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The Electric Conductivity of Nitric Acid

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IX. *The Electric Conductivity of Nitric Acid.*

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INTRODUCTORY.

OF the commoner mineral acids the chemical changes of Nitric Acid, from their evident complexity, have formed the subject of numerous memoirs, while those of sulphuric acid, from their assumed simplicity, have been to some degree neglected ; on the other hand, the physical properties of the latter have been studied with considerable elaboration, while those of the former have been passed over, doubtless on account of the corrosive nature of the acid and the difficulty of preparing and preserving it in a reasonable degree of purity. Further, with certain exceptions, the alterations in physical properties induced by the products of reduction, be they nitrogen peroxide or nitrous acid, either singly or conjointly, have attracted but little attention, though it is a common matter of observation that the current intensity of a Grove's or other cell containing nitric acid remains constant, even though the fuming acid, originally colourless or red, has become of a deep green tint. It is more than probable that of the factors of OHM's law, both the E.M.F. and internal resistance are continually varying.

At the earliest stages of the enquiry it was found that the passage of a few bubbles of nitric oxide gas into a considerable volume of nitric acid produced an alteration of one per cent. in the resistance, and the same result could be effected to a less degree by exposure to sunlight, and to a still less degree by exposure to artificial illumination. Therefore, we determined to investigate the alterations of conductivity produced by changes of concentration and temperature in samples of acid purified with necessary precautions, more especially as former workers upon the subject have either used samples of acid confessedly impure, or have been silent as to any method of purification, or have adopted no special care in dealing with a substance so susceptible of polarisation.

At the outset we desire to state that it is proposed to view our results from the standpoint of the hydrate theory, and to point out any abrupt alterations of physical properties of nitric acid corresponding to any particular concentration, adopting in

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outline the methods and arguments used by PICKERING* in his investigations on sulphuric acid.

Pure acids and clean vessels are glib phrases, which represent unattainable ideals; we only trust that we have adopted reasonable precautions of purification, and that even if our determinations are not of absolute exactitude, yet the arguments deducible from them are not seriously affected.

Lastly, we desire to express our obligations to the Rev. F. JERVIS-SMITH, of Trinity College, Oxford; Mr. E. H. GRIFFITHS, of Sydney Sussex College, Cambridge, for assistance in the experimental portion; to Mr. R. T. GUNTHER, for photographs; to the Chemical Department of the University of Oxford, for loan of apparatus; to Mrs. V. H. VELEY, for certain illustrations; and to the Government Grant Committee of the Royal Society for moneys to defray a moiety of the expenses. The work was conducted partly in the Chemical Department of the University Museum, and partly in the laboratory of Magdalen College.

FORMER INVESTIGATIONS ON ELECTRIC CONDUCTIVITIES.

KOHLRAUSCH and GROTRIAN† determined the conductivity of dilute nitric acid of concentrations varying from 6·32 to 62·07 per cent., seven points in all, and at three different temperatures for each concentration, in order to deduce the values of the constants α and β in the equation

$$K_t = k_0 (1 - \alpha_t + \beta_t^2).$$

These writers adopted their well-known method of alternating currents, but allowed that the acid used was impure, as they wrote:—"Die concentrirte Salpetersäure, ursprünglich farblos, hatte nach längerem Stehen eine hellgelbe Färbung angenommen, offenbar durch Bildung eines Spurs von salpetriger Säure unter dem Einfluss des Lichtes." Their investigations, however, brought out an interesting detail, namely, that the conductivity increases with the percentage concentration up to 30 to 33 per cent., and subsequently decreases; in the sequel this point will be more fully discussed.

OSTWALD,‡ adopting KOHLRAUSCH's telephone method with slight modifications, made a number of determinations of the molecular conductivity of nitric acid, diluted so as to contain a gram-molecular weight in volumes of water varying from 2 to 8,192 litres.

Finally, BOUTY§ studied the changes in conductivity caused by the solution in

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* 'Journal of the Chemical Society,' 1890, Trans., 64–184.

† 'Ann. Phys. Chem.,' vol. 154, pp. 215–239.

‡ 'Journ. Prakt. Chem.,' vol. 30, p. 228, and vol. 31, p. 437; also 'Zeits. Physickal Chem.,' vol. 1, p. 75.

§ 'Compt. Rend.,' vol. 106, p. 595.

nitric acid of small quantities of metallic nitrates. This work has, however, only an indirect bearing upon the present investigation.

Preliminary Experiments.

In consequence of certain initial difficulties, experiments were made upon the effects produced by (1) an added impurity of nitrous acid; (2) sunlight; and (3) imperfect insulation of the electrolytic cell. The results obtained may serve to explain certain discrepancies between our values and those of previous workers.

(1.) *Added Impurity of Nitrous Acid.*—The following experiment serves to illustrate this point, to which reference was made in the introductory section:—The resistance of a mixture of 1 vol. of acid (1·48 sp. gr.) and 4 vols. of water was found to be 6·97 ohms; a few bubbles of nitric oxide gas passed in so as to form a trace of nitrous acid caused an increase of ·07 ohm, or 1 per cent. in round figures.

(2.) *Sunlight.*—It is a common matter of observation that the space above the liquid in a partially-filled bottle of concentrated nitric acid contains coloured fumes, though the liquid itself may be almost colourless. This would show that the vapour rather than the liquid was decomposed by the action of light. In order to decide this point a comparative experiment was made by taking two stoppered flasks of the same capacity, and presumably of the same glass. One of these was completely, and the other partially filled with acid of 85 per cent. concentration, which contained one part per million of nitrous acid. Both flasks were exposed to the direct sunlight of an April day for two hours thirty minutes. Though the amount of nitrous acid in the former sample was unaltered, that in the latter was increased to 21 parts per million, and it had become bright yellow in colour.

As a further illustration, the following experiment may also be quoted:—The resistance of a certain length of acid (1 : 4 as above) was found to be 7·18 ohms, but after exposure for six hours to the diffuse daylight of a dull and cloudy day in October, the resistance had altered to 7·31 ohms, or an increase of 2 per cent. in round numbers, both experiments being made under the same conditions of temperature.

(3.) *Imperfect Insulation of Electrolytic Cell.*—As it appears from the diagrams given in certain standard text-books on physical chemistry that the electrolytic cells may be kept rigid by metallic clamps, it was thought desirable to ascertain if such an arrangement might lead to incorrect determinations. Our experiment showed that (1) winding the ends of a copper wire around the cell in the neighbourhood of the electrodes, (2) wrapping tin-foil round the whole cell, produced a diminution of resistance amounting to 0·3 and 1·6 per cent. respectively.

PURIFICATION OF WATER.

Ordinary distilled water was purified by redistillation with a few crystals of potassium permanganate and a few cubic centimetres of concentrated sulphuric acid instead of potassium hydrogen sulphate, as recommended by STAS. A slow current of purified hydrogen was passed through the water during the operation, which was conducted in a laboratory used for no other purpose. The condensation was purposely kept somewhat imperfect to prevent any ammonia gas from being redissolved in the cool water; the first and last fifths of the distillate were rejected, and the intermediate portion again distilled over barium hydrate to remove any sulphuric acid. On the day before any conductivity experiments were made the water was distilled a third time in a platinum still fitted with a condensing tube and receiver of the same material, and again also with imperfect condensation. It was observed that after several litres of the water had been distilled a deposit of silica, distinctly crystalline, was formed on the still. Finally, a few hours previous to the commencement of a series of experiments, the water contained in small bottles was partially frozen (by immersion in a freezing mixture) so as to obtain a hollow tube of ice; the central core of water was poured off, the ice quickly melted and mixed with a quantity of nitric acid necessary for the concentration required. It is not, of course, presumed that, by the method adopted, water was obtained of the degree of purity arrived at by KOHLRAUSCH and HEYDWEILER;* indeed, it was not considered necessary to use such precautions, when the solutions to be measured would possess a conductivity many million times greater than that of the purified water.

PURIFICATION OF NITRIC ACID.

Two different methods were adopted for this purpose according as the concentration required was less or greater than 68 per cent. In the former case, acid of sp. gr. = 1·4, sold as pure, and nearly colourless, was distilled continuously under a pressure of a few millimetres in an apparatus constructed entirely of glass, as to the essential parts, namely, the still, condenser and receiver. The acid could be drawn up into the still, and syphoned off from the receiver by glass tubes provided with stop-cocks; it was stored in tubes of hard glass (a precaution adopted by STAS in his investigations upon atomic weights) the ends of which were drawn off but not sealed, as it was found that the vapour of the acid given off at ordinary temperatures decomposed to produce nitrous fumes in the operation of sealing.

When acids of concentration greater than 68 per cent. were required, a proportion of the water was removed by distillation of such an acid with an equal bulk of sulphuric acid; the pale yellow acid thus obtained was then redistilled with barium

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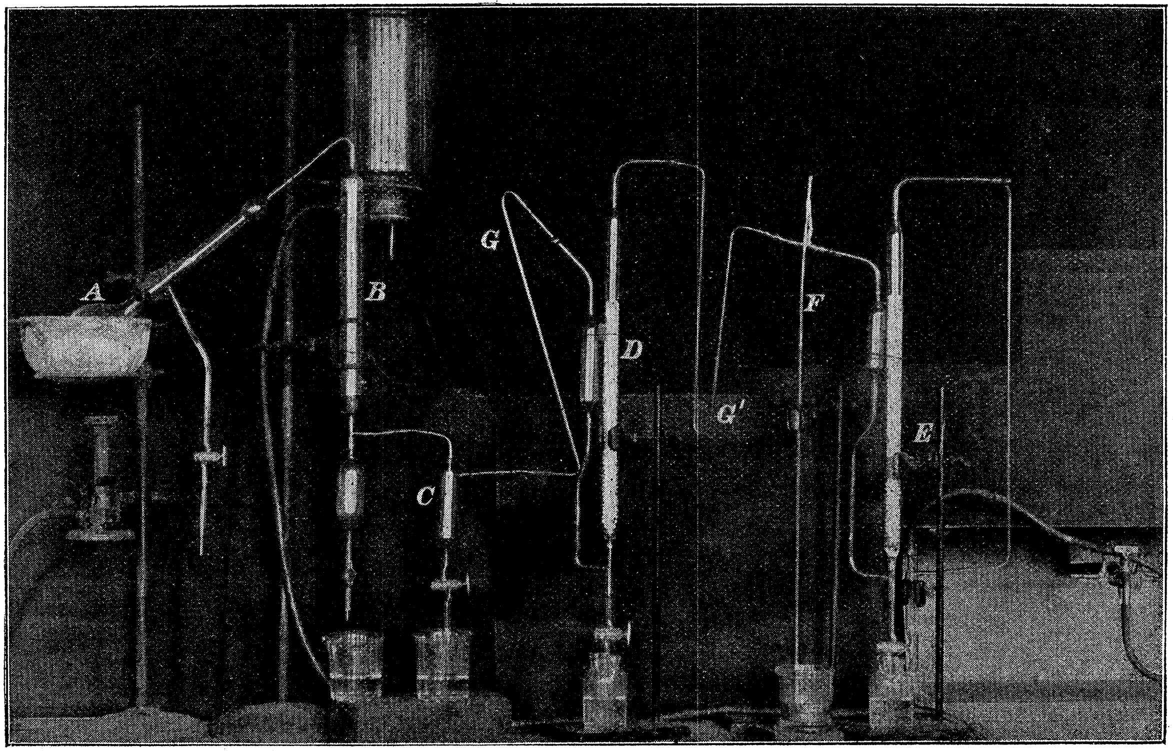
* 'Zeits. Physikal Chem.,' vol. 14, p. 317.

and silver nitrates dissolved in it, the former to remove any sulphuric acid which might have been mechanically carried over, the latter to remove haloid acids remaining dissolved.* The acid thus obtained was subjected to a third process of fractional distillation † in an apparatus constructed all of glass as follows.

Fig. 1.



A (fig. 1) is a distillation flask of about 400 cub. centims. capacity, the neck of which, considerably lengthened out, was sealed at its upper end to the top of a spiral condenser, B, kept cool by a current of ice-cold water; to the lower end of the latter the receiver was attached, which was provided with a stop-cock for drawing off the condensed acid from time to time. A side trap, C, was sealed on to the upper end of the receiver, in order to retain any accidental spirting from the sulphuric acid towers, D and E; these latter were about half a metre high, and filled for three-quarters of their length with glass beads moistened with sulphuric acid, which could be renewed by means of stop-cocks sealed at their lower extremities. This process of cleansing and renewal was repeated not only previous to, but also during each distillation. It was found by experience that these towers were sufficient to prevent any moisture from passing from the water pump to the anterior portion of the apparatus. The

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* This process of purification was previously adopted by Kolb, 'Ann. Chim. Phys.' [4] vol. 10, p. 140.

† Attempts were made to remove the water present by means of phosphorus pentoxide, but were unsuccessful owing to the rapid decomposition of the 99 per cent. acid by this substance.

gauge, F, introduced between the two towers served to indicate the pressure, generally a few millimetres, under which the distillation was conducted, while the glass springs, G and G′, decreased the rigidity of the apparatus. The process of distillation consisted in drawing up the acid into the flask by means of the stopcock; the whole apparatus was then exhausted, and the water-bath surrounding the distillation flask gently warmed. The nitrous fumes present in the acid were for the most part immediately swept through the apparatus, and the remainder collected in the first portions of the nitric acid condensed in the receiver. This was drawn off and the whole process repeated until a small test sample of the acid produced no decoloration of a drop of standard potassium permanganate solution after the lapse of thirty minutes. The most effective method, according to our experience, for removing the last trace of nitrous fumes without either diluting the acid or adding any other impurity, consists in passing a stream of dried ozonised oxygen through the acid, and then subsequently distilling it in the above vacuum apparatus to eliminate any dissolved gas.

Detection and Estimation of Impurities.

The principal impurities likely to be present in any sample are (i.), nitrous acid, formed from the decomposition of the liquid itself, or its superincumbent vapour, (ii.), sulphuric acid, (iii.), the haloid acids, namely, hydrochloric and hydriodic, derived from the previous manufacture of the acid from "caliche," and, (iv.), alkaline silicates or silica from the glass of the containing vessels. The methods used to estimate the three first-mentioned impurities are described in detail.

(i.) *Nitrous Acid.*

For this purpose the metaphenylene-diamine method was employed, by means of which 1 part in 20 millions (according to Griess, its author) can be detected, and according to our own observation a quantity less than 1 in 15, but greater than 1 in 20 millions is revealed. The standard test adopted was that of 1 part nitrous acid in 1 million parts of water, produced either by the liberation of that amount of nitrous acid by the acidification of sodium nitrite (obtained from silver nitrite) or by an imitation tint formed from Bismarck-brown dissolved in dilute alcohol; the comparisons were made by the tintometer described by one of us in a previous communication.

(ii.) *Halogen Acids.*

The solubility of silver chloride was fully investigated by Stas[*] in the course of his investigations upon the atomic weights. According to this writer, the solubility

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[*] 'Ann. Chim. Phys.' [4], vol. 25, p. 22, and [5], vol. 3, p. 145.

varies according as the chloride is in the pulverulent or caseous condition. More recently the same subject has been investigated by J. P. COOKE,* who states the solubility is not affected by nitric acid. The method of estimating the traces of halogen acids in the samples was as follows:—

10 cub. centims. of the sample to be examined were placed in a miniature flask and 1 cub. centim. of a silver nitrate solution containing ·05 gram of the salt was added; the turbidity, if any, was compared with that produced by the same quantities of purified water, the silver nitrate solution and a fractional part of 1 cub. centim. of a solution of hydrochloric acid of known strength. It was found in the course of experiment that a sample of nitric acid of 20 per cent. concentration gave no turbidity with the silver nitrate, but on addition of ·5 per million of hydrochloric acid a turbidity was produced which appeared to be equal in amount to a blank experiment, made at the same time, with water only; but after standing for some hours the turbidity in the former case was less than that in the latter, and remained nearly white, instead of changing to a violet tint on exposure to diffuse daylight. It was probable, therefore, that the chloride was being slowly decomposed by the nitric acid. As a result of this observation, acids of concentration greater than 20 per cent. were diluted down to this strength, and the comparison made with the blank water experiment after the interval of one hour. It is not presumed that the estimations are of absolute accuracy, especially as the greatest quantity of haloid acids found in any sample was 3·8 parts per million, the average being less than 2·0 parts. The correction to be applied for these amounts of impurity is of the second order, and may reasonably be neglected.

(iii.) *Sulphuric Acid.*

The observations upon the solubility of barium sulphate in water and in dilute nitric acid appear to be very discordant. According to FRESENIUS and HINTZ† one part of barium sulphate in 400,000 water can be detected provided that a slight excess of barium chloride is added, but only 1 in 100,000 parts if no such excess is present; under the same conditions, in presence of nitric acid of 7·8 per cent. concentration, only 1 part of barium sulphate in 33,000 can be detected.

These estimations were made with a view of examining the accuracy of the quantitative determination of sulphuric acid by barium chloride, as the precipitant, in the presence of various salts and acids which might be present in the course of analytical experience; otherwise the use of barium chloride rather than the nitrate in the presence of nitric acid might be open to objection. Furthermore, it is evident that the delicacy of the reaction between a barium salt and sulphuric acid will depend *cæteris paribus* on the relative masses of the reacting substances. The work

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* 'American Journal of Science,' vol. 21, p. 220.

† 'Zeits. Analyt. Chem.,' 1896, vol. 33, p. 170.

of the above writers has been criticised by KÜSLER,* who found by an electric resistance method that a saturated solution of barium sulphate in water contains 1 part of salt in 425,000 water (equals 2·35 parts per million), a result in accordance with the former observations of ROSE, KOHLRAUSCH, and HOLLEMANN.

In the estimation of the amount of impurity of sulphuric acid in the samples used, 1 cub. centim. of a 10 per cent. solution of barium nitrate was added to 10 cub. centims. of the nitric acid, which had been neutralised previously by a solution of ammonia; the quantity of the barium nitrate was more than a hundredfold in excess of that required to precipitate the greatest amount of sulphuric acid likely to be present. In a blank experiment with water which had been distilled over baryta it was found that 2·3 parts of sulphuric acid per million water produced a turbidity with the barium nitrate; but in the case of a sample of nitric acid of 50 per cent. concentration, after neutralisation with ammonia, 2·8 parts of sulphuric acid per million produced a turbidity. The mean of these two numbers, namely 2·5, may reasonably be taken as the limit of delicacy of the reaction within the limit of ·0650 per cent.; from the results calculated upon this basis the greatest quantity of sulphuric acid found was 4·3 parts per million. A selection is given below (p. 385) of various acids used in order to show the degree of purity attained.

DETERMINATION OF THE CONCENTRATION OF THE SOLUTIONS.

For this purpose standard solutions of sodium hydrate were made from metallic sodium, purified by melting it in vacuo and filtering the molten metal through iron gauze; it was then placed in a silver dish and allowed to hydrate slowly in the vapour of water from a dilute soda solution; the method adopted has previously been fully described.

The solution thus obtained was made up to a definite volume and standardised as against (i.) sulphuric and (ii.) hydrochloric acid; the acidity of the former was determined volumetrically by sodium carbonate, and gravimetrically as barium sulphate, that of the latter (i.) volumetrically by pure metallic silver, by the method of STAS, and (ii.) volumetrically by sodium carbonate. Three different methods and two different indicators, namely, litmus and methyl-orange, were used by two different individuals. The degree of concordance obtained for one such standard solution of soda is shown by the following table:—

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* 'Zeits. Anorgan. Chem.,' vol. 112, p. 261.

TABLE I.

Acid.	Method.	Sodium hydrate in 1 cub. centim.
		gram.
Sulphuric	Barium sulphate	0·03912
,,	Sodium carbonate	0·03912
,,	,,	0·03914
Hydrochloric	Silver	0·03914
,,	,,	0·03912
,,	Sodium carbonate	0·03912
,,	,,	0·03912

For the determination of the nitric acid solutions a weighed quantity was expelled from a pyknometer, neutralised by a slight excess of the standard sodium hydrate, and the amount of such excess added determined by a solution of hydrochloric acid of $\frac{1}{100}$ equivalent strength of the soda.

STANDARDISATION OF THERMOMETERS.

The thermometers employed were graduated to ·1° C., and were compared with (i.) a standard Kew thermometer which could be read to ·05° F., and (ii.), within certain limits, with another standard graduated to ·05° C., constructed by BAUDIN and formerly in the collection of the 8th Duke of MARLBOROUGH.

The zero displacements of all the instruments were determined by immersing them in a cylinder filled with washed ice, and surrounded by an outer jacket packed with the same material. The readings were made with a telescope, furnished with cross wires and mounted on glass plates, after the manner of QUINCKE's reading microscope. For the estimation of the errors at higher temperatures, the thermometers were suspended in a deep tank (containing several gallons of water), so that the thread of mercury at the point to be observed was just visible above the surface; the instruments were arranged in a line with the standard in the middle, so that by a slight rotatory movement of the telescope stand each of them could be brought into the field of view in rapid succession. The water was warmed about 2° above the point required, allowed to cool slowly, while thoroughly stirred, and a first set of readings taken; the process of stirring was repeated, and a second set taken; in case of any variation, the mean value was accepted. At the commencement and conclusion of each set of observations, the standards were read, and their constancy throughout was regarded as a safe criterion that the temperature of the large mass of water had not appreciably altered. The whole series of observations was repeated for every 5° within the range required, and in the case of two thermometers found to be less uniform in bore than the others, readings were taken at an interval of each degree.

This method of standardisation, though tedious, probably eliminates the errors due to a lag of the mercury thread to a greater degree than a more rapid process. It was not thought necessary to apply the corrections for variations of atmospheric pressure, or others adopted by the Bureau International, as the methods of determining the electric conductivity of a highly decomposable electrolyte are not susceptible of such a degree of accuracy that such corrections would materially affect the result.

CALIBRATIONS OF ELECTROLYTIC CELL.

In order to determine the mean cross-sectional area of this apparatus, two methods were adopted: (i.) that described by BUNSEN (Gasometrische Methode), namely, by pouring in equal volumes of mercury and reading the different levels by a telescope, the absolute volume of the measuring tube being subsequently ascertained by two independent weighings of mercury at the temperature of the observation; (ii.) by pouring in from a funnel such a weight of mercury as would fill the burette for every tenth graduation in cubic centimetres, the temperature being noted at the time. The following results are given to illustrate the concordance obtained by the two methods:—

TABLE II.

Method I.	Method II.	Difference.
cub. centims.	cub. centims.	cub. centims.
10·12	10·04	+·08
10·02	10·02	Nil
10·02	9·99	+·03
10·33	10·36	−·03
10·02	10·04	−·02
9·82	9·82	Nil
10·02	9·96	+·06
9·82	9·88	−·06
10·02	10·06	−·04
10·02	10·05	−·03
10·22	10·25	−·03

The mean values were accepted as the true volumes.

In order to measure the different lengths so as to deduce the cross sectional areas, a pair of slide callipers was used, reading to ·01 centim. and compared with a standard metre. The highest and lowest value for the area within the limits of observation were 4·4732 and 4·3839 sq. centims. respectively, so that the burette was of a fairly uniform bore.

RESISTANCE COILS.

The resistance coils, supplied by Messrs. ELLIOT BROS., and marked as true ohms at 16° were standardised by Mr. E. H. GRIFFITHS as against his coils, which had been compared with the standards in the possession of the Cavendish Laboratory, Cambridge. We desire to express our appreciation of Mr. GRIFFITHS' courtesy and kindness in this matter. Two sets of determinations were made at different times and at slightly different temperatures. The results are given as true ohms, when the thermometer used always for the box registered a temperature of 16°.

TABLE III.

Coils as marked.	Series I.	Series II.	Mean.
ohms.	ohms.	ohms.	ohms.
50	49·9994	49·9927	49·9961
20	19·9999	20·0003	20·0001
10 A	10·0026	10·0026	10·0026
10 B	10·0031	10·0028	10·0029
5	4·9995	4·9996	4·9996
2	2·0022	2·0034	2·0028
1 A	1·0026	1·0018	1·0022
1 B	1·0022	1·0018	1·002
·5	·5027	·5017	·5022
·2 A	·2005	·2007	·2006
·2 B	·2001	·2007	·2004
·1	·1005	·1007	·1006

With the exception of the 50-ohm coil the results are concordant to within ·001 ohm, and in the majority of cases to ·0005 ohm, which is within the limit of experimental error.

The values of the higher coils were referred to the 50-ohm coil by reducing the bridge arm to $\frac{1}{100}$; they are not, therefore, of such a high degree of accuracy, but these coils were seldom required.

Coils as marked.	Values.
ohms.	ohms.
100 A	99·9895
100 B	99·9956
200	200·0117
500	500·1618

TEMPERATURE COEFFICIENT OF BRIDGE WIRE.

The bridge wire, supplied by Messrs. JOHNSON and MATTHEY, was of platinum- (90 per cent.) iridium (10 per cent.) alloy; its mean diameter was 1·5 millim.

In order to determine its temperature coefficient, a small portion was drawn out to ·005 millim. diameter, and the wire introduced into a Callendar-Griffiths pyrometer. Its resistance at the three temperatures of steam, ice, and 20·15 was determined by one of their platinum resistance boxes, in which the compensating leads are thrown into one arm of the bridge, while the coil and its leads are in another arm thus, changes in resistance of the leads produce no effect on the readings. The values for R in steam and ice were ascertained by different arrangements of plugs, and hence different bridge wire readings. The coils used are indicated by letters.

STEAM.

Coils.	Readings.	Temp. of resistance box.	Bar.	R. con.
			millims.	
C.F.H.	+ 6·04	19·95	748·8	191·351
C.F.H.	+ 6·04	20·03	748·76	191·355
C.F.G′.	+ 1·11	20·01	748·76	191·359
C.F.G.H.	− 4·05	20·12	748·78	191·353
		Mean	748·78	191·353

The boiling point of water for $p = 748{\cdot}78$ is 99·59; hence the value for R under this condition is 191·355.

ICE.

Coils.	Readings.	Temp. of resistance box.	R. con.
C.G.	+ 2 04	20·38	172·288
C.G.H.	− 3·095	20·4	172·286
C.G′.	+ 2·04	20·4	172·289
		Mean	172·288

Hence $R = 172{\cdot}288$, if $t = 0$; similarly, for $t = 20{\cdot}15$ R was found in the same manner to be 176·149. Taking R at 0 as 1, R at 20·15 = 1·02241, and at 99·59 = 1·11067, the curvature is very slight, and is expressible by the equation

$$R_t = 1 + {\cdot}0011123\,t\,;$$

but if $R_{15} = 1$, then $R = {\cdot}0010911$, and the equation for the temperature coefficient is

$$\delta R_t = R_{15}\,(1 + (t - 15) \times {\cdot}001094),$$

with a probable error of 1 in 1000.

CONSTRUCTION OF THE BRIDGE.

In preliminary experiments with the ordinary form of metre bridge used with a telephone and small induction coil as described by KOHLRAUSCH and others, difficulty was experienced in obtaining silence in the telephone within the limits desired. This was eventually traced to imperfect insulation of the wooden board, even though well seasoned and previously soaked with paraffin wax (figs. 2 and 3). It was therefore thought desirable to construct a bridge in which the wire was an air line, and all the strappings were mounted upon ebonite pillars. The wire was stretched between two massive brass castings, *aa*, and insulated from them by ebonite plates, *bb;* at one end it was fixed to a brass pin, and at the other to a stretching screw, *s′*, so arranged

Fig. 2.

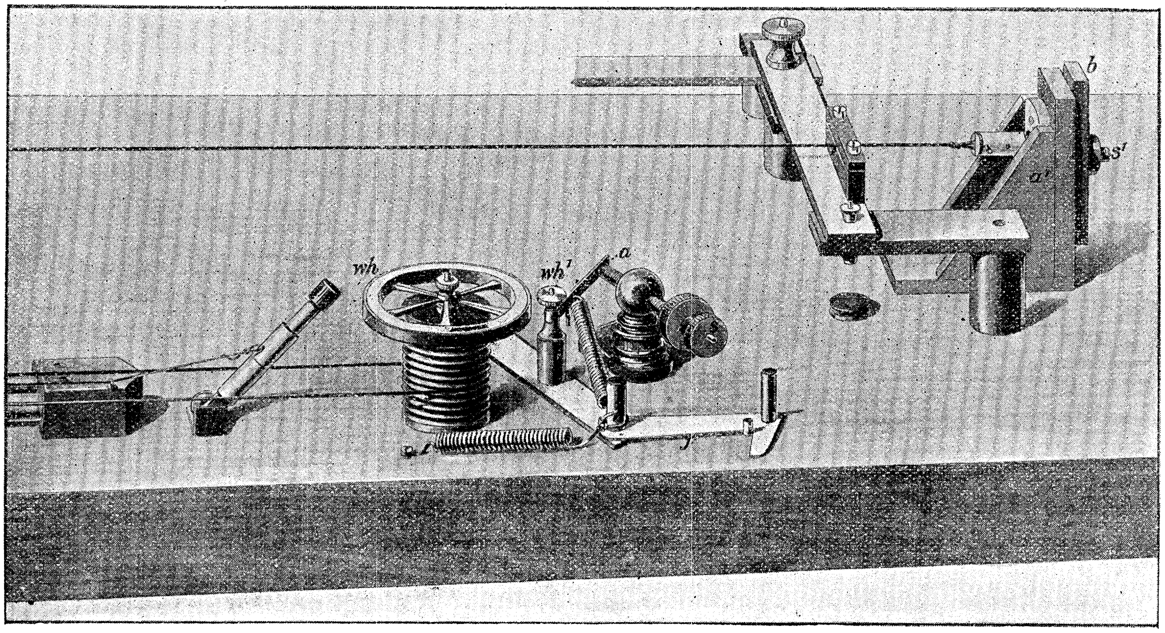
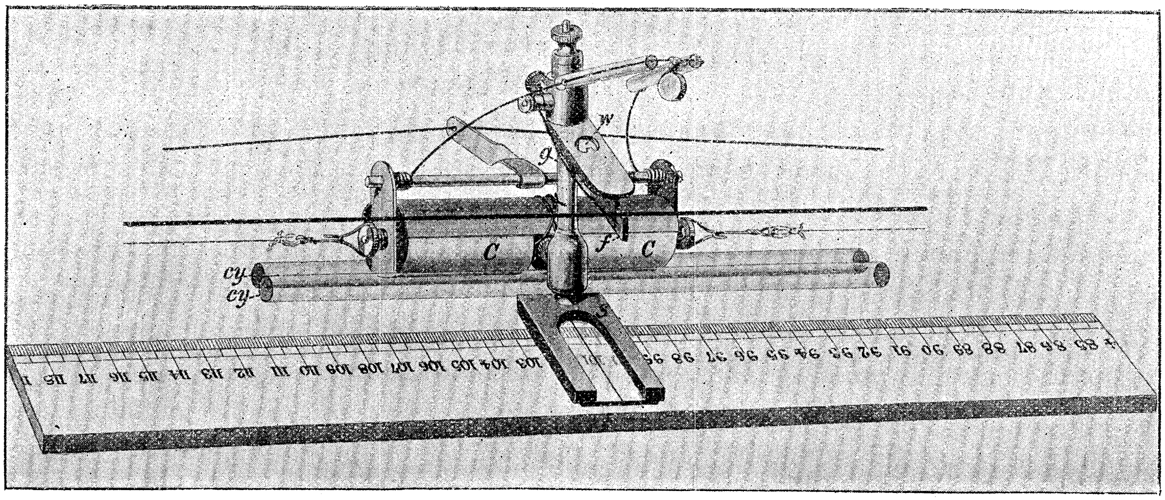


Fig. 3.



as to tighten but not twist the wire; its effective length was 2 metres. As this arrangement obviously required a special form of slider to tap, without sagging the wire, the following plan was adopted: two weighted opposed cones, *cc*, moved upon two uniform glass cylinders, *cy*, placed side by side and set parallel to the wire, according to the principle of Lord KELVIN, that a body provided with four points will always move parallel to itself along a cylinder. A brass shoe, *s*, carrying a glass plate projected from the centre of the cones at a right angle and rested upon the millimetre scale of the bridge; the position of the slider was indicated by a line etched upon the lower surface of the glass plate, and observed through a little window, *w*, situated vertically above it. A platinum contact piece, *f*, mounted upon an ebonite rod, *g*, was adjusted to within a fraction of a millimetre of the wire. When it was desired to make contact, an insulated arm, *H*, was brought down upon the wire from above by tilting the lever, *I*. In order to move the slider a wheel, *wh*, was attached to one of two pulleys, over which passed a cord kept stretched by a spiral spring. For the purpose of fine adjustment, the wheel, *wh*, was furnished with a rubber band, cemented at its edge, on which a second and smaller wheel, *wh'*, could be brought to bear by releasing the lever, *J*; from the latter wheel projected an arm, *A*, which rested upon the end of the milled head screw, *S*. By this arrangement the slider could be moved by the observer from the extremity of the bridge, and all thermo-currents due to his proximity and direct handling were avoided.

CALIBRATION OF BRIDGE WIRE.

The wire was placed in the bridge, stretched to the requisite extent, and allowed to rest undisturbed for nine weeks; then it was calibrated by CAREY FOSTER'S method, using as a gauge a short length of the same wire soldered on to massive copper terminals and a copper connector of the same length, both of which were joined to the bridge by mercury cups furnished with stout copper tags. The process of calibration was conducted on two different dates. The wire was found to be very uniform throughout, the highest and lowest values for the resistance of 1 millim. being ·0001516 and ·0001510 ohm respectively.

The total resistance of the 851 millims. in the centre of the bridge, as also of the ends of the bridge, were determined by a fall of potential method, using one Daniell cell working through a resistance of 200 ohms, a standard coil of ·1 ohm value, and a high resistance galvanometer; the current was uniform within limits of time greatly in excess of those required for the observation; the necessary corrections for the temperature coefficient were subsequently applied. Ten independent observations were made of the total resistance, one set of two on one date, and another set of eight after an interval of a week. For the interchange of the standard coils and electrolyte, a switch board, constructed upon S. P. THOMPSON'S pattern, was used. The mercury cups were mounted upon ebonite stems to secure better insulation, and for the purpose of better contact between the copper connectors and tags the former were furnished with leaden weights instead of the more troublesome elastic bands generally used.

The Commutator.

In our earlier experiments a small induction coil was used according to the well-known Kohlrausch method, but owing to the susceptibility of the nitric acid to polarisation, this apparatus was found to be unsatisfactory. A commutator of the disc pattern was therefore substituted, being driven by a small water-motor served through a Kelvin tap to secure a regular flow of water; the necessary electric current was obtained from a one-quart Daniell cell.* The speed of the commutator disc was determined by a kymograph, a lever arrangement being fitted up so as to give one vibration for each revolution. A number of experiments showed that the revolutions varied between the extreme limits of 16 and 20 per second; as the disc carried nine commutators, there were for each revolution 18 makes and breaks and 9 reversals; this gives per second 288–360 of the former and 144–180 of the latter. In order to test the efficacy of this method, the alternating currents were led directly into nitric acid of various concentrations for one hour. No evidence of polarisation could be detected when the commutating arrangement was switched off and the electrodes simultaneously connected up with a very sensitive galvanometer, and, further, no trace of nitrous acid could be detected by the metaphenylene-diamine test.

The commutator, working-cell, and water-motor were placed in a different wing of the building, the current being brought into the experimental room by leads twisted together.

General Arrangement of Apparatus (Diagram I).

C represents the commutator, L its leads, K a key for either short-circuiting the current (position 1), or connecting up with the bridge and electrolytic cell E (position 3) or breaking connection altogether (position 2). R_3 is a small bifilar coil to the extremities of which the leads of a call telephone, *t*, were attached, the latter serving to detect any alteration or failure of the commutator. R_1 is a resistance box, the coils of which were adjusted so as to approximately compensate any alteration in the standard resistance, R, and therefore to maintain the current uniform through the whole series of experiments; B is a switchboard, R_2 a box of auxiliary cells used in connection with Carey Foster's method, and t_1 a balancing telephone. The leads L_1 and L_2 connecting the switch-board with the bridge consisted of ten strands of

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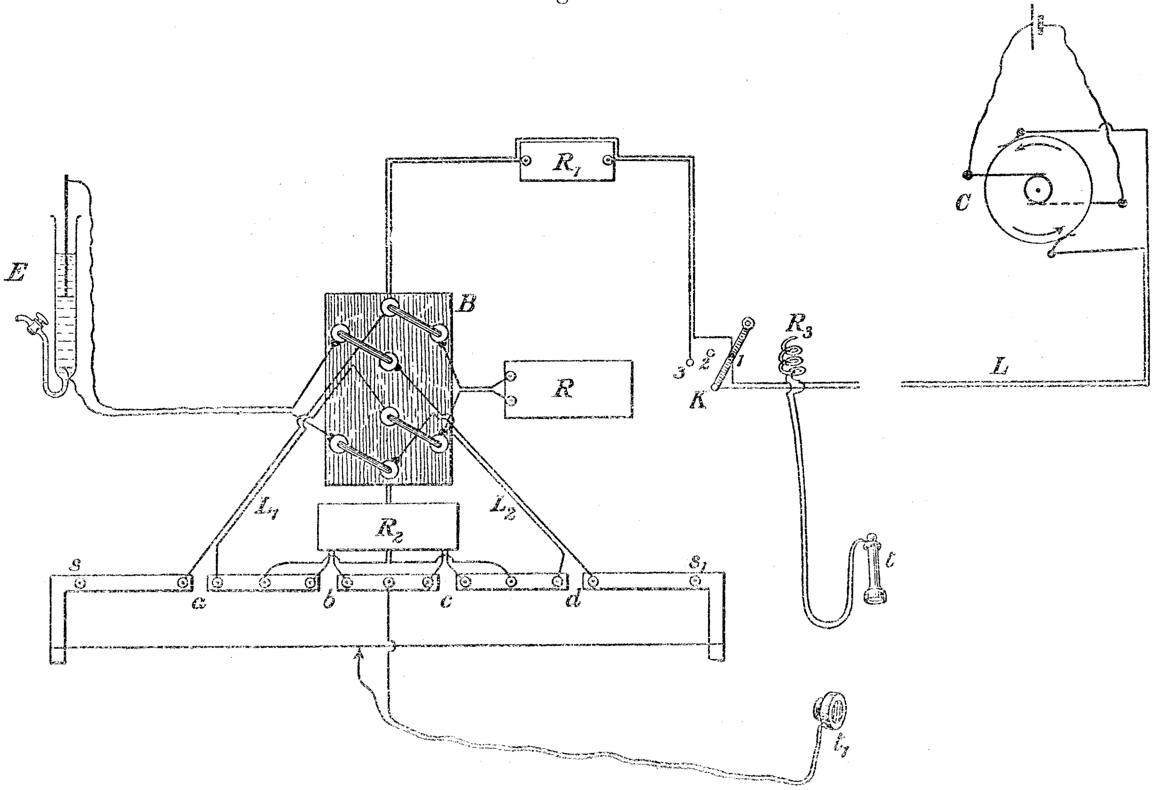
* The current of this cell, measured by a standard tangent galvanometer, was found to be ·22 ampere when flowing through the commutator at rest, but it would probably be rather less when the commutator was rapidly running, owing to a consequent increase of resistance in the contacts.

Diagram I.



Showing general arrangement of the apparatus.

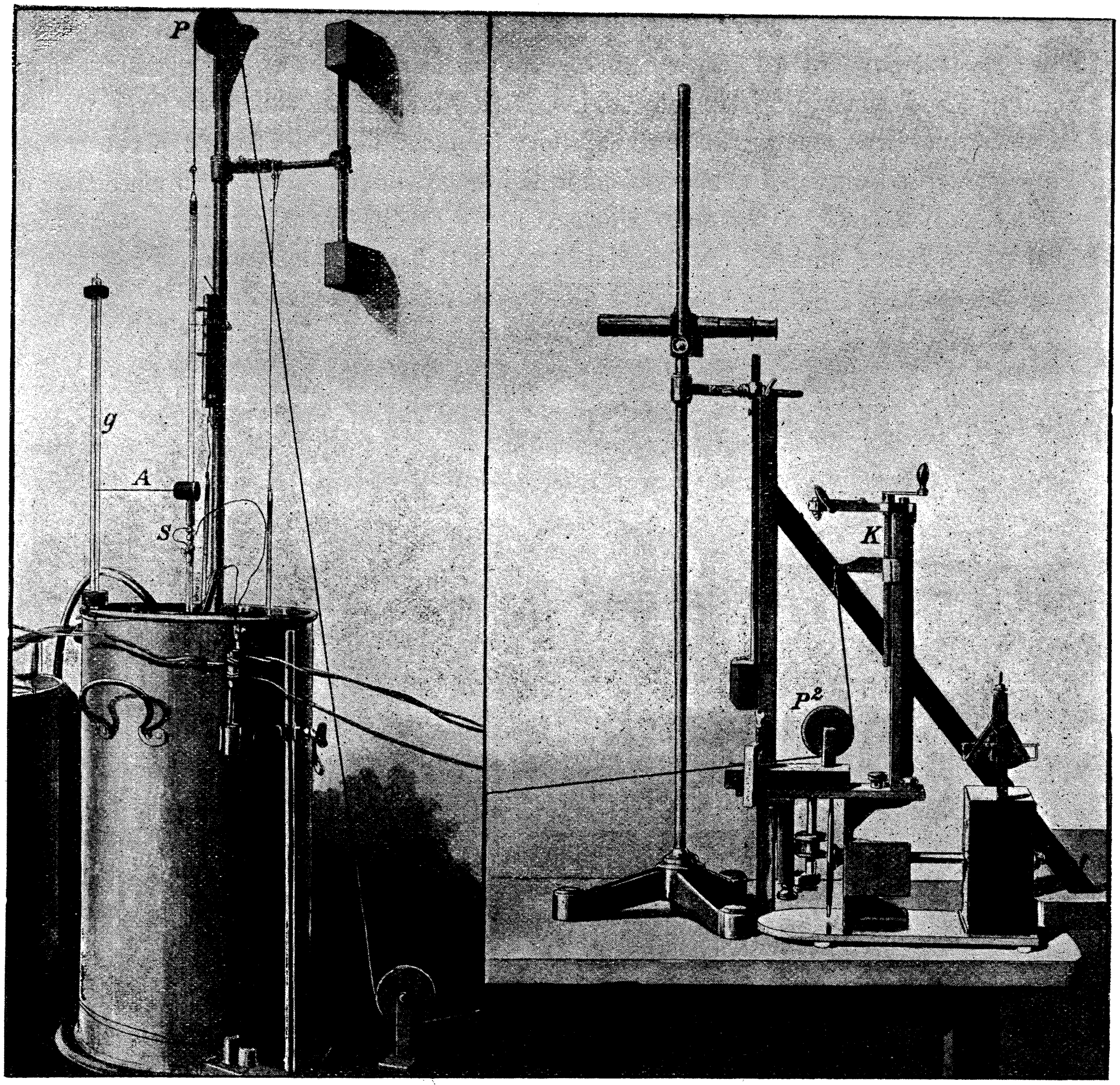
No. 18 copper wire soldered on to massive copper tags; their resistances were determined in position and found to be as nearly as possible equal; L_3 the leads (of similar construction) to the standard coils were of resistance ·005 ohm., a constant factor added to all values of R.

The Electrolytic Cells.

(i.) *Standard Cell.*

Several forms of cell were adopted in the earlier experiments, but as all those of the **U** or bottle pattern, as described by Kohlrausch, involve their calibration by a solution of an electrolyte of known conductivity, it was resolved to use a cell of a straight burette form, with one electrode fixed, and the other movable, so as to throw different lengths of the acid into circuit, and thus obtain independent measurements. For this purpose the movable electrode was welded on to a platinum wire passing through a glass tube to the binding-screw, S (fig. 4); above this a similar tube was fastened, upon which was etched a centimetre scale copied directly from the standard. In order to ensure that the whole arrangement should slide parallel to its axis, the graduated tube was allowed to run in **V** grooves mounted upon a block of ebonite, and provided with a small spring to avoid accidental displacement; their rotation was prevented by a small arm, A, working in glass tube guides, *g*. A cord passing over the pulleys, P, P_1 and P_2, was attached to the upper end of the graduated tube, and the other end to an arm; this cord could

Fig. 4.



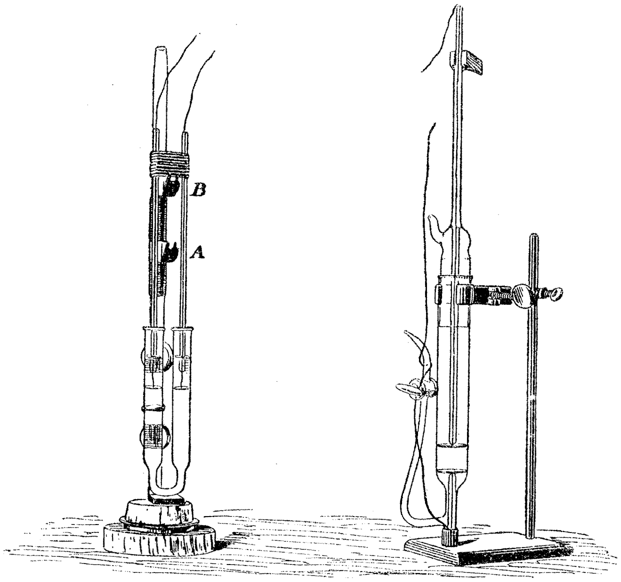
be shortened by suitable loops, and the final adjustments effected by means of the kymograph screw, K. The divisions of the tube were observed by a telescope mounted on a rigid stand.

To secure perfect insulation the cell rested upon and against blocks of ebonite, *a*, *b* and *c*, the two latter being V grooves, against which it was kept pressed by elastic bands. Preliminary experiments already described showed that all fastenings of a conducting nature should be avoided, especially if high tension currents are used. So far as can be judged by the description and diagrams of certain previous writers, sufficient attention does not seem to have been given to this essential point. Finally, to avoid contamination of the acid by dust, the cell was closed by a platinum disc.

(ii.) *Temperature Coefficient Cell* (fig. 5).

This was a **U** tube of 1·77 sq. centims., cross sectional area, rigidly attached to an insulating stand containing the electrodes, both movable in this case and welded on to platinum wires passing through capillary tubing. The upper ends of these were tied and cemented on to an ebonite block which could be made to rest upon either of two brackets furnished with a hole, slot and plane arrangement similar to that used for a Kelvin galvanometer. When the block rested on the lower bracket (position A), measurements were made of the resistance of the leads and the acid in the bend of the **U**; when, on the upper bracket (position B), the total resistance was made up of these factors, together with the introduced length of acid, being double that of the height through which the electrodes had been lifted. To obtain, so far as possible, independent measurements the process of raising and lowering the electrodes was repeated during any one series of experiments. The top of each limb of the **U** tube was closed with platinum discs.

Fig. 5.



Temperature coefficient cell. Electrolytic cell No. 2.

(iii.) *Cell for Acids from* 70 *to* 99·8 *per cent. Concentration.*

As the acid above 70 per cent. is very hygroscopic and its fumes are liable to attack the electric connections, a cell for use not only at a particular but also at any required temperature was devised, as follows: a cylinder of glass, with an etched centimetre scale, was drawn out at its lower end and a vacuum tap sealed on; the upper end was closed by an accurately ground glass cap carrying a tube on which were etched two lines at a distance of 10·24 centims. apart. Within this tube moved a piece of thermometer tubing so as to form a stuffing-box arrangement containing within it the platinum lead from the movable electrode; one line was etched upon it, which could be made to coincide with either line upon the outer tube. The method of measurement was similar to that described in (i.) (standard cell), and the whole was, as in previous cases, thoroughly insulated. It was found that acid could be preserved in this cell for a considerable time without any appreciable change of concentration.

The electrodes for all the above cells were coated with the velvet-like deposit of platinum, which, according to the experience of KOHLRAUSCH and successive writers, gives the most satisfactory results. After preparation they were kept immersed for some weeks in the prepared distilled water, which was frequently changed.

TANKS FOR ELECTROLYTIC CELLS.

Two zinc tanks, of many gallons capacity, and furnished with covers, were used in the course of the investigation; they were both similarly constructed, one of two, the other of three concentric chambers; the innermost, of small dimensions, containing the electrolytic cell with its accessories, stood on three legs, so as to raise its level about six inches; the other, of large dimensions, furnished with ring stirrers, was filled with water to a level above that of the top of the electrolytic cell. It was found that a difference of 20° between the tank and room temperatures caused only a fall in the former of 1° after two hours; there was, therefore, no appreciable alteration of temperature in the course of any set of experiments lasting only a few minutes. Standardised thermometers were placed both in the outer and inner chambers; when their corrected readings differed only by 0·1 it was assumed that equilibrium of temperature in the outer and inner chambers had been established.

When a temperature of 0° was required, the outer chamber of the triple-chambered tank contained air only, and the middle chamber was filled with finely-powdered ice, the water melting from which was continuously drained off. For other temperatures, water was run into the outer chamber, and steam blown in, if necessary.

THE METHOD OF PERFORMING AN EXPERIMENT.

The electrolytic cell was charged with the required mixture of nitric acid and recently-melted ice as previously described, then placed in the inner chamber of the tank and its electrodes connected up with the bridge leads. When an hour had elapsed after equilibrium of temperature had been first observed, preliminary measurements were made in order to ascertain approximately the conductivity of the acid, and thus not only to facilitate the final measurement, but also to eliminate the risk of decomposition. The cell was then emptied, recharged with a second portion of the acid, and connections made as before; after an interval of some hours the final measurements were made as follows:—

The graduated glass tube was adjusted so that division 5 of its scale coincided with the point of intersection of the cross threads of the telescope; the standard coils were placed in the left gap (L) and the electrolytic cell in the right gap (R) of the bridge; if then the current from the commutator was found satisfactory, connection was made with the bridge and its accessories, and a first balance obtained.

The current was then switched off, the position of the coils and electrolytic cell interchanged, the current switched on, and a second balance obtained. The movable electrode was then raised to division 15 on the scale, and the value of the standard coils altered so that their combined resistances were approximately equal to those of the introduced length of acid and leads (as determined by the preliminary experiment), while simultaneously the resistances in the control box were also changed so as to maintain the current intensity uniform. Then balancings were obtained with the electrolytic cell successively in the R and L gaps as before. The whole series of operations were repeated for the introduction of the second length of acid caused by raising the graduated glass tube through another five divisions.

The thermometers in the standard resistance box, bridge and tanks were read before and after each set of observations, and any necessary corrections for alteration of temperature subsequently applied.

As an illustration, all the measurements and observations for two samples of acid, namely of 1·299 and 30·52 per cent. concentration are given; these particular values have been selected as those of maximum and minimum conductivity for each form of electrolytic cell.

TABLE IV.

Series.	Percentage of acid.	Impurities in parts per million.
I.	1·299	Halogen acids = 0·5 Sulphuric acid = 1·0 Nitrous acid = 0·07
II.	30·52	Halogen acids = 3·7 Sulphuric acid = 2·3 Nitrous acid = nil
Other samples used in the course of the investigation	45·01	Halogen acids = 0·29 Sulphuric acid = 2·3 Nitrous acid = 0·16
	58·2	Halogen acids = 2·7 Sulphuric acid = 3·6 Nitrous acid = 0·75
	73·82	Halogen acids = 1·1 Sulphuric acid = 3·16 Nitrous acid = nil.
	90·37	Halogen acids = nil Sulphuric acid = nil Nitrous acid = 0·83
	98·87	Nitrous acid = 1·1

TABLE V.

	Position of movable electrodes.	Temperature (corr.) before and after each observation.			Resistance (corr.) of coils + leads.	Resistance of acid + leads.	Mean cross sectional area of tube.	Resistance of acid.
		Tank.		Resistance coils.				
		Outer chamber.	Inner chamber.					
					ohms.	ohms.	sq. centims.	ohms.
Series I.	5	15·7	15·6	16·5	15·0106	14·9658 = R_1		
	15	15·7	15·6	16.5	48·0260	48·2660 = R_2	4·4591	33·0002 = $R_2 - R_1$
	20	15·7	15·6	16·5	65·0179	65·0179 = R_3	4·4560	50·0521 = $R_3 - R_1$
Series II.	5	13·7	13·6	14·2	22·9031	22·9031 = R_1		
	15	13·7	13·6	14·2	25·8988	25·9505 = R_2	4·4591	3·0474 = $R_2 - R_1$
	20	13·7	13·6	14·2	27·3989	27·4810 = R_3	4·4560	4·5779 = $R_3 - R_1$

The following table serves to illustrate the method of determining the temperature coefficients, the acid used in Series II. being selected as an example :—

Table VI.

Temperature.	Resistance (corr.) of acid and leads.	Difference (B—A).
	ohms.	ohms.
0·2	17·2093 (A) 29·7130 (B)	12·5037
14·5	15·9365 (A) 25·7957 (B)	9·8592
27·9	15·1748 (A) 23·4070 (B)	8·2322

Hence, from these data, the values for the constants α and β in the equation $R_t = R_0 (1 \pm \alpha t \pm \beta t^2)$ can be deduced.

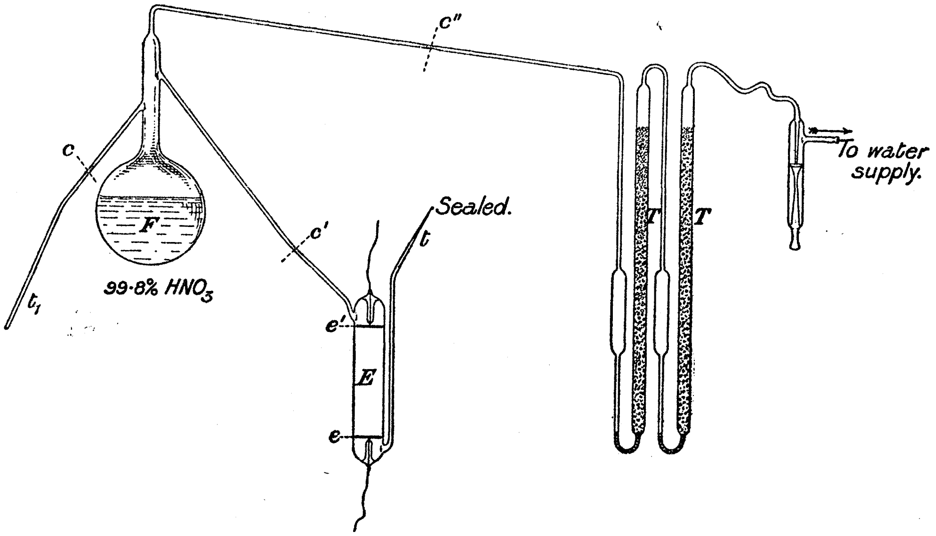
Preparation and Properties of Anhydrous Acid (HNO_3).

By the vacuum apparatus described in the previous part of the paper it was not found possible to obtain acid of concentration greater than 99·88 per cent. With a view of eliminating the remainder of the water, another apparatus was constructed, all of glass, but without any glass taps, through which, however perfect, moist air may find a passage.

TT (Diagram II.) are drying towers similar to those in the first form of apparatus. c, c', c'' are thick-walled capillary tubes, which can be sealed off in succession, F is the distillation flask of about 200 cub. centims. capacity, and E the electrolytic cell furnished with another capillary, t, sealed before distillation, but which subsequently served to withdraw a sample of acid for analysis after the determination of conductivity. The apparatus anterior to the towers was dried by exhausting through the capillary, t, and subsequently admitting dry air, the whole process being repeated a number of times, while the glass was kept continuously warmed by a flame; t is then sealed, acid of 99·8 per cent. drawn up into the distillation flask through the suction tube, which was then sealed off. The whole apparatus was then exhausted by the pump, and the flask gently warmed until the acid began to distil over into the towers; when this was observed the source of heat was removed, and the whole of the tube c''

continuously heated to free it from any condensed acid; then it was sealed off at the lowest possible temperature while the pump was kept in action. By immersing E in a freezing mixture acid passed over from F, and this process was allowed to continue until the upper electrode was well covered; the electrolytic cell was then detached by cutting off at *c′*, plugging the opening immediately by a sealed capillary, and covering the whole with a glass cap. Though it is true that a trace of moisture might be introduced here, yet the error due to this would be less than that caused by the decomposition of the vapour of acid if *c′* had been sealed in a flame; thus, of two evils, the less was chosen.

Diagram II.



Apparatus employed for the preparation of the anhydrous acid (HNO_3).

The acid thus obtained was perfectly colourless. Analyses made after measurement of conductivity gave the following values:—

$$\text{Acid, per cent.}\left\{\begin{array}{l}(1)\ 99\cdot97\\(2)\ 99\cdot98\end{array}\right.$$

$$\overline{99\cdot975\text{ mean.}}$$

Determinations were made of its density at 4°, 14·2°, and 24·2° (*vide infra*), and a further pair of analyses made, with the result:

$$\text{Acid, per cent.}\left\{\begin{array}{l}(1)\ 99\cdot97\\(2)\ 99\cdot97\end{array}\right..$$

The acid may therefore be regarded as anhydrous (HNO_3) within the limits of experimental error. Hitherto the highest recorded values appear to be 99·45 per cent. (PERKIN),[*] 99·67 per cent. (LUNGE and REY),[†] and 99·84 per cent. (KOLB),[‡] but doubts have been expressed as to the correctness of the determinations of the last observer.

CALIBRATION OF CELL AND WIRES USED FOR ANHYDROUS ACID.

As the method originally proposed by KOHLRAUSCH and adopted by subsequent workers for determining the "resistance capacity" of their cells appeared in this particular case to involve manipulative difficulties and errors consequent therefrom, the following method was used. The distance between the inner surface of the electrodes was determined along nine different lengths; the mean value found was 9·77 centims.; the volume of the portion of the cell between the electrodes was measured by water delivered from a calibrated burette connected with the cell by pressure-tubing, readings being taken for the levels of the upper surface of the lower electrode and lower surface of the upper electrode. Five or six series of experiments were conducted, different burette levels being taken in each such series; the mean of all the values was 35·2 cub. centims., with an error of ± ·1 per cent. From these data the mean cross sectional area was calculated to be 3·603 sq. centims. In order to determine the resistance of the platinum leads sealed into the cell, their lengths were measured and the resistance of a known length of the same wire determined by CAREY FOSTER'S method; the value thus calculated was added to that of the copper wire leads which joined the cells to the bridge, due allowance being made in each case for its coefficient at the temperature of the experiment. Such indirect measurements cannot, of course, lay claim to absolute accuracy, but appeared to be the best attainable after the cell had been fitted up and used for the experimental determinations.

(i.) *Chemical Properties of Anhydrous Acid.*

As a considerable quantity of the anhydrous acid was prepared in the course of the enquiry some of its properties were examined. It has no action upon the following metals (i.) copper, (ii.) silver, (iii.) cadmium, (iv.) mercury, all of a high degree of purity, and (v.) commercial magnesium at ordinary temperatures; purified iron and commercial granulated tin were unaffected by the acid even when boiling. Zinc purified by frequent distillation in vacuo was slightly acted upon at ordinary temperatures, but sodium immediately caught fire. The acid has no action whatever

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[*] 'Journal of the Chemical Society,' 1893 (Trans.), p. 65.

[†] 'Journal of the Society of Chemical Industry,' 1891, p. 543.

[‡] 'Ann. Chim. Phys.' [4], vol. 10, p. 140.

on finely-powdered calcium carbonate (Iceland spar and marble) either at ordinary temperatures or the boiling point. Vitreous phosphorus at first melts in the acid and then catches fire, while a considerable quantity of a dark-red sublimate (probably phosphorus suboxide P_4O) condenses in the walls of the tube above the surface of the liquid; flowers of sulphur, as also iron pyrites, dissolve quickly and completely in the gently-warmed acid. Nitration of aromatic hydrocarbons is readily effected by the acid, whilst such a substance as chloral hydrate is decomposed, with complete conversion of the chlorine into hydrochloric acid.

(ii.) *Determination of Density.*

For this purpose the form of Sprengel pyknometer, as modified by **Dittmar**, was used, and of capacity about 54 cub. centims.; the ends of both limbs were closed by caps, and on account of the high coefficient of expansion a series of bulbs were blown on one limb of the U tube.

The necessary corrections were made for reducing the observations to weighings in vacuo.

The following results were obtained :—

Density 4/4 = 1·54216 (i.)
= 1·54209 (ii.)
Mean . . 1·54212

Density 14·2/4 = 1·52236 (i.)
= 1·52231 (ii.)
Mean . . 1·52234

Density 24·2/4 = 1·50390 (i.)
= 1·50398 (ii.)
Mean . . 1·50394

The values obtained by former observers are given for the sake of comparison.

Observer.	Percentage of acid.	Values.
Kolb	99·84	D_0 = 1·559 D_{15} = 1·530
Lunge and **Nef**	99·65	$D_{15/4}$ = 1·520
Perkin	99·45	$D_{15/15}$ = 1·5191 $D_{25/25}$ = 1·5043

The results of **Lunge** and **Nef**, as also of **Perkin**, do not differ materially from those obtained by us after allowance is made for the slightly higher percentage strength and lower temperature, while those of **Kolb** are considerably higher; the method adopted by the last for the determination of acidity was, however, open to considerable objection, though his preliminary methods of purification were similar to those described above. It is proposed to publish shortly an account of the determination of densities and of other physical properties of the acid to confirm the conclusions drawn from the present work.

Supplementary Note on the Application of Carey Foster's Method for Comparison of Resistances.

It was thought advisable to obtain certain measurements by Carey Foster's method for the comparison of resistances, not only to serve as a check upon the rest of the work, but also to ascertain if this method could readily be applied in the case of a decomposable electrolyte.

For this purpose the auxiliary coils were wound upon glass tube frames and soaked in paraffin wax; the frame was then enclosed in a box which was placed in a larger one, the space of two inches between them being packed with cotton wool. Two thermometers were introduced through the lids, so that their bulbs were in the centre. The maximum change registered during an hour was never more than one-tenth of a degree.

The process of working was as follows :—The ordinary method was first employed to obtain the value for $K \times 10^8$, then the auxiliary coils introduced into circuit and the determinations repeated. It will be seen from the following table that the results obtained by the two methods are concordant when due allowance is made for the slight variation of temperature.

Table VII.

Strength of acid per cent.	$K \times 10^8$ by C. Foster's method.	Temperature.	$K \times 10^8$ by Kohlrausch's method.	Temperature.	Difference.
25·23	7094	17°·6	7079	17°·3	−15
45·34	5984	12·6	5980	12·6	− 4
51·77	5294	12·0	5277	11·8	−17
56·07	4402	6·6	4398	6·6	− 4
61·60	3829	5·5	3841	5·6	+12
64·37	3521	4·7	3514	4·7	− 7

As a matter of experience it was found that for Carey Foster's method the electrodes should be continually recoated with the platinum deposit, otherwise it was difficult to ascertain exactly the point of minimum sound in the telephone.

Experimental Results.

The approximate temperatures selected for observation were 0°, 15°, and 30° for acids of percentage concentration from 1·3 to 50, but 0°, 10°, and 20° above this strength, as the more concentrated acids are not only extremely volatile, but also liable to decomposition.

In Table VIII. the values are given for the specific resistances in true ohms, corrected at 0°, 15°, and 30° for temperature coefficients; these of the first and second order, multiplied by 10^4 and 10^6 respectively, are shown in the fifth and sixth columns.

TABLE VIII.

Percentage concentration.	Specific resistance in true ohms.			Temperature coefficients.	
	At 0.	At 15.	At 30.	$\alpha 10^4$.	$\beta 10^6$.
1·30	19·924	14·883	11·974	−204	+238
3·12	8·739	6·53	5·279	−205	+244
5·99	4·767	3·593	2·927	−200	+237
10·13	3·022	2·306	1·895	−192	+224
15·32	2·236	1·723	1·416	−184	+206
20·11	1·910	1·478	1·224	−182	+206
25·96	1·746	1·368	1·120	−169	+165
30·42	1·722	1·342	1·105	−174	+183
33·81	1·740	1·351	1·109	−177	+188
35·90	1·771	1·372	1·195	−178	+184
39·48	1·837	1·415	1·146	−181	+186
45·01	1·969	1·511	1·222	−183	+190
51·78	2·248	1·694	1·366	−198	+225
53·03	2·316	1·726	1·427	−211	+275
58·20	2·571	1·916	1·576	−210	+277
61·20	2·755	2·016	1·375	−190	+ 77
65·77	3·074	2·317	1·963	−208	+292
69·53	3·227	2·523	2·150	−177	+228
73·82	4·153	3·270	2·831	−174	+237
76·59	4·7584	3·599	2·302	−153	− 6
78·90	6·239	4·836	4·493	−206	+377
84·08	10·188	8·164	7·177	−166	+226
86·18	12·535	10·106	8·874	−161	+212
87·72	16·624	13·320	12·220	−177	+294
89·92	24·012	19·929	15·847	−120	+ 46
91·87	37·618	31·077	27·967	−146	+202
94·32	53·847	45·270	41·108	−133	+182
96·12	73·663	66·069	63·517	−192	+152
98·50	54·733	56·057	60·730	− 4	+136
98·85	50·182	51·586	53·966	+122	+ 43
99·27	26·554	25·075	26·164	− 69	+215
99·97	25·688	24·286	23·713	− 47	+ 71

In Table IX., the values for $K_{15} \times 10^8$ for the different concentrations obtained in Cell No. I. represent for each length of acid the mean of two, and in some cases three, four, and six, independent observations; the values are concordant in the majority of cases to ·05 per cent., which is probably within the limit of experimental error; the values for Cells II. and III. also represent the mean of several experiments.

In Table X., the values for $K_0 \times 10^8$ and $K_{30} \times 10^8$ are given for the sake of comparison of our results with those of other observers. Throughout the conductivity of mercury at 0° is taken as unity, and its specific resistance as 94·07 microhms per 1 cub. centim.

TABLE IX.

Measurements with Cell No. I.

Percentage concentration. I.	Values of $K_{15} \times 10^8$.		
	II. Length of acid =15 centims.	III. Length of acid =10 centims.	IV. Mean.
1·30	631·86	632·25	632·06
3·12	1440·2	1441	1440·6
5·99	2617·3	2618·9	2618·1
10·13	4077·9	4080·4	4079·2
15·32	5458·9	5462·2	5460·5
20·11	6361·8	6365·7	6363·8
25·96	6873·6	6877·8	6875·7
30·42	7006·1	7010·4	7008·2
33·81	6960·7	6964·9	6962·8
35·90	6855·5	6859·7	6857·6
39·48	6646·5	6650·5	6648·5
45·01	6224·1	6227·8	6225·9
51·78	5552·5	5555·9	5554·2
53·03	5448·2	5451·5	5449·8
58·20	4907·3	4910·3	4908·8
61·20	4663·7	4666·6	4665·1
65·77	4059	4061·5	4060·3
Measurements with Cell No. II.			
69·53	3728·7		
73·82	2877		
76·59	2613·5		
78·96	1945·1		
84·08	1152·2		
86·18	930·86		
87·72	706·23		
89·92	472·02		
91·97	302·7		
94·32	207·8		
96·12	142·38		
98·50	167·81		
98·85	182·36		
99·27	375·15		
Measurement with Cell No. III.			
99·97	387·34		

TABLE X.

Percentage concentration.	Values of $K_0 \times 10^8$.	Values of $K_{30} \times 10^8$.
1·30	492·15	785·63
3·12	1076·4	1781·9
5·99	1973·3	3213·8
10·13	3112·7	4963·6
15·32	4206·5	6641·0
20·11	4925·4	7686·1
25·96	5386·2	8399·1
30·42	5464·4	8515·4
33·81	5405·7	8480·1
35·9	5312·3	8402·9
39·48	5119·5	8205·7
45·01	4777·1	7701·2
51·78	4183·9	6884·5
53·03	4061·4	6594·5
58·20	3658·6	5967·8
61·20	3414·9	6842·5
65·77	3059·8	4792·1
69·53	2915·3	4375·9
73·82	2265·2	3323·2
76·59	1976·9	4085·8
78·90	1507·75	2093·5
84·08	923·3	1310·6
86·18	750·5	1060
87·72	555·9	769·8
89·92	391·8	593·6
91·87	250·1	336·4
94·32	174·7	228·8
96·12	127·7	148·1
98·5	171·9	154·9
98·85	187·5	174·3
99·27	354·3	359·5
99·97	366·2	396·7

From the data given in Table VIII., it is evident that the specific resistance of nitric acid decreases for percentage concentrations from 1·3 to 30, at first more, then less rapidly; from this point the resistance increases slowly up to 76 per cent., thence more rapidly, until a maximum is reached at 96·12 per cent., when a sudden reversal takes place.

KOHLRAUSCH (*vide supra*), by interpolation of his results, gives the points of maximum conductivity at 29 per cent. at 0°, 29·7 per cent. at 18°, and 30·2 per cent. at 40°, data which are in general accordance with our results, though it is evident that the exact minimum point could only be ascertained to within one-tenth per cent., by a number of experimental determinations made on either side of the point in question, whereas KOHLRAUSCH gives data only for 23, 30·95, and 37·36 per cent., respectively.

As the reversal between 96·12 and 98·5 was wholly unexpected, and at first sight appeared anomalous, the determinations were continued within small percentage limits, and the results thereby confirmed.

It will also be observed that whereas nitric acid behaves as other electrolytes, namely, in possessing a positive temperature coefficient of conductivity for percentage concentrations from 1·3 up to 96·12, yet from this point up to 99·27 per cent. it behaves as a metallic conductor in possessing a negative temperature coefficient.

Formerly, negative and positive coefficients were regarded as the essential point of differentiation between metallic and electrolytic conductors respectively, until ARRHENIUS,[*] led by theoretical considerations, based upon the ionic dissociation hypothesis, observed negative coefficients in the cases of hypo-phosphorous acid (of concentration = 1·014 normal) and phosphoric acid (of concentration = 3 × ·95 normal). Upon this matter ARRHENIUS expressed himself as follows :—"Es ist wohl kaum denkbar dass man nach den bisherigen Ansichten ohne Zuhilfenahme der Dissociationstheorie die Existenz von negativen Temperaturkoeffizienten erklären könnte." OSTWALD, and other writers of the same school, when quoting the results of ARRHENIUS, have adopted the same view, with greater or less modification. But in the case under discussion, nitric acid of concentration 96–99·97 per cent. would, *ex hypothesi*, contain few, if any, free ions, and, therefore, the theory would lead to a totally opposite conclusion. For the present it is not proposed to offer any explanation of the phenomenon observed, but merely to call attention to the somewhat analogous example of the density of sulphuric acid, which attains its maximum at 98·78 per cent. (PICKERING, LUNGE, NEF, and ISLER) and thence decreases up to 99·86 per cent. (PICKERING).[†]

In the paper quoted above, ARRHENIUS calculates, by interpolation, the temperature of maximum conductivity of nitric acid as at 668°, but to our minds it is idle to speculate upon its properties at a temperature far above that at which it could have any existence.

HYDRATES OF NITRIC ACID.

The existence of definite hydrates of nitric acid has been discussed by various writers[‡] from the standpoints of (i.) direct experimental observations ; (ii.) analogy of the composition of the metallic nitrates and of the phosphoric acids ; (iii.) differentiations of observed values ; cumulative evidence from the first of the methods appears the most cogent. The following *résumé* gives briefly the conclusions of the several writers :—

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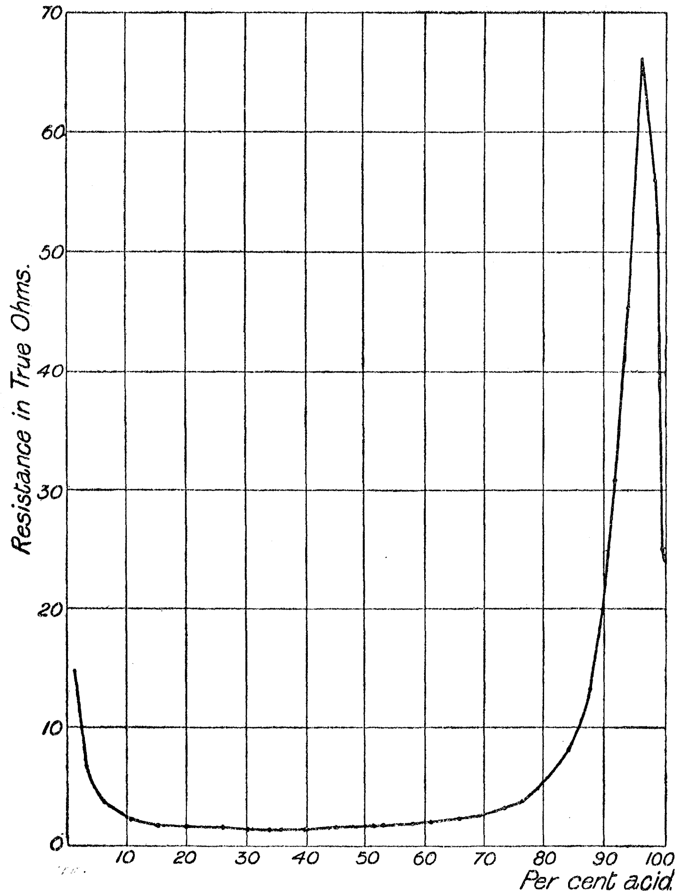
[*] 'Zeits. f. Physikal. Chem.,' vol. 4, p. 96.

[†] Note added June 17, 1898.—Since the above was written, the suggestion has been put forward that in the case of nitric acid of 96–99·7 per cent., there is an initial decomposition into water and the anhydride N_2O_5, precisely as sulphuric acid to a greater degree at a higher temperature, and to a less degree at a lower temperature, decomposes into water and its anhydride SO_3.

[‡] MENDELEEFF, "Principles of Chemistry"; W. H. PERKIN, Sen., 'Journal of Chemical Society,' Trans., 1889, p. 724, and 1893, p. 65; KOLB (*vide supra*); BERTHELOT, 'Mécanique Chimique,' pp. 1, 397; PICKERING, 'Journal of Chemical Society,' Trans., 1893, p. 436; CROMPTON, *ibid.*, 1888, p. 121; VELEY, 'Ber. Deutsch. Chem. Ges,' vol. 28, p. 928.

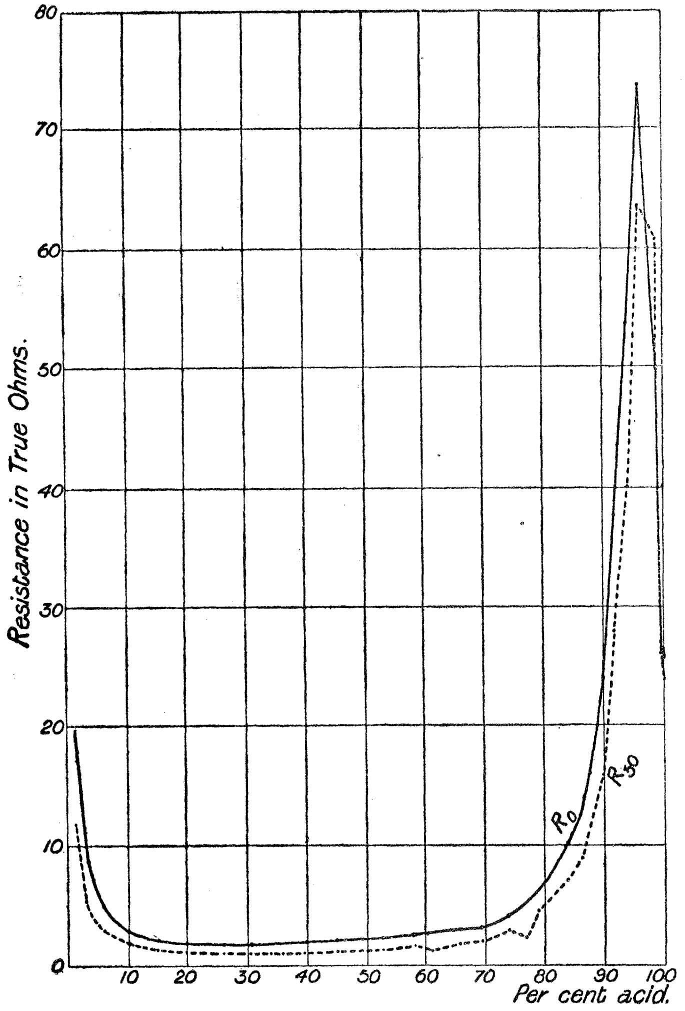
HNO_3 $10H_2O$	25·5	per cent. HNO_3	Differentiation of density curve (Pickering).
HNO_3 $7H_2O$	33·3	„ „	Specific magnetic rotation (Perkin). Freezing of solution (Pickering). Chemical activity towards metals (Veley).
HNO_3 $5H_2O$	41·2	„ „	Density curve (Mendeleeff).
HNO_3 $3H_2O$	53·85	„ „	Isolation in crystals (Pickering). Metallic nitrates (Mendeleeff).
HNO_3 $2H_2O$	63·63	„ „	Vapour pressure (Mendeleeff). Heat of dilution (Berthelot).
HNO_3 H_2O	78·02	„ „	Density determinations (Kolb). Isolation in crystals (Pickering). Specific magnetic rotatory power, metallic nitrates and analogy with H_3PO_4 (Perkin).

Curve 1.



Specific resistance ρ of nitric acid at 15° C.

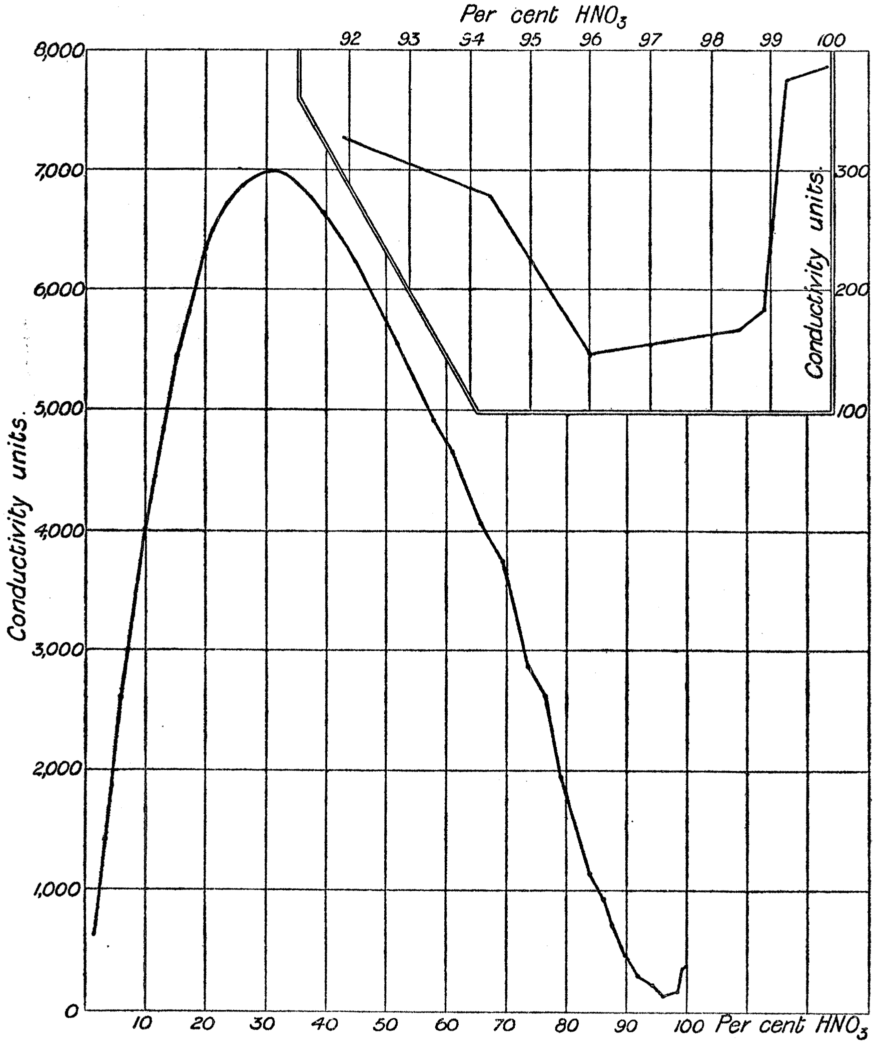
Curve 2.



Specific resistance ρ of nitric acid at 0° to 30° C.

In Table XI. the values for $\alpha \times 10^4$ and $\beta \times 10^6$ are given in relation to the *molecular* proportions of water from 3·07 to ·07, as it would seem that the method adopted by comparatively few writers on such a subject as the present is the more rational, as nature deals with molecules, but art with percentages.

Curve 3.



Conductivity in mercury units of acid at 15° C.

TABLE XI.

Molecular proportions of water.	Value of $\alpha \times 10^4$ (−).	Value of $\beta \times 10^6$ (+).
3·07	211	275
2·43	210	277
2·25	190	77
1·84	208	292
1·59	177	228
1·30	174	236
1·09	153	6
0·99	206	377
0·78	166	226
0·65	161	212
0·58	177	294
0·47	120	46
0·39	146	202
0·27	133	182
0·18	192	152
0·07	4	136

From these figures it will be observed that the minima values for $\alpha 10^4$ and maxima for $\beta 10^6$ occur in the cases of 3·07, 1·84, ·99, and ·55 molecular proportions of water, or very approximately $HNO_3.3H_2O$, $HNO_3.2H_2O$, $HNO_3.H_2O$, and $2HNO_3.H_2O$, and the curve representing the conductivity units in terms of percentages is markedly discontinuous at points corresponding to the three last hydrates, the existence of which has also been confirmed by a series of experimental determinations of the densities and contractions of samples of acid of various concentrations. Further evidence is thus added by an independent method to that already accumulated as to the existence of definite combinations of nitric acid with water.

In conclusion, we trust that these observations may serve as an addition to our knowledge of the electric and chemical properties of dilute, and especially of the most concentrated nitric acid, purified, as we hope, with such methods as are available in the present state of chemical art. It appears that for this and similar investigations a material, which should at once be perfect in its transparency, its non-conductivity, and its unalterability by the strongest reagents, remains still an ideal.

Fig. 1.

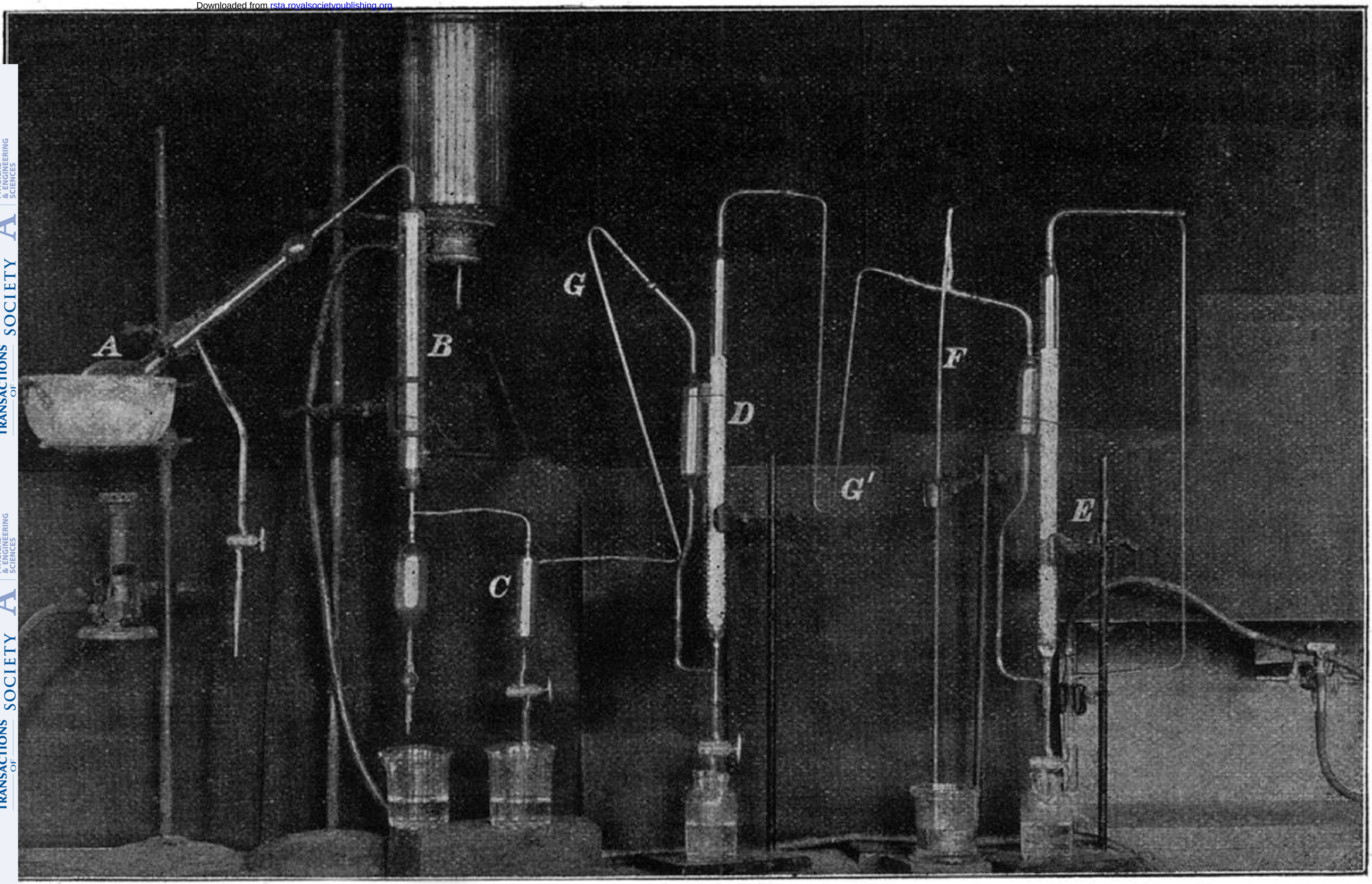


Fig. 2.

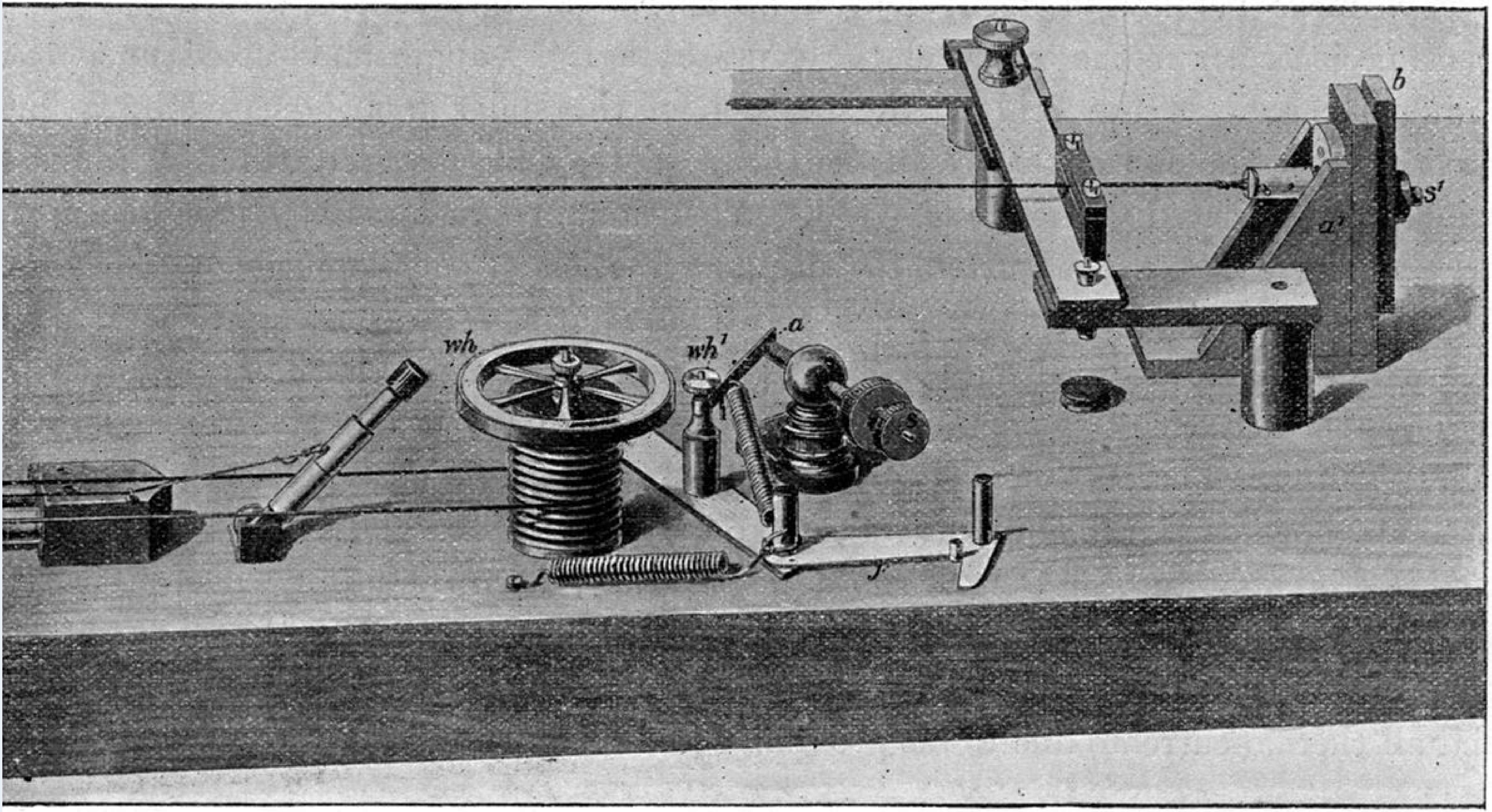


Fig. 3.

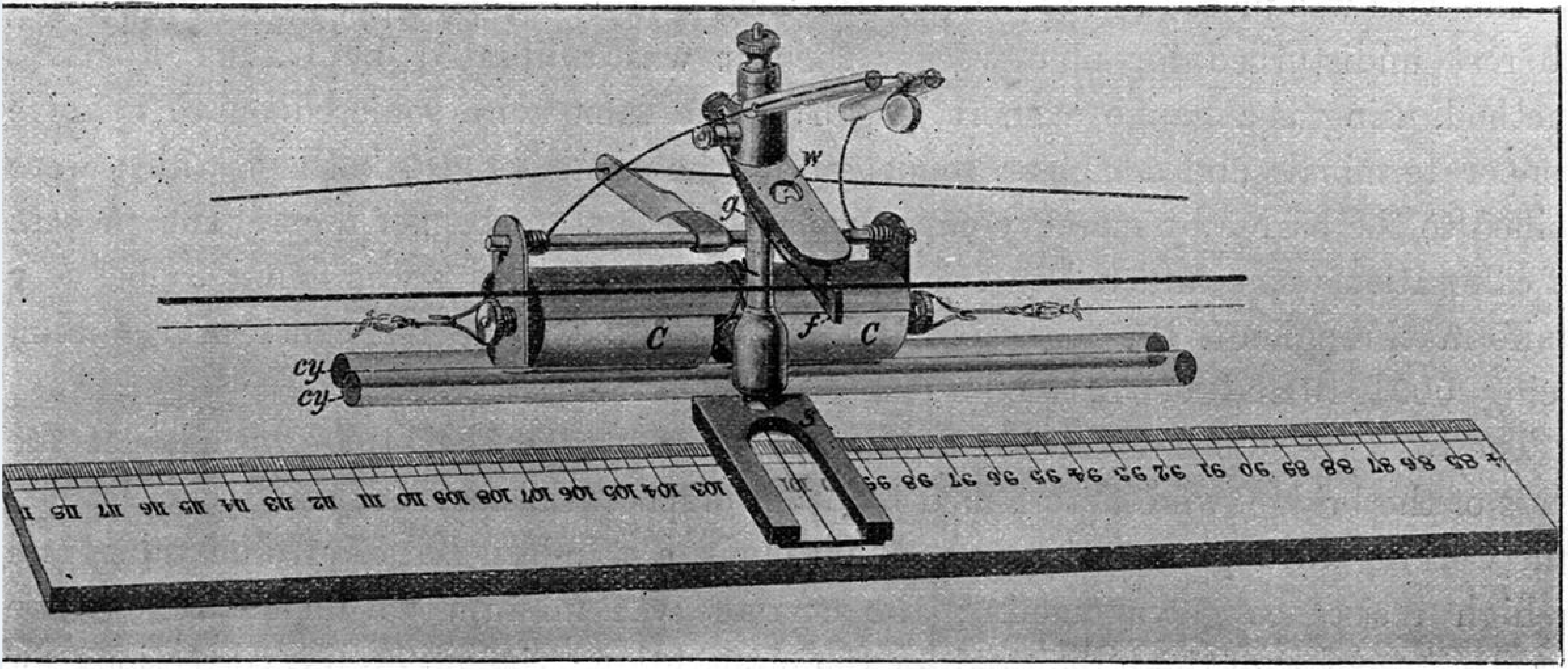


Fig. 4.