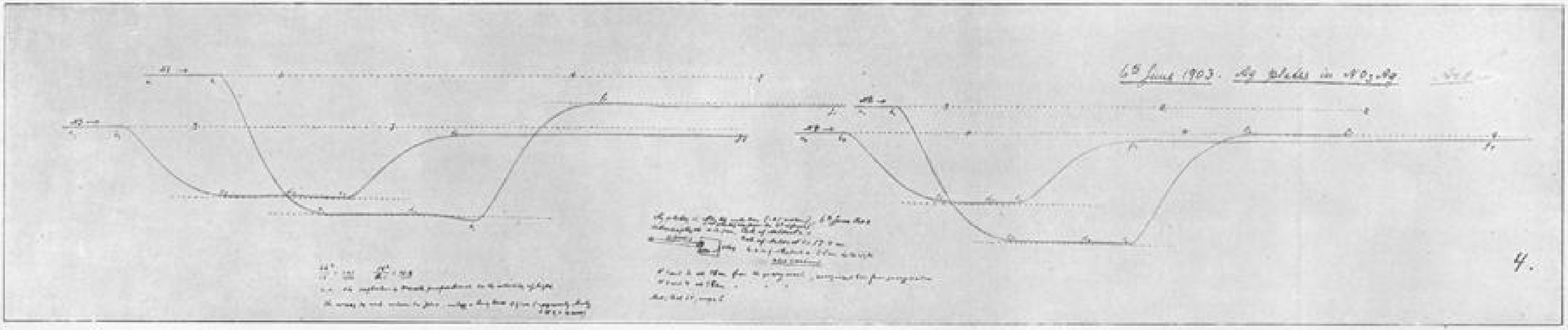


Plate N4.

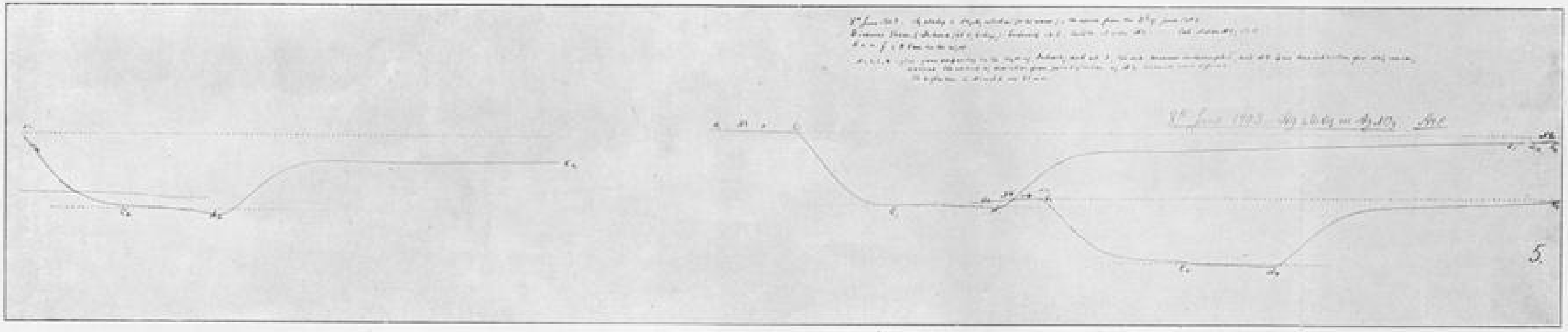


Plate N5.

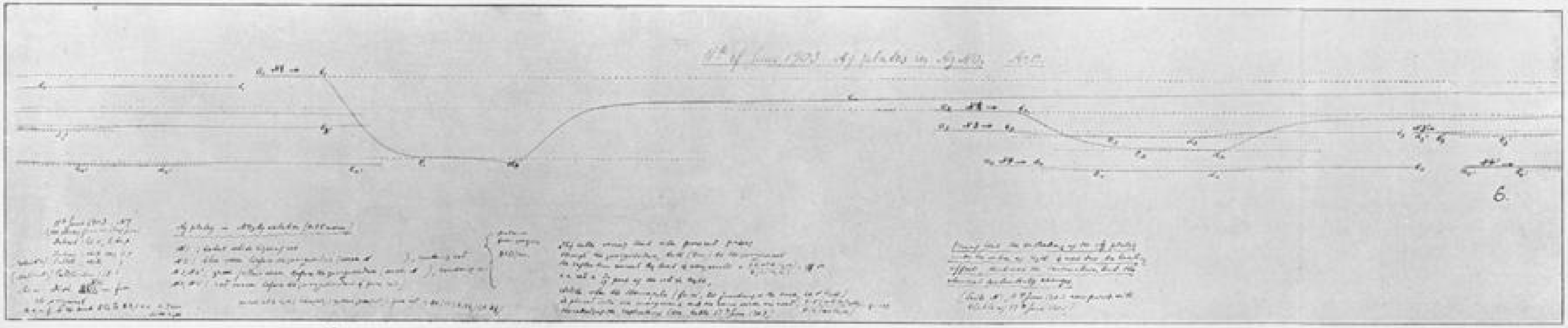


Plate N6.

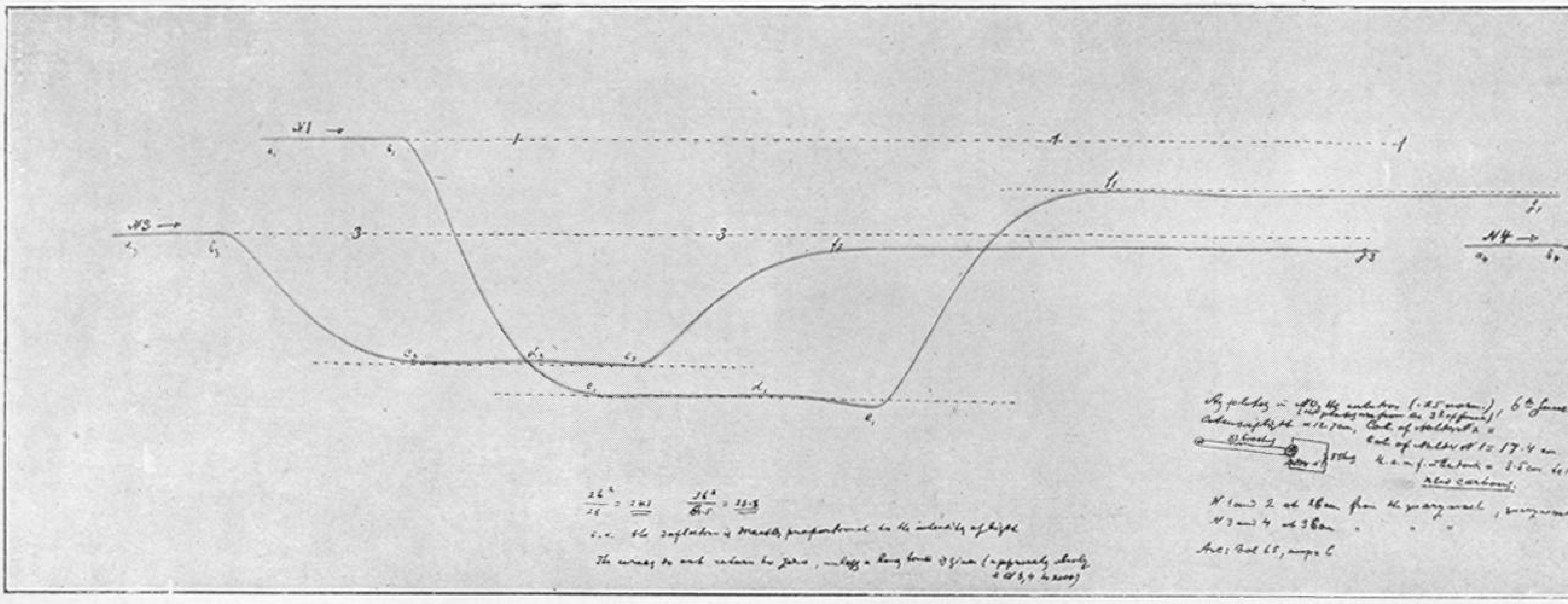


Plate N4.

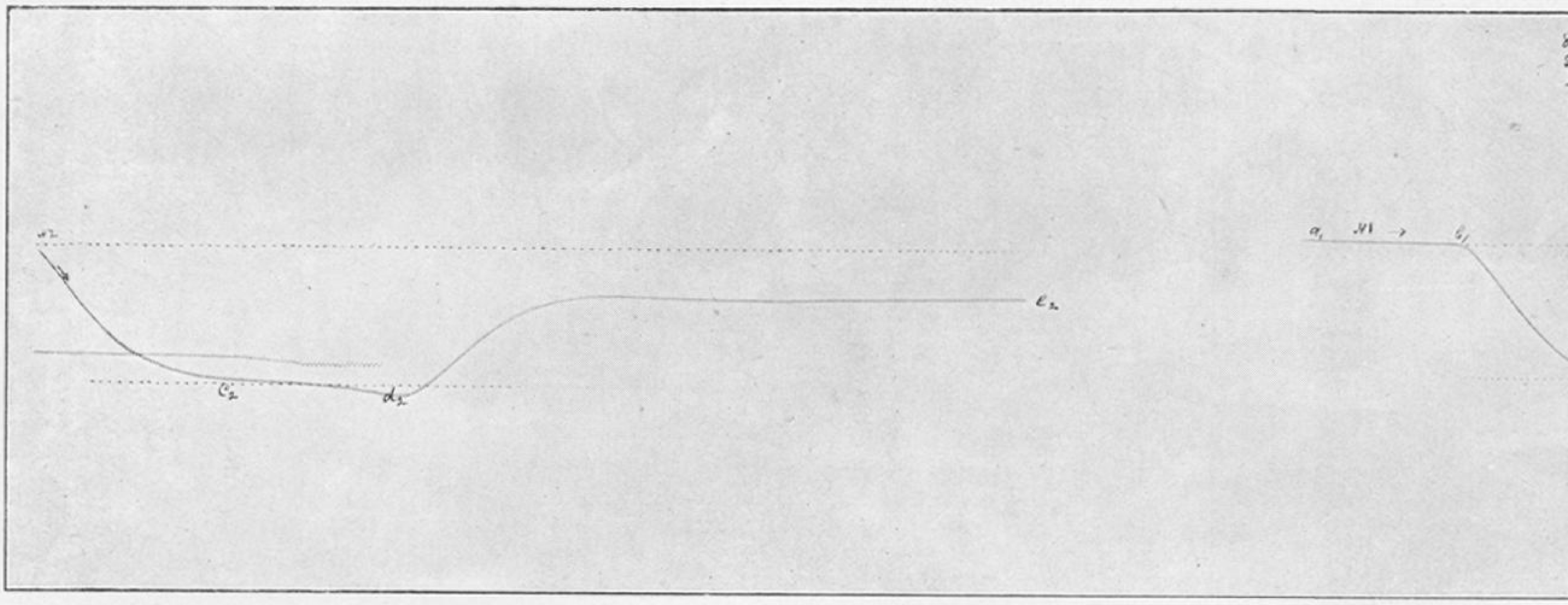


Plate N5.

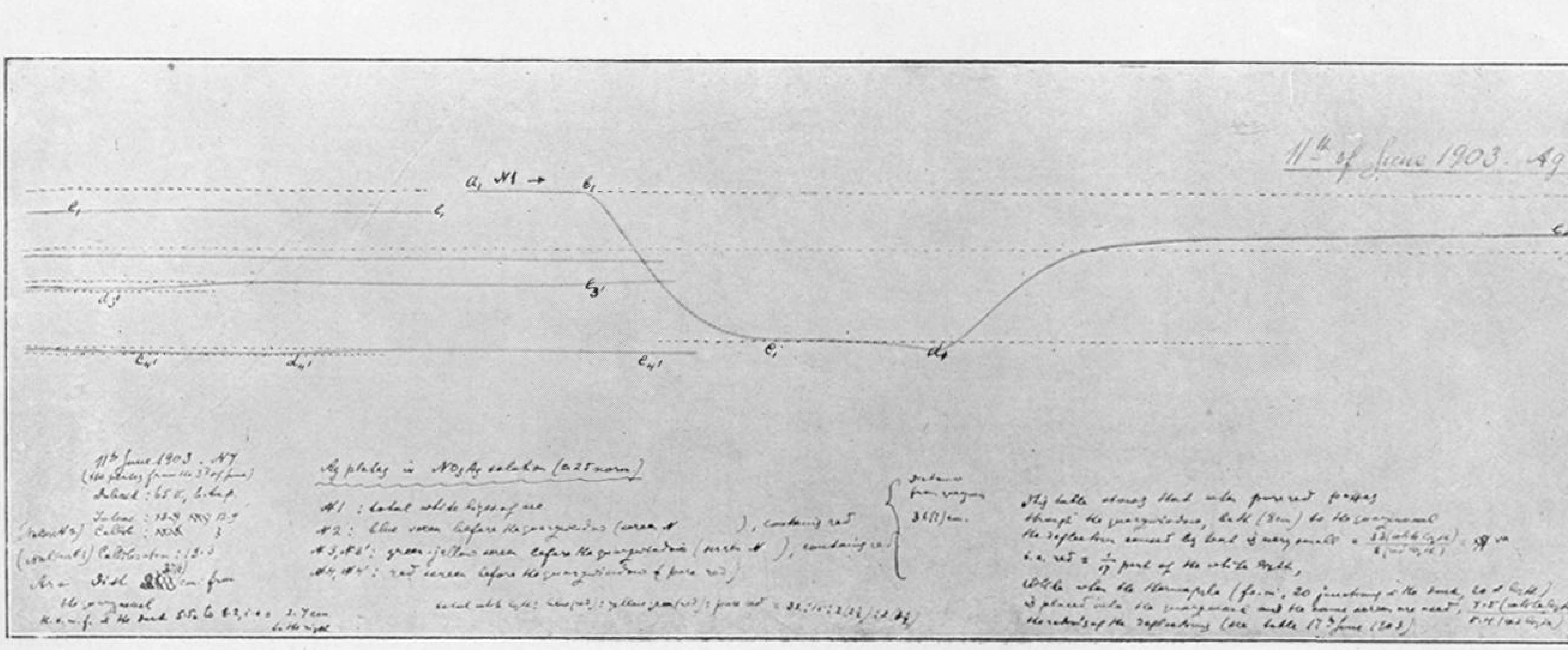
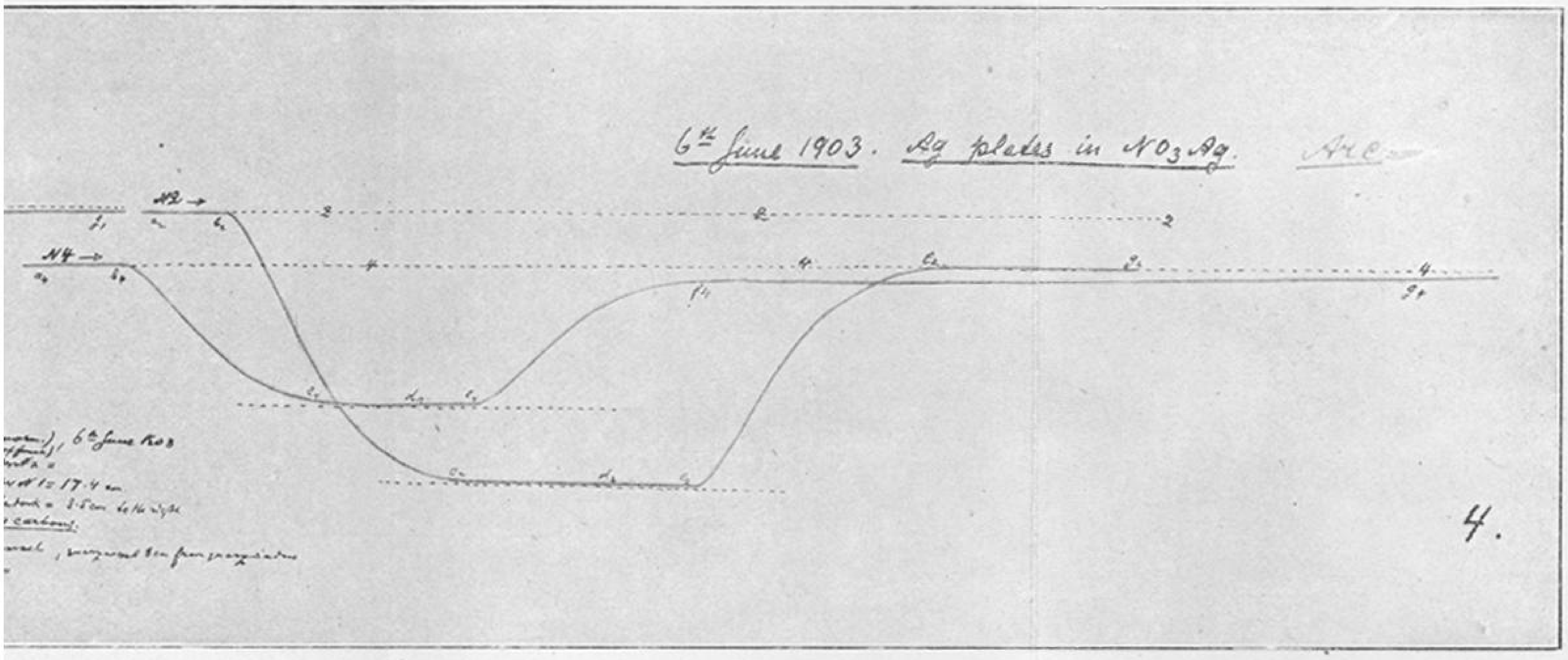
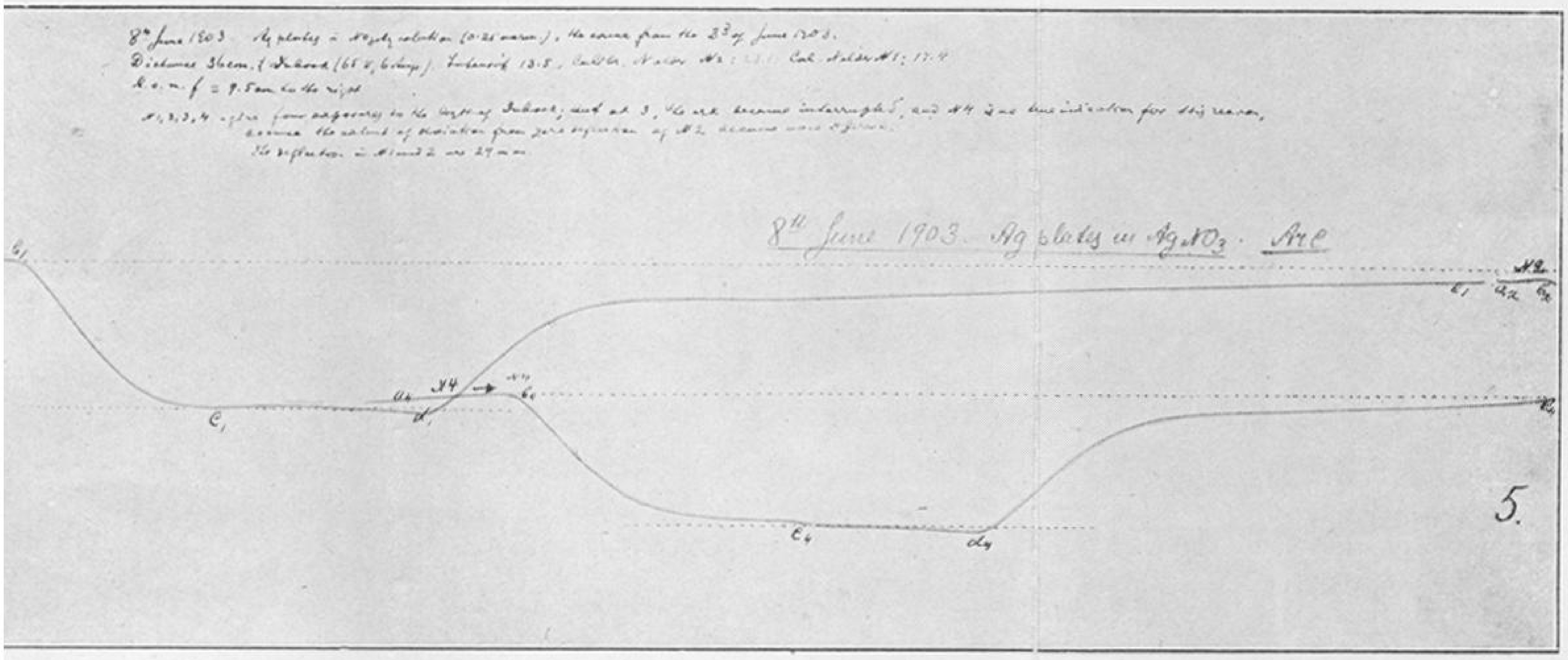


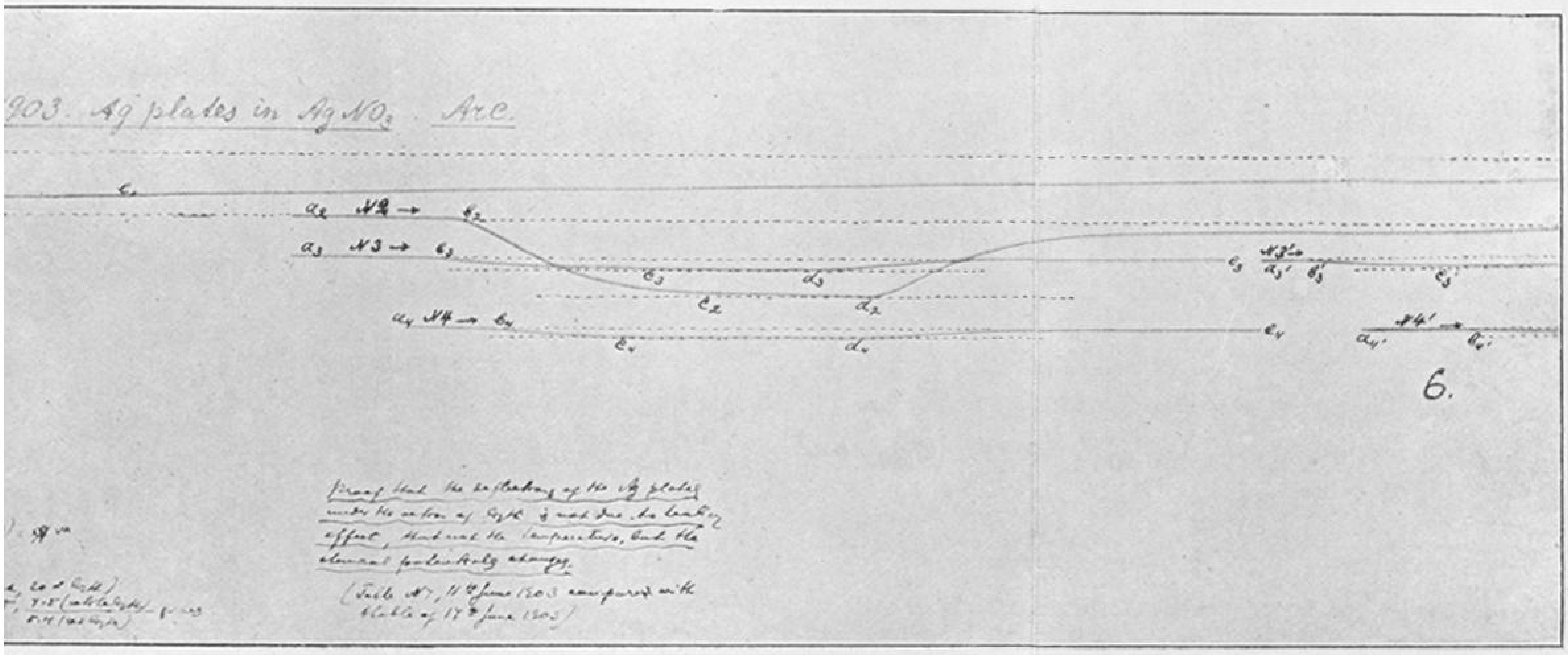
Plate N6.


6th June 1903. Ag plates in NO3Ag. Arc
N2 →
N4 →
2
4
4.
6th June 1903
N1 = 17.4 cm
3.5 cm to the right
carbons

N4.


8th June 1903. Ag plates in NO3Ag solution (0.25 norm.), the same from the 3rd of June 1903.
Distance 3 cm.; Dubois (65 V, 6 days). Laboratory 13.5, Cal. Holder N2: 23.1 Cal. Holder N1: 17.4
E.m.f = 9.5 cm to the right
N1, 2, 3, 4 after four exposures to the light of Dubois; but at 3, the arc became interrupted, and N4 gives the indication for this reason, because the extent of deviation from zero deflection of N2 became more 5 [?]
The deflection in N1 and 2 was 29 mm
8th June 1903. Ag plates in AgNO3. Arc
N4 →
N2
5.

N5.


1903. Ag plates in AgNO3. Arc.
N2 →
N3 →
N4 →
N3' →
N4' →
6.
Proof that the deflections of the Ag plates under the action of light is not due to heating effect, that was the temperature, and the element practically changing.
(Table N7, 11th June 1903 compared with table of 17th June 1903)

N6.

Plate N6.

N6.

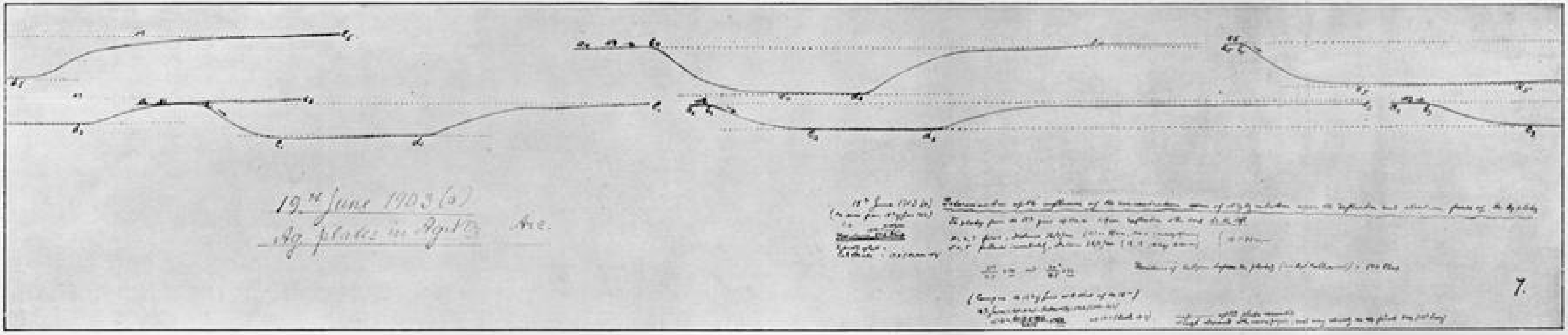


Plate N7.

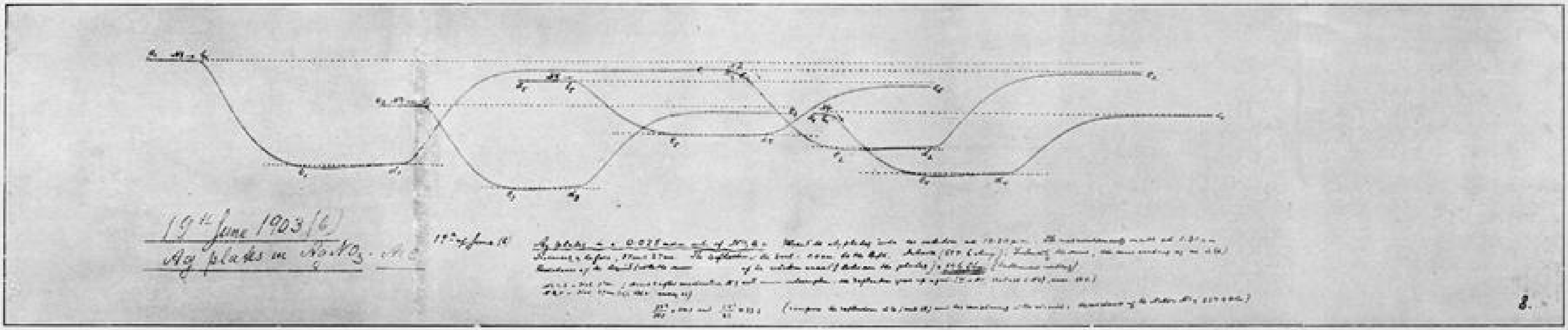


Plate N8.

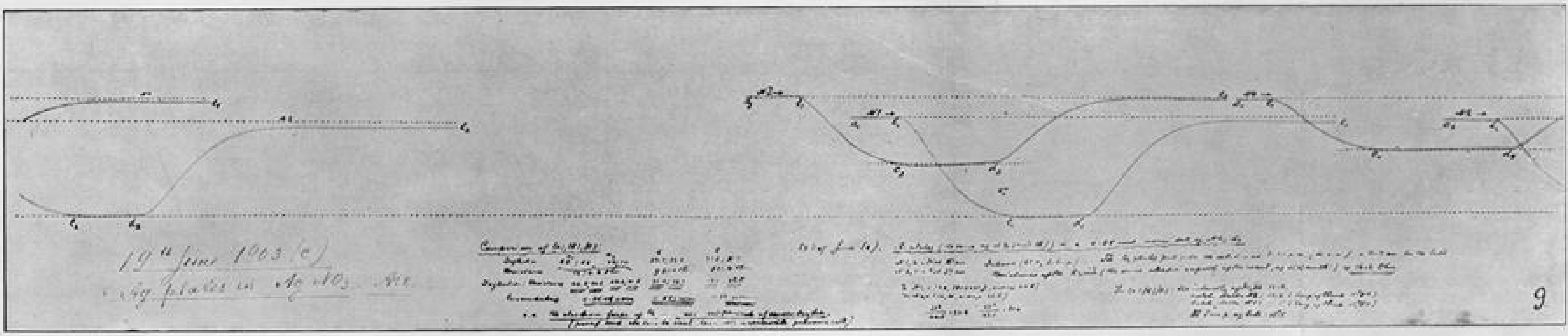
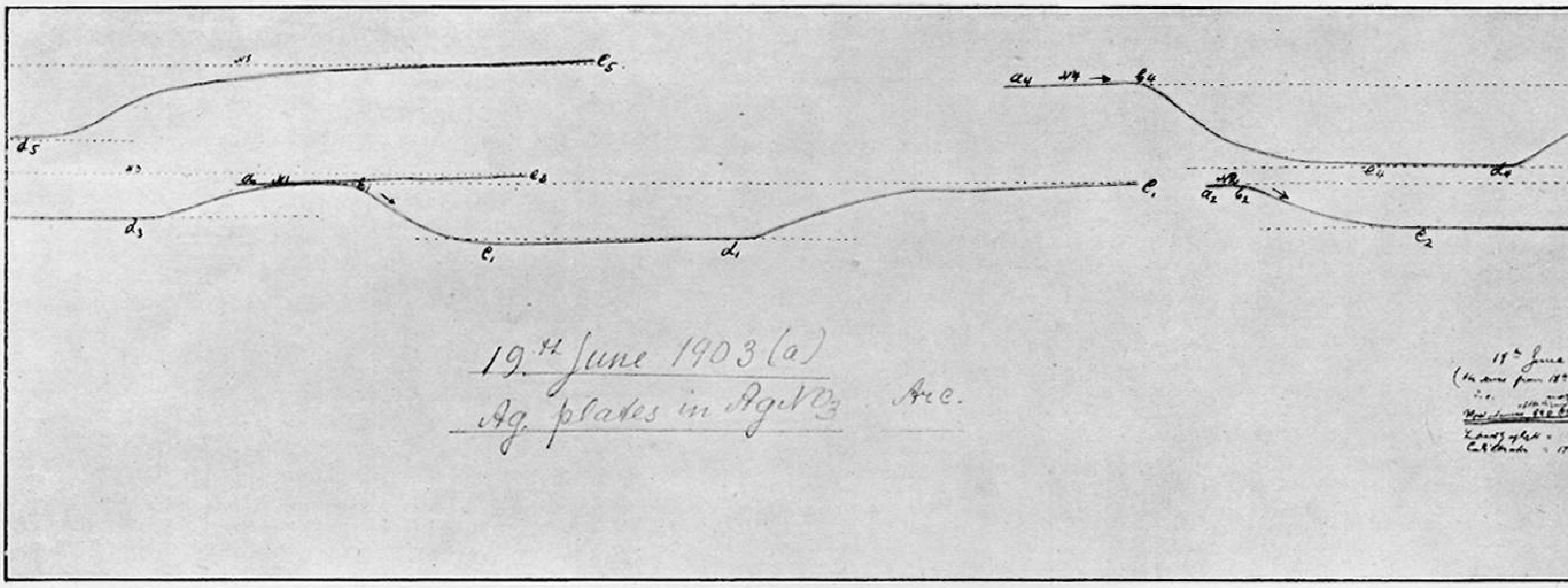
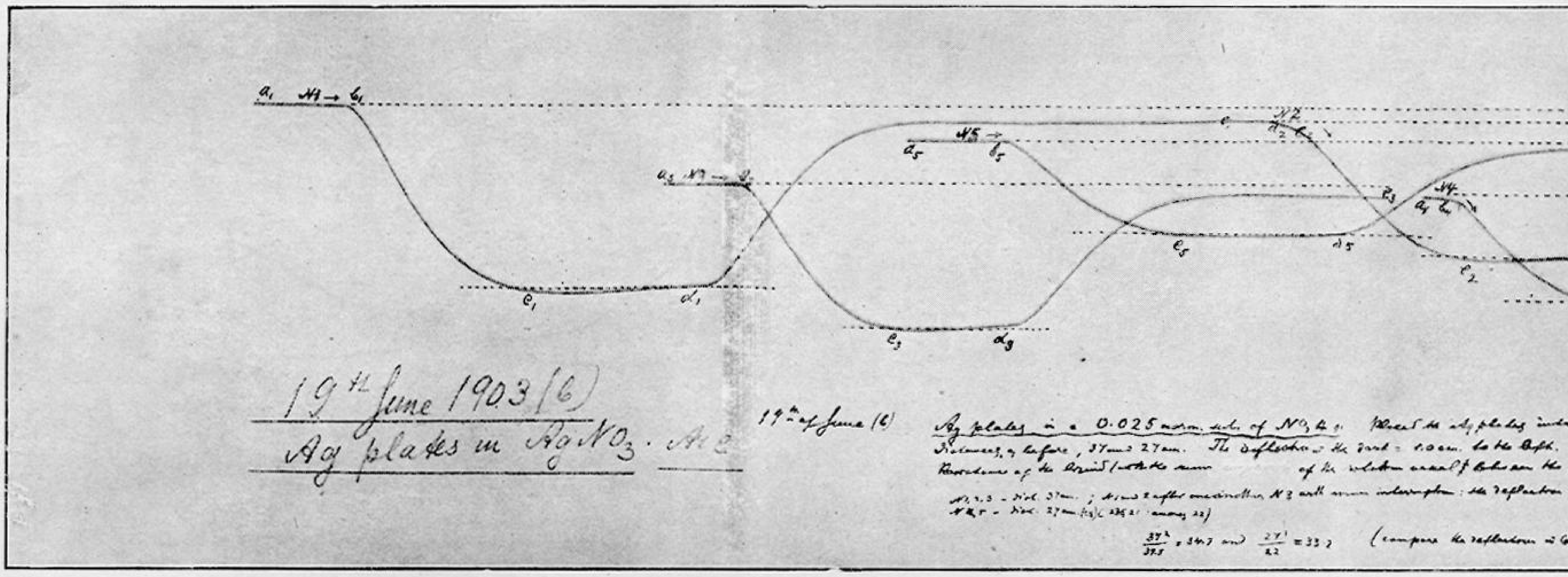


Plate N9.



19th June 1903 (a)
Ag plates in AgNO3. Arc.

Plate N7.

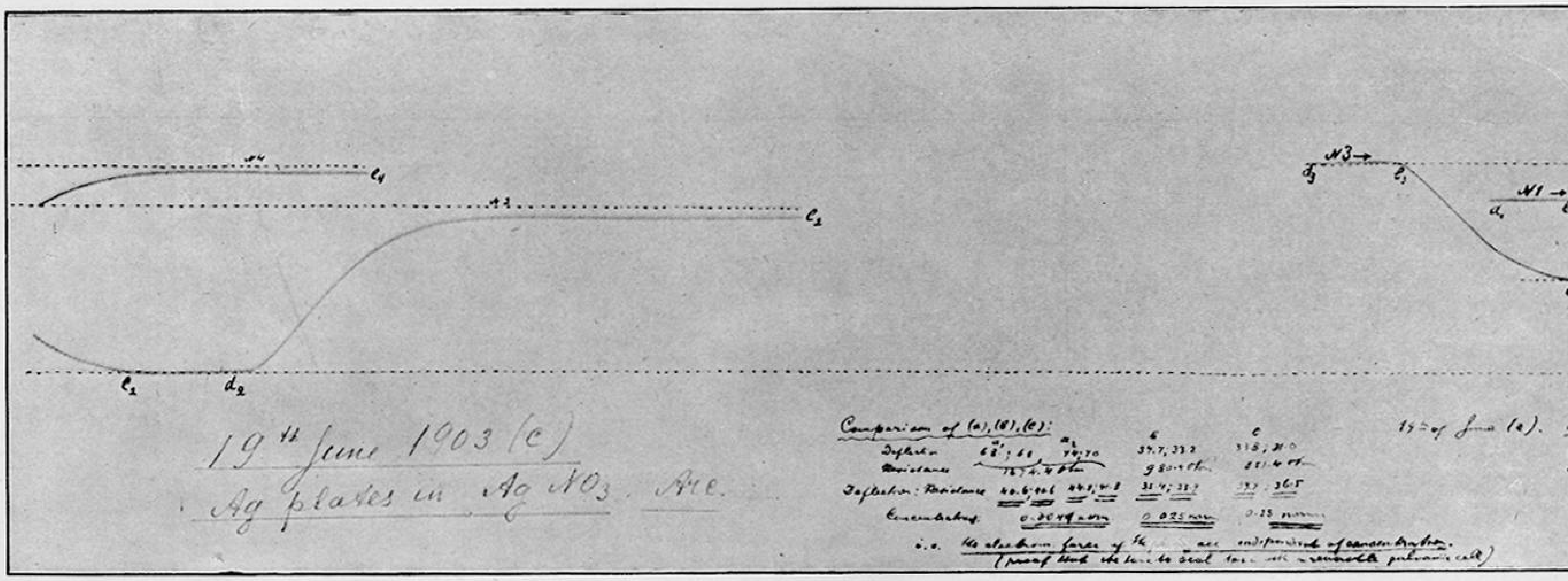


19th June 1903 (b)
Ag plates in AgNO3. Arc.

19th of June (b)

Ag plates in a 0.025 norm. soln. of NO3 Ag. Placed the ag plates [illegible]
Distances, as before, 37 and 27 mm. The deflection in the [illegible] = 1.0 cm. to the left.
Resistance of the liquid (with the same [illegible] of the solution as all of [illegible]
N1, 2, 3 – dist. 37 mm.; 4 and 5 after [illegible] N3 with [illegible] interruption: the deflection
N4, 5 – dist. 27 mm. (13) (33, 21 among 22)
$\frac{37^2}{37.5} = 34.7$ and $\frac{27^2}{22} = 33.3$ (compare the deflections in

Plate N8.



19th June 1903 (c)
Ag plates in Ag NO3. Arc.

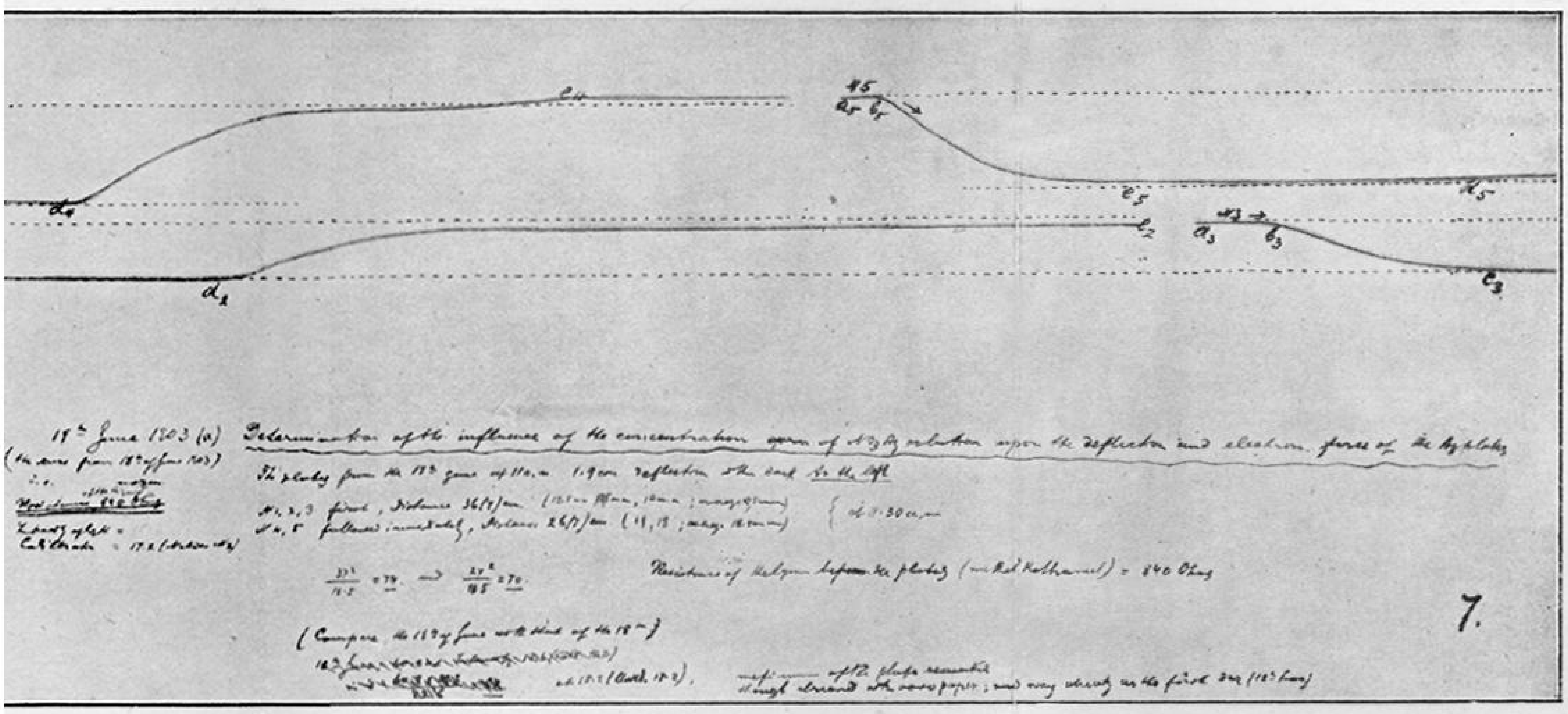
Comparison of (a), (b), (c):

	a	a1	b	c
Deflection	68; 66	74; 70	34.7; 33.3	33.5; 31.0
Resistance	1674.4 ohm		980.4 ohm	851.4 ohm
Deflection : Resistance	40.6; [illegible]	44.3; 41.8	35.4; 33.9	39.3; 36.5
Concentration	0.0044 norm		0.025 norm	0.23 norm

i.e. the electromotive forces of the [illegible] are independent of concentration.
(proof that we have to deal here with a reversible galvanic cell)

19th of June (a).

Plate N9.



19th June 1903 (a) (the same from 18th of June 1903)

Determination of the influence of the concentration of NO3Ag solution upon the deflection and electrom. force of the Ag plates

The plates from the 18th June at 11 a.m. 1.9 cm deflection of the dark to the left

N1, 2, 3 first, distance 36(?)cm [illegible] at 3.30 [illegible]

N4, 5 followed immediately, distance 26(?)cm (19, 18; [illegible])

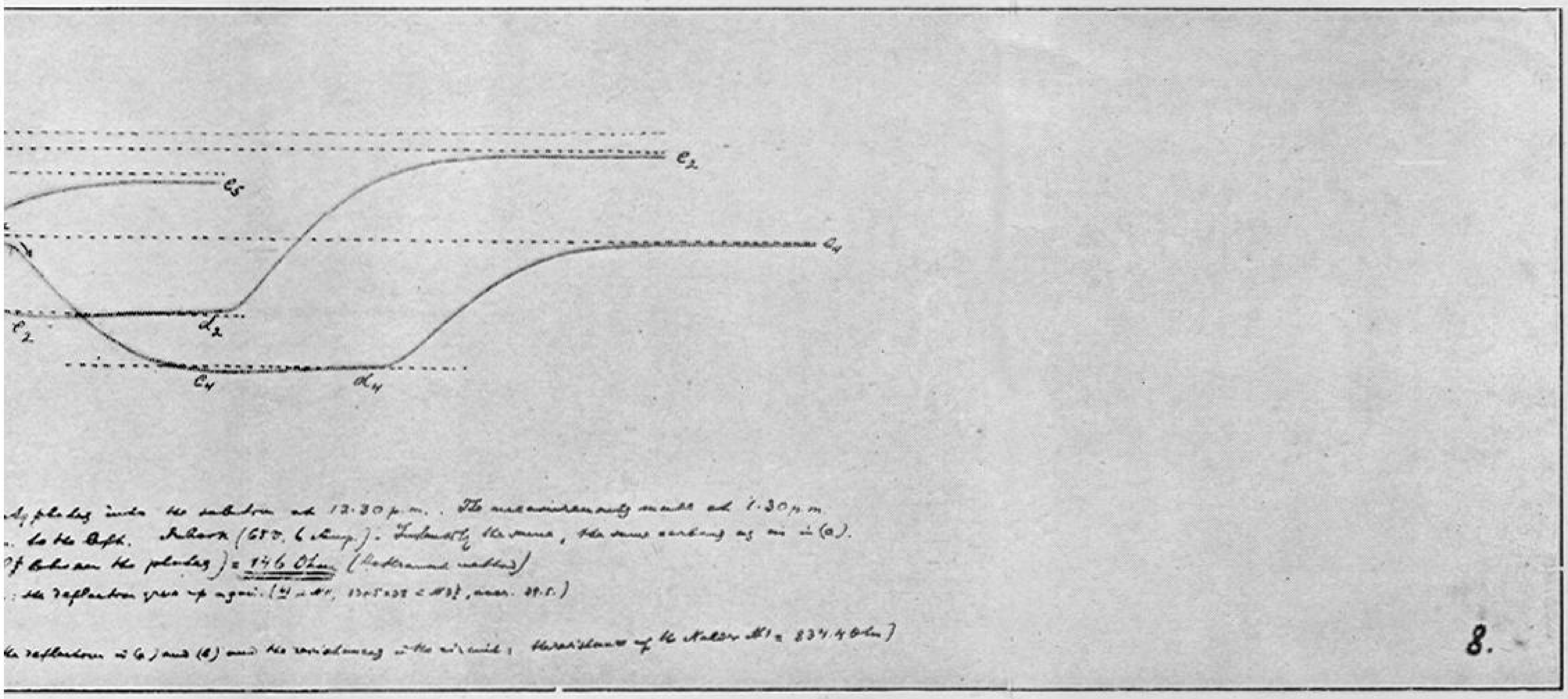
$\frac{37^2}{18.5} = 74$ and $\frac{27^2}{10.5} = 70$

Resistance of the Ag between the plates ([illegible] Kohlrausch) = 840 Ohms

(Compare the 18th of June with that of the 18th)

[illegible]

7.



Ag plates into the solution at 12.30 p.m. The measurements made at 1.30 p.m.

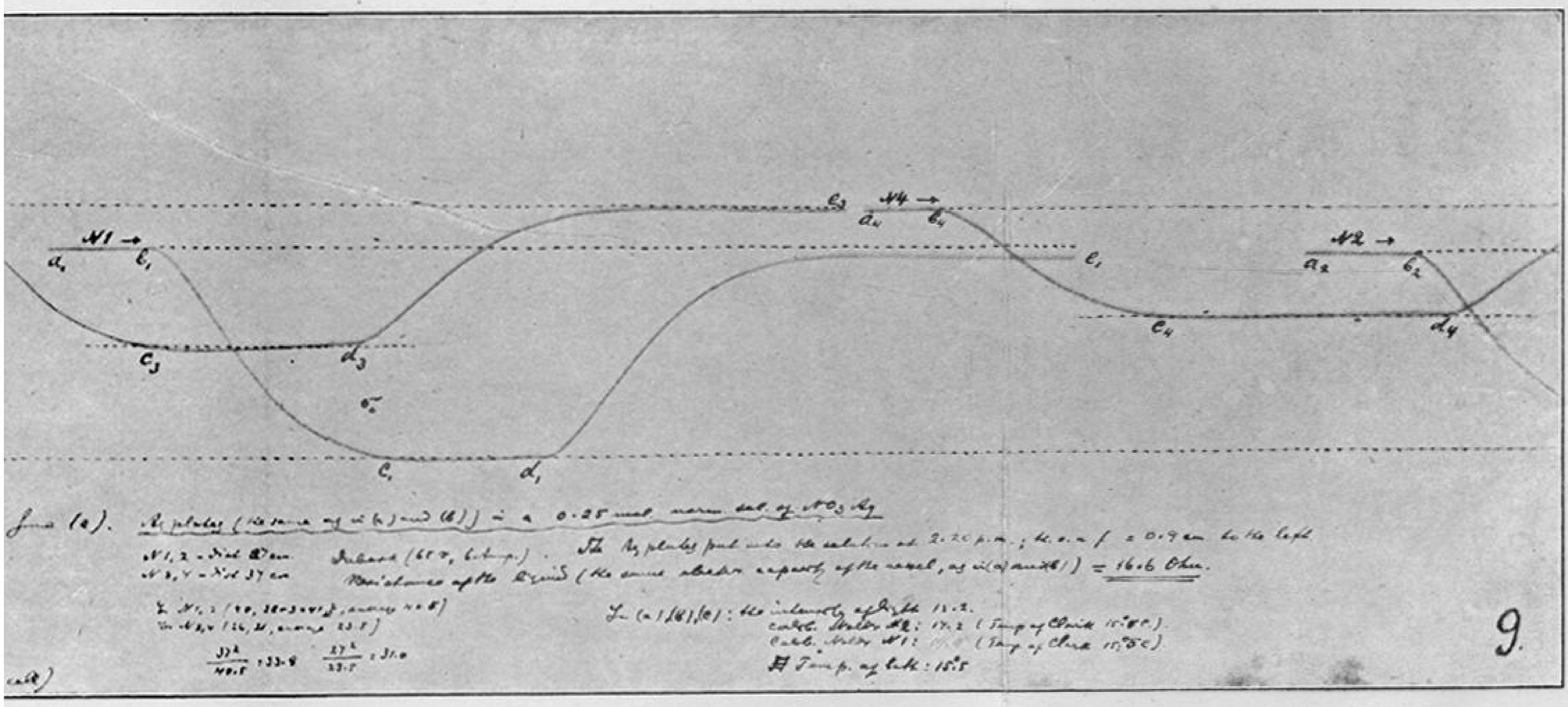
to the left. Daniell (68°, 6 [illegible]). [illegible], the same as in (a).

of between the plates) = 146 Ohm (Kohlrausch method)

: the deflection goes up again. ([illegible])

the deflection in (a) and (b) and the resistance in the circuit; the resistance of the [illegible] N1 = 834.4 Ohm]

8.



June (c). Ag plates (the same as in (a) and (b)) in a 0.25 mol. norm. sol. of NO3Ag

N1, 2 = Dist 40 cm

N3, 4 = Dist 37 cm

Daniell (68°, [illegible]). The Ag plates put into the solution at 2.20 p.m.; [illegible] = 0.9 cm to the left.

Resistance of the liquid (the same electr. capacity of the vessel, as in (a) and (b)) = 16.6 Ohm.

In N1, 2 ([illegible]), average 40.5)

In N3, 4 ([illegible], average 23.5)

$\frac{37^2}{40.5} = 33.8$ $\frac{27^2}{23.5} = 31.0$

In (a) (b) (c): the intensity of light 15.2.

Calib. [illegible] N2: 17.2 (Temp of Clark 15.8° C).

Calib. [illegible] N1: [illegible] (Temp of Clark 15.5° C)

Temp. of bath: 15.5

9.

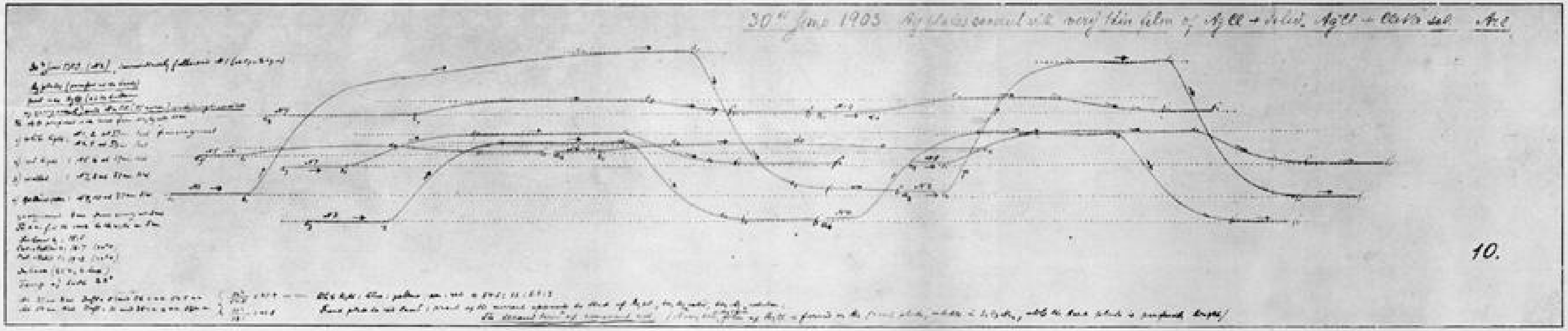


Plate N10.

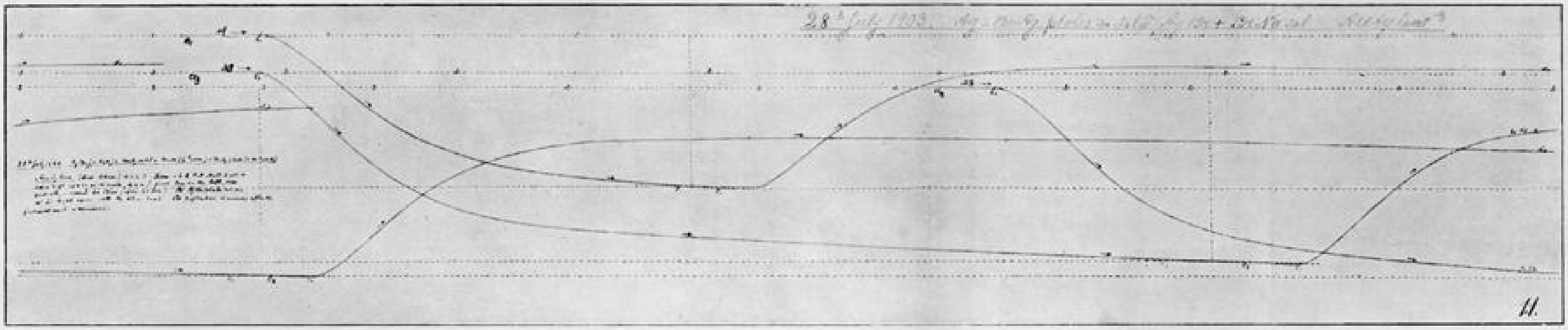


Plate N11.

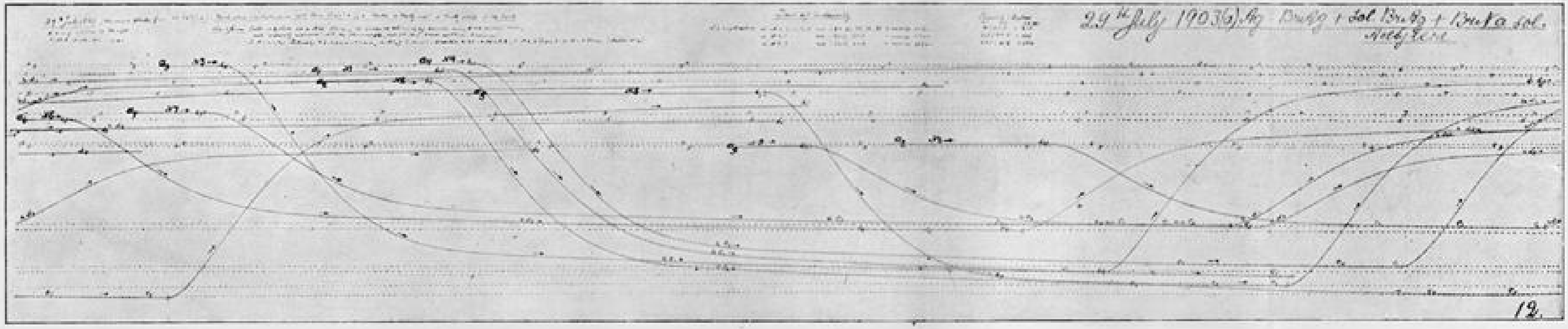


Plate N12.

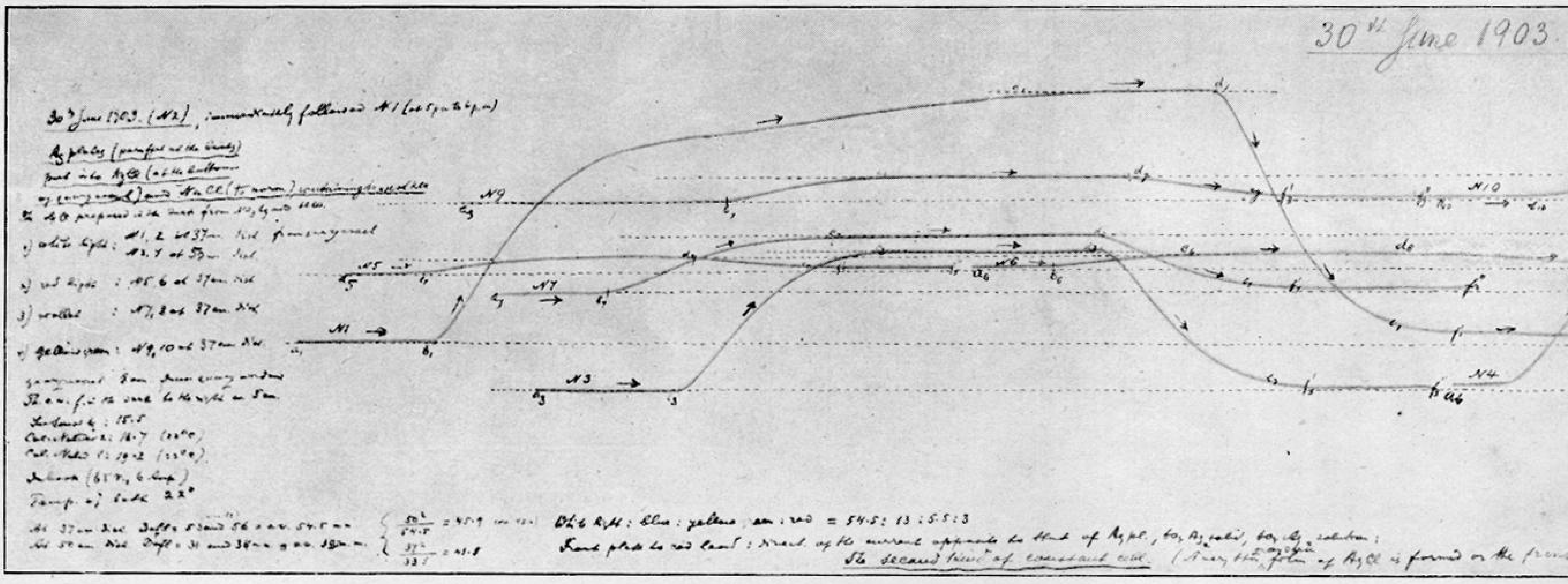


Plate N10.

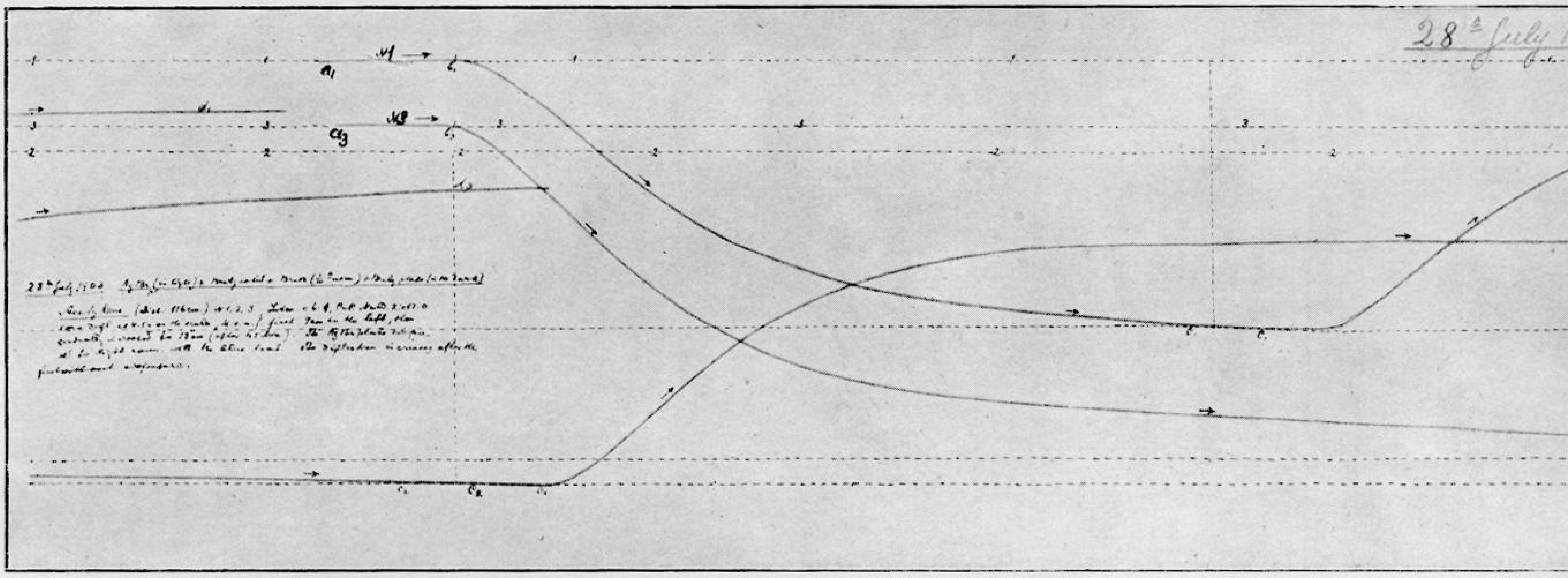


Plate N11.

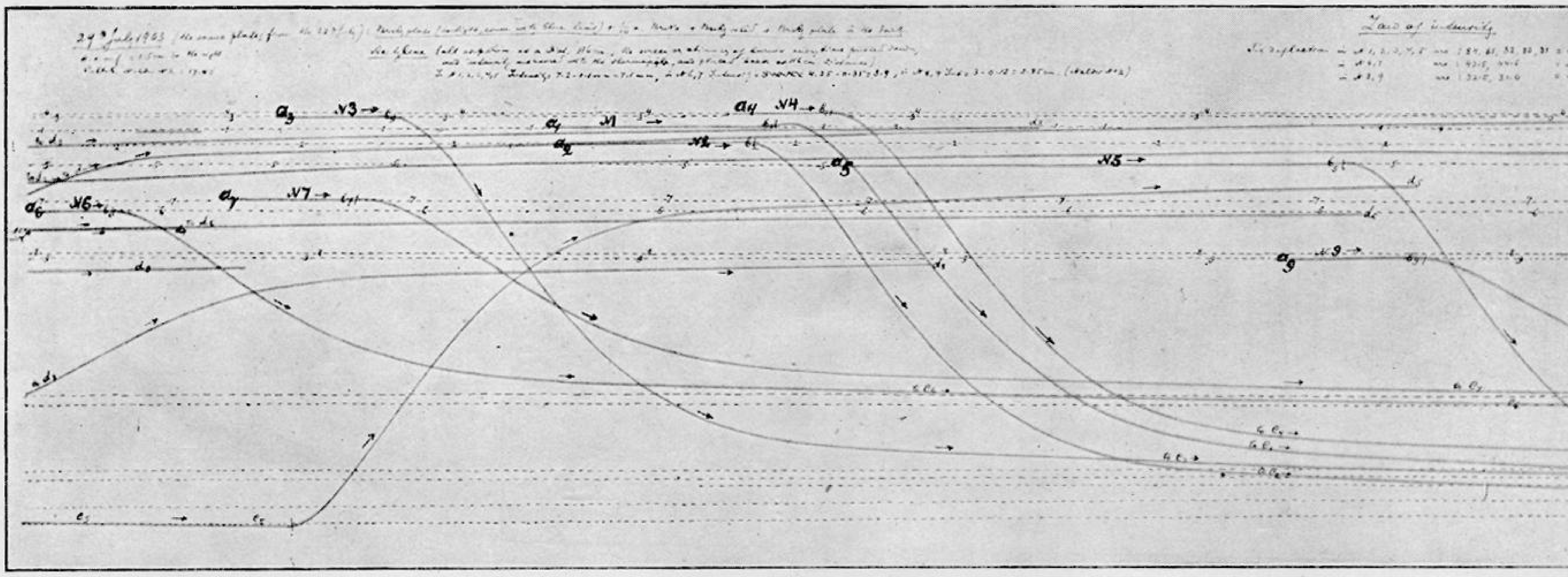
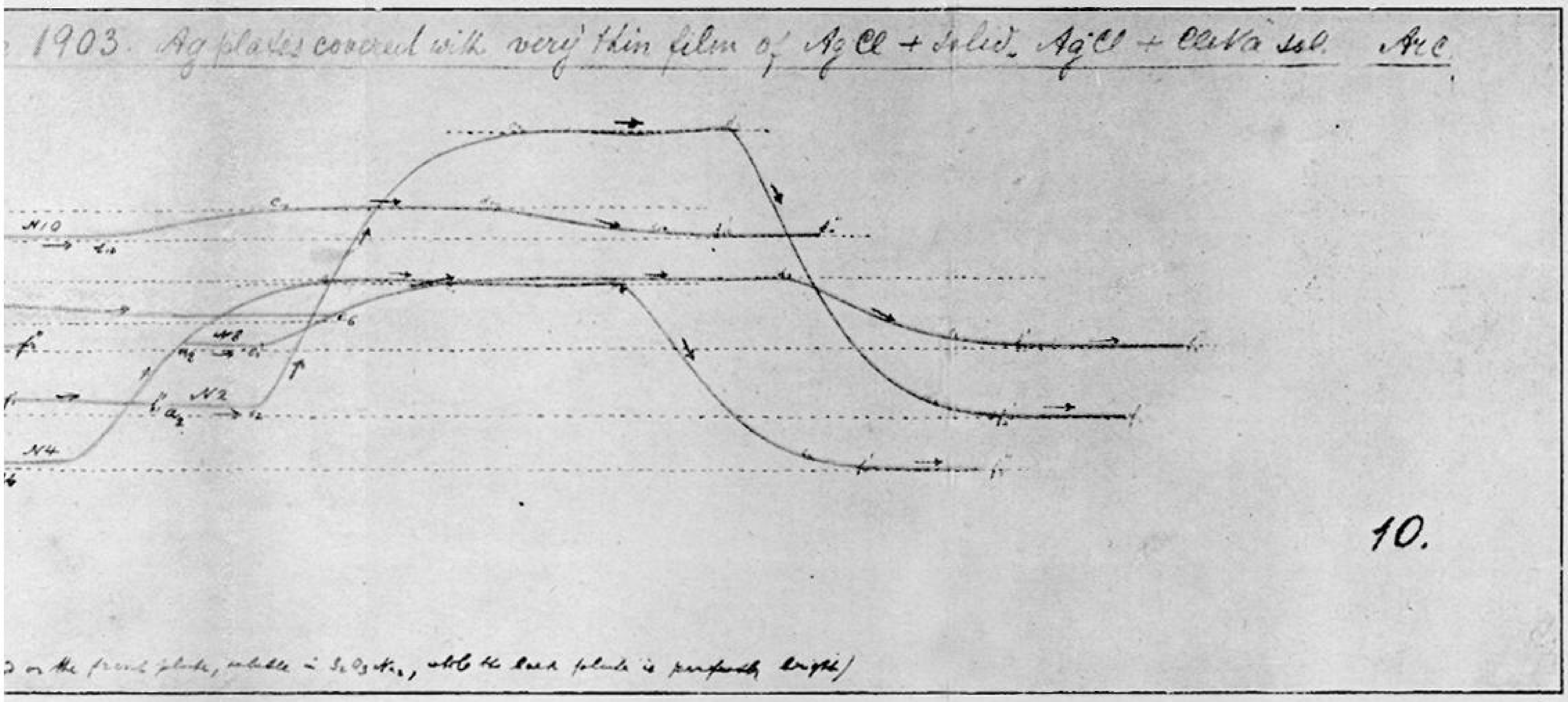
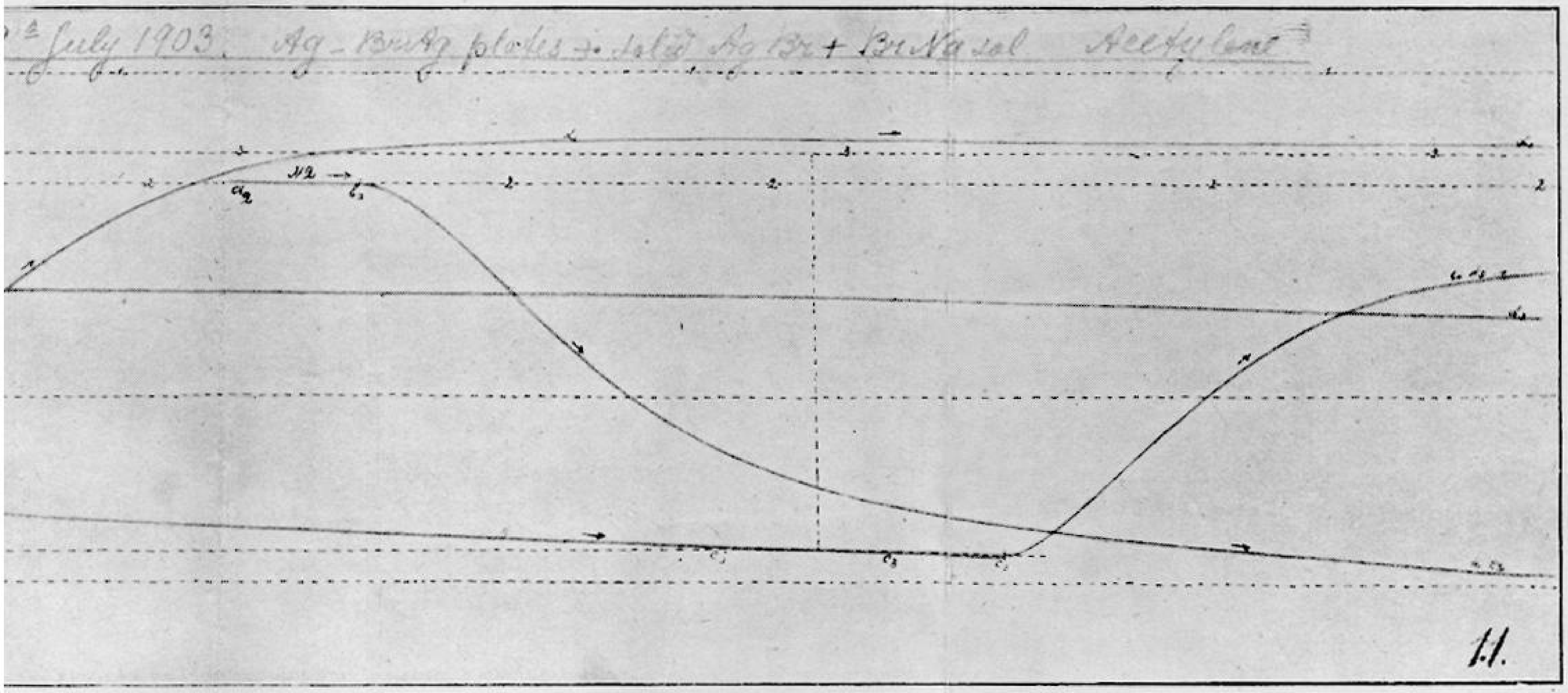


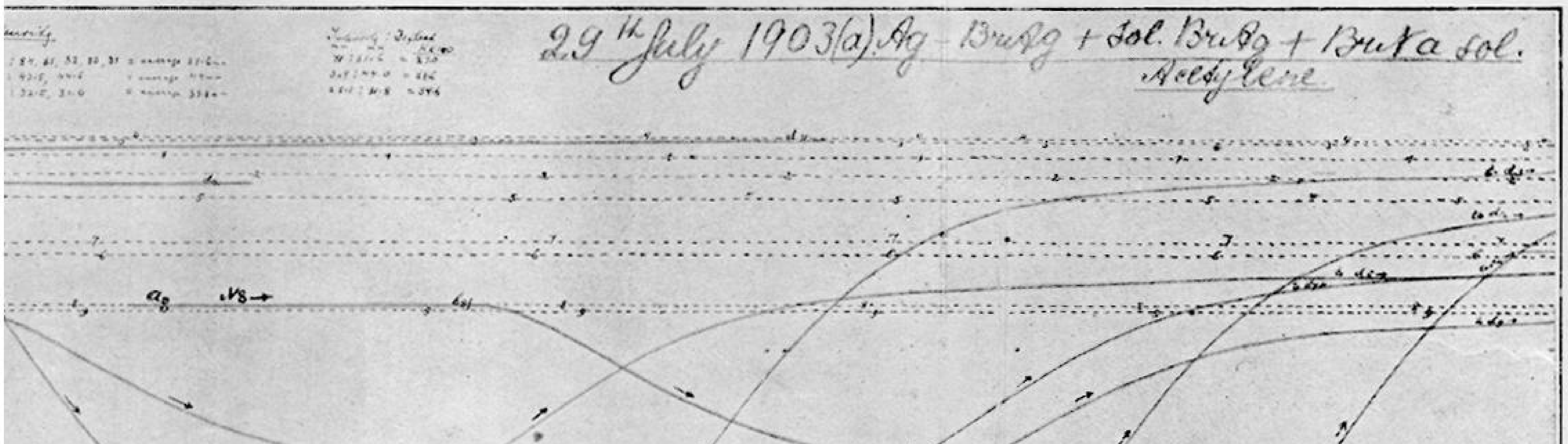
Plate N12.


1903. Ag plates covered with very thin film of AgCl + solid AgCl + ClNa sol. Arc
N10
N8
N2
N4
a2
on the front plate, soluble in S2O3Na2, while the back plate is perfectly bright)

10.


July 1903. Ag–BrAg plates + solid AgBr + BrNa sol Acetylene
N2
a2

11.


29th July 1903(a). Ag–BrAg + sol. BrAg + BrNa sol.
Acetylene
a8
N8

12.

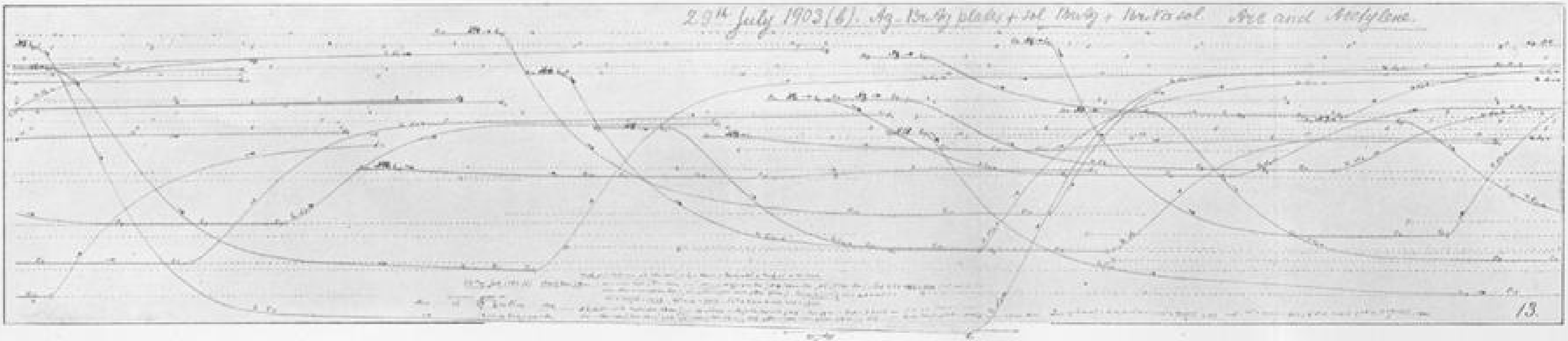


Plate N13.

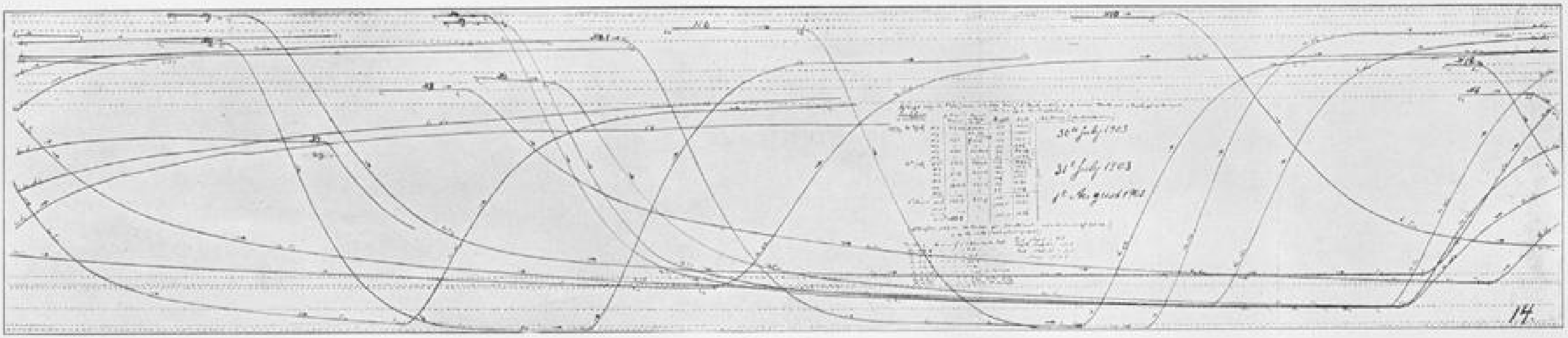


Plate N14.

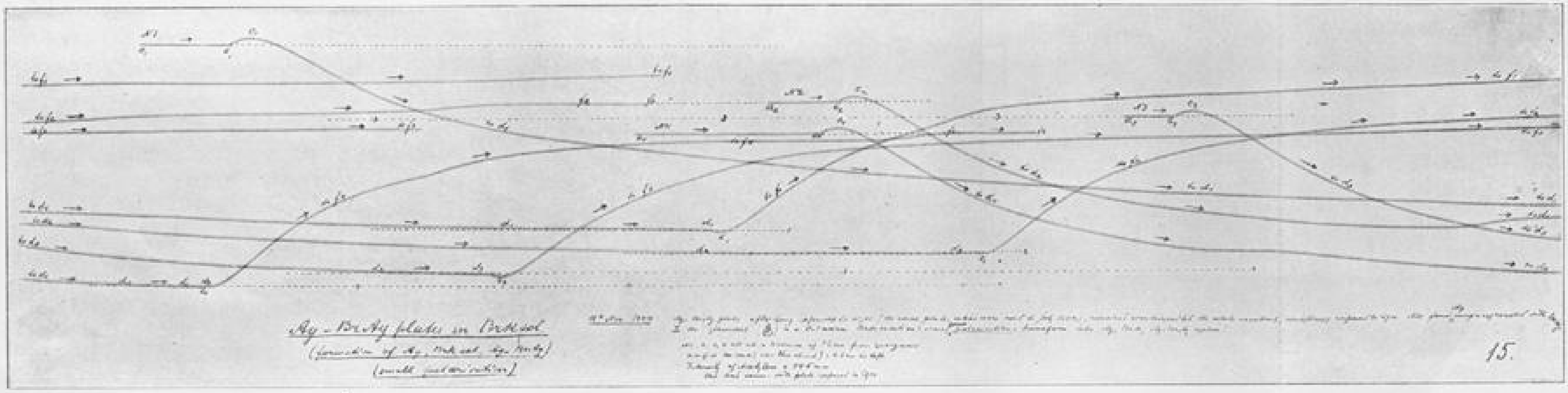


Plate N15.

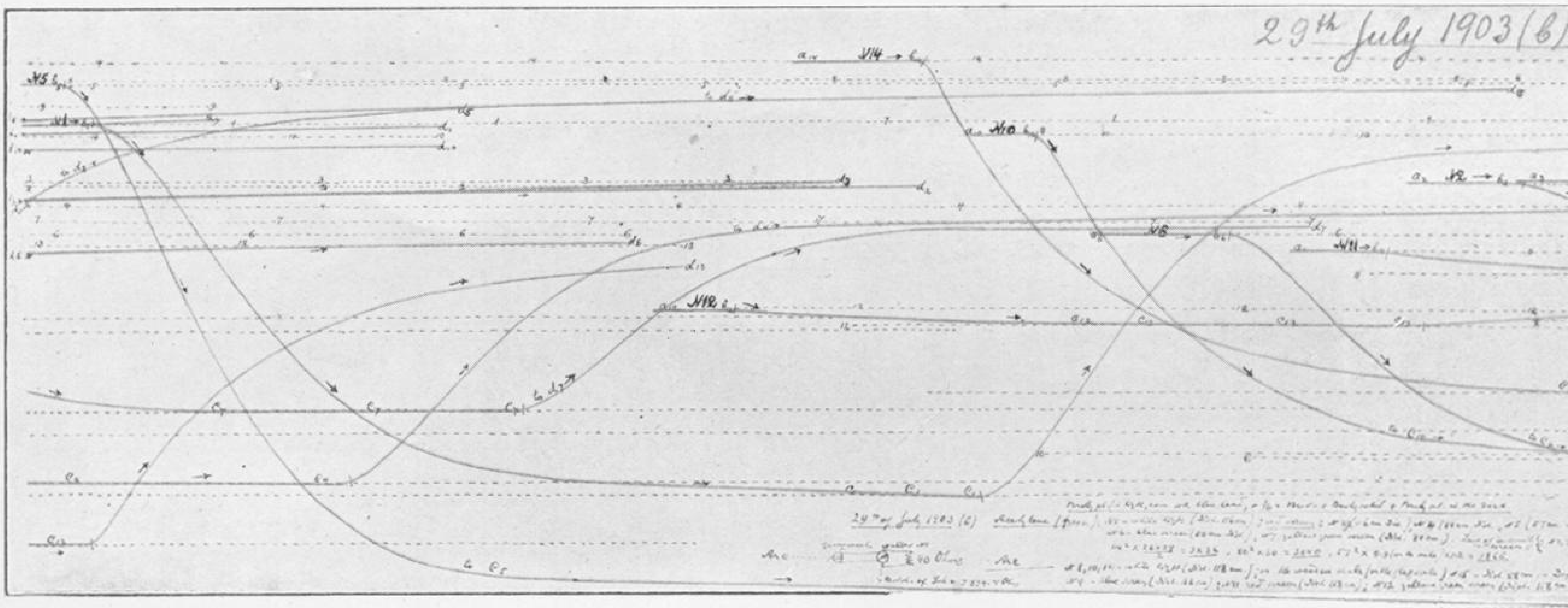


Plate N13.

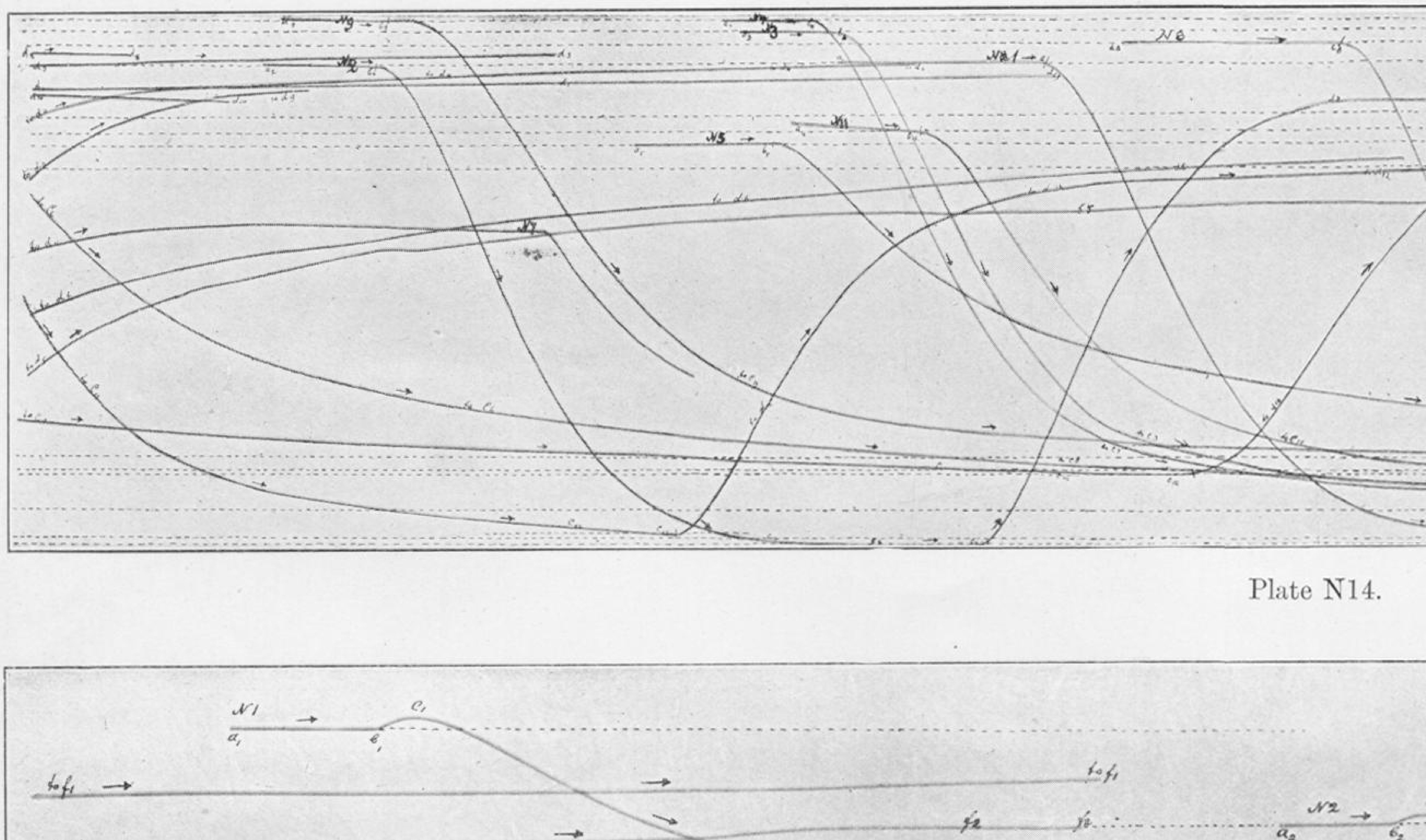
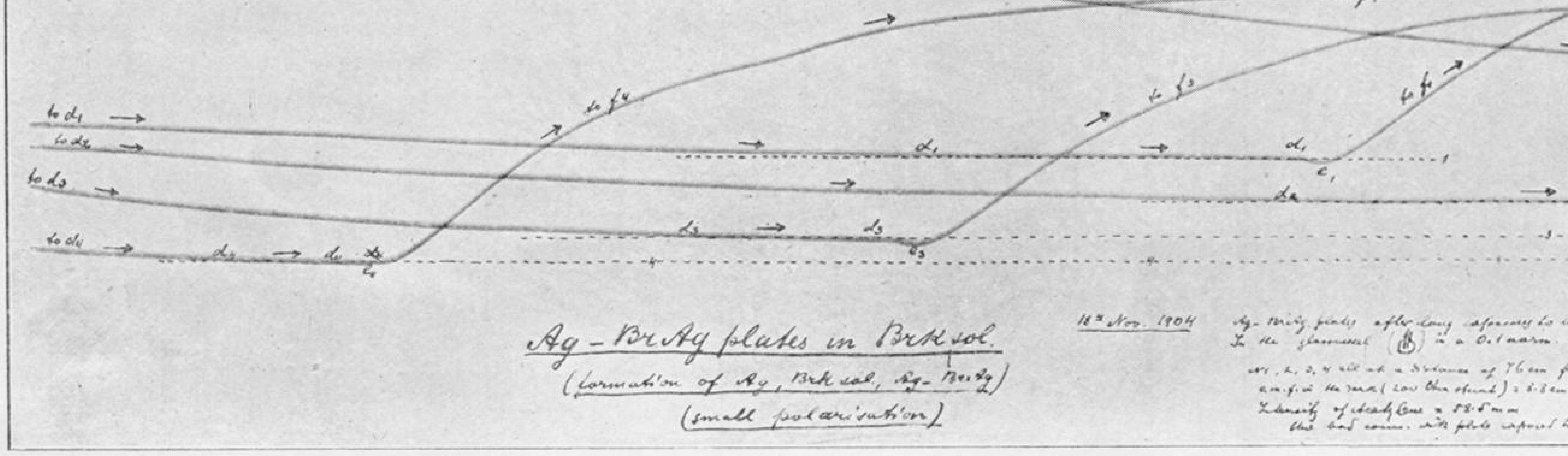
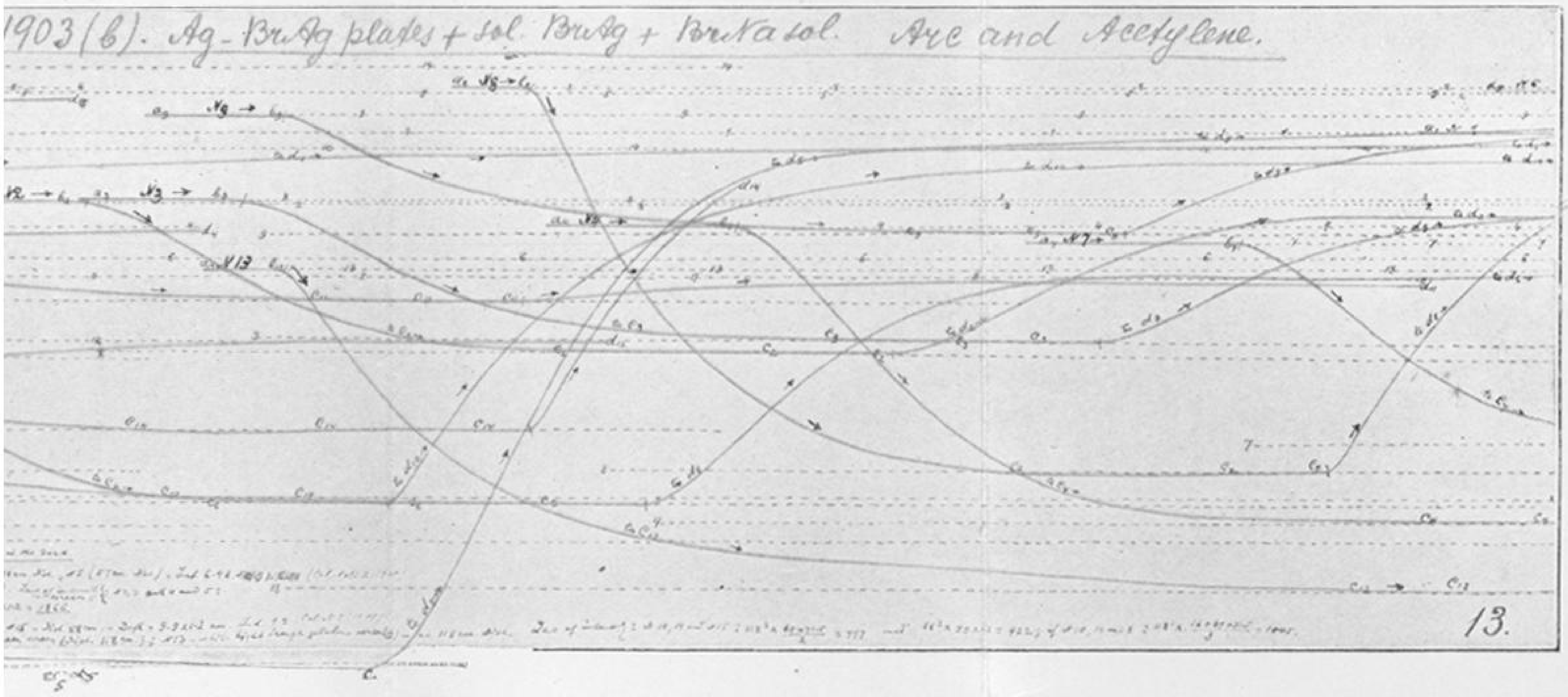
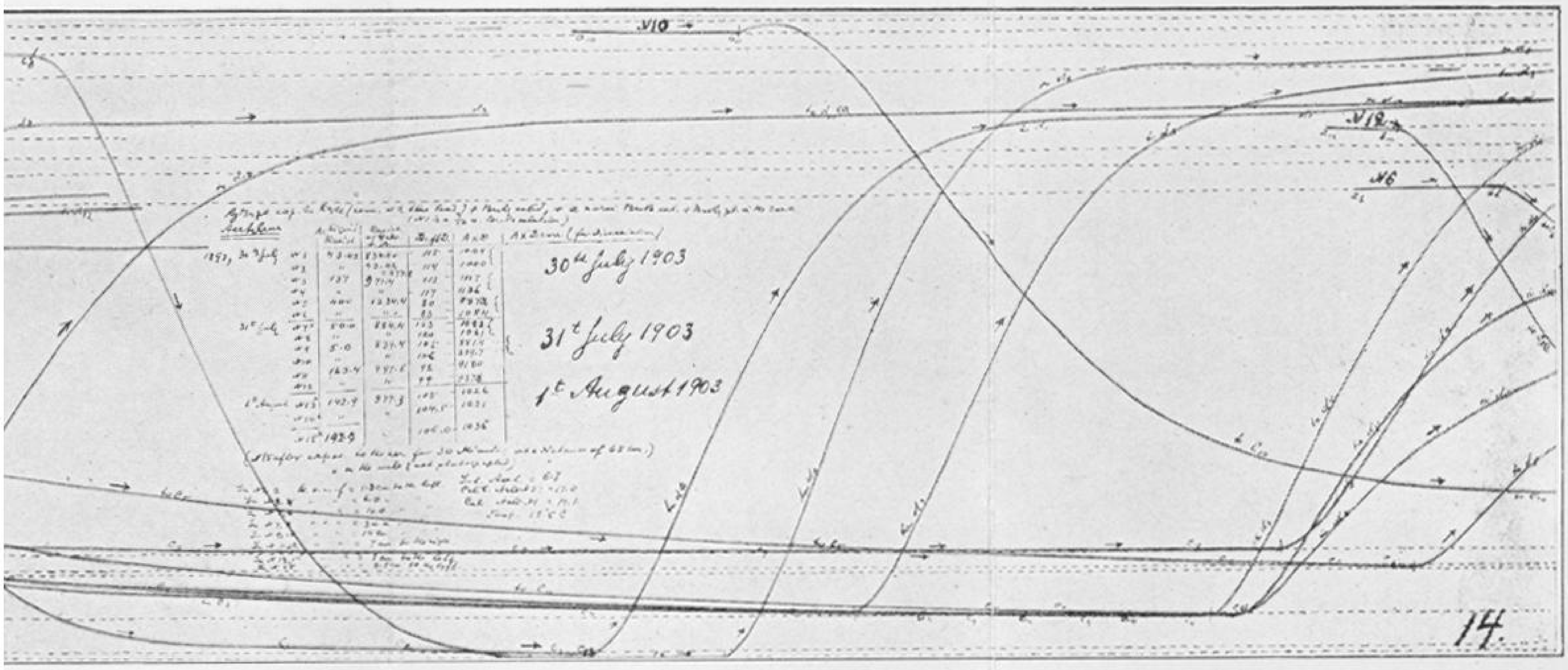


Plate N14.

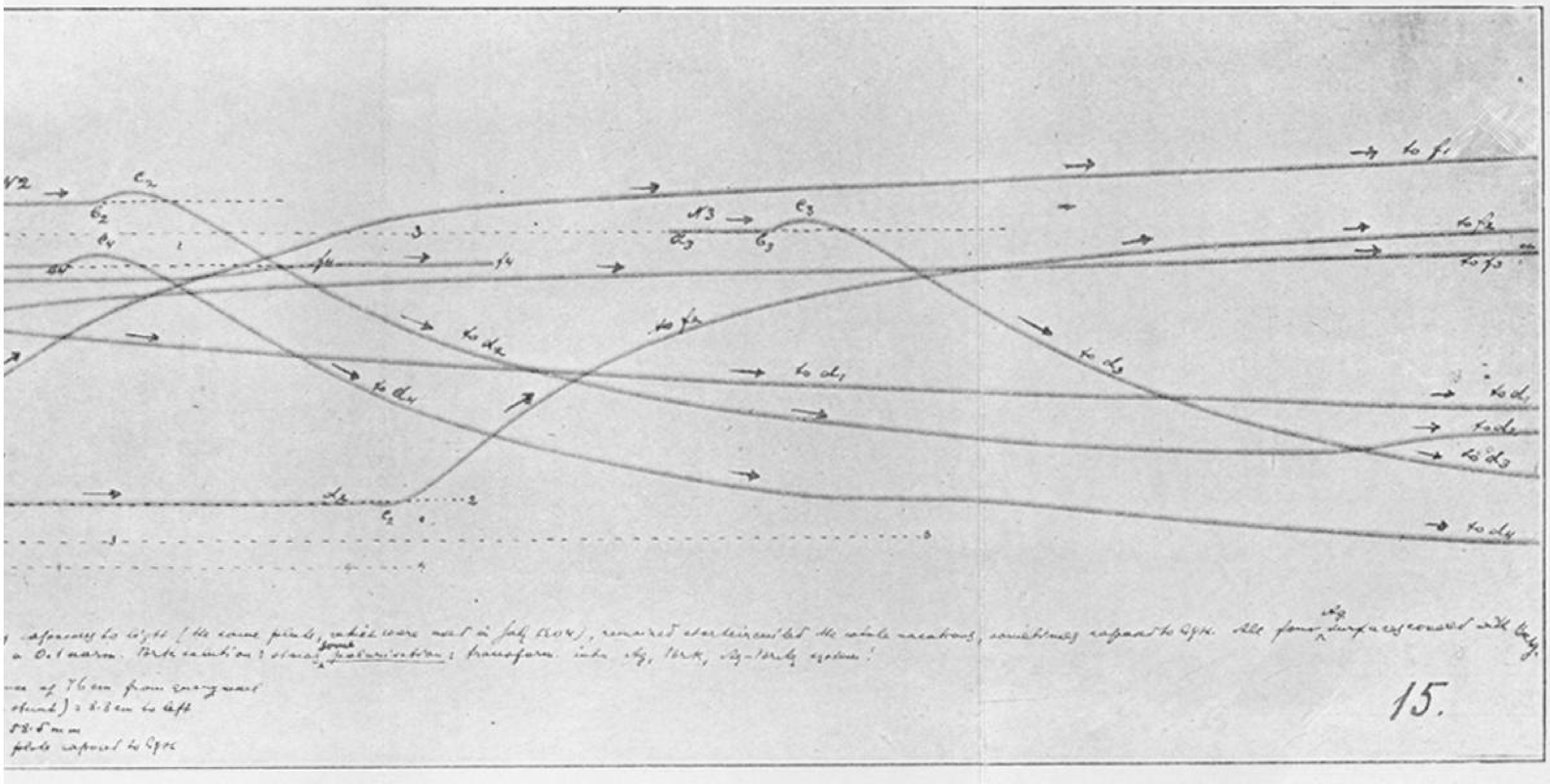


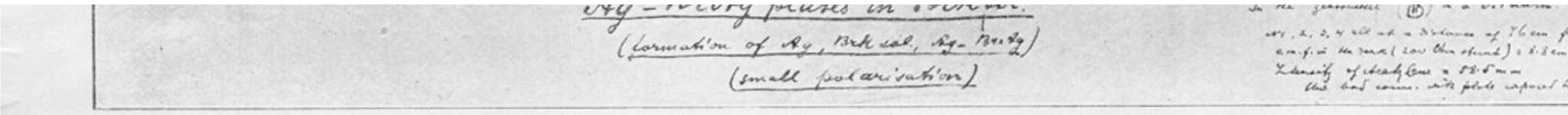

1903(b). Ag-BrAg plates + sol. BrAg + BrNa sol. Arc and Acetylene.
N8
N2
N3
N13
N7
13.

N13.


N10
N18
N6
30th July 1903
31st July 1903
1st August 1903
14.

N14.


N2
N3
to f1
to f2
to f3
to d1
to d2
to d3
to d4
15.



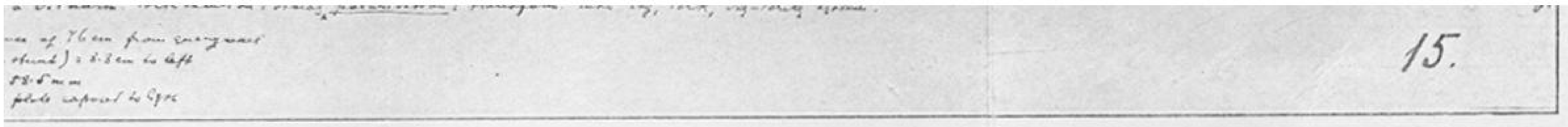
(formation of Ag, Brk sol, Ag- Br Ag)

(small polarisation)

No. 1, 2, 3, 4 all at a distance of 76 cm

Intensity of Acetylene = 58.5 mm

Plate N15.

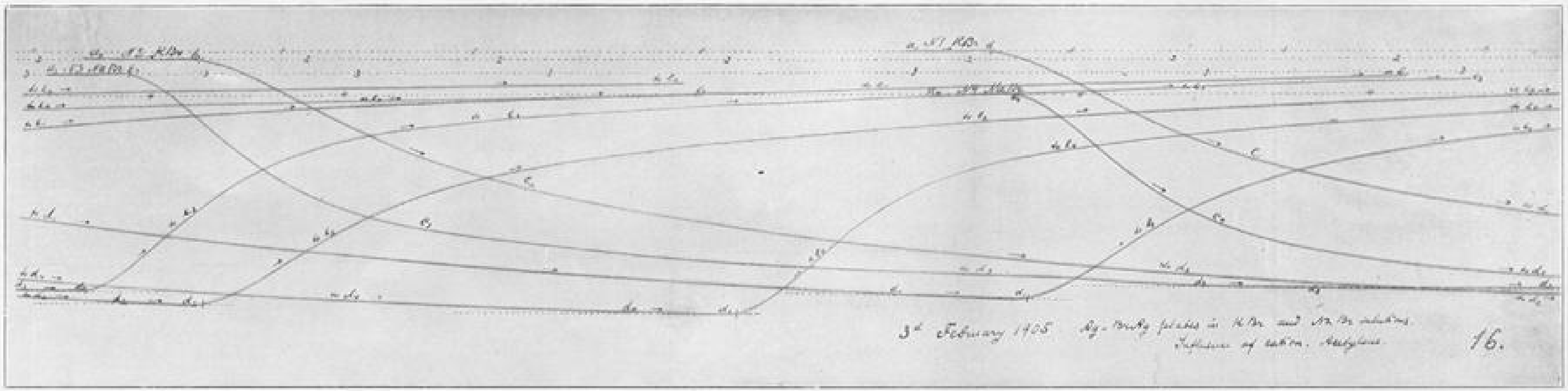


[illegible] regularly spaced.

ce of 76 cm from emergence
obtained) = 8.3 cm to left
58.5 mm
plate exposed to 6 sec

15.

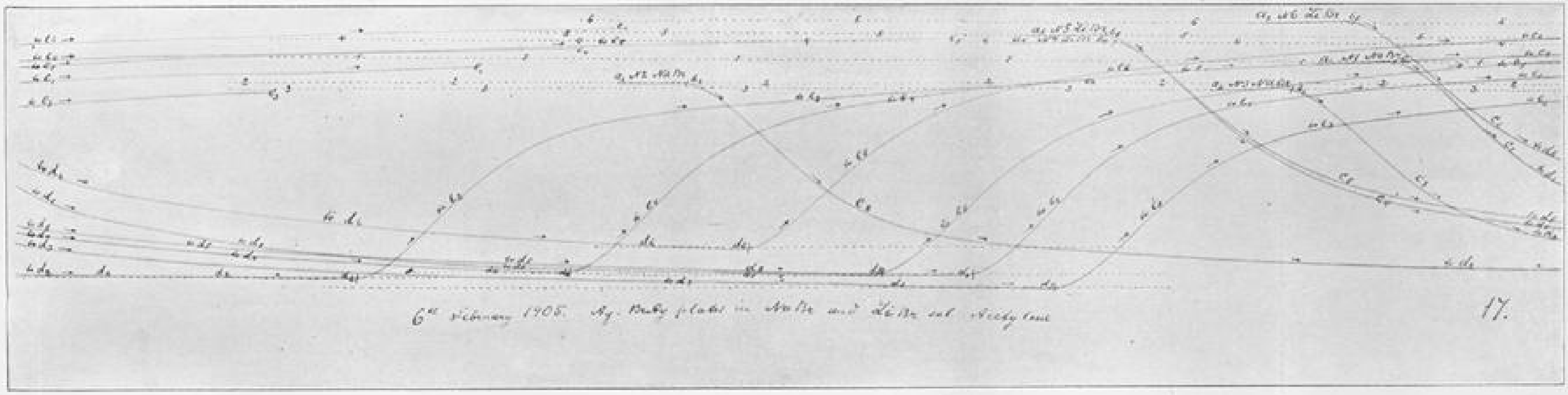
N15.



3rd February 1905 Ag-AgBr plates in KBr and NaBr solutions. Influence of carbon. Acetylene

16.

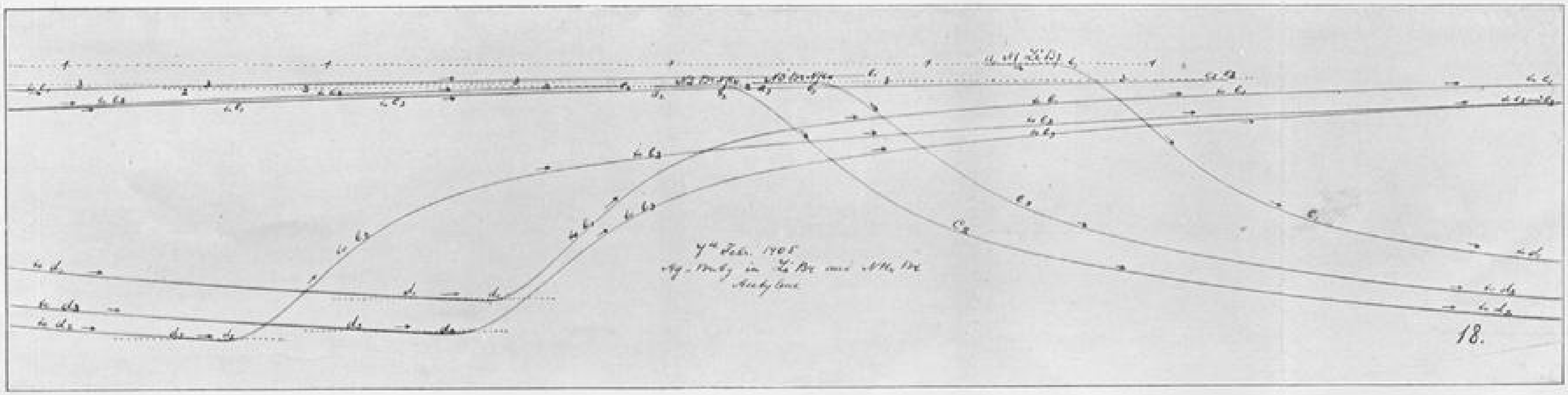
Plate N16.



6th February 1905. Ag-AgBr plates in NaBr and LiBr sol. Acetylene

17.

Plate N17.



7th Feb. 1905 Ag-AgBr in LiBr and NH4Br Acetylene

18.

Plate N18.

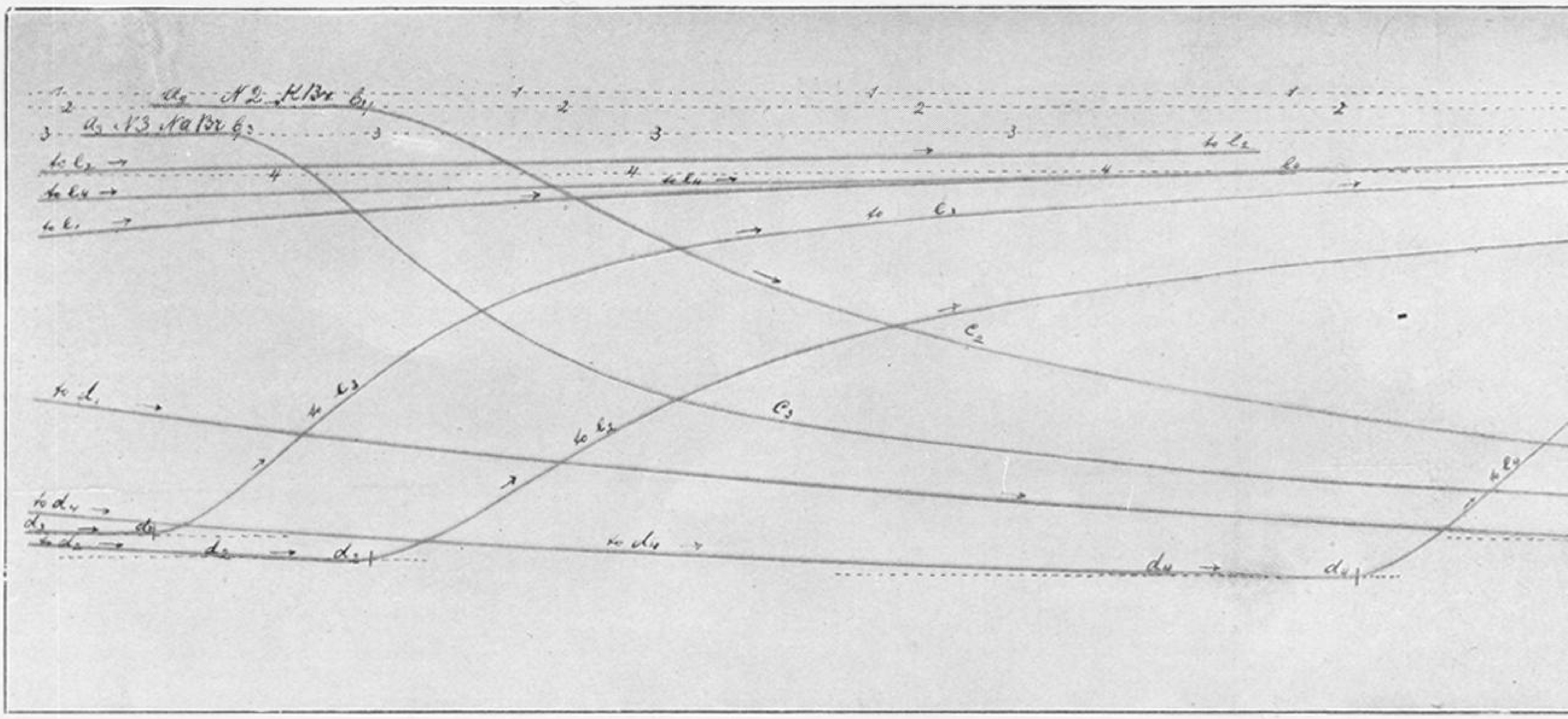


Plate N16.

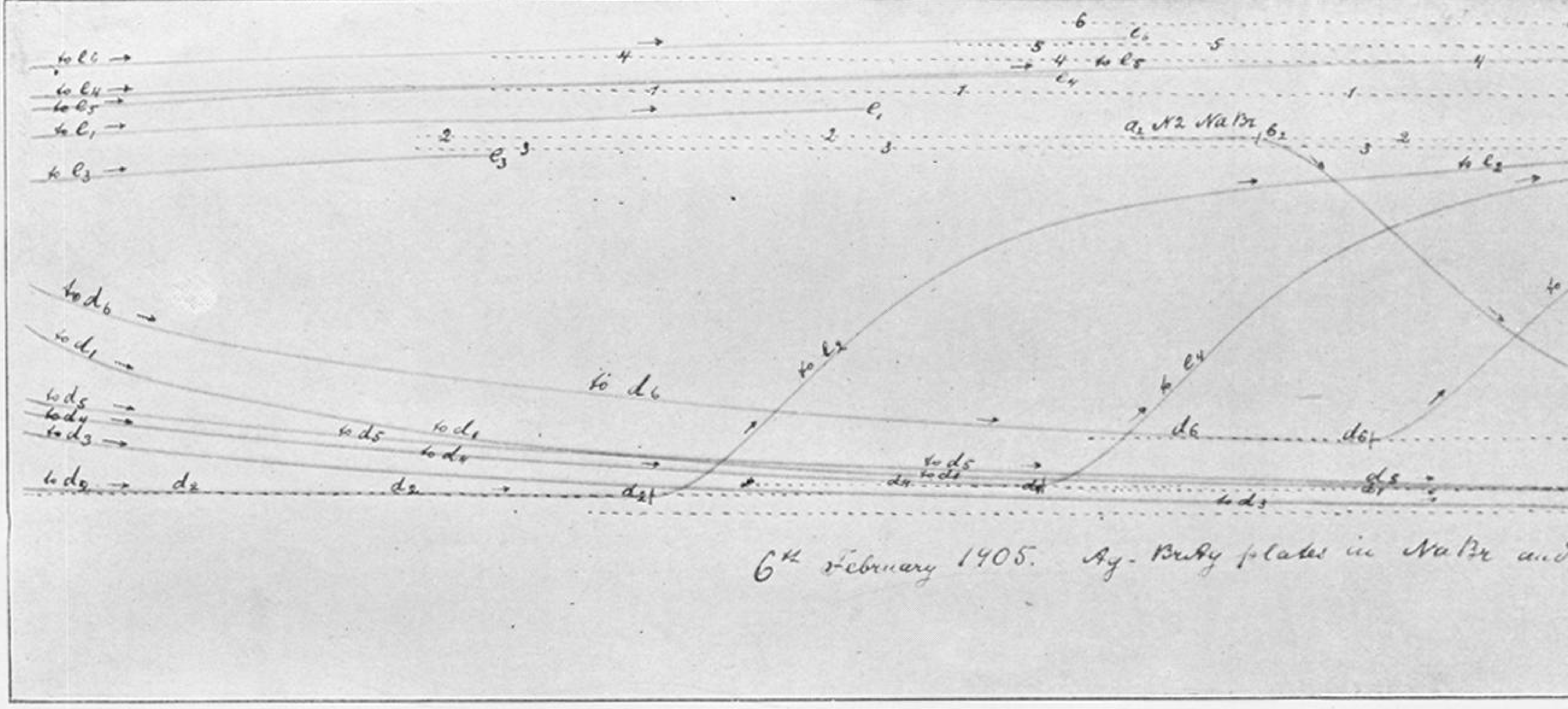
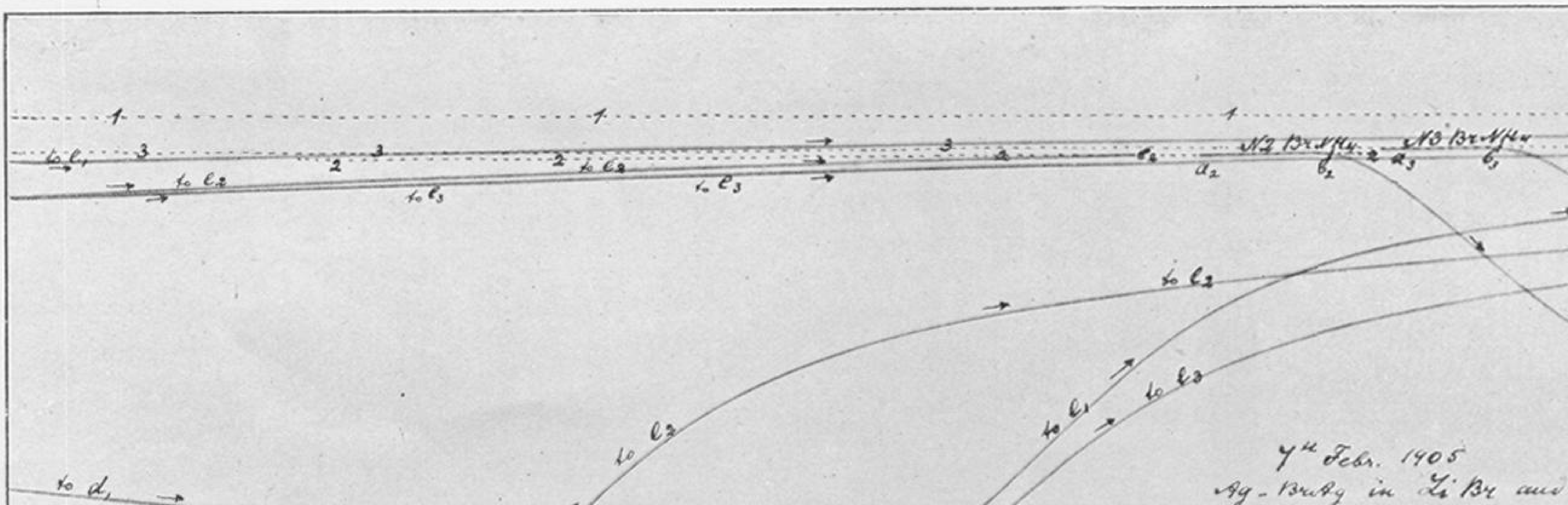
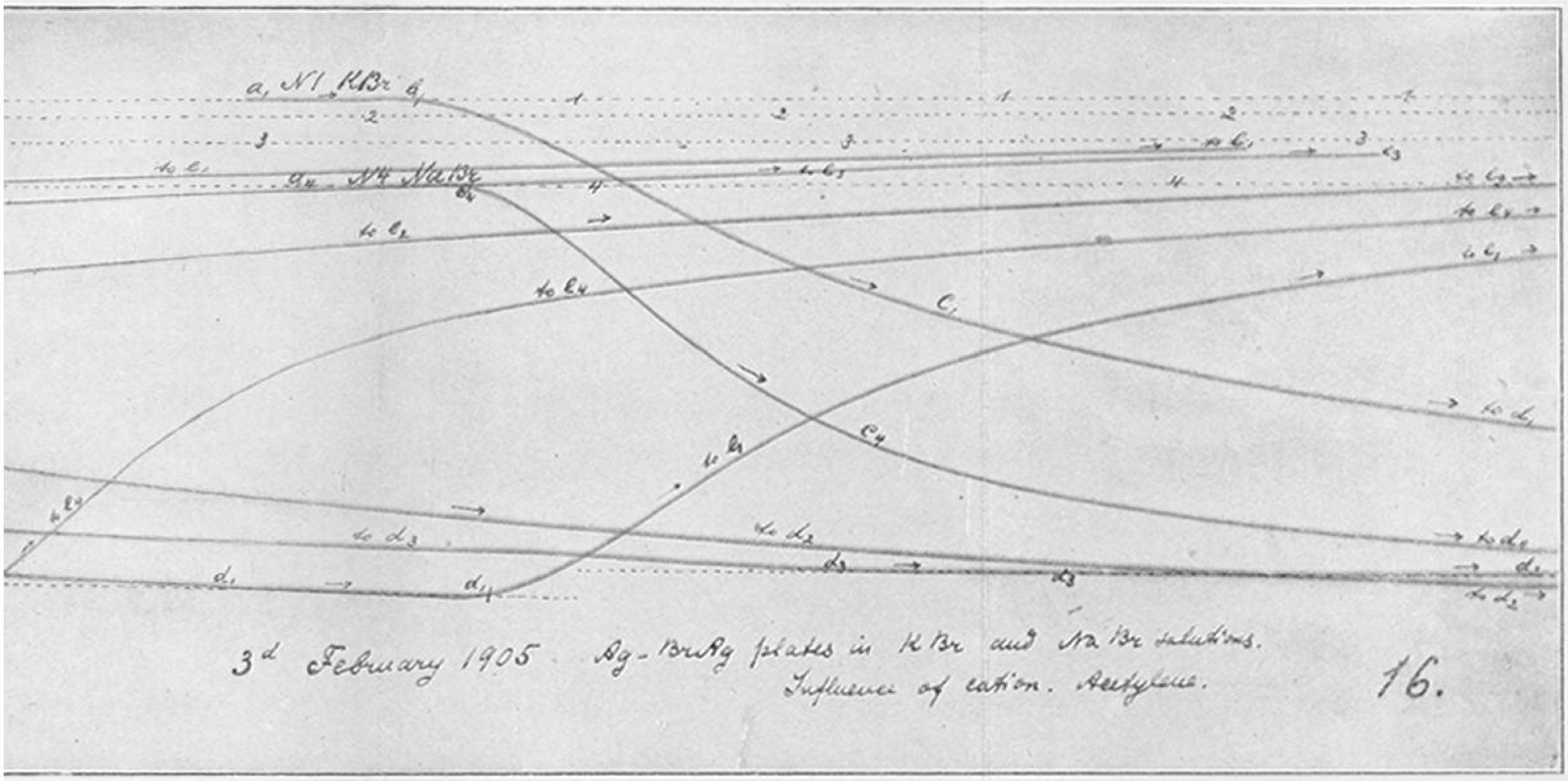


Plate N17.

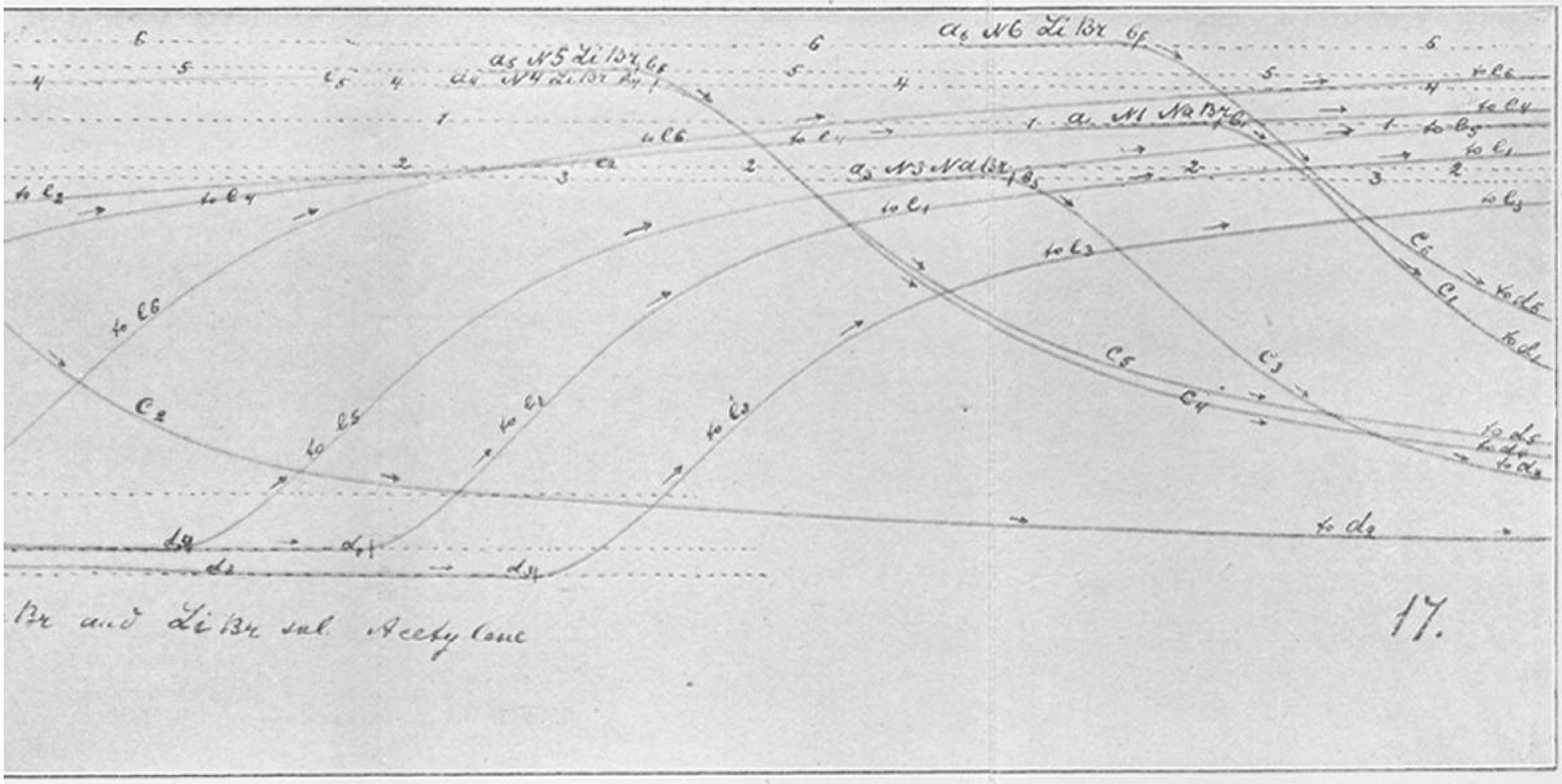




3d February 1905 Ag-BrAg plates in KBr and NaBr solutions.
Influence of cation. Acetylene.

16.

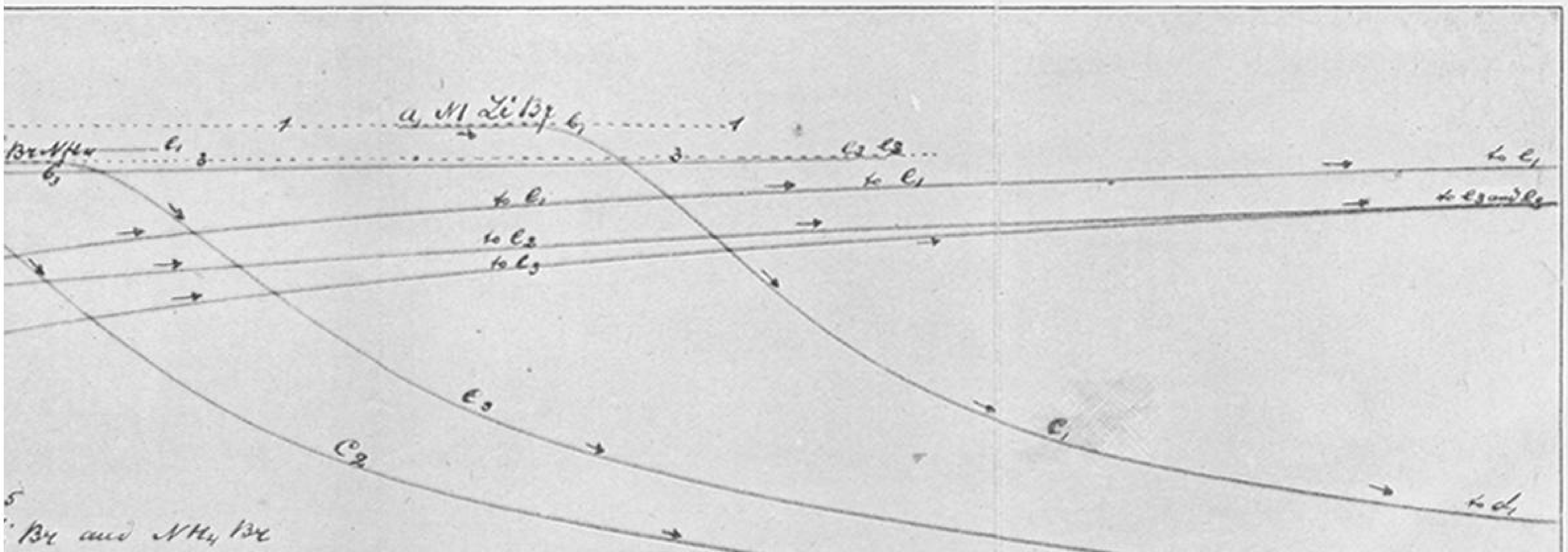
N16.



Br and LiBr sol. Acetylene

17.

N17.



Br and NH₄ Br

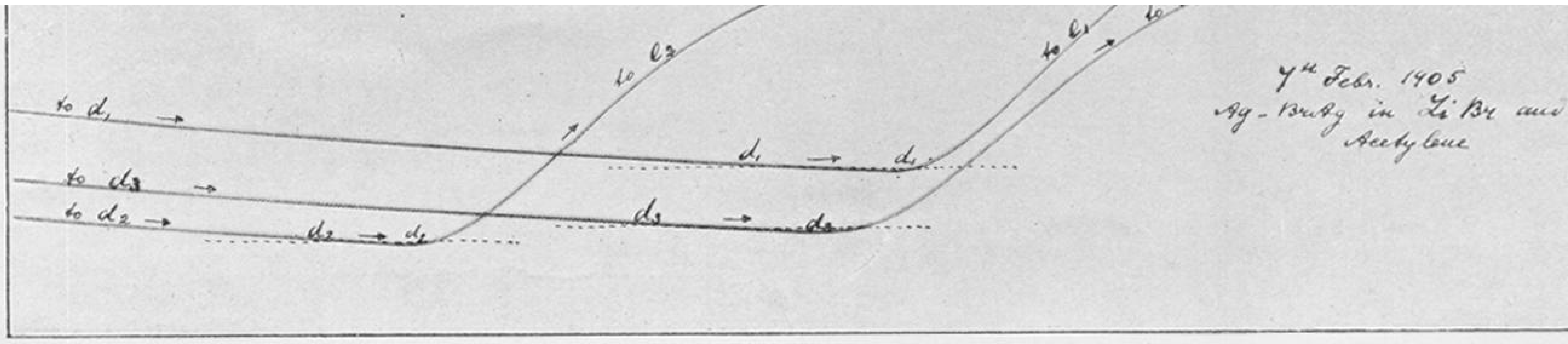
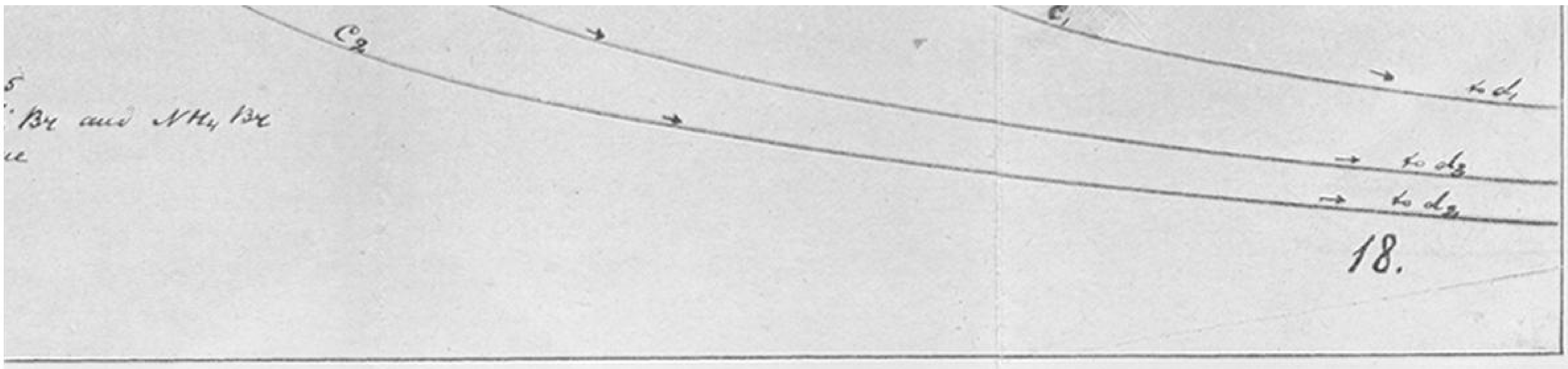

7th Febr. 1905
Ag - BrAg in LiBr and
Acetylene
to d_1 →
to d_3 →
to d_2 →
d_2 → d_2
d_1 → d_1
d_3 → d_3
to l_2
to l_1
to

Plate N18.



18.

N18.

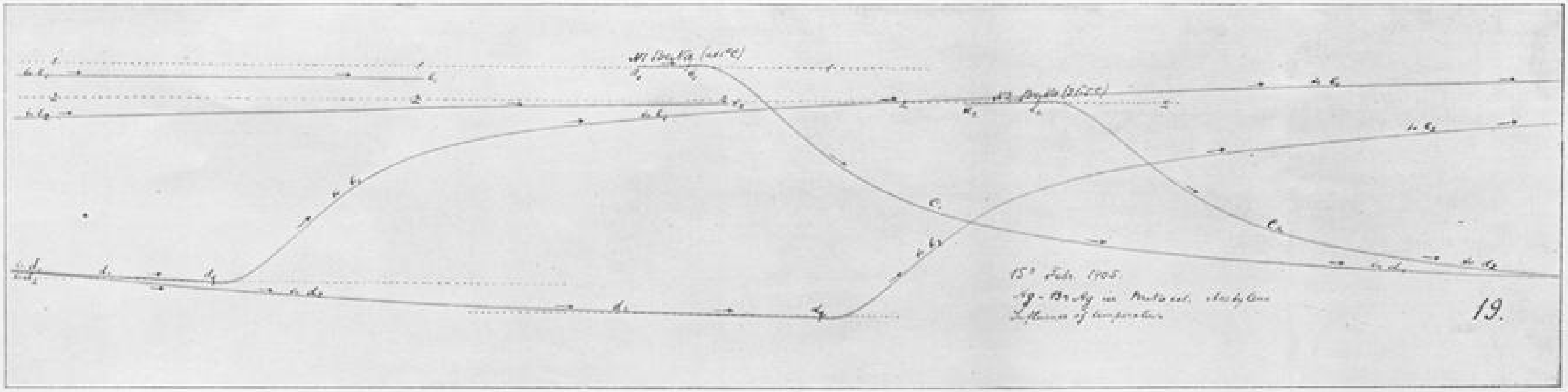


Plate N19.

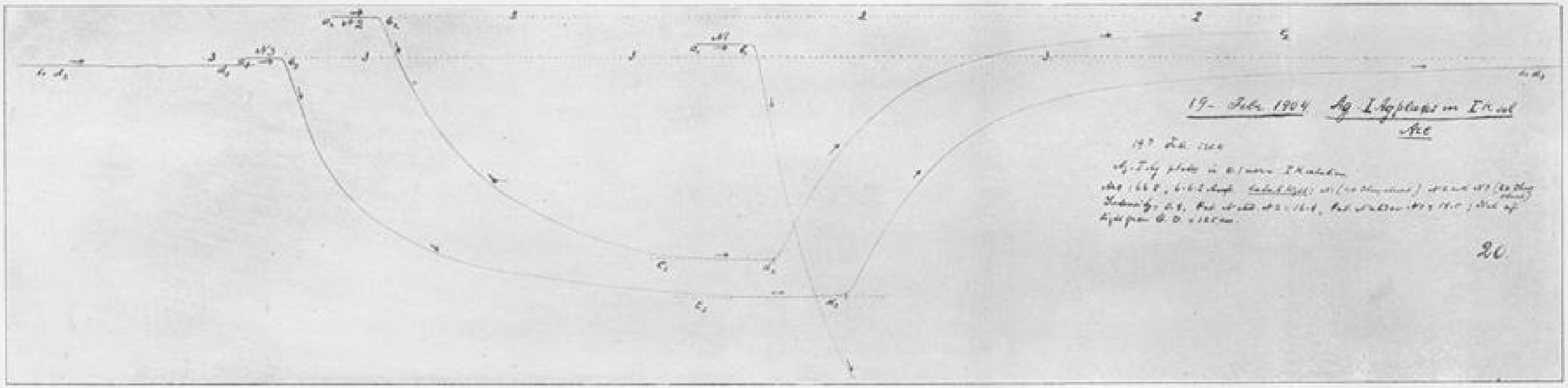


Plate N20.

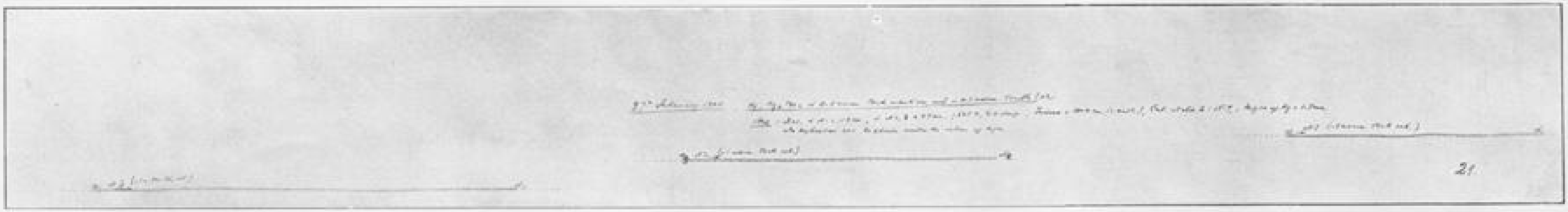


Plate N21.

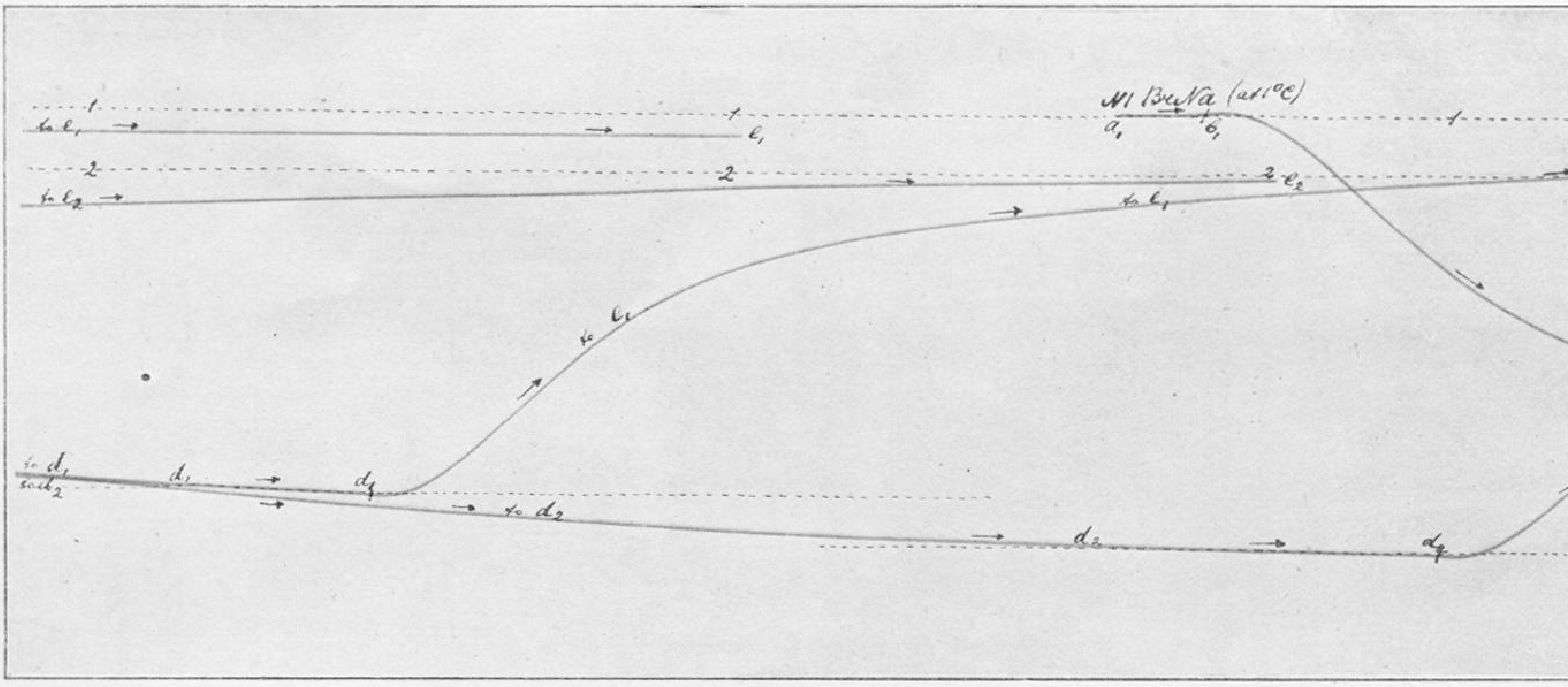


Plate N19.

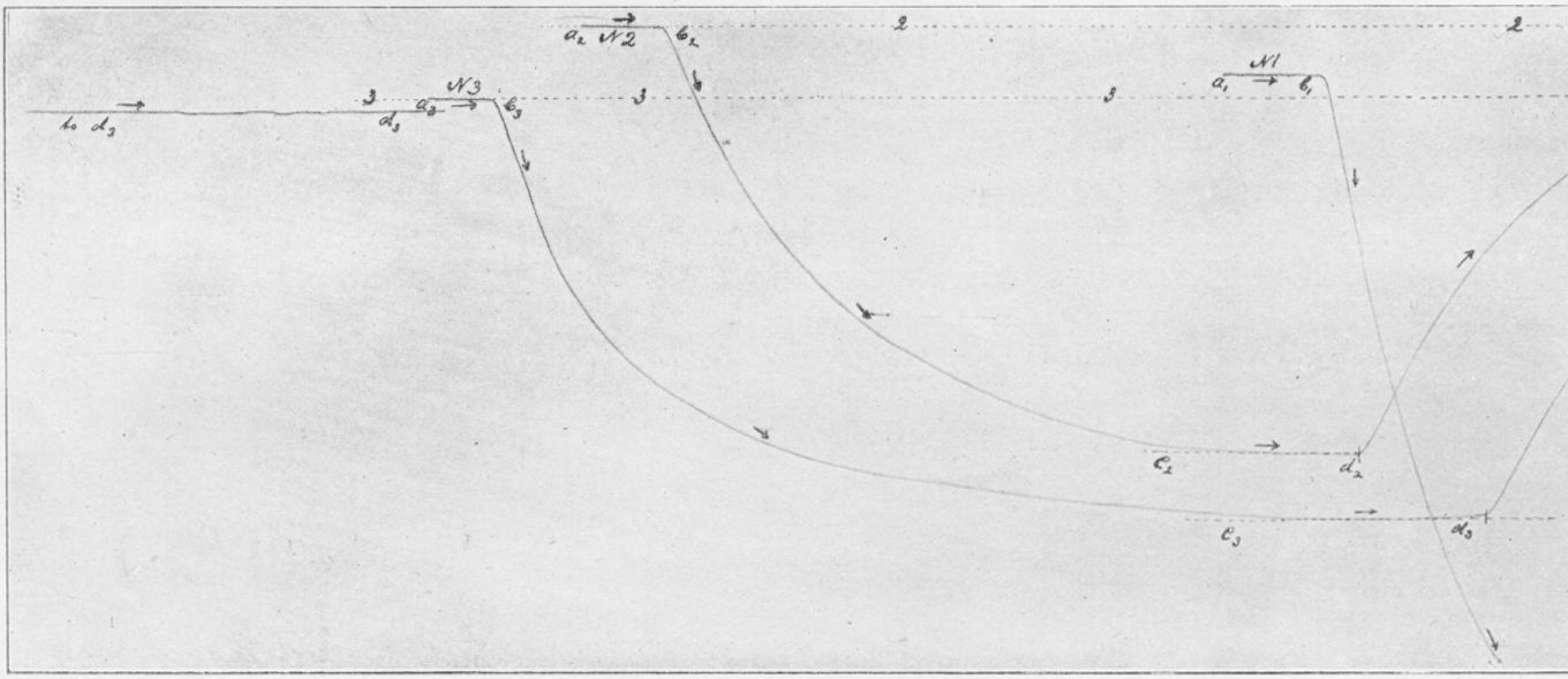


Plate N20.

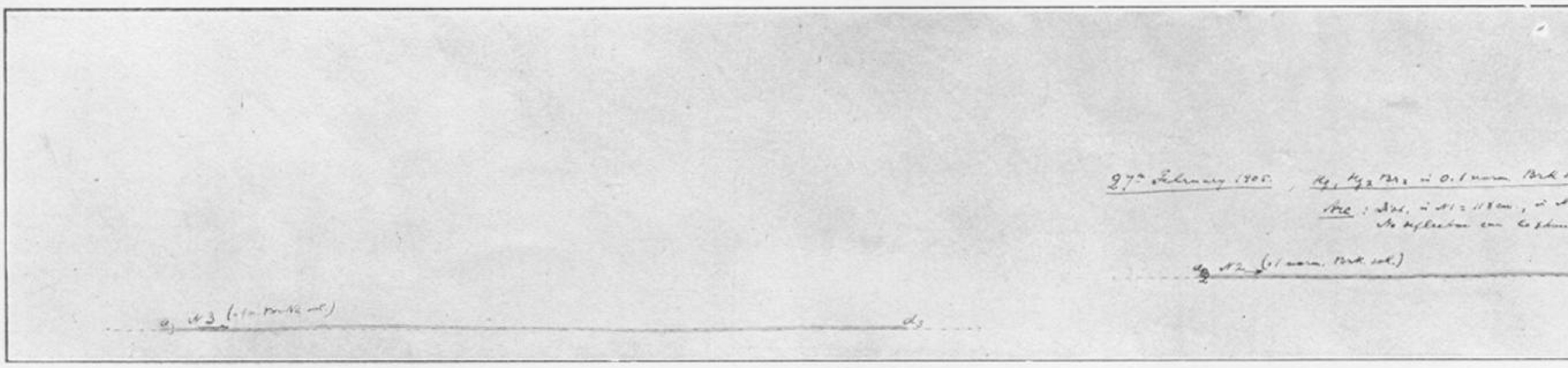
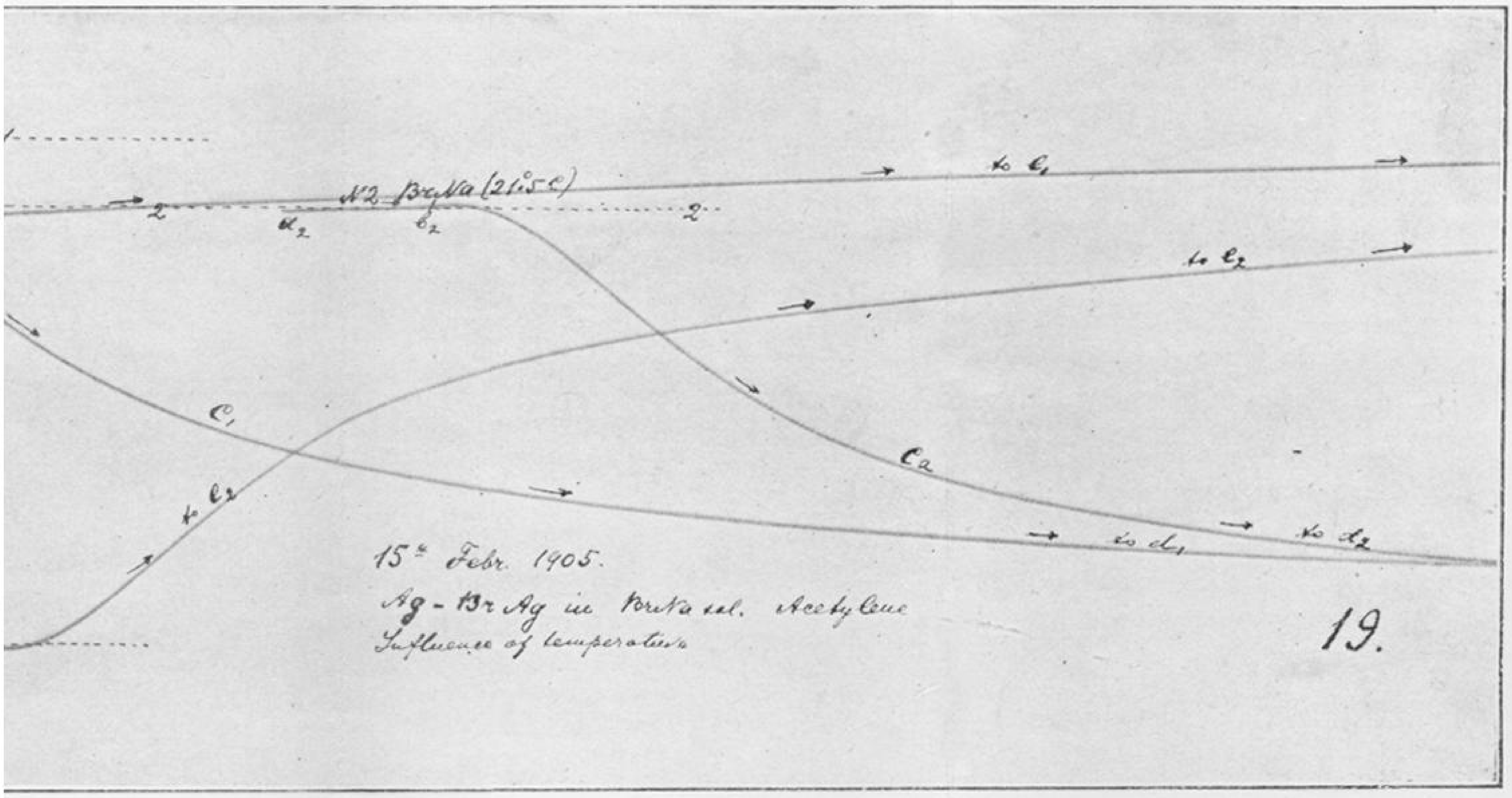
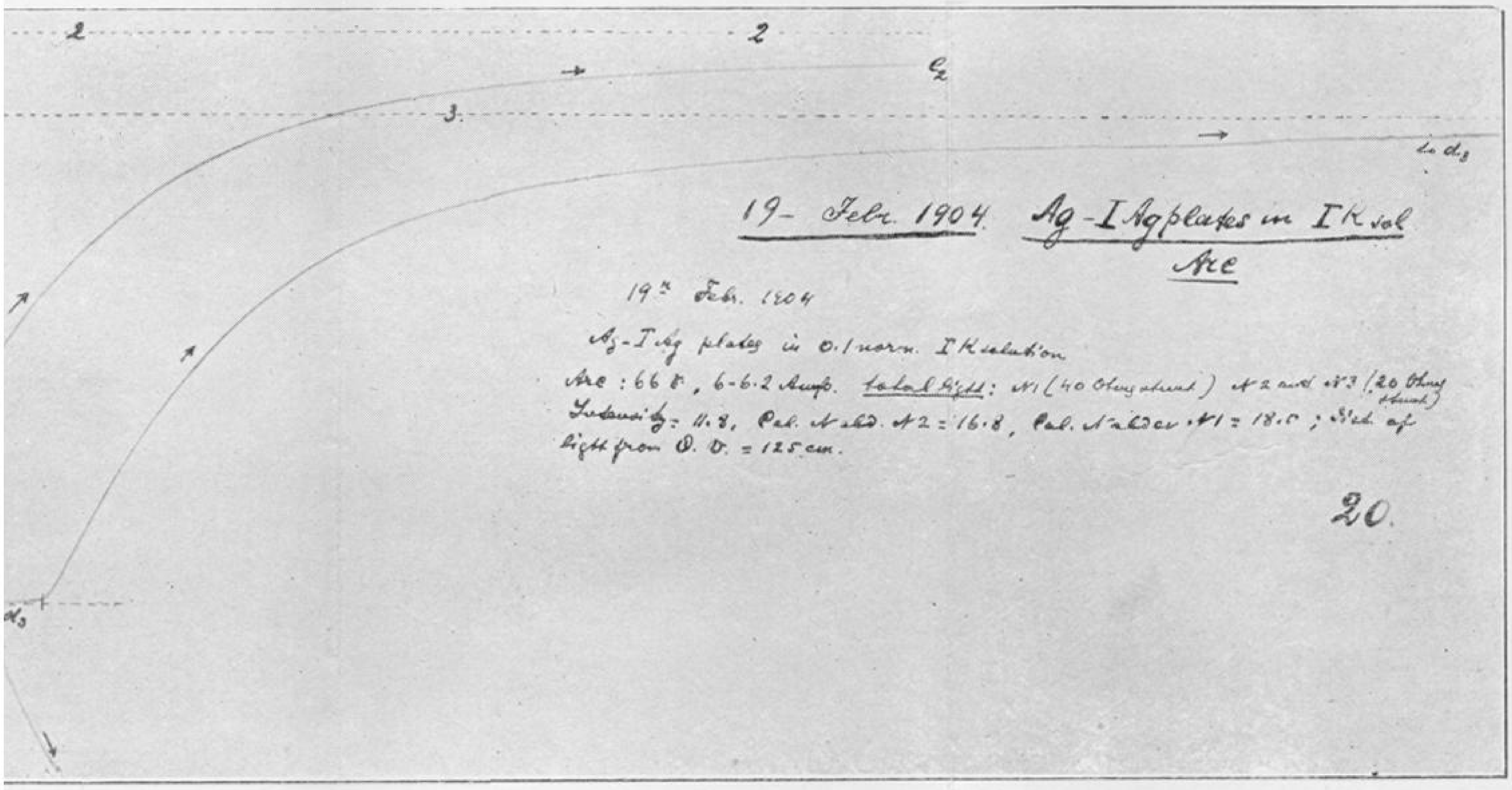


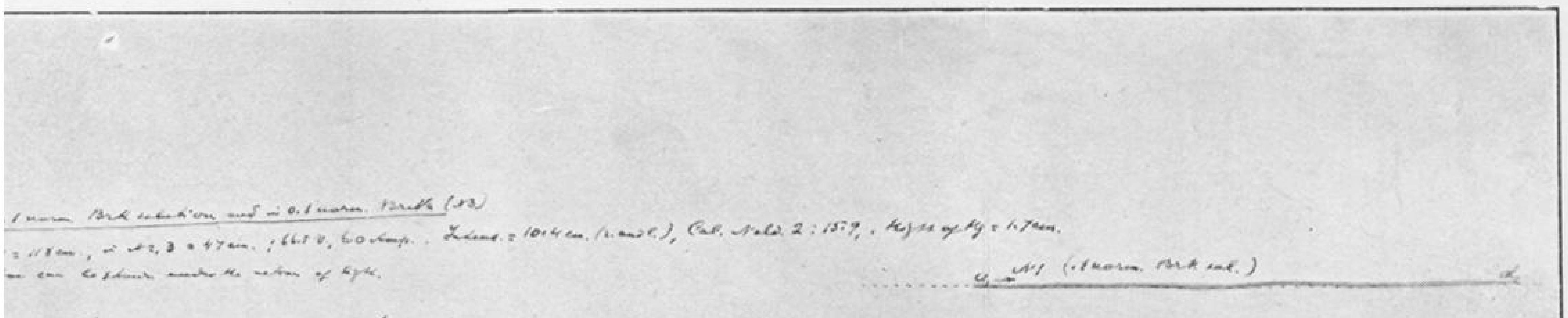
Plate N21.


2
N2 BrNa (21.5°C)
a₂
b₂
2
to c₁
to c₂
c₁
c₂
to c₂
to d₁
to d₂
15th Febr. 1905.
Ag - Br Ag in BrNa sol. Acetylene
Influence of temperature

19.


2
2
c₂
3
to d₃
19- Febr. 1904. Ag-I Ag plates in I K sol
Arc
19th Febr. 1904
Ag-I Ag plates in 0.1 norm. I K solution
Arc: 66 V, 6-6.2 Amp. total light: N1 (40 Ohm shunt) N2 and N3 (20 Ohm shunt)
Intensity = 11.8, Cal. Nald. N2 = 16.8, Cal. Nalder N1 = 18.5; dist. of light from O. V. = 125 cm.
d₃

20.


1 norm. BrK solution and in 0.1 norm. BrK (N3)
= 118 cm., in N2, 3 = 47 cm.; 66 V, 60 Amp. Intens. = 1014 cm. (c.and.), Cal. Nald. 2: 15.9, Height of Hg = 1.7 cm.
can be found under the action of light.
N1 (1 norm. BrK sol.)
a₂

21.

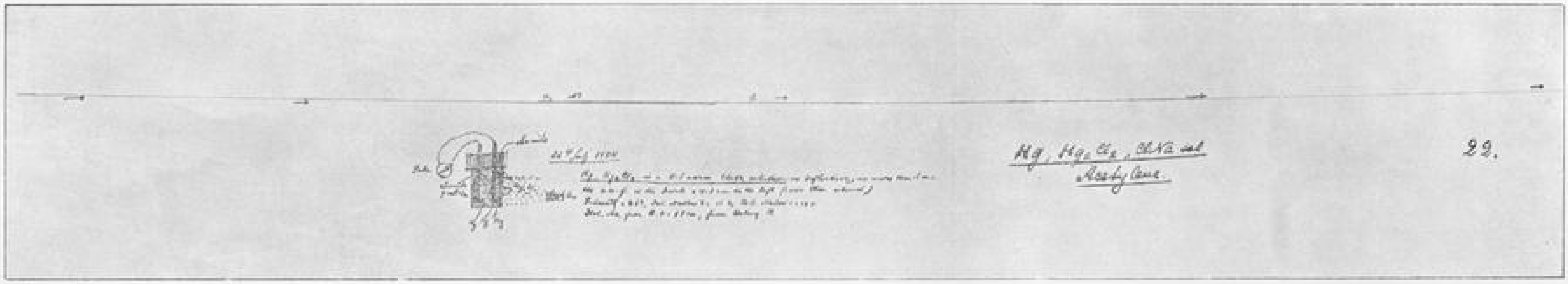


Plate N22.

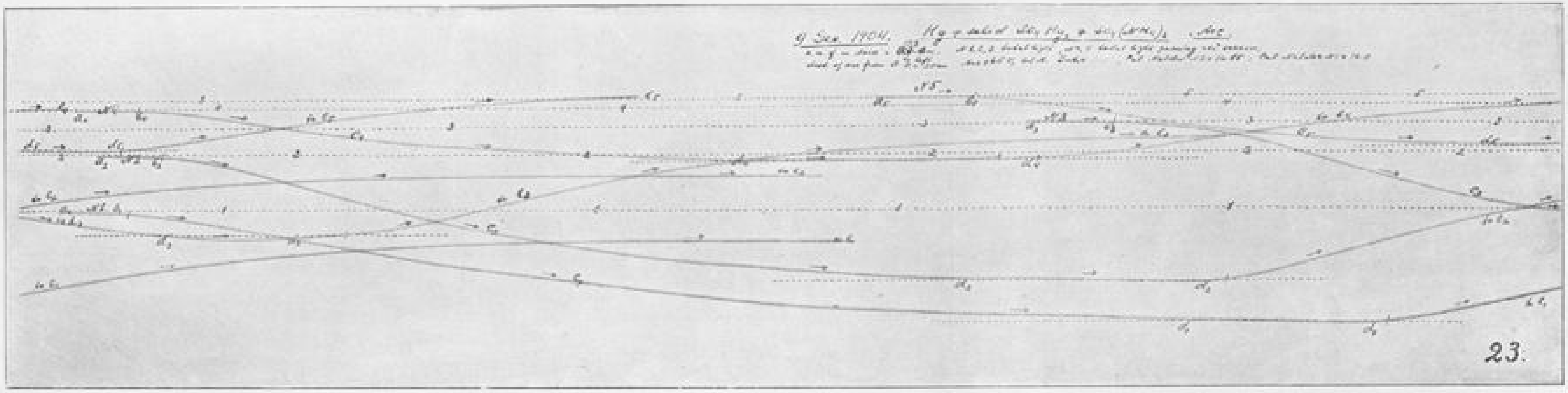


Plate N23.

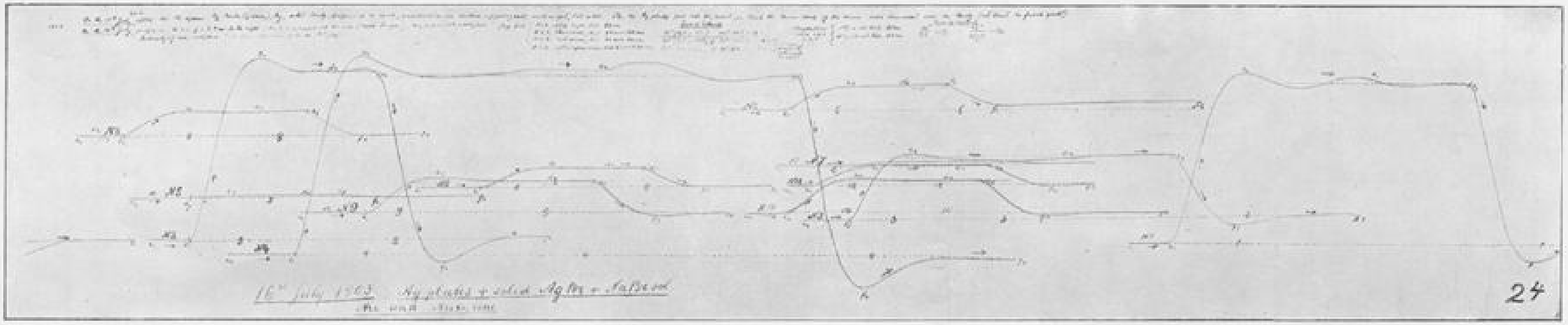


Plate N24.

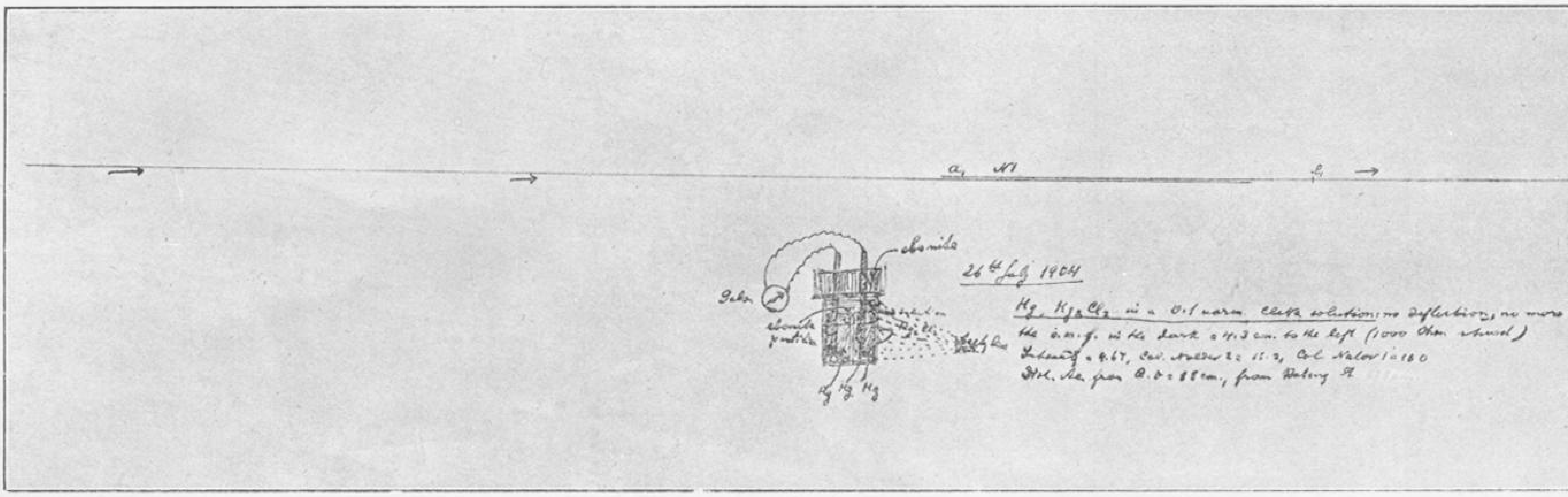


Plate N22.

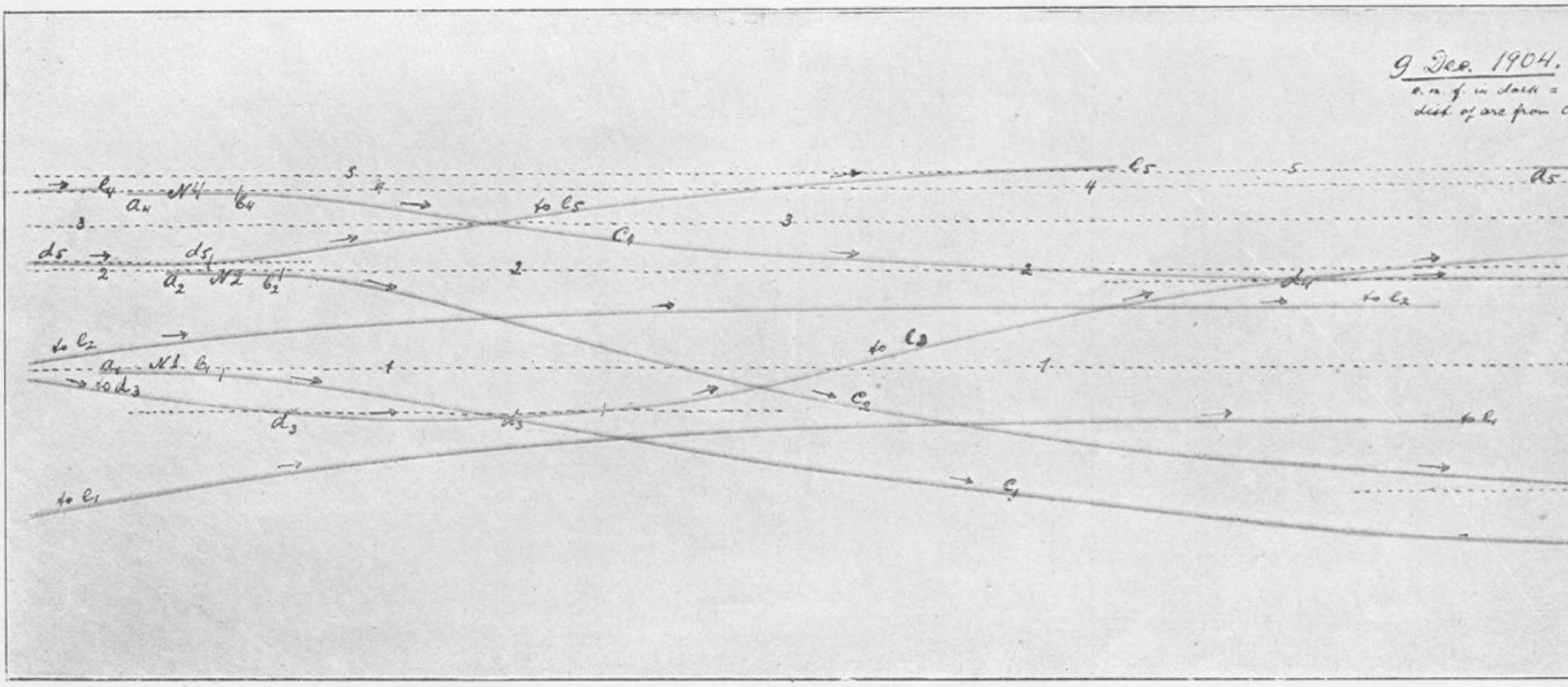


Plate N23.

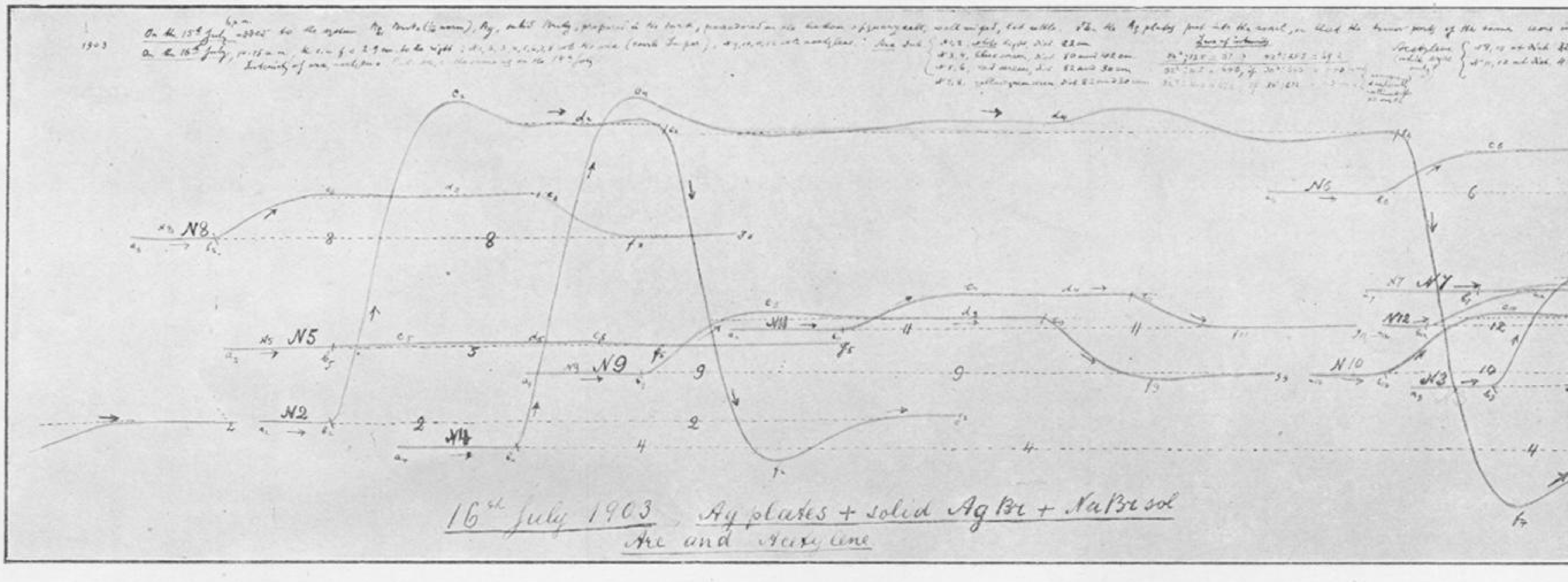
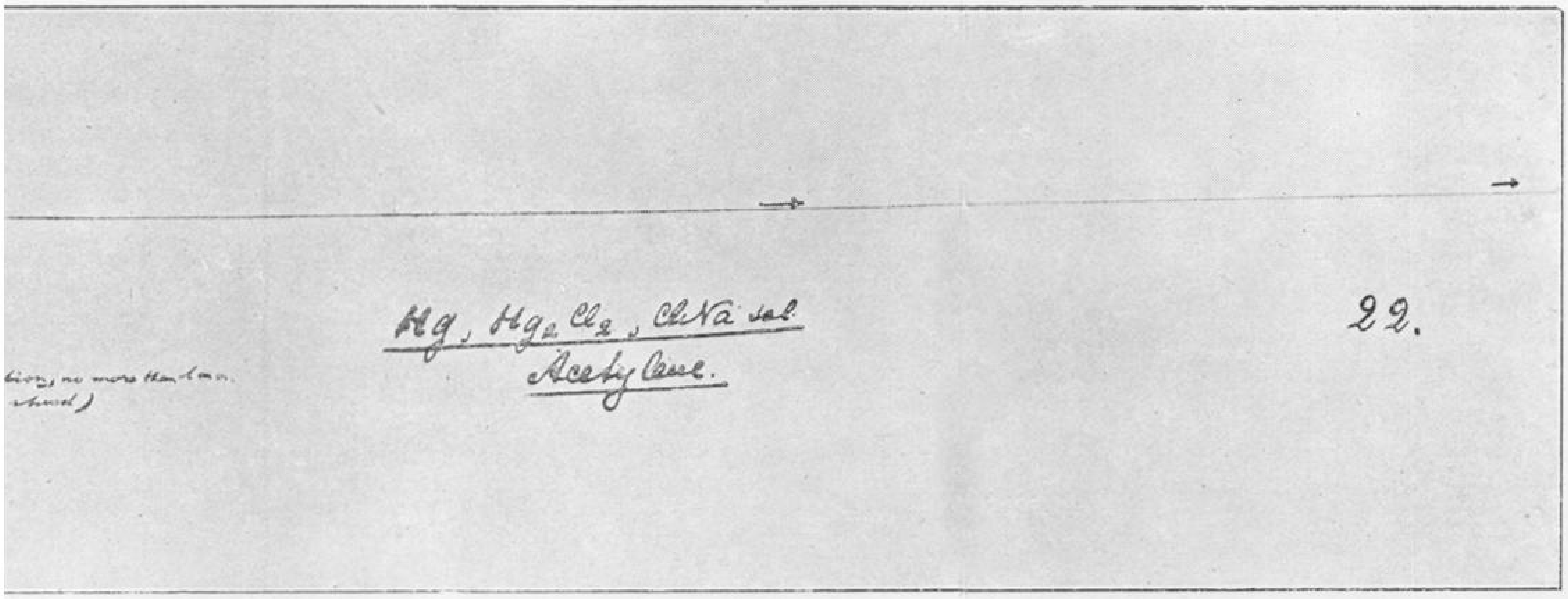
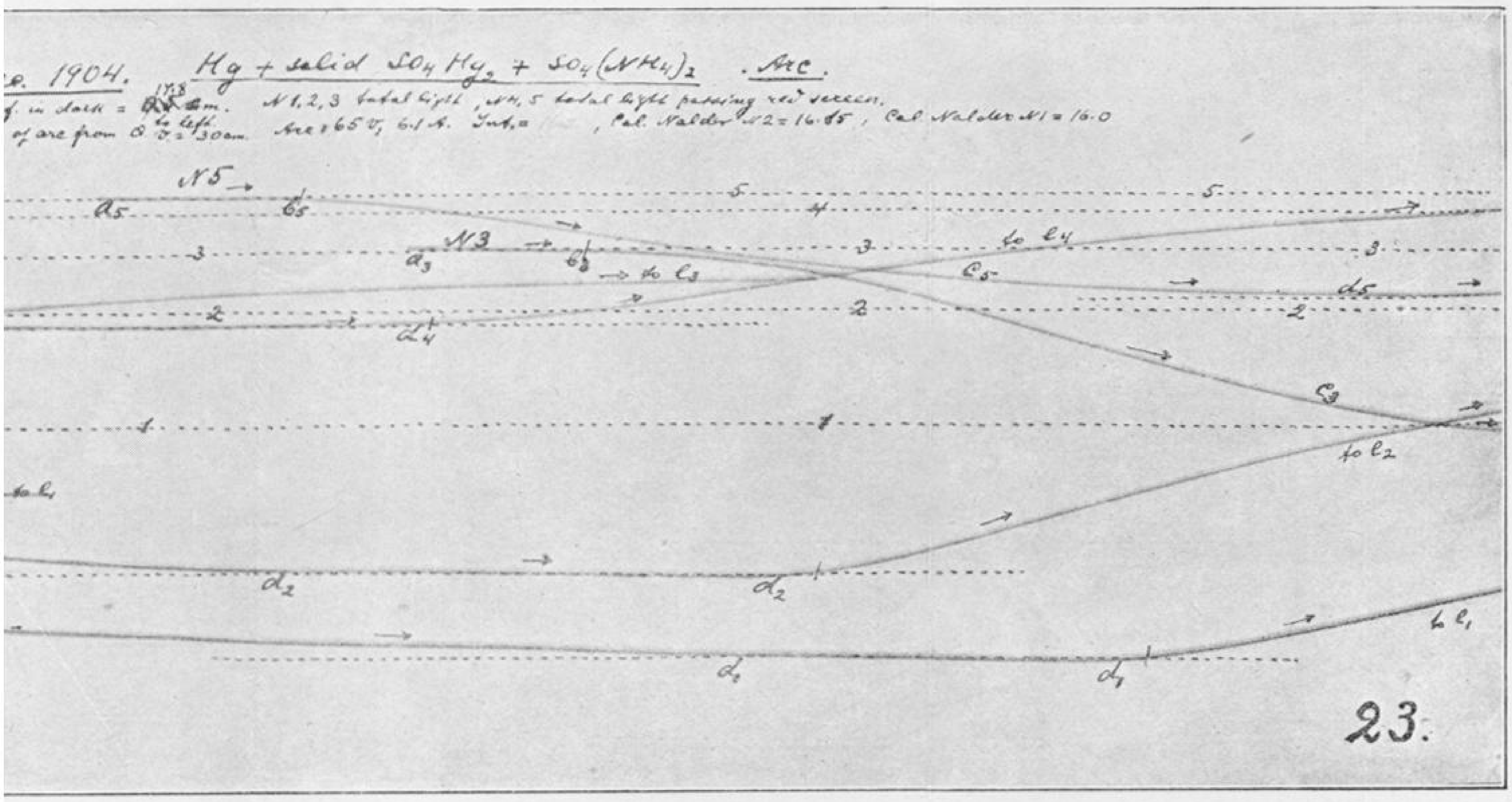


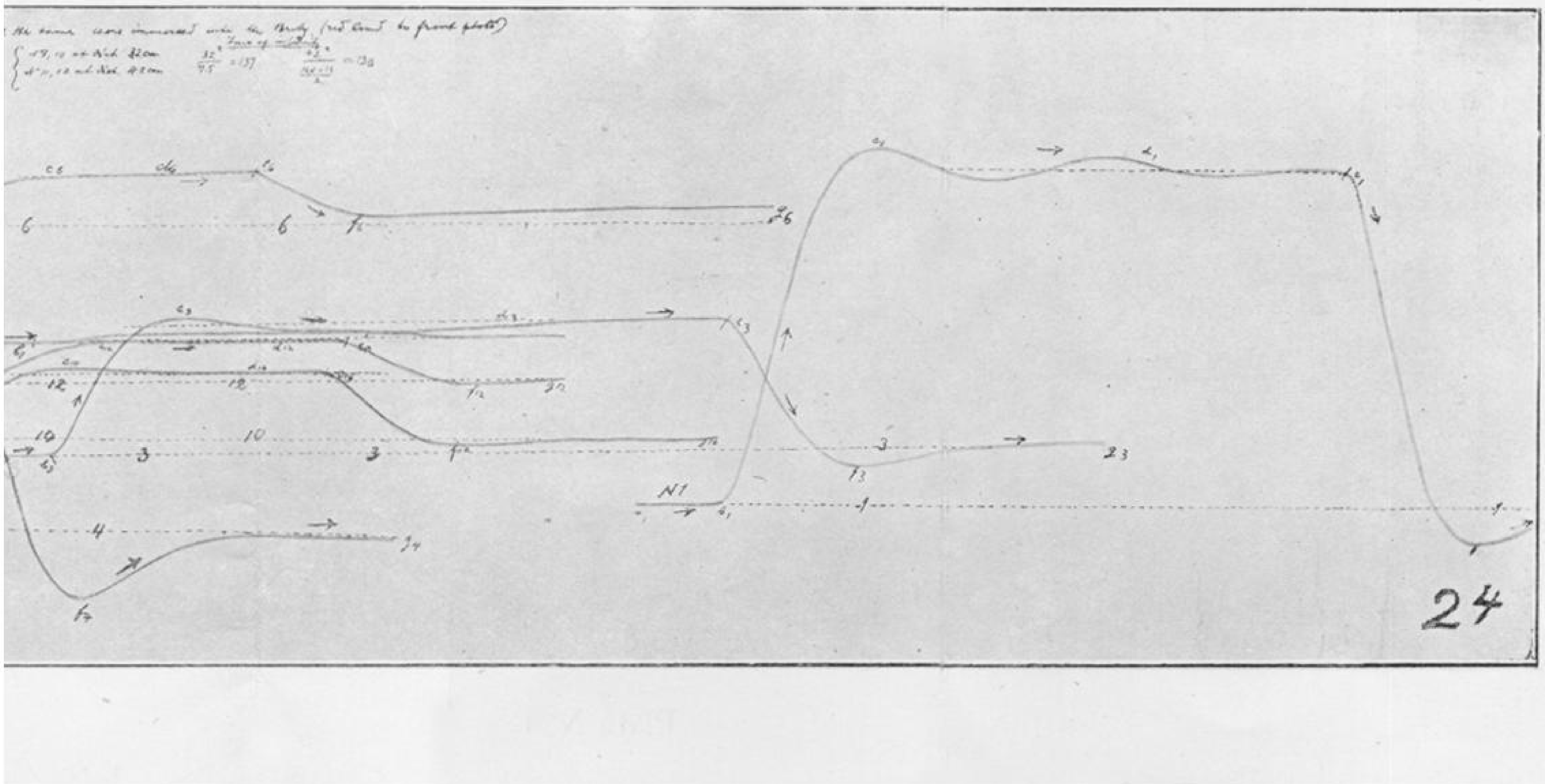
Plate N24.


Hg, Hg₂Cl₂, ClNa sol.
Acetylene.
tion, no more than 1mm.
shown)

22.


. 1904. Hg + solid SO₄Hg₂ + SO₄(NH₄)₂ . Arc.
f. in dark = 17.8 cm. N1,2,3 total light, N4,5 total light passing red screen.
of arc from C. to left = 30cm. Arc 65 V, 6.1 A. Int.= , Cal. Nalder N2 = 16.85, Cal. Nalder N1 = 16.0
N5
a₅
c₅
N3
a₃
c₃
to e₃
to e₄
c₅
d₅
a₄
e₃
to e₂
to e₁
d₂
d₂
d₁
d₁
5
4
3
2
1

23.


c₆
d₆
e₆
f₆
6
c₃
d₃
e₃
f₃
12
10
3
4
f₄
N1
a₁
d₁
e₁
1

24