VIII. *On the Electrical Resistance of Thin Liquid Films, with a revision of* NEWTON'S *Table of Colours.*

By A. W. REINOLD, *M.A., Professor of Physics in the Royal Naval College, Greenwich, and* A. W. RÜCKER, *M.A., Professor of Physics in the Yorkshire College, Leeds.*

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[PLATES 59, 60.]

I.

IN a preliminary note read before the Royal Society in June, 1877,[*] we stated the results of some observations in which an electric current was used in investigating the properties of soap films. These observations were made in the course of an enquiry (then incomplete) as to whether the resistance offered by a soap film to an electric current is inversely proportional to its thickness, and our object in undertaking this was to obtain, by a novel method, evidence as to the value of previous experiments by which various physicists had from time to time attempted "to obtain from the phenomena of capillarity, or from observations on liquid films, an indication of the magnitude of the radius of molecular attraction."

Since that date we have had but few opportunities of carrying out our research in common (as was necessary), and hence the long delay which has taken place; but we are now in a position to state the results of our later experiments, in which the method has been in several respects altered, and the apparatus considerably improved.

In the first place, it will be well to give a summary of the conclusions of previous observers. QUINCKE,[†] as the result of a well-known research, conducted by immersing in water and mercury plates of glass covered by wedge-shaped films of silver, collodion, and other convenient substances, arrived at the conclusion that the radius of molecular attraction is approximately equal to 50×10^{-7} centims. PLATEAU[‡] estimates it at less than 59×10^{-7} centims. LÜDTGE,[§] on the other hand, asserts that the thickness of a soap film becomes almost immediately after its formation less than twice the radius

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[*] Proc. Roy. Soc., No. 182, 1877.

[†] Pogg. Ann., 1869, Bd. cxxxvii., p. 402.

[‡] 'Statique des Liquides,' 1873, tom. i., p. 210.

[§] Pogg. Ann., 1870, Bd. cxxxix., p. 620.

of molecular attraction. This conclusion, if correct, would show that QUINCKE's number is at least ten times too small.

The values derived from the dynamical theory of gases are, however, much smaller. VAN DER WAALS[*] finds $0{\cdot}23 \times 10^{-7}$ centims. to be an inferior limit, but considers QUINCKE's value too high.

O. E. MEYER,[†] on the contrary, thinks that the cause of the discrepancy is to be found in the fact that the expression "radius of molecular attraction" (*Wirkungssphäre*) is used in the theory of capillarity in a sense different from that in which it is employed in the theory of gases. He believes that, if we possessed a kinetic theory of liquids, the magnitude investigated by QUINCKE and PLATEAU would be found to be that of the free path of the molecules in the liquid, or would acquire some similar meaning.

PLATEAU's experiments consisted in measuring the pressure of the air confined in a soap bubble by means of a water manometer. A decrease in that pressure might be expected if the thickness of the film became less than twice the radius of molecular attraction. His conclusion is based on the fact that no regular change was observed in the case of a bubble which lasted for three days, and thinned to the pale yellow of the first order of NEWTON's scale.

LÜDTGE formed a liquid film at one end of a cylindrical tube, and, when it had become thin, closed the other end by a newly formed film. A small quantity of air was then forced into the enclosed space through an orifice in the side of the tube. The films assumed the form of spherical segments, and it was found that that produced by the thinner film was the less curved. The inference that the superficial tension increased as the thickness of the film diminished, was supported by other experiments, for an account of which we must refer to the original paper. We may, however, remark that the large magnitude assigned to the radius of molecular attraction, and the statement that the superficial tension is increased instead of diminished when the thickness of a film is less than twice that magnitude, are opposed to the views of most physicists.[‡] The observations both of PLATEAU and LÜDTGE are open to the objection that there is no proof that the soap solution used remained unaltered during the experiments.

A mixture of glycerine and water will gain or lose water according to the magnitude of the tension of the aqueous vapour in its neighbourhood. The superficial tension of a soap solution would thus tend to increase in damp, to decrease in dry, air. The direct effects of absorption or evaporation might, however, be diminished or even reversed by the changes of temperature with which they were accompanied. PLATEAU, to prevent the absorption of moisture, enclosed the bubble in a small glass vessel, at the bottom of which were placed some sticks of caustic potash. This arrangement would tend, and

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[*] 'Beiblätter,' Bd. i., p. 19.

[†] 'Die Kinetische Theorie der Gase,' 1877, p. 236.

[‡] See 'Statique des Liquides,' PLATEAU, tom. i., p. 205, 1873. Also 'Théorie Mécanique de la Chaleur,' DUPRÉ, p. 358, 1867.

in fact was designed, to reduce the thickness of the film by evaporation, and would thus alter its constitution.

LÜDTGE, anticipating the objection that the effect observed may have been due to the larger proportion of water absorbed by the older and thinner film, points to similar results obtained with a decoction of Quillaja. He appears to have overlooked the fact that if the experiments were performed in a dry atmosphere, the cold produced by evaporation might have been the true cause in both cases.

The difficulty of estimating accurately what the magnitude of the effect of such a cause might be was much enhanced by the fact that no observations had been made on the amount of water gained or lost by a soap film in a given time. The retrogression of the colours, which, after indicating for some time a decrease, often show an increase in thickness, had indeed been observed by PLATEAU. It was, however, impossible to say how far this change was directly due to absorption. Considerable masses of liquid are, as we shall hereafter show, often drawn into a film from the reservoir furnished by the relatively thick portions in contact with its solid supports. An imperceptible current of this kind might, whatever its cause may be, increase the thickness of the film without altering the proportions of its constituents. On the other hand, films thinning under the influence of gravity might, and, as our observations prove, often do, absorb large quantities of vapour without any sign of retrogression in the colours. Under these circumstances, the results of previous observers being in conflict, and so little being known as to the magnitude and rapidity of the changes of constitution which a soap film could undergo without rupture, it appeared desirable to investigate the subject from a novel point of view.

SONDHAUS* had attempted to study the passage of an electric current through a soap film, but failed, as his apparatus was not sufficiently delicate. With this exception, no investigation had, so far as we are aware, been made previous to our own on the resistance of liquid films. Experiments of this kind nevertheless seemed likely to afford information as to the probability of gaining, from observations on liquid films, any accurate knowledge of the magnitude of the radius of molecular attraction. In the entire absence of experimental results it was doubtful whether the specific resistance of a film is the same as that of the liquid from which it is produced. If the magnitude of the radius of molecular attraction is as great as is supposed by LÜDTGE or even by QUINCKE, some indication of the approach of a film to double that magnitude might be given by a change in its mean specific resistance. On the other hand, something might be learnt by properly contrived experiments as to the alterations in the constitution of a film wrought by variable hygrometric conditions.

The object then of our investigation has been to trace the effect on the specific resistance of a soap film—

(1.) Of change of thickness ;

(2.) Of change in the hygrometric condition of the surrounding air.

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* Pogg. Ann. 1876, Bd. clvii., p. 95.

By comparing the results with observations on the liquid in mass, we are able to draw certain conclusions as to the light thrown on the molecular constitution of liquids by experiments on soap films.

The investigation divided itself into two parts, viz.: the determination (1) of the thickness, (2) of the resistance, of a film at any particular epoch, and as these, though carried on at the same time, were to a great extent independent, it will be convenient at first to treat of the former alone.

II. *The Liquid.*

The soap films were made in accordance with the receipt given by M. PLATEAU, with the exception that a small quantity of saltpetre was added to increase the conductivity. One part by weight of oleate of soda was dissolved in 40 parts of water, together with (in general) either 3, 5 or 7 parts of saltpetre to 100 of water. Three parts by volume of this liquid were then mixed with 2·2 parts of PRICE'S glycerine. It will be convenient to call a solution containing *n* parts of saltpetre to 100 of water an *n* per cent. solution. The solutions thus prepared produced in the course of a few days a flocculent precipitate which could not be separated by filtering. They were therefore placed in long vertical glass tubes furnished with caoutchouc stoppers at the upper, and stop-cocks at the lower ends. In time the liquids cleared by the precipitate rising to the top, and became sufficiently transparent to allow of their refractive indices being measured. They could then be drawn off for use without disturbing the impurities on the surface. This operation of clearing occupied several months, and was always carefully performed in order to ensure the homogeneity of the liquids. It will be convenient to refer to a liquid thus prepared as a *standard solution;* others containing greater or less proportions of glycerine will be called *derived solutions.*

III. *Refractive Index.*

The following table (Table I.) gives the refractive indices, for sodium light, of several solutions, the composition of which is indicated in the first three columns.

TABLE I.

Percentage of salt in standard solution.	Parts of standard solution by volume.	Parts of water or glycerine by volume.	Refractive index.
5	100	0	1·3969
5	95	5 H_2O	1·3947
5	95	5 glycerine	1·4002
. .	0	100 glycerine	1·4715
8·82	75·6	24·4 glycerine	1·4155

The refractive index no doubt varied from film to film, as the composition of the liquid from which they were formed was often considerably altered by the absorption or evaporation of water. As a knowledge of the amount of water thus gained or lost was one of the objects in view, it was necessary to assume as a first approximation that the refractive index was constant. The method of testing and improving upon this assumption will be explained hereafter.

IV.—*Revision of* NEWTON'S *Table of Colours.*

The determination of the thickness of the films involved a knowledge of (in addition to the refractive index) (1) the angle of incidence, (2) the colour of the film, (3) the thickness of a plate of air exhibiting that colour when illuminated by light at normal incidence. The method of measuring the angle of incidence will be described when an account is given of the apparatus employed (see p. 461). It is sufficient to say here that the films experimented upon were in the form of cylinders with vertical axes. Light was reflected upon them from a fixed mirror; a brightly illuminated vertical band was thus produced, and the thickness at any point was determined by the colour exhibited by this band. To increase and test the accuracy of the observations, two mirrors and therefore two beams of light, incident at different angles, were used.

The apparent thickness of a film is defined to be the thickness of a plate of air which shows, when illuminated at normal incidence, the same colour as that displayed by the more obliquely illuminated of the two bands. A good deal of labour was saved in the calculations by the use of this quantity instead of the real thickness, which could of course be readily deduced from it.

NEWTON, in describing the rings which bear his name, gives two lists of colours. In the first* seventeen colours are enumerated in the first four orders. In the second, which is reproduced in WATTS' 'Dictionary of Chemistry' (Art. *Light*), this number is increased to twenty-six. In this more extended list many tints are included which shade into those nearest to them by gradations too subtle to be readily appreciated; and since for purposes of measurement it is of little use to retain the names of colours unless the eye is able to distinguish with some approach to certainty where they begin and end, the following list, but little more extended than NEWTON'S first, was employed. The colours in brackets are those which are not included in NEWTON'S first list. The blue of the first order is omitted.

First order: Black, white, yellow, [orange], red.
Second order: Voilet, blue, green, yellow, [orange], red.
Third order: Purple, blue, green, yellow, red, [bluish red].
Fourth order: Green, [yellowish green], red.

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* NEWTON'S 'Opticks,' 3rd Edition, London, 1721, pp. 174 and 206.

In the other orders NEWTON'S two lists and our own agree in distinguishing only two colours, green and red.

It was soon found that a more precise method of nomenclature and a convenient system of symbols for the tints were needed. Each colour was therefore sub-divided into ten equal parts which were indicated by numerals from 0 to 9 in the order of increasing thickness. Any tint could be readily expressed by writing down the first letter of its name followed by a bracket containing two numbers, the first of which showed the order, and the second the part of the colour referred to. Thus B [3, 0,] B [3, 9] and B [3, 5] indicate the divisions of the blue of the third order nearest to the purple, nearest to the green, and halfway between the boundaries of those colours respectively. The last of these corresponds to the thickness answering to the same colour in NEWTON'S scale.

If a single tint is alone presented to the eye, it is often difficult to assign the precise value to be attached to it. The films, however, generally displayed several colours in the same vertical line, and it was thus possible to reinforce the judgment as to the tint at any point by estimating the distances of that point from the boundaries of the colour in which it lay. The increment in thickness corresponding to the entire range of a colour, varies considerably, and thus the tenth of a tint has also different values in different parts of the scale. As a rule it is less than one per cent. of the thickness, though in the blue of the second order it rises to 3 per cent. It was thus sometimes necessary and possible to estimate to the twentieth of that colour.

A valuable check on the accuracy of the observations was afforded by the use of the two mirrors. The light reflected from the first was incident on the film at about 45°, and the angle of incidence of that reflected from the second was made as small as possible and varied on different occasions between 2° and 7°. When the thickness of the film at any given level was to be measured, the horizontal spider line of a cathetometer-telescope was brought to that level, and the colours were noted at the points were it crossed the two bright strips.

The thicknesses corresponding at normal incidence to the colours at these points (T_1 and T_2), and the true thickness of the film (T) are connected by the equations

$$T = \frac{T_1}{\cos i_1'} = \frac{T_2}{\cos i_2'},$$

where i_1' and i_2' are the angles of incidence on the internal surface of the film. Two simultaneous but independent measures of the thickness were thus obtained, the mean of which was adopted as correct.

This method presented the additional advantage of affording a means of checking the accuracy of the scale of colours employed. The ratio $T_1 \div T_2$ depends only on the nature of the liquid and the magnitude of the angles of incidence. On calculating it for a number of observations, it was soon found that although tolerably constant for any particular colour, it varied considerably for different colours. This shewed that the thicknesses corresponding to the colours were not identical with those furnished by NEWTON'S scale, even when readjusted on account of the omissions already referred to. Nor was this surprising. The above description of the method of estimation is sufficient to show that in all probability no two observers would agree as to the positions of the boundaries between neighbouring tints. If accuracy is required each must construct his own scale.

This might be undertaken by observations on a set of NEWTON'S rings. Two difficulties, however, here arise, the first due to the fact that, even when NEWTON'S rings are produced on a large scale, the colours are far more crowded than on the films, and thus not only is their appearance somewhat changed, but differences of hue clearly distinguishable in the one case are lost in the other. The second difficulty has its origin in the distortion of the lenses, used in the production of NEWTON'S rings, in the neighbourhood of their point of contact. Calculations based on the assumed sphericity of the lenses are thus of little use near the central black patch. For these reasons it was determined to supplement the observations on NEWTON'S rings by those made on the films, to determine the thicknesses corresponding to a few clearly marked colours by the first, and the ratios of the thicknesses of the intermediate tints by the second.

As it was necessary to produce the rings on a large scale, a pair of the curved plates, sold for this purpose by Mr. LADD in a brass case, were placed in a vertical plane. The diameters were measured by the cathetometer. The light employed was reflected from a mirror and passed through a slit about two feet distant from the rings. By placing a soda flame behind the slit, daylight and homogeneous light incident at the same angle could be used in turn. If T be the thickness corresponding to a ring of colour of diameter Δ, which lies between the n^{th} and $(n+1)^{\text{th}}$ dark rings formed by the soda flame, the diameters of which are δ_n and δ_{n+1},

$$T=\frac{588}{2}\left\{n+\frac{\Delta^2-\delta_n^2}{\delta_{n+1}^2-\delta_n^2}\right\}.$$

By thus deducing the value of T from the diameters of the dark "soda" rings in its immediate neighbourhood, errors due to the non-sphericity of the lens are much diminished, and the observation is independent of the closeness of contact between the two plates of glass in the centre of the system.

To obtain accurate results in the neighbourhood of the first dark soda ring it was necessary to determine some additional fixed points. A plate of blue cobalt glass was therefore interposed between the mirror and the rings. The light thus obtained was not homogeneous, but was sufficiently nearly so to make it safe to assume that the thicknesses corresponding to the first few dark rings were proportional to the natural numbers.

The diameters of the four smallest rings were measured, the wave length of the light was computed from the larger pair by means of the above formula, and this being known, the inner pair could be used as reference lines for colours in their immediate neighbourhood. On one occasion, four measures, each made on a single ring, gave 431, 429, 431 and 438 millionths of a millimetre as the wave length respectively; on another occasion two measures gave 432 and 438. As none of these numbers differ from their mean by more than 1·2 per cent. these measurements enable us to estimate the accuracy of the method. Red glass (coloured with oxide of copper) was used in the same way, and two measures agreed in giving the wave length as 615. In the case of the blue of the second order the difficulty was much increased by the fact that the boundary of a colour so near the centre of the rings is very irregular. If we except this tint, however, no measurement ever differed from the mean of the measures on the same colour by more than 1·6 per cent. As three sets of measurements were taken at intervals of nine and six months respectively, and as in most cases three, and in some five, observations were made in each colour, it seems that the errors of recognition and measurement combined did not (except in the case mentioned) exceed 1·6 per cent.

Side by side with these experiments, which were purposely made at long intervals to test the constancy of the colour estimations, other supplementary observations were made upon the films themselves. The scale of colour at first used was obtained by assigning to each tint the thickness ascribed to that of the same name in NEWTON'S second scale, and adjusting the boundaries so that the number thus assigned to any tint should be the mean of those assigned to its boundaries. The scale so formed was then tested in the following way. The angles of incidence and the refractive index being known, the ratio of the cosines of the angles of internal incidence could be calculated. The colours at the points where the horizontal cross wire cut the illuminated bands on the film having been noted, the air-thicknesses corresponding to them at normal incidence were taken out from the table of colours, and the ratio of the larger to the smaller calculated and divided by the ratio of the cosines. The number so obtained will be referred to as the *quotient*, and the difference between it and unity was taken as a measure of the accumulated errors of the scale and of the observation. The mean apparent thickness of the film was easily deduced from the quotient.

As has been already stated, the observations proved that the table of colours required revision. This was effected by assigning the quotients to the colours shown by the more obliquely illuminated band in the observations by which they were obtained, and re-arranging the table so as to make the mean of the quotients assigned to each colour as nearly as possible unity. Care was taken to make the revised table agree closely with the observations on NEWTON'S rings.

In January, 1879, 600 double colour observations were made on the two illuminated bands, and the table of colours as corrected by them was again revised by means of 1,142 observations made in September and October, 1879. No further change has been found necessary, although the accuracy of the table thus corrected has been further tested by more than 500 observations made in September and October, 1880. It is hardly necessary to state that these revisions were carried out without any reference to the electrical experiments with which the results obtained by them were to be combined. As, however, the conclusions arrived at in this paper with respect to the specific resistance of soap films depend only on the final series of experiments made during September and October, 1880, it is satisfactory to note that the table of colours in no way depends upon these experiments, but that they are used below only to test the results arrived at a year before.

The following details will serve to show the accuracy attained in the two sets of experiments, in the calculation of which the table as finally adjusted was used:—

Experiments made in September and October, 1879.—The films were examined under very varying hygroscopic conditions, and it was thought advisable to see whether the value of the quotient was affected by the varying dilution of the films. The value of the quotient would have been about 2 per cent. greater for pure water than for a standard solution. Twenty films were selected, which gave tolerably constant specific resistances, and the means of the ratios given by observations on each colour were calculated for each film. The mean of these numbers for the ten films which had the lowest specific resistance, and were therefore (as will be shown hereafter) the more dilute, was 1·004, for the other ten films it was 0·994. A precisely similar result was attained when the quotients were compared film by film instead of colour by colour. As the effects of evaporation or absorption seemed, therefore, to appear on the means of a large number of observations, and as we had not at that time all the data for calculating the theoretical quotient in each case, the mean of the quotients for each colour was divided by the mean of all the quotients. These numbers are inserted in column VII. of Table II.

Experiments made in September and October, 1880.—These experiments being, for the reasons already stated, the more valuable as tests of the table of colours, we give the following rather fuller details:—516 observations were made, and (omitting fractions) in the case of 52, 84, and 95 per cent. of these the difference between the quotient and unity was less than ·01, ·02, and ·03 respectively. Hence in 84 per cent. of the observations the mean value adopted differed from both of those from which it was derived by less than 1 per cent. The mean value of the mean quotients for all the colours was 0·9985. The ratio of the two cosines was the same in all cases, viz.: 1·157. Both these numbers were calculated with the refractive index of the standard solution.

In comparing the new table with that of NEWTON, it is best to take from the latter only such colours in the second list as have on each side of them colours which also occur in our own list, *i.e.*, to confine the comparison to those cases when no question as to the boundaries of the colours can arise.

In Table II.—Column I. contains the names of the colours.

Column II. the symbols.

Column III. the thickness in terms of 10^{-5} centims., according to NEWTON'S scale.

Column IV. the thickness according to the observations on NEWTON'S rings.

Column V. the thickness according to the corrected scale.

Column VI. the difference of thickness corresponding to a tenth of a tint in each of the colours measured.

Column VII. the mean quotient for each colour obtained in September and October, 1879, each (for the reasons given) divided by their mean.

Column VIII. the mean quotients obtained in September and October, 1880, also divided by their mean to make them comparable with the preceding.

Column IX. the difference between unity and the mean of the numbers in columns VII. and VIII., expressed in terms of 0·001.

TABLE II.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
First order—								
Red	R (1, 5)	. .	. .	2·84	·032	. .	1·003	+ 3
Second order—								
Violet	V (2, 5)	. .	. .	3·05	·011	. .	1·010	+10
Blue	B (2, 5)	. .	3·34	3·53	·081	1·000	0·998	− 1
Green	G (2, 5)	3·78	. .	4·09	·034	1·003	0·999	+ 1
Yellow	Y (2, 5)	4·07	4·50	4·54	·054	0·998	1·000	− 1
Orange	O (2, 5)	4·31	. .	4·91	·022	0·996	0·995	− 4
Red	R (2, 5)	. .	. .	5·22	·040	1·006	1·003	+ 5
Third order—								
Purple	P (3, 5)	. .	. .	5·59	·035	0·996	0·995	− 4
Blue	B (3, 0)	. .	5·73	5·77	·053	0·997	0·993	− 5
,,	B (3, 5)	5·85	. .	6·03	. .	. .	. .	. .
Green	G (3, 5)	6·29	. .	6·56	·053	1·006	1·000	+ 3
Yellow	Y (3, 5)	6·79	7·11	7·10	·056	1·001	1·002	+ 2
Red	R (3, 5)	7·25	. .	7·65	·051	1·003	0·994	− 1
Bluish-red	BR (3, 5)	8·00	. .	8·15	·051	1·001	0·997	− 1
Fourth order—								
Green	G (4, 0)	. .	8·58	8·41	·103	0·997	1·004	+ 1
,,	G (4, 5)	. .	. .	8·93	. .	. .	. .	. .
Yellow-green	YG (4, 5)	9·00	9·71	9·64	·041	1·004	1·002	+ 3
Red	R (4, 5)	10·08	. .	10·52	·134	0·994	0·997	− 4
Fifth order—								
Green	G (5, 0)	. .	11·29	11·19	·141	0·995	1·000	− 2
,,	G (5, 5)	11·50	. .	11·88	. .	. .	. .	. .
Red	R (5, 0)	. .	12·66	12·60	·150	0·996	0·997	− 3
,,	R (5, 5)	13·12	. .	13·35	. .	. .	. .	. .
Sixth order—								
Green	G (6, 0)	. .	14·01	14·10	·138	. .	1·001	+ 1
,,	G (6, 5)	14·68	. .	14·79	. .	. .	. .	. .
Red	R (6, 0)	. .	15·44	15·48	·157	. .	1·009	+ 9
,,	R (6, 5)	16·25	. .	16·27	. .	. .	. .	. .
Seventh order—								
Green	G (7, 0)	. .	16·99	17·05	·164	. .	. .	. .
,,	G (7, 5)	17·75	. .	17·87	. .	. .	. .	. .
Red	R (7, 0)	. .	18·49	18·69	·135	. .	. .	. .
,,	R (7, 5)	19·25	. .	19·36	. .	. .	. .	. .
Eighth order—								
Green	G (8, 0)	. .	20·04	20·04	·111	. .	. .	. .
Red	R (8, 0)	. .	21·15	21·15	. .	. .	. .	. .

We are unable to place much confidence in the observations of the violet of the second and the red of the first order, as they were very few in number. Even in the case of the blue of the second order, though the quotients agreed well together, the difference between the figures in columns IV. and V. is too large to be satisfactory. We have therefore in most of our work taken 4×10^{-5} centims. as the smallest apparent thickness which could be used where great accuracy was required. For the rest, the difference between the observations on NEWTON'S rings and the corrected table rarely exceed one per cent., while NEWTON'S scale in parts differs from both by as much as ten per cent. of the thickness. On the whole we think the optical observations alone show that the corrected scale above the blue of the second order is accurate to one per cent.

V. *Method of Experiment.*

In our previous experiments, described in the paper already referred to, a cylindrical film was formed, supported above and below by cylindrical platinum cups, and its resistance was measured by WHEATSTONE'S bridge. This method was unsatisfactory, first, because it took no account of any "polarisation" which might occur at the extremities of the film; and secondly, and this is the more important disadvantage, because it compelled us to measure the resistance of the film as a whole, instead of selecting any part which might be suitable to our purpose.

The method since adopted and now to be described is free from the above-mentioned disadvantages. It depends upon the measurement of the difference of potential, produced by the passage of a current, between two horizontal sections of the film. Steel sewing needles or gold wires (preferably the latter) are inserted in the film, and the difference of potential between them measured by an electrometer, and compared with that between two other points in the same circuit separated by a known resistance. Three needles were actually employed, supported horizontally, and about 15 millims. apart, the upper one being about 5 millims. below the upper cylindrical cup, and the lowest 10 millims. from the lower cup. Calling the needles 1, 2 and 3, counting from top to bottom, the difference of potential between 1 and 2, between 2 and 3, or finally between 1 and 3 could be measured as might be desirable. It is clear that this method disposes of any difficulties that may arise (1) from counter-electromotive force set up at the electrodes by the passage of the current, and (2) from irregularities in the substance of the film itself at or near its supports. Observation shows that such irregularities are of frequent occurrence. For example, it happens not unfrequently that a film, after thinning continuously for some time, begins to thicken from the bottom, the colours rising and being so crowded together that it is difficult to distinguish them. Again, white flecks occasionally appear at the top, and more frequently black patches, forming themselves gradually into a ring of black, the resistance of which is, as we have already shown,* enormously great in comparison with that of a

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* *Loc. cit.*

coloured ring of the same width, even when the colour is of the second or first order.

In discussing the method it is necessary to show that no sensible error was caused by the disturbance of the equipotential lines which accompanied the introduction of the needle points into the films. The distance between any two needles being greater than those between the upper and lower needles and the metal rings by which the cylinder was supported, it will be sufficient to consider the extremities of the film only.

A small aggregation of liquid was always observed around the needle points. Its dimensions were variable, but the diameter was never greater than a millimetre and a half. If we assume that the resistance of this mass (of radius a) was infinitely small, compared with that of the surrounding film, and that the dimensions of the cylinder were infinitely greater than a, the equation to each of the disturbed equipotential lines would be of the form

$$y\left\{1-\frac{a^2}{x^2+y^2}\right\}=\text{constant},$$

where the axes of x and y are horizontal and vertical respectively.

The maximum displacement, by the introduction of a needle, of the equipotential line which passes through $x=0$, $y=\eta$ would therefore be $\frac{a^2}{\eta}$. The condition of accuracy is that this quantity shall be negligible at a distance from the needle equal to that of the metal ring which bounds the cylinder. This distance was generally greater than 5 millims., and therefore 0·11 is the limit of error. The distance between two needles being 15 millims., it is therefore possible that an occasional error of 0·75 per cent. may have been caused, but we doubt whether it ever reached this amount; and in all the more important experiments, viz.: those made after September 20, 1880, it certainly did not, as the two lower needles were exclusively used, and the error must therefore have been halved.

The thickness of the film between two needles was taken as the mean of the thicknesses at the needles. These were measured in turn, the time of each observation being noted, and curves were drawn of which the ordinates represented the thicknesses and the abscissæ the times. It was found that to make and record a measure of the thickness occupied about half a minute, but, when the film was thinning slowly, observations were made at longer intervals. The curves were used to correct errors of observation by smoothing off irregularities. On a few occasions errors amounting to 2 per cent. of the thickness were thus detected. In the curves themselves the error of observation probably nowhere exceeds 1 per cent., and approaches that amount only when the films were very thin.

The electrical observations on the resistance of the film were carried on simultaneously with the above, and curves showing the relation between the resistance and time were in like manner constructed. By taking out from these two sets of curves the thickness and resistance at any particular time, the specific resistance could be calculated by the formula given in our previous paper.

When the films became thin they were generally so uniform in tint that it was sufficient to determine the thickness half way between the two needles.

VI. *Description of the Apparatus.*

The experiments were made in a room with a south aspect, the film apparatus being supported in the window recess. Plate 59, fig. 1, represents a sectional elevation of this apparatus from front to back, taken very nearly through the centre. Plate 60, fig. 5, shows the same in plan, with the mirrors and the telescope of the cathetometer. A and B (fig. 1) are iron cylindrical cups, each 33 millims. in diameter, placed vertically one above the other, between the edges of which the cylindrical liquid film is formed. A small brass tube C, attached to A, slides with easy friction through another tube F, and enables the length of the film to be adjusted at will. F has a brass flange which carries a binding screw, and is cemented to a glass disc G, for closing the circular aperture at the top of the glass case HH. Through this aperture the cup A, with attached tube, &c., can be removed from the case for purposes of cleaning. A piece of indiarubber tubing fastened to the end of the tube C passes through the base board of the apparatus at the point *a* (fig. 5), and is connected with a reservoir of air.

The lower cup B is soldered to the top of a brass tube DD, which slides in a slightly larger tube, and can hence be removed when required. The smaller brass tube E was originally intended to afford a means of filling or emptying the cup from the outside. In the later experiments it was not used for this purpose, but, its upper end being stopped up with sealing wax, it merely served as a metallic connexion between the film and the source of electricity.

A film, when under examination, is surrounded by two glass cases, the front and side faces of which are constructed of specially polished glass. The top of each is of ordinary plate glass, and the back of wood. The inner case HH fits tightly down by its wooden base upon the square ebonite platform I, by which the lower cup is insulated. The outer case H′H′ slides down upon the inner by grooves *cc*, fig. 5, and is held firmly in its place by the back of the inner case, and by the base board I′ (fig. 1). The object of the outer case is to prevent sudden changes of temperature or hygrometric state in the interior of the apparatus.

The needles (*nnn*, fig. 1, shewn also in figs. 2, 3, and 5), were, in the experiments described in this paper, made of gold wire. They pass through small holes drilled in a vertical pillar of ebonite. Fine silk-covered copper wires soldered to their extremities make connexion with the mercury cups M, and hence with the electrometer. To provide against the ebonite pillar being wetted by the bursting of the films, and the insulation of the needles from each other, and from the base of the apparatus being thereby impaired, a small glass shield is also supported by the pillar (figs. 1, 2, 3), in which holes are drilled large enough for the needles to pass through without touching it.

Figs. 2 and 3 show in detail the arrangements for moving the needles from the outside when the inner and outer cases are in their places, and for adjusting them to their proper position in the film. A brass tube, *g*, passes through the chamber below the glass case, and has at its lower end a milled head, *h*, by which it can be rotated about its axis. A brass rod, *f*, passes through it, having below a milled head, *k*, and above a pinion, *e*, which engages with the rack, *d*, carrying at one extremity the ebonite pillar and gold needles. It will thus be seen that motions of two distinct kinds can be given to the needles from without; they may be moved to and fro parallel to themselves by turning the milled head, *k*, which works independently of the outer tube, and they may be turned round a vertical axis by means of the milled head, *h*. In the figures the needles are represented at right angles to the rack, *d*, but they may be placed at any other suitable angle by turning the ebonite pillar in its socket.

Arrangement for forming the films.—This is shown on the right hand side of figs. 1 and 5. A rectangular portion of the ebonite base board is cut away, and communication thus made between the interior of the glass case and the chamber PP beneath. This aperture can be closed by a wooden trap-door, shown in dotted lines in fig. 1, and turned up or down by a milled head, *t*, at the back of the case. When it is turned down, its edges dip into a rectangular groove filled with mercury. K is a brass rod with screw thread cut upon it, which serves as a rack for the pinion, worked by the screw head, *l*. It carries eccentrically at the top a circular brass platform, on which is placed a shallow glass dish, of diameter a little greater than that of the cylinder A, containing the liquid for forming the films. The position of the rod K is such that when the platform is raised through the aperture by the screw head, *l*, and rotated by the screw head, *m*, the glass dish can be brought immediately under the cylinder A, and a horizontal film thus formed over the mouth of the latter. This done, the dish is lowered through the aperture which is then closed by the trap-door.

The object of the lower chamber PP will now be evident. It serves as a storehouse for the liquid, which can be thus introduced into and withdrawn from the film-chamber without establishing any connexion between the latter and the outward air. Its base is of ebonite, with holes in it for the electrometer wires to pass through. The cylinder DD is in contact with no material except ebonite.

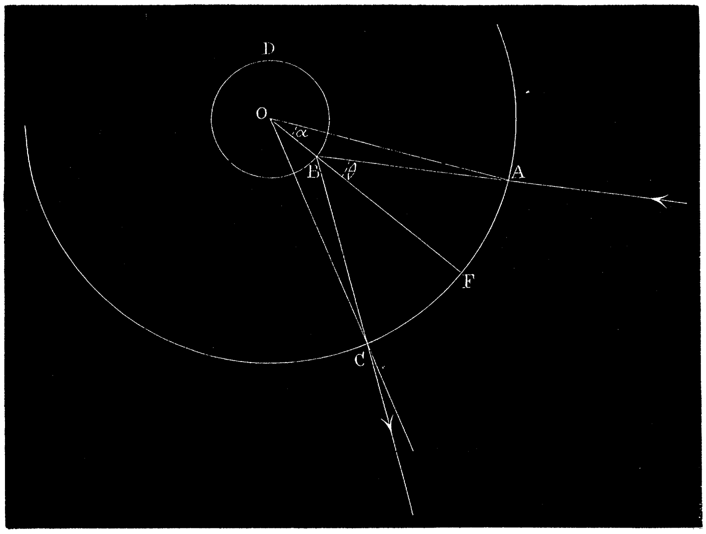
The horizontal film mentioned above is converted into a cylinder as follows:—Air being forced from the reservoir, the film becomes spherical, and increases in size until it adheres to the edge of the lower cup B, which is about three quarters full of the same liquid. It is then only necessary to withdraw air until the barrel-shaped film becomes cylindrical, an adjustment which can be accurately made with the telescope.

The needles are now made to pierce the film, an operation which can in general be effected without endangering its existence, and their position so adjusted that the points at which they meet the film may lie upon one of the vertical bands of light seen from the cathetometer.

Method of measuring the angle of incidence.—In Plates 59, 60, figs. 1 and 5, NN is a stout mahogany board which supports the whole apparatus. It has the form of an incomplete circle, the centre of which coincides with the centre of the cup B, and a paper scale graduated to half degrees is attached to its outer edge. It rests upon a long wooden slab SS, fixed in the window recess, by three points, viz.: the knob *q*, and the two levelling screws *p*, *p*. A portion of the slab SS has been cut away to make room for the lower chamber.

T is the telescope of the cathetometer, placed at a distance of about 2 metres from the film, and Q and R are the mirrors for reflecting light upon the film. The angle of incidence in the case of either mirror was determined in the following manner :—

In the accompanying figure, let B D represent the film and A F C the graduated circle, and let the light fall on the film in the direction A B and be reflected along B C. Join O A, O C.



If

$$OA(=30{\cdot}4\text{ centims.})=a,\quad\text{the angle } AOB=\alpha$$

$$OB(=1{\cdot}65\text{ centim.})=b,\quad ,,\quad ,,\quad ABF=\theta$$

then

$$\frac{a}{b}=\frac{\sin\theta}{\sin(\theta-\alpha)},$$

whence

$$\tan\theta=\frac{a\sin\alpha}{a\cos\alpha-b}$$

and thus θ is known if α is known.

The vertical cross wire of the telescope of the cathetometer being directed to the centre of the illuminated band, a plumb line is passed along the edge of the graduated circle, until it arrives at the point C, when it coincides with the cross wire. This point is noted on the circle. Similarly when the plumb line is at A, its image formed by reflection coincides with the cross wire. We thus know the arc AC and consequently the angles α and θ.

Successive readings made in this way rarely differed by more than 10′, and as the mean of several determinations was always taken, the accuracy of the method was amply sufficient for our purpose. The values of α during the experiments described in this paper were 42° 41′ and 2° 44′.

The Hygrometer.—Fig. 4 represents the hair hygrometer and the thermometer attached to it. The hair was cleaned according to the method prescribed by REGNAULT. The index is of ivory, and is graduated in degrees of arc. When the instrument was placed under a receiver, dried by sulphuric acid, and left for 24 hours, the index stood at 0°. When the receiver was saturated with aqueous vapour the index stood at about 60°. In the experiments described, the hygrometer was only used for the purpose of ascertaining whether any change in the hygrometric state of the air surrounding the film took place while the film lasted. No attempt was made to obtain the actual values of the hygrometric state corresponding to the indications of the instrument.

The position of the hygrometer in the case is shown at V, fig. 5. A strip of glass was placed in front of it to protect it from the spray caused by the bursting of the films.

Method of maintaining a constant hygrometric state.—In many of the experiments it was necessary to prevent as far as possible any absorption of vapour by or evaporation from the films. To check evaporation, the lower cup B was filled with liquid to within about 2 millims. of the edge. Two dishes containing the liquid and exposing an evaporating surface of about 20 square centims. were also placed in the inner chamber. On and after September 24 these were replaced by a much larger dish with an evaporating surface of about 52 square centims. Sheets of blotting paper moistened with the liquid were attached to the back and one of the sides of the inner case. One of these dipped in a small vessel containing the liquid and could be moistened by a pipette introduced through a small hole cut in the back of the apparatus.

As the inner glass case, though fitting the ebonite base board, I, sufficiently well to prevent the ready passage of air or aqueous vapour, was not absolutely air tight, small dishes containing the liquid with pieces of blotting paper, also moistened with the liquid, dipping into them, were placed in the outer case. A dish of the liquid was also placed in the chamber below the case.

The air for forming the films was contained in a bladder, fitted with pressure boards. On being forced from the bladder it passed first through two tubes containing caustic potash and pumice soaked in strong sulphuric acid respectively, and then over a surface of *liquide glycérique* contained in a horizontal tube about 2 centims. in diameter. When a constant state was required, the first film made was never used; it was left until the hygrometer and thermometer had become steady, was then broken without opening the case by giving it a sharp blow with the needles, and replaced by another. If during this operation the hygrometric reading altered by more than one or two tenths of a division, the second film was also rejected, and so on. In general, the films used had been formed without any appreciable change in the hygrometric state. Minute and even excessive as these precautions may appear, we found, as will be shown hereafter, that they were barely sufficient for our purpose.

The principal use of the chamber P was to enable us to keep the liquid used in making the films unchanged, when for special purposes we wished to charge the inner case with aqueous vapour at a greater or less tension than that proper to the *liquide glycérique.*

Insulation tests.—As before stated, the ebonite pillar carrying the three needles was protected from the spray of the bursting films by a glass shield, with holes in it for the needles to pass through. As, however, the precautions just described filled the case with large quantities of vapour, it was possible that in the course of a few hours a deposit of moisture might be formed on the ebonite pillar, or upon the glass sides of the apparatus, of such conducting power as seriously to interfere with the accuracy of the experiments. To guard against error from this source, the insulation of the needles from each other, and of the needles and the upper and lower cups from the case, was tested at the end of each set of observations. The observations were regarded as satisfactory so long as the greatest resistance measured did not exceed 0·3 per cent. of the insulation resistance. When, as happened on one or two occasions, it greatly exceeded this limit, the preceding observations were rejected.

VII.—*Description of method employed for measuring the electrical resistance of the films.*

The battery consisted of 4 LECLANCHÉ cells of the ordinary pattern. A simple circuit was formed, comprising the battery, three boxes of resistance coils, and the film to be experimented upon. The resistances consisted of (1) a box of coils ranging from 1 to 10,000 ohms, (2) ten coils each of 10,000 ohms, and (3) ten coils each of 100,000 ohms. In the case of most of the films recently observed, the resistance in the boxes was either 500,000 or 1,000,000 ohms, and two binding screws, one on each side of this resistance, could be connected by carefully insulated wires with the electrometer. The current always passed through the film from the top to the bottom.

The Electrometer.—The electrometer used is one of Sir WILLIAM THOMSON'S quadrant instruments, made by WHITE; it retains its charge remarkably well, a few turns of the replenisher being sufficient to bring the hair up midway between the two dots after the instrument has been left to itself four or five days, and no re-charging has been found to be necessary during the last eighteen months. We have found it convenient to connect the outer case of the electrometer to earth, and one of the electrodes to the induction plate. This, though not the most sensitive arrangement, has been found to give the best results. The two electrodes are also connected by fine silk-covered wires to short copper rods which dip into mercury cups placed on a sheet of glass immediately in front of the electrometer. Two other mercury cups, connected with the points whose difference of potential is required, stand close by, and gutta-percha-covered copper wire bridges, which can be arranged parallel or cross-wise, enable the electrification of the quadrants to be reversed, and readings to be obtained right and left. This arrangement was found to work quite satisfactorily, and was more to be depended on than Sir WILLIAM THOMSON'S reversing key, which was tried for a time and abandoned.

The deflection of the needle of the electrometer, as measured on the scale, not being proportional to the difference of potentials of the quadrants, it was necessary to correct it. It was thought that, A—B being the difference of potential of the quadrants and d the deflection, a value might be assigned to μ which would make A—B approximately proportional to $d\left(1-\frac{d}{\mu}\right)$; and it was found on trial that the value $\mu = 10{,}000$ satisfied the requirements sufficiently well.

A circuit was formed containing a battery of six DANIELL'S cells and a constant external resistance of 12,000 ohms. Two points in the circuit separated by a resistance varying from 1,000 to 6,000 ohms were connected with the electrometer, and the deflections read off. The following table shows the proportionality between the deflections corrected according to the above rule, and the difference of potential obtained by multiplying the smallest corrected deflection by 2, 3, 4, 5, 6 in succession. The agreement may be regarded as perfectly satisfactory, when it is remembered that the electrometer readings cannot be relied on to much less than 0·5 of a division.

TABLE III.—Calibration of electrometer scale.

Resistance =1000 n.	Deflection $(=d)$.			$\frac{d^2}{10^4}$	$d-\frac{d^2}{10^4}$	52 n.
	Right.	Left.	Mean.			
6000	328·5	320	324·2	10·5	313·7	312
5000	266·5	267	266·7	7·1	259·6	260
4000	214·5	210	212·2	4·5	207·7	208
3000	158·5	159	158·7	2·5	156·2	156
2000	104·5	106·5	105·5	1·1	104·4	104
1000	52·5	52	52·2	0·2	52·0	52

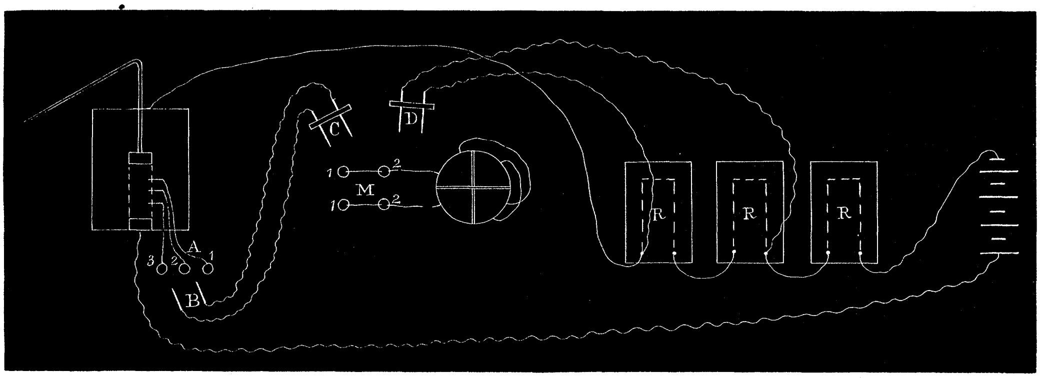
The distance of the electrometer from the scale and lamp was about a metre, and the deflections were, as a rule, within the limits 80 and 250 divisions. In some of the experiments the lamp and scale were removed to a distance of 1·6 metres from the electrometer, and a sharp image of the slit on the scale obtained by means of a lens. In both positions of the scale it was found that the above empirical rule was approximately true, and that the difference of potential corresponding to a given electrometer deflection d was proportional to $d\,(1-d\times 0{\cdot}0001)$. Similar observations were from time to time repeated, and always with the same result.

According to MAXWELL ('Electricity and Magnetism,' vol. i., p. 274), the deflections of the electrometer, when of moderate magnitude, are proportional to the product

$$(A-B)\left(C-\frac{A+B}{2}\right)$$

where C is the potential of the needle and A and B those of the quadrants. Now, in calibrating the electrometer, the potential of one pair of quadrants (say B) was kept constant, and the other gradually raised, and thus our empirical correction is made up partly of the conversion of arcs into tangents, and partly of the change due to increasing values of A+B. But since a correction which holds for one constant value of B will not hold for another, it was necessary to test the validity of our formula for the range of potentials studied. For this purpose two resistances, each of 100,000 ohms, were included in a circuit, and a piece of carbon paper with a resistance of about 700,000 ohms interposed between them. The mean electrometer deflections corresponding to the equal resistances were 127·85 and 127·55, which differed by only 0·3 of a division. Hence the formula may be regarded as valid, whatever be the position in the circuit of the resistance considered.

Fig. 6.



Method of observation.—The order of observations of the electrical condition of a film was as follows: The film having been formed and adjusted, and the needles fixed in their proper places, the copper wires B (fig. 6) were inserted in the mercury cups belonging to the particular pair of needles between which the resistance was to be measured. The connecting pieces C and D, consisting each of a strip of ebonite with stout copper wires passing through, were inserted in succession in the mercury cups (M 1, 1), and the deflections written down in order, the time of each observation, given by a chronometer, being noted by the side.

It was generally found that the needles were of slightly different potentials even when no current was passing, and it was necessary to correct for this which would affect the apparent resistance of the film. This difference was measured after the film was formed and before the current was allowed to traverse it. It was generally small, and sometimes vanished, but as a rule caused a deflection of from 1 to 5 divisions of the scale. Frequently its direction was constant for the same film, and even for the same day, but, as its magnitude could not be relied on to remain unaltered during the life of a film, the current was interrupted at intervals of 5 or 6 minutes and the condition of the needles examined. The deflections observed were added to or subtracted from those obtained for the needles when the current was passing, according to their direction.

The same phenomena were observed with steel and platinum needles in an augmented degree, and were less under control. It was always found that the difference of potential between needles 1 and 3 was equal to the sum of the differences between 1 and 2, and 2 and 3. This difference was not altered in any constant manner by the passage of the current. Sometimes during the life of a film and with the current continuously passing it increased, sometimes it diminished, and again at other times showed no signs of alteration. But in what direction it would change, if at all, could not be predicted.

Polarisation so-called has nothing to do with the phenomenon, since its direction and magnitude do not depend upon the direction or continuance of the current. The cause is to be found in the difference of chemical condition of the needles produced by the action of the liquid quite independently of the current. The needles are affected to a different extent, and thus a difference of potential is set up between them. That this is the cause of the phenomenon was shown as follows: Two steel needles, not specially cleaned, were inserted in a film, and their extremities connected by wires with the electrometer. The deflection was +6. The lower needle was then passed through the fingers, and the deflection rose to +9. The lower needle was then washed, rubbed with emery paper, washed again, and connected with the electrometer, which now showed a deflection of −3. Thus by cleaning the needles unequally, either could be made to be of a higher potential than the other. With gold wires these changes occurred to a less degree than with either steel or platinum, and hence gold was the metal employed in the latest experiments. In these it was usual each morning to wash the gold needles in boiling nitric acid and then in distilled water. But even when the greatest care was taken in cleaning the needles, it was impossible to ensure their being in such a state as to exhibit when immersed in the film no difference of potential.

As a specimen of the observations made in measuring the resistance of a film, we give the following: The symbols × and || mean that the wire bridges of the electrometer reversing arrangement are crossed and parallel respectively.

SEPTEMBER 27, 1880.—Film I., needles 2–3, resistance in boxes =508,000 ohms=R.

Part of circuit which is connected with electrometer.	× Deflection.	Time.			|| Deflection.	Time.		
		h.	m.	s.		h.	m.	s.
Needles (no current passing)	0	. .			2 right	Mean =1		
Film	80 right	12	54	12	75·5 left	12	55	6
Resistance	174		54	42	166		55	30
Film	82·5		56	0	79		57	0
Resistance	167		56	30	159·5		57	30
Film	85·5		58	0	82		59	0
Resistance	159·5		58	30	151·5		59	30
Needles	0	. .			2 right	Mean =1		
Film	91·5	1	1	0	85·5	1	2	0
Resistance	149·5		1	30	140		3	12
Film	93		3	42	90		4	30
Resistance	140		4	6	133·5		5	0
Film	96·5		5	30	91·5		6	30
Resistance	135·5		6	0	127		7	0
Needles	·5 right	. .			2·5 right	Mean =1		

These observations were continued until $1^h\ 22^m$, when the film burst. The numbers thus obtained were then plotted down on a sheet of curve paper, times being represented as abscissæ and deflections as ordinates. Thus, four curves were drawn, of which F (right) and F (left) gave the mean film curve, and R (right) and R (left) the mean resistance curve. The curves F (right) and F (left) were always very close together and sometimes coincident, but, as the zero of the electrometer was liable to change, the curves for both right and left deflections were always drawn and the mean taken. The same remarks apply to the curves of resistance-deflections. From the two mean curves thus obtained a third is deduced as follows: The ordinates of the curves are read off at points separated by intervals of four minutes, and when the proper corrections, described above, have been made, the film-deflection is divided by the resistance-deflection and the quotient multiplied by the resistance of the coils. A curve passing through the series of points so obtained enables us to determine the resistance of the film between the two needles at any epoch.

Example.—September 27. Film I.; at 12^{h} 58^{m} the deflections are, for film 83 [or 84 when allowance is made for the independent difference of potential of the needles], and for resistance 159·6.

$$84\ (1-84\times 10^{-4})=83{\cdot}4 \text{ nearly}$$
$$159{\cdot}6\ (1-159{\cdot}6\times 10^{-4})=157 \quad ,,$$

Hence the resistance is $\frac{83{\cdot}4}{157}\times 508{,}000=269{,}400$ ohms.

VIII. *Method of testing the accuracy of the experiments.*

Observations with the Galvanometer.—With the object of ascertaining whether the apparatus was in satisfactory working order, the following experiment was occasionally made. A strip of Dr. MUIRHEAD'S carbon paper was attached to a piece of glass by brass clips and carefully insulated. Its extremities were connected to a WHEATSTONE'S bridge and also to the electrometer, and its resistance measured by the two methods in succession. Usually an observation by galvanometer was made between two observations by electrometer, care being taken to prevent changes of temperature of the carbon paper. It is unnecessary to give details of these experiments, but the following may be quoted as indicating the character of the results obtained :—

	Galvanometer.	Electrometer.	Difference.
			Per cent.
September 24 . .	1,620,000	1,633,000	0·8
,, 25 . .	1,455,000	1,457,000	0·14
,, 26 . .	1,910,000	1,920,000	0·52

The differences in the resistance of the carbon paper from day to day were due partly to differences of temperature, but chiefly to changes in the hygrometric state of the atmosphere.

The experiments with the carbon paper were repeated at intervals. If the difference of the resistances obtained exceeded 1 per cent. the observations on the films were interrupted, until, the apparatus having been overhauled, the two methods gave results with the carbon paper in sufficiently close agreement. A similar experiment was sometimes performed with the films themselves. The specific resistance was calculated both from measurements made on a portion of the film by the electrometer, and also from the resistance of the whole length measured by WHEATSTONE'S bridge. To effect this, the thicknesses at top and bottom, and, if necessary, at intermediate points, were measured.

These observations confirmed our opinion of the superiority of the electrometer method. Results were sometimes obtained agreeing to about 0·5 per cent., but generally the difference was greater, and sometimes it was as large as 6 per cent. The fact that the most discordant results were obtained with films which had exhibited a considerable number of black specks at the top shows the advantage of working in the middle of the film. We may here remark that the effect of these black specks upon the electrometer was carefully noted. They generally travelled round the film at varying speeds, and it was found that a speck much larger than was usual was required to produce any effect on the electrometer by its passage over the nearest needle.

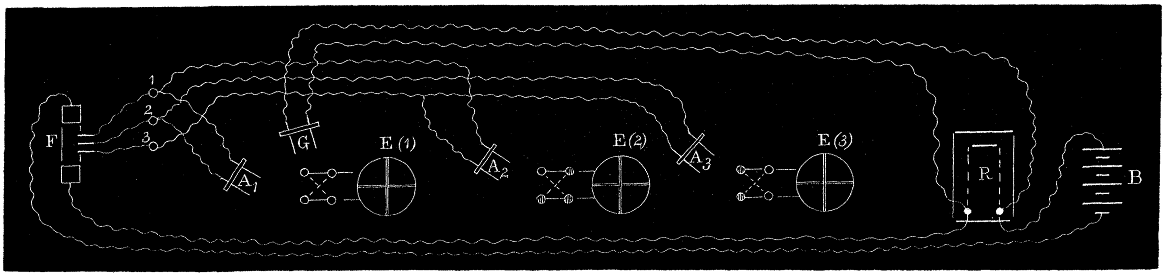
Observations with three Electrometers.—It may be desirable to state why three needles were used for the films rather than two. The object in view was twofold. In the first place, when a film begins to thin, it often happens that its upper part, the region between needles 1 and 2, shows recognizable colours, and is in a fit condition for observation and measurement, before the colours of the region between needles 2 and 3 become well defined, and thus time is gained by attacking the upper part of the film while the lower part still remains thick. Again, it happened not unfrequently that during the observation of the region between needles 1 and 3, a thickening of the film would occur from below, the colours rising steadily from the lower cup and being separated by a sharp line of (apparent) discontinuity from the portion—often perfectly uniform in tint—towards which they were advancing. Such a "thickening from below" was always carefully watched, and as soon as it approached needle 3 the electrical connexions were readjusted and the examination transferred to the region between needles 1 and 2.

In the second place, it appeared very important to be able to prove by direct experiment that the electrometer method of measuring the conductivity of a film was to be relied on, and that the results obtained were not dependent upon the conditions of the instrument employed. The galvanometer method of testing the electrometer measures was not, as has already been stated, always applicable. It was therefore determined to measure the resistances of the film between needles 1–2, 2–3, and 1–3 respectively by three independent instruments. We were fortunate in securing, through the kindness of Professors W. G. ADAMS and F. GUTHRIE, the loan of two quadrant electrometers similar to the one already in use. The electrometers were arranged as shown in fig. 7.

The first operation was to compare the electrometers with each other, which was effected in the following manner:—A simple circuit was formed, traversed by a current of constant strength, the resistance in it being about 15,000 ohms. Two points in the circuit, separated by resistances gradually increasing from 1,000 to 12,000 ohms, were connected in succession with the electrometers, and the deflections, right and left, noted. The numbers so obtained enabled comparison curves to be drawn, by which deflections of electrometers (2) and (3) could be referred to scale readings of electrometer (1).

The comparison of the electrometers was repeated each day while the experiments were going on. When a film was to be examined the connecting pieces, A_1, A_2, A_3, being all inserted in the corresponding mercury cups, the deflections right and left of the three electrometers were observed, the time of each reading being noted. A_1 was then removed, and G inserted in its place, and the deflections right and left again observed. These observations were repeated without cessation so long as the film lasted. The time occupied in taking a complete set of readings for the three needles and for the resistance was from 2 to 3 minutes.

Fig. 7.



F is the film with the three needles inserted in it, connected respectively to the mercury cups 1, 2, 3.
E (1) the electrometer which measures the difference of potentials between needles 1 and 2.
E (2) „ „ „ „ 1 and 3.
E (3) „ „ „ „ 2 and 3.
R, box of resistance coils.
B, battery of 4 Grove's cells.

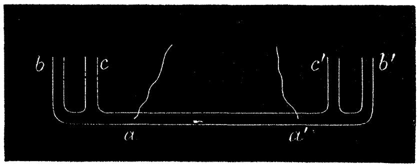
The deflections being plotted down on curve paper, as before described, curves representing the actual resistances between needles 1–2, 2–3, and 1–3 were deduced. The resistance between needles 1–3 ought of course to be equal to the sum of the resistances between needles 1–2 and 2–3. Sometimes the agreement was perfect, and the difference was rarely in excess of 1 per cent.

IX. *Description of the Apparatus for measuring the resistance of the liquid in mass.*

The method finally adopted for measuring the electrical resistance of the soap solutions was in principle the same as that employed in the examination of the films. A current was passed through a known resistance and a tube containing the liquid to be examined; and the difference of potential between two points in the tube which could be connected with an electrometer was compared with that between two other points in the same circuit separated by a known resistance.

A piece of tube was selected, as nearly cylindrical as possible, about ·8 centim. in diameter and 32 centims. in length. Its two ends were bent at right angles to it, as shown in the accompanying diagram, and two short pieces of the same tubing were fused into it near the turned up ends for the insertion of thermometers. At *a*, *a*′, about

13 centims. apart, two fine holes were drilled in the tube, and pieces of platinum wire, the ends of which just projected beyond the inner surface of the glass, were cemented into these by sealing wax. The distance between these two points was measured by a cathetometer and the diameter was determined by weighing the quantity of mercury which occupied a portion of the tube a little longer than the distance between *a* and *a′*.



If

$l=$ the distance between *a* and *a′* ;
$r=$ the radius of the tube ;
$R=$ the resistance in ohms of the liquid between the two points ;
$\rho=$ the specific resistance, *i.e.*, the resistance per cubic centimetre ;

then

$$\rho=R\times\frac{\pi r^2}{l}$$

The value of the constant $\frac{\pi r^2}{l}$ for the tube with which all the soap solutions were measured was ·030001. The specific resistances were thus readily obtained by multiplying the observed resistances by ·03.

The points *a*, *a′* were sufficiently far from the bent up portions of the tube to ensure that the lines of flow between them would be parallel to the generating lines of the cylinder, and, as in the films, the platinum points *a*, *a′* would not sensibly interfere with this symmetrical flow.

The two electrodes connecting with the battery consisted of flat spirals of platinum wire, the diameters of which were such as to allow them to move freely in the tubes *b*, *b′*. The object of using a spiral wire rather than a continuous disc was to facilitate the escape of the bubbles of gas formed by the decomposition of the liquid.

The thermometers used had a range of 40° C, and were graduated to 0°·5, but could be read to 0°·1 without difficulty. They were compared with a thermometer graduated to 0°·1 which had been verified at Kew. Pieces of cork through which they passed supported them in their places in the tubes *c*, *c′*.

It is well known that the electrical resistance of a liquid depends in a very important degree upon its temperature; and hence the necessity of knowing accurately the temperature of the soap solution at the time when its resistance was measured. To this end a water bath was contrived containing a chamber sufficiently large to hold the resistance tube, thermometers, &c.

The water bath, which was made of tin plate, is represented in Plate 60 fig. 8, with the front detached for the purpose of showing the paddles, B, B, B, B, for stirring the water and producing uniformity of temperature throughout. These are moved up and down by means of strings passing over a pulley. The rectangular chamber A, A, A, A, is 33 centims. long, 21 centims. high, and 20 centims. deep. It is surrounded on four sides by water, and is closed on the remaining sides, viz.: front and back, by glass windows. In these experiments the window at the back was not used as such, being covered by thick felt. The window in front is provided with felt packing, and is held firmly in its place by four nuts. The bath is supported on an iron stand about a foot from the table.

Four tubes C, C, D, D, each about 2·5 centims. in diameter, pass through the base of the apparatus and are closed by caoutchouc stoppers. Through C, C pass the battery wires, and through D, D two other wires connecting with the electrometer. Similarly three tubes E, E, E pass through the upper part of the apparatus, the standard thermometer F being supported in the centre one. H, H are mercury cups for connecting the electrodes of the tube with the battery wires; and K, K similiar cups for making the electrometer connexions. By placing BUNSEN burners beneath the lateral bent tubes G, G′, which are also made of tin plate, the water could be heated. As a rule the range of temperature employed was between 10° and 35°; within these limits it was easy to obtain any required temperature and to maintain it constant during an interval sufficiently long for two or three complete sets of observations to be taken. No observations were made until the thermometers *f*, *f* gave the same readings and the thermometer F indicated a temperature not differing by more than two or three tenths of a degree from that of the others. The mean between the readings of *f*, *f* and of F was then assumed to be the temperature of the liquid in the tube.

The mode of connecting with the electrometer, first the wires in the liquid and then the points in the circuit on either side of the known resistance, was identically the same as that already described as employed in the measurement of the resistance of a film. The required temperature having been reached, the resistance in the box of coils was adjusted to give an electrometer deflection not very different from that of the liquid. The potential difference of the points a, a' was then examined, the battery circuit being broken meanwhile. As in the case of the films this difference was found to be very irregular both in magnitude and direction. As a rule the deflection produced by it did not exceed 2 divisions of the scale, but occasionally it rose to as much as 6 or 7 divisions. The circuit was then completed and after an interval of 3 or 4 minutes, when the rate of weakening of the current (due to polarisation, &c.) appeared to be uniform, the electrometer readings right and left were taken

(1) When the liquid was connected with the electrometer.
(2) „ resistance „ „ „
(3) „ liquid again „ „ „

The circuit was now broken, and the potential difference of the points a, a' again determined. The temperature at the beginning and end of each set of observations (which occupied about four minutes) was noted. Two sets of observations were always made at each temperature. The mean liquid-deflection derived from (1) and (3) was then divided by the resistance-deflection, after the proper corrections (already described) had been applied to both, and the quotient multiplied by the value of the resistance in the box of coils.

Calculation, based on JOULE'S law, showed that the rise of temperature of the liquid in the tube, due to the passage of the current, could not in an extreme case, supposing the current to flow continuously for 10 minutes, exceed the one-thirtieth of a degree Centigrade.

A series of experiments was carried out with the view of determining how far the resistance of liquids measured by the electrometer method were in agreement with those obtained by other methods. Since the determinations of the electrical conductivities of liquid, made by KOHLRAUSCH, and by KOHLRAUSCH and GROTRIAN are more complete, and their results more consistent and trustworthy than those of other observers, it was resolved to test the electrometer method by comparing the resistance of a liquid furnished by it with that of the same liquid given by KOHLRAUSCH. Sulphuric acid was selected for the purpose, and three solutions were prepared, their specific gravities at 18° being 1·1993, 1·4119, and 1·611. A new tube was made, the radius of which was about 0·15 centim. Pieces of the larger tubing were fused to the ends for the insertion of electrodes and thermometers. The distance between the small holes made in it for the reception of thermometers was 12·742 centims., and the constant $\frac{\pi r^2}{l}$ was determined to be 0·00563376.

I. SULPHURIC acid, spec. grav. at 18° =1·1993, computed from determinations made at 12°·5 and 17°.

Temperature.	Specific resistance (=ρ).
Centigrade.	Ohms per cub. centim.
15·38	1·48235
20·61	1·36730
21·46	1·32820
22·78	1·32450
26·26	1·24865

These values were plotted down on a piece of curve paper. From the curve so obtained the specific resistance at 18° was found to be 1·4198.

KOHLRAUSCH (Pogg. Ann., Bd. 159, p. 233) gives for sulphuric acid

$$k_{18}10^8=6701, \text{ spec. grav. at } 18^\circ=1{\cdot}1799$$
$$k_{18}10^8=6911 \quad ,, \quad ,, \quad =1{\cdot}2201$$

where k_{18} is the conductivity at 18° C. referred to that of mercury at 0° as unity.

Assuming that, between the two specific gravities given above, the change in conductivity is proportional to the change in specific gravity, we have

$$k_{18}10^8=6802, \text{ for sulphuric acid of spec. grav. } 1{\cdot}1993 \text{ at } 18^\circ.$$

hence

$$\rho=\frac{1}{k_{18}}\times\text{specific resistance of mercury}$$
$$=\frac{10^8}{6802}\times{\cdot}970=1{\cdot}4260.$$

The value assumed here for the specific resistance of mercury, viz. : ·970, is that given by Kohlrausch himself. Matthiessen gives 0·9619 (Everett's 'Physical Units'), but it was thought desirable in transforming Kohlrausch's numbers for liquid conductivities to make use of the specific resistance of mercury which he had himself obtained.

II. Sulphuric acid, spec. grav. at 18°=1·4119, computed from measurements made at 12°·5 and 16°·5.

The resistance was measured at four temperatures, and from the curve so obtained the specific resistance at 18° was deduced =2·001.

Kohlrausch gives

$$k_{18}10^8=5112, \text{ spec. grav. at } 18^\circ=1{\cdot}3946$$
$$k_{18}10^8=3494 \quad ,, \quad ,, \quad =1{\cdot}5014$$

whence

$$k_{18}10^8=4849{\cdot}9, \text{ for spec. grav. } 1{\cdot}4119$$
$$\therefore \rho=\frac{10^8\times{\cdot}97}{4849{\cdot}9}=2{\cdot}000$$

III. Sulphuric acid, spec. grav. at 18°=1·611.

The resistance was measured at 17°·56 and at 22°·25. Specific resistance at 18° deduced =4·725.

Kohlrausch gives

$$k_{18}10^8=2554, \text{ spec. grav. } =1{\cdot}5707$$
$$k_{18}10^8=1823 \quad ,, \quad =1{\cdot}6315$$

whence

$$k_{18}10^8=2069{\cdot}5 \text{ for spec. grav. } 1{\cdot}611.$$
$$\therefore \rho=4{\cdot}687.$$

The experiments with sulphuric acid were not carried further, as they were intended merely to test the trustworthiness and accuracy of the method. Tabulating the above results, we have—

SULPHURIC Acid.

	Spec. grav. at 18°.	Specific resistance at 18°.		Difference.
		By electrometer.	Deduced from KOHLRAUSCH'S experiments.	Per cent.
I.	1·1993	1·420	1·426	0·44
II.	1·4119	2·001	2·000	0·05
III.	1·6110	4·725	4·687	0·80

The agreement of the resistances measured by the electrometer, with the values obtained for similar solutions by KOHLRAUSCH by a totally different method, is sufficiently close to justify us in placing reliance upon this method for the investigation of other liquids.

X. *Relations between the specific resistance, temperature, and constitution of a liquid.*

A number of experiments were made at different times, by the method just described, on standard and derived solutions of different constitutions. Each liquid was observed at several different temperatures, and the results were plotted down in curves. Between the limits of temperature at which the observations on the films were made (17° C. to 22° C.), these curves were very approximately straight lines, and the equation to any of these might be expressed by the formula

$$\rho=\rho_{20}\{1+a(20-t)\}$$

where ρ_{20} is the specific resistance at 20° C.

The quantity a varied only between the limits 0·027 and 0·032 for standard solutions containing 3, 5, and 7 per cent. of salt respectively, and for derived solutions to which not more than 100 per cent. of water had been added. Addition of glycerine to the standard solution increased the value of a, but, within the range of the change of constitution observed in the films, it did not exceed 0·039. The mean value for all the standard solutions studied, viz.: 0·03, was therefore taken as correct for all others differing but little from them in composition. For the five films mentioned in Section XI., which lost considerable quantities of water, a was taken equal to

$$0·03+0·00013\,\delta$$

where δ is the difference between the specific resistances of the solution and of the standard solution from which it was derived.

In the following table a few out of a large number of examples of the accuracy of this formula as applied to the liquid in mass are given :—

Column I. gives the percentage of salt in the standard solution.

Column II. p or the number of parts by volume of water or glycerine added to $100-p$ parts of standard solution to produce the derived solution.

Column III. gives the value of a obtained from the above rules.

The other columns explain themselves.

TABLE IV.

I. x.	II. p.	III. a.	IV. ρ_{20}.	V. t°.	VI. ρ_t (observed).	VII. ρ_t (calculated).
3	0	0·0300	208·1	16·8	229	228
. .	. .	. .	. .	19·5	211	211
3	30 H_2O	0·0300	176·0	22·5	160	163
5	0	0·0300	135·0	18·5	142	141
. .	0	. .	. .	22·3	125	126
5	20 H_2O lost	0·0355	177·4	18·2	188	189
. .	. .	. .	. .	21·7	167	167
5	25 H_2O lost	0·0390	203·4	14·9	244	244
. .	. .	. .	. .	24·5	172	168

It is unnecessary to quote experiments not made near the temperature limits of the observations on the films. With regard to the value of ρ_{20} it was found that the addition of glycerine increased, of water (within certain limits) diminished, the specific resistance of a standard solution. If, however, the quantity of water added exceeded a certain amount, which varied with the percentage of the solution, further additions increased the specific resistance. As in all the instances of considerable change of constitution to be discussed hereafter, the specific resistance was greater than that of the standard solution, while the hygrometer showed that the air was drier than when the precautions to fill it with aqueous vapour at the tension of that given off by the solution were taken, it follows that, on the assumption also to be discussed hereafter that the specific resistance of the film and the liquid in mass are identical, the only case to be considered is that of a solution which has lost water by evaporation.

A soap film, made from a standard solution, which has lost water by evaporation, may be considered as a mixture of another standard solution, containing a greater percentage of salt and of glycerine.

If x and X be the percentages of the first and second standard solutions respectively, p the number of volumes of water lost in 100 of solution, s and g the number of volumes of standard solution and glycerine in 100 parts of the derived solution, of which the altered film is formed, respectively; then since a standard solution contains 2·2 volumes of glycerine to 3 of water

$$X=x\frac{300}{300-5\cdot2p},$$

$$g=\frac{2\cdot2}{3}\,\frac{100p}{100-p}, \qquad s=100-g$$

Solutions were made up in accordance with the numbers given by these formulæ to represent films composed originally of a 5 per cent. standard solution, which had lost 15, 20, and 25 parts of water respectively. The standard solution used had a specific resistance of 135 at 20°, somewhat lower than that given by other similar solutions which varied from 140 to 143.

It was found that the specific resistances and parts of water lost were connected by the convenient formula

$$p^2=10(\rho-\rho')=10\,\delta$$

where ρ' is the specific resistance of a standard x per cent. solution.

TABLE V.

$\rho'=135$.		
ρ.	p.	p (calculated).
135	0	0·0
157	15	14·8
177	20	20·5
203	25	26·0

XI. *Results of the experiments.*

Specific resistance of films.—The observations on the liquid in mass showed, as has been already pointed out, that additions of water diminished, and additions of glycerine increased, the specific resistance. In agreement with this a large number of preliminary experiments proved that the specific resistance of a soap film was higher in dry than in damp air, and that the changes due to variations in the hygroscopic state of the atmosphere were very much larger than any which might be due to the diminishing thickness of the film. As our latest experiments were however in several respects the most full and trustworthy, we confine ourselves in this paper to giving an account of them, premising only as the result of our preliminary work, that any large change in the specific resistance of a film might be safely attributed to the absorption or evaporation of water.

The observations were made between September 13 and October 1, 1880. Several films were rejected either because the insulation was found to be faulty, or because irregular masses of the black or white of the first order, which must have deflected the lines of flow, were collected at the top. Twenty-three films were observed without these defects, and on them our conclusions are based. All were made of the same liquid, which contained 5·05 per cent. of salt, and of which the specific resistance at 20° was 140·5.

The temperatures at which experiments were made varied only between 17°·5 and 22°·5, and, in the first instance, the observations were arranged according to the indications of the hygrometer. Thus, the specific resistances of all the films, during the experiments in which the hygrometer stood between 50 and 51, were calculated for a thickness equal or nearly equal to 9×10^{-5} centims., and the mean taken. All the other films were treated in the same way and the results tabulated. The value 9×10^{-5} centims. was chosen because nearly all the films were observed at that thickness.

TABLE VI.

Hygrometer.	Number of films.	Mean value of ρ_{20}.
48–49	1	167·9
49–50	5	161·6
50–51	8	156·5
51–52	4	153·7
52–53	..	..
54–55	5	145·7

From this table we learn that on the average the specific resistance of the films was lower and nearer that of the liquid in mass, as the hygrometer stood higher. This result had been anticipated.

The method of moistening the air in the case was open to the objection that the air would probably be a little too dry. Water would evaporate from the blotting paper soaked with the liquid, and the air would therefore be in contact with surfaces moistened with a liquid containing a rather larger percentage of glycerine than the soap solution itself. A small tin tray was made to cover as large a part of the base of the chamber containing the film as was consistent with perfect insulation, and filled with soap solution. A surface of liquid, 52 square centims. in area, was thus exposed, and two films were observed with the air moistened with this alone, and without the blotting paper.

With this arrangement the specific resistances were found to be very high and to rapidly increase, as shown below:—

Thickness.	Specific resistance.	
	Film I.	Film II.
14×10^{-5} centims.	178·8	169·4
4×10^{-5} „	201·6	192·0

These compared so unfavourably with observations made when the blotting paper was used, that it was again employed—in conjunction with the tray—a corner of the paper dipping in the liquid. Occasionally if the paper appeared to be getting dry, it was moistened by liquid introduced by means of a fine pipette through a small hole cut for the purpose in the back of the case.

As in spite of these precautions the air would probably remain a little too dry, there was evidently good reason for excluding from the comparison with the liquid in mass all films for which the reading of the hygrometer was low, and 51° was taken as a provisional limit. Another equally important condition of accuracy was that the hygrometric state of the chamber should be constant, *i.e.*, that the hygrometer and thermometer should be steady during the observations. Changes in the hygrometric state of the air might evidently involve the loss or gain of water by the film. We found that ten films satisfied the conditions that neither hygrometer nor thermometer should vary more than 0°·3 while they were under observation, and that of these four were inadmissible, as the hygrometer stood below 51°. The smallest thickness for which all of the remaining six were examined was 9×10^{-5} centims., and the results at that thickness are given below :—

Date and number of film.	h.	t.	Observed specific resistance.	ρ_{20}.
September 27, III. .	53·1	20·6	141·9	145
,, 28, III. .	53·1	18·9	148·2	143
,, 28, I. .	53·1	18·8	151·7	146
,, 27, II. .	53·0	20·9	142·4	146
,, 30, II. .	51·2	17·9	145·8	137
,, 30, I. .	51·1	17·8	151·6	142
				Mean 143

The mean value of ρ_{20} differs only by 1·8 per cent. from that of the liquid in mass, and the probable error is ± 1 or $\pm 0·71$ per cent.

The conclusion to which this result points, viz.: that the specific resistance of a liquid film is the same as that of a mass of the liquid of the same constitution, is greatly strengthened by another line of argument.

A film, produced in an atmosphere charged with aqueous vapour at a tension differing but slightly from that proper to the liquid from which it was formed, would rapidly adjust itself to that tension. The extremely small quantity of vapour which would have to be absorbed or given off before the condition of equilibrium was attained, and the comparatively large changes of temperature which this absorption or emission would produce in a body of such small mass, would both conduce to this result. It might therefore be that a film the constitution of which differed from that of the liquid sufficiently to produce an appreciable effect upon the specific resistance, might nevertheless have reached a stable state during the first few minutes after its formation and while still too thick to admit of any optical observations being made upon it. If, then, the films, the specific resistances of which agreed most closely with that of the liquid in mass, were also those which obeyed OHM's law with the greatest accuracy, this result would evidently point to the conclusion that the variations in specific resistance were due to changes in constitution and not to the diminishing thickness of the film.

To put this to the test the specific resistances of the films were calculated for apparent thicknesses which were multiples of ten millionths of a centimetre above and for multiples of five millionths of a centimetre below 9×10^{-5} centims. The results, which are too long to be given in full, will be sufficiently indicated by the following table. The films are divided into four classes. Those in Class I. satisfy the three conditions as to constancy of hygrometer, constancy of temperature, and height of hygrometer. Those in Class II. satisfy the first two of these conditions, but not the third. Those in Class III. fail to satisfy the third and one at least of the other conditions. In the case of the films included in Class IV. the arrangements as to moistening the air differed in some respects from those above described (pp. 462, 478).

Column I. gives the date on which the film was observed.

Column II. the number of the film.

Column III. the amount by which the ratio of the specific resistance at the least to that at the greatest observed thickness differs from unity.

In each class μ_1 is the mean of these numbers without reference to sign, μ_2 is the algebraical mean. One film (September 29, V.) is omitted from this list. It was purposely observed under conditions (to be presently described) such as first to increase, and then to diminish the specific resistance, and is therefore useless for the purposes of such a comparison.

TABLE VII.

Class I.		
I.	II.	III.
September 27 .	II.	−0·003
„ 27 .	III.	+0·017
„ 28 .	I.	−0·017
„ 28 .	III.	0·000
„ 30 .	I.	−0·017
„ 30 .	II.	−0·005
		$\mu_1=$ 0·010
		$\mu_2=-$0·005

Class II.		
I.	II.	III.
September 18 .	I.	+0·022
„ 20 .	III.	+0·039
„ 23 .	I.	+0·019
		$\mu_1=$ 0·027
		$\mu_2=+$0·027

Class III.		
I.	II.	III.
September 18 .	II.	+0·050
„ 20 .	I.	+0·171
„ 20 .	II.	+0·084
„ 22 .	I.	+0·021
„ 27 .	I.	+0·046
		$\mu_1=$ 0·074
		$\mu_2=+$0·074

Class IV.		
I.	II.	III.
September 24 .	I.	+0·136
„ 24 .	II.	+0·169
„ 25 .	I.	−0·029
„ 29 .	I.	+0·073
„ 29 .	II.	+0·128
October 1 . . .	I.	+0·003
„ 1 . . .	II.	+0·024
„ 1 . . .	III.	+0·116
		$\mu_1=$ 0·085
		$\mu_2=+$0·078

The conclusion to be drawn from this table is obvious. The divergence from OHM'S law increases rapidly as the conditions become less and less favourable to the preservation of the film in a constant state. The amount of the divergence shown by films in the same class varies considerably; but this is accounted for by the fact that the range of thickness observed, the time during which the film lasted, and the amount of change in the hygrometer and thermometer during that time, are very irregular. There is only one film, however, for which the figure in column III. is less than those which occur in Class I. In the case of this film (October 1, I.) none of the usual precautions were taken, but two dishes of dilute sulphuric acid (specific gravity 1·159) were introduced into the inner chamber. The hygrometer and thermometer read 50° and 17°·5 respectively at the commencement of the observations, and each had risen only 0·1 of a degree at the end. The specific resistance of the film at 20° was 153·4. This number differs less from the specific resistance of the liquid in mass than those often obtained, and, combined with the extreme constancy of the thermometer and hygrometer, proves that a state of things was accidentally produced very similar to and of even greater constancy than that attained by the ordinary methods of moistening. With this single exception, however, all the films included in Class I. obey OHM's law better than any of the others.

In order to test this agreement more fully the following method was adopted. The simplest plan for combining the results of a set of films would be to take the means of the specific resistances at each of the thicknesses at which they were observed. In the case of the films in Class I. the range of comparison possible with this method would have been only from 14×10^{-5} to 9×10^{-5} centims., the greatest and least thicknesses at which all the films were observed.

To get over this difficulty the specific resistance obtained at each thickness for any film was divided by that corresponding to a thickness of 12×10^{-5} centims. for that film. If OHM's law were not obeyed, each of the columns of figures thus obtained ought to give increasing or decreasing values of the ratios as the thickness diminished, and this divergence from the law would have been still more strongly marked in the means of the numbers corresponding to any particular thickness.

The results of this calculation are exhibited in the following table.

Column I. gives the apparent thickness in terms of 10^{-5} centims.

Column II. the colour corresponding to this thickness correct to the nearest tenth of a tint.

Column III. the actual thickness.

Columns IV.–IX. the ratios for the six films.

Column X. the means of these ratios.

The date and number of the film and the readings of the hygrometer and thermometer at the beginning and end of the observations are placed at the head of the column which refers to it.

The thickness 12×10^{-5} centims. was selected as the point of comparison, as at that thickness the specific resistances differed least from their mean value.

Table VIII.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
			Sept. 27, II.	Sept. 27, III.	Sept. 28, I.	Sept. 28, III.	Sept. 30, I.	Sept. 30, II.	Mean.
		Hygrometer	53·0 53·1	53·1 53·2	53·2 53·1	53·1 53·2	51·1 51·2	51·2 51·3	
		Thermometer	20·9 20·6	20·6 20·4	18·8 18·9	18·9 18·7	17·8 17·9	17·9 18·1	
16·0	R (6, 3)	13·30	. .	1·014	. .	. .	1·013	1·012	1·013
15·0	G (6, 6)	12·47	1·002	1·012	. .	1·006	1·008	1·003	1·006
14·0	R (5, 9)	11·64	0·999	1·006	1·005	1·010	1·001	1·004	1·004
13·0	R (5, 3)	10·80	1·001	1·006	1·003	1·016	1·001	1·007	1·006
12·0	G (5, 6)	9·97	1·000	1·000	1·000	1·000	1·000	1·000	1·000
11·0	R (4, 9)	9·14	0·994	0·994	0·997	0·992	1·001	1·000	0·996
10·0	R (4, 1)	8·31	0·990	0·987	0·989	0·986	0·998	1·001	0·992
9·0	G (4, 6)	7·48	0·992	0·976	0·987	0·989	0·996	1·011	0·992
8·5	G (4, 1)	7·06	0·994	0·983	. .	0·988	. .	1·015	0·995
8·0	BR (3, 2)	6·65	0·994	0·988	. .	0·984	. .	1·010	0·994
7·5	R (3, 2)	6·23	0·983	0·987	. .	0·988	. .	1·005	0·991
7·0	Y (3, 3)	5·82	0·992	0·985	. .	1·006	. .	1·004	0·997
6·5	G (3, 4)	5·40	0·999	0·983	. .	. .	. .	1·011	0·998
6·0	B (3, 4)	4·99	0·999	0·992	. .	. .	. .	1·002	0·998
5·5	P (3, 2)	4·57	. .	1·010	. .	. .	. .	1·010	1·010
5·0	O (2, 9)	4·16	. .	1·004	. .	. .	. .	1·007	1·005
4·5	Y (2, 4)	3·74	. .	1·026	. .	. .	. .	1·007	1·016
								Mean	1·001

The constancy of the numbers in the last column of this table is extremely satisfactory. In no case do they differ from their mean value by more than 1·5 per cent., and this result is certainly as good as could be expected when it is remembered that the thickness is measured by a colour estimation only. It is, however, worth while to investigate the outstanding discrepancies a little more closely. The numbers in column X. are a little less for medium than for large or small thicknesses. The reality of such an alternate decrease and increase in the specific resistance is very improbable, while on the other hand the method of correcting the table of colours by the quotients is likely to produce small periodic errors. Each observation on Newton's rings is, however, independent of the rest, and another table (Table IX.) was therefore prepared as follows:—

Column I. gives in terms of the corrected scale the thicknesses corresponding to the colours measured directly by means of Newton's rings.

Column II. gives numbers proportional to the mean specific resistances of the six films in Class I. at those thicknesses; these are deduced approximately from column X. in the above table.

Column III. gives similar numbers calculated with the thicknesses deduced from NEWTON'S rings instead of those given by the corrected table.

TABLE IX.

I.	II.	III.
15·48	1·009	1·006
14·10	1·004	·998
12·60	1·003	1·008
11·19	·997	1·006
9·64	·992	·999
8·41	·995	1·015
7·10	·996	·997
5·77	1·004	·997
4·54	1·016	1·007

In the last column of this table there is no regular increase or decrease in the value of the specific resistance and the largest numbers are those which correspond to medium thicknesses. A comparison therefore of the two tables seems to place it beyond question that a soap film thicker than $3·74 \times 10^{-5}$ centims. obeys OHM'S law at all events to within one per cent.

The results of the experiments may be summed up as follows :—

(1.) It is difficult to form a soap film under conditions such as to preclude a slight evaporation or absorption of water. The more nearly such conditions are attained the more closely does the specific resistance of the film agree with that of the liquid in mass. The mean specific resistance of six films observed at a real thickness of $7·48 \times 10^{-5}$ centims. under the most favourable circumstances agreed with that of the liquid to 1·8 per cent.

(2.) The same films obeyed OHM'S law with great accuracy and much better than the others. This was tested between thicknesses of $13·3 \times 10^{-5}$ and $3·74 \times 10^{-5}$ centims. Within these limits the specific resistance never differed from its mean value by more than 1·5 per cent., and showed no tendency to increase or decrease regularly as the thickness diminished.

We may therefore conclude that the specific resistance of a soap film thicker than $3·74 \times 10^{-5}$ is independent of the thickness and is equal to that of the liquid from which it is formed.

The experiments afford no indication of an approach to a thickness equal to the diameter of the sphere of molecular attraction, but if QUINCKE'S result be correct they enable us to determine a superior limit to the difference between the specific resistance of the surface and interior of the liquid respectively.

Let us suppose that the thickness of the film (T) is greater than twice the length of the radius of molecular attraction (ϖ). Let R, ρ, and r be the apparent specific resistance of the film, the specific resistance of the liquid in mass, and the mean specific resistance of the surface layer, the thickness of which is equal to the radius of molecular attraction respectively. Then we have

$$\frac{\mathrm{T}}{\mathrm{R}}=\frac{\mathrm{T}-2\varpi}{\rho}+\frac{2\varpi}{r}$$

Now the experiments certainly prove that there is no regular increase or decrease in the specific resistance of the film between the thicknesses of 13×10^{-5} and $3{\cdot}7\times10^{-5}$ centims. amounting to as much as 3 per cent. of its value. But if we assign to 2ϖ the value found by QUINCKE, about 1×10^{-5} centims., it may readily be shown from the above formula that, if r differed from ρ by as much as 17 per cent., R would vary 3 per cent. between those thicknesses. As no such variation is observed we must conclude either that the radius of molecular attraction is less than QUINCKE's value or that the mean specific resistance of the surface layer, the thickness of which is equal to the radius of molecular attraction, does not differ by more than 17 per cent. from that of the liquid in mass.

It is obvious that the electrical experiments confirm the accuracy of the revised scale of colours. Had NEWTON'S scale been used, the numbers analogous to those given in columns II. and III. of Table IX. would have varied from 0·884 to 1·012.

Change of composition of the films.—The fact that films formed under constant hygrometric conditions obey OHM'S law having thus been proved, the second part of the enquiry refers to the change of composition which might under other circumstances be produced.

This is illustrated by experiments on five films.

In the case of some of these the observed specific resistance rose as high as 204, indicating, as that of the liquid in mass was only 140·5, a considerable loss of water.

To determine this the specific resistance was first reduced to 20° C. by the formula

$$\rho=\rho_{20}\{1+(0{\cdot}03+0{\cdot}00013\,\delta)(20-t)\}.\quad \text{(See p. 475.)}$$

The number of parts of water lost out of 100 of the original standard solution was then approximately calculated from the formula

$$p^2=10\,\delta.\quad \text{(See p. 477.)}$$

The loss of 25 parts of water having been proved to increase the refractive index by 0·018, a corrected value of that quantity was obtained from the formula

$$\mu=1{\cdot}397+0{\cdot}00072\,p,$$

which would be very nearly true up to $p=25$.

This number was then used to correct the thickness of the film, and the new value of ρ thus obtained gave a second approximation to the value of p.

The following table (Table X.) refers to films I. and II., September 24, and films I. and II., September 29. In the case of the first two the air in the case was moistened by the tray of liquid alone without the aid of the blotting paper. When the second pair were observed no precautions were taken to moisten the air.

Column I. gives the date and number of the film.

Column II. the apparent mean thickness in terms of 10^{-5} centims.

Column III. the number of minutes (m) since the formation of the film.

Column IV. p or the number of parts by volume of water lost out of 100 parts of the original standard solution.

Column V. the values of $\frac{\Delta p}{\Delta m}$.

TABLE X.

I.	II.	III. m.	IV. p.	V. $\frac{\Delta p}{\Delta m}$
September 24, I. . .	14·0	10·8	19·0	0·13
	8·0	20·8	20·3	0·17
	4·5	38·3	23·3	
September 24, II. . .	14·0	6·1	16·2	0·16
	8·0	15·6	17·7	0·22
	4·5	33·6	21·7	
September 29, I. . .	14·0	9·9	12·5	0·28
	8·0	18·2	14·8	
September 29, II. . .	14·0	6·4	17·3	0·12
	8·0	13·8	18·2	0·25
	4·5	24·7	20·9	

Bearing in mind that the inner surfaces of these films were in the immediate neighbourhood of the liquid contained in the lower cup to the edge of which the cylinder was attached, we may from this table draw the following conclusions :—

(1.) A soap film, the area of the external surface of which is about 45 square centims., enclosed in a space about 3900 cubic centims. in volume, and the inner surface of which is in contact with air permanently nearly saturated at the tension proper to the solution from which it is formed, may in the course of 40 minutes lose 23·3 out of the 57·7 volumes of water originally contained in every 100 volumes of the solution.

(2.) The values of $\frac{\Delta p}{\Delta m}$ increase as the film gets thinner, but in all cases are much smaller than the value of the same quantity calculated from the moment at which the film was formed to that at which it reached a thickness of 14×10^{-5} centims. Hence, as we should expect, the greater part of the loss, whether measured by the total amount of water evaporated or by the change in the constitution of the film, takes place in the first few minutes. As the film thins, however, the evaporating surface of a given quantity of liquid increases, and thus after a time the rate of change of constitution increases too, no doubt again to diminish when the tension given off by the film is approaching equilibrium with that in the air.

Another film (September 29, V.) was in like manner formed when no precautions had been taken to regulate the amount of moisture in the air. When it was about 11¼ minutes old, a dry sheet of blotting paper hung up inside the inner case was damped by water introduced by a pipette through the hole in the back of the apparatus. The film continued to thin and the electrical resistance to increase, but the specific resistance which had been rising immediately began to fall.

In the following table (Table XI.), column I. gives the number of minutes elapsed since the formation of the film, column II. the apparent thickness of the part between the needles, column III., p, which has the same signification as above.

The table illustrates the rapid changes which a film may undergo. Similar experiments were made with many other films, and always with the same result.

TABLE XI.

I. m.	II.	III. p.
5·6	14·0	15·8
6·4	13·0	16·6
7·2	12·0	16·9
8·2	11·0	17·7
9·2	10·0	18·5
10·7	9·0	18·2
11·2	Water introduced.	
11·4	8·5	17·8
12·1	8·0	17·3
12·9	7·5	16·5
13·6	7·0	15·6
14·9	6·5	15·0
16·3	6·0	14·7
18·0	5·5	14·4
20·1	5·0	13·9
23·4	4·5	13·4
28·1	4·0	12·1

All experiments on films which are absorbing or losing water are, of course, subject to some uncertainty as to their temperature. These observations however seem to show that the temperature of the film does not differ much from that of the air. While the film was losing water the temperature would be lower than that of the air, and the error thus introduced would exaggerate the loss, while the heating of the film by the absorption of water would exaggerate the gain. We should therefore expect the change of constitution to appear very rapid about the time when the water was introduced, as at that time the temperature of the film would be changing most rapidly. The low value of p found at 10·7 minutes (see Table XI.) makes it difficult to draw any absolutely certain conclusions. If however we suppose that at the moment the blotting-paper was moistened the value of p was as high as 21, the sudden fall to 17·8 would be explained by a change of temperature not much exceeding 1° C. There is therefore no evidence of any considerable change in temperature when a film suddenly ceases to lose and begins to absorb water.

Turning next to the bearing of these observations on the experiments of MM. PLATEAU and LÜDTGE, it is evident that arguments based upon a substance subject to such rapid and considerable changes of composition as are indicated by our observations are open to grave suspicion.

It is indeed true that large changes in the constitution of a soap solution are attended with but trifling alterations in its surface tension. We have for instance proved by experiment that the loss of 25 parts of water alters the tension of a 5 per cent. standard solution by less than 3 per cent. But on the other hand it is evident that, under other circumstances than those detailed above, much larger quantities of water might be gained or lost. In our observations the period of the ultimate slackening of the rate of change of constitution was never reached unless the films were formed in air filled with moisture of the right tension by means of the precautions we have described.

The introduction of a small leaden dish of strong sulphuric acid into the case produced the most violent commotion in a film. Streams of liquid circulated round it with great rapidity, it became spotted with white flecks, and generally broke in less than five minutes. The irregular colouring and the short duration alike prevented accurate measurement in these cases, but it is probable the rate of change was far greater than in those above detailed. The bubble observed by M. PLATEAU lasted for three days, and was placed in a beaker containing caustic potash. The inner surface was, on the other hand, in contact with air which was itself in contact with the water in the manometer. Under these circumstances water may have been either lost or absorbed, and the phenomenon sought for, viz.: a change in surface tension, might have been either caused or masked by the changing constitution of the film.

On the whole, then, we think that the study of the electrical resistance of soap films offers better opportunities of investigating their nature than any other method which has been hitherto proposed. It is far more sensitive to slight changes in constitution, and it provides, as it were, a means of analysing the films, such as measurements on no other of their physical properties afford.

It has been suggested that it would be impossible for a soap film to exist, the thickness of part of which is less than twice the radius of molecular attraction. The surface tension being in this part less than in the remainder, rupture, it is contended, must ensue. This argument might perhaps be conclusive if it were known that the difference of surface tension was considerable. If however it is small while the surface viscosity is high, the force thus set up might for a long time only accelerate the thinning of the film without actually tearing it asunder. In any case while soap films present so many paradoxical phenomena, such as the sudden augmentation of thickness noticed by us in the paper already referred to, it seems unsafe to rest satisfied with conclusions for which direct experimental evidence cannot be adduced.

In conclusion we must express our thanks to Mr. A. HADDON, Demonstrator in the Physical Laboratory of the Royal Naval College, Greenwich, for the ready and able assistance which he has rendered to us during the whole of our investigation.

Our acknowledgments are also due to the late Mr. F. WENTWORTH and to Mr. C. C. STARLING, both of the Yorkshire College, for aid in the tedious calculations required for the revision of the table of colours.

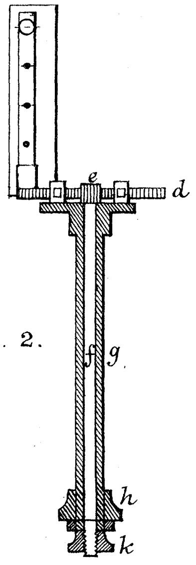
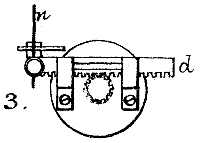


Fig. 2.



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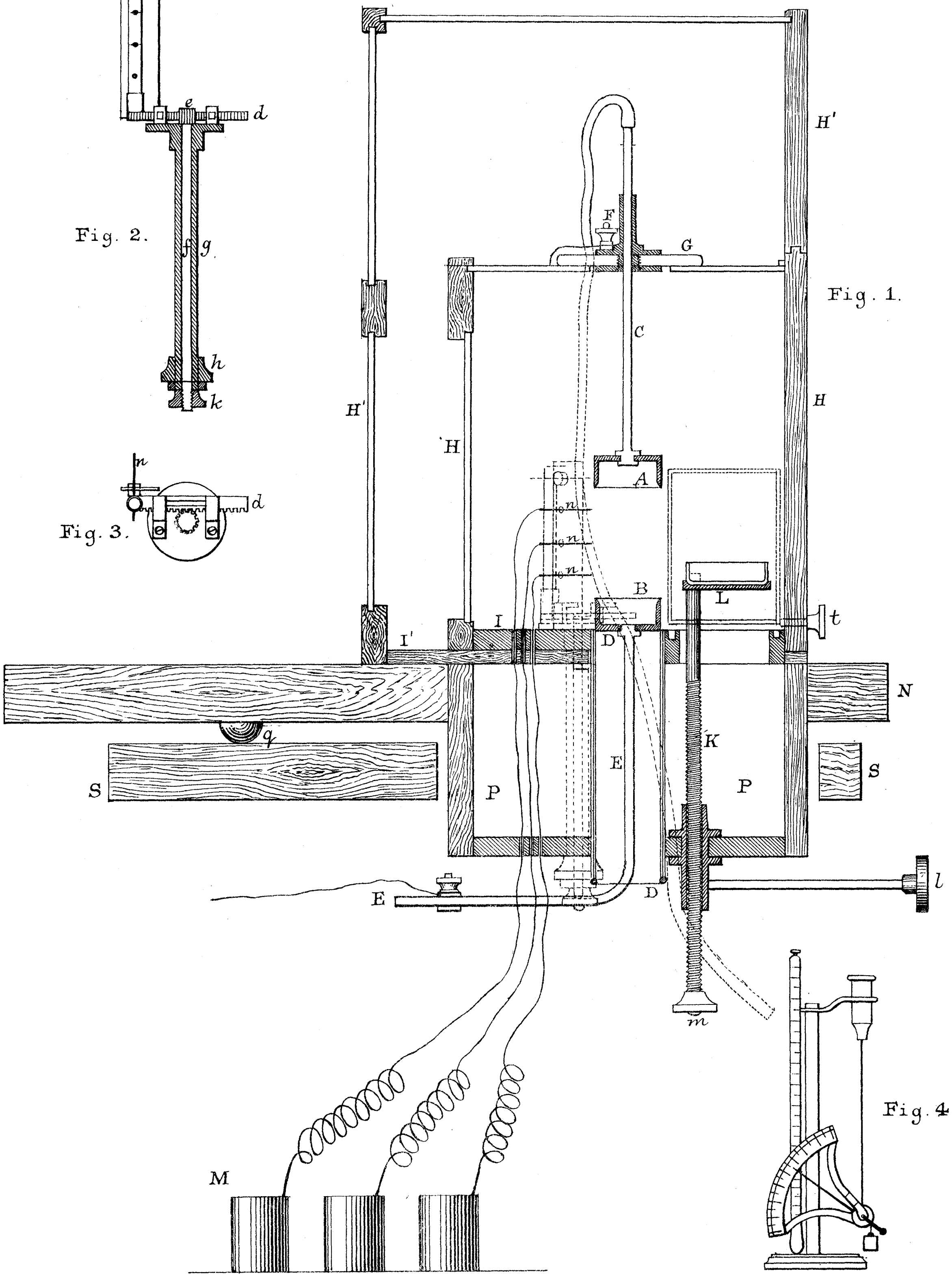

Fig. 1.

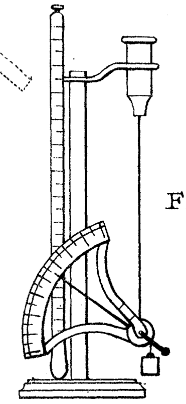

Fig. 4.

Scale $\frac{1}{3}$ *of full Size.*

West, Newman & C^o. lith.

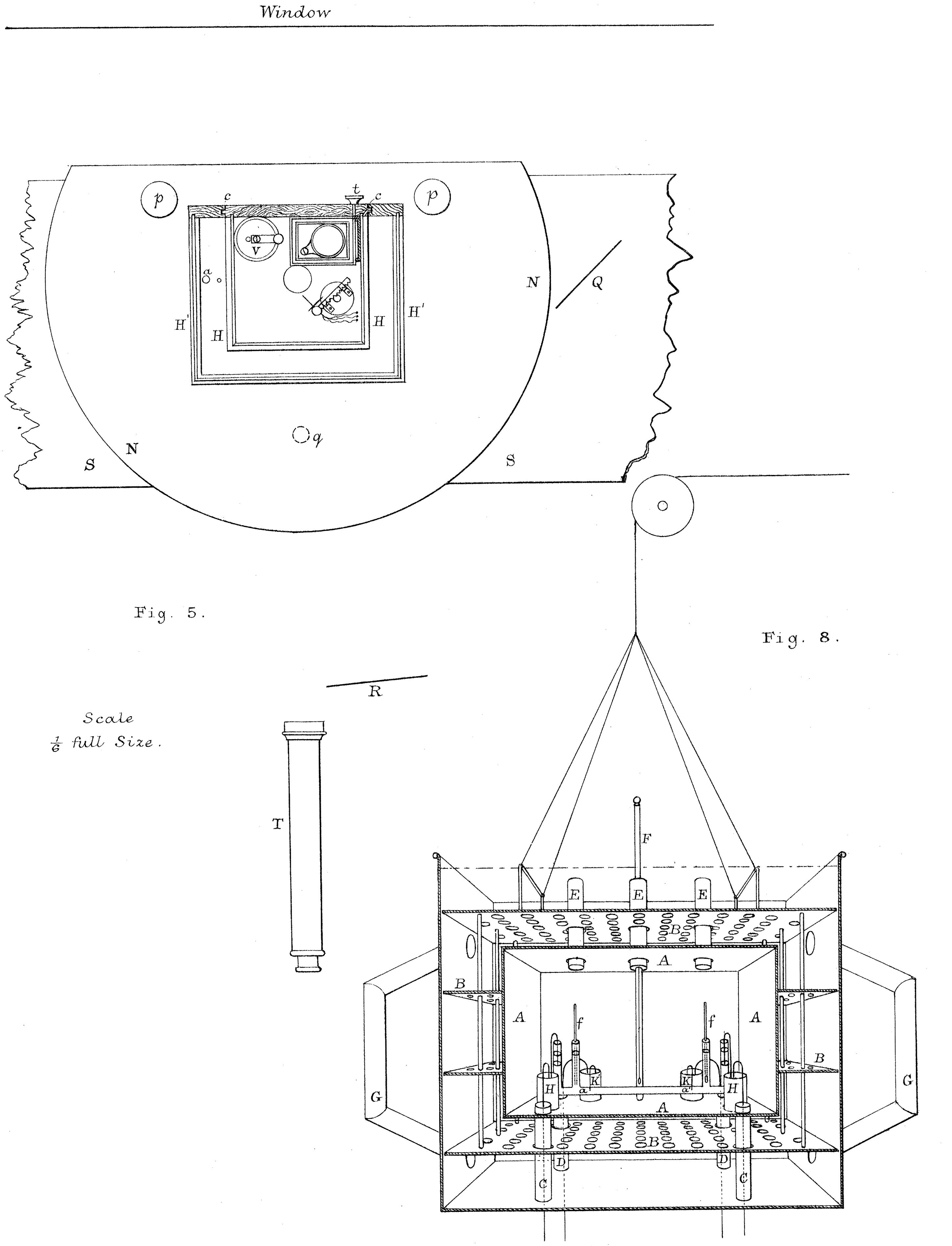

Fig. 5.

Scale
$\frac{1}{6}$ full Size.

Fig. 8.

West Newman & Cº lith.