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ON THE SURFACE TENSION OF LIQUIDS UNDER THE INFLUENCE OF ELECTRO-STATIC INDUCTION.

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THE beginning of experimental inquiry into the relations subsisting between the capillary phenomena of a liquid and its state of electrification dates back to the middle of the last century. The subject has proved attractive to a host of physicists, and numerous investigations have been made and numerous phenomena described. Most of these phenomena may be referred to three general groups, according to the nature of their physical causes:

I. The first group includes those phenomena which are to be attributed principally to ordinary electrostatic forces of attraction and repulsion between the various (finite) portions of the liquid, or liquid and connected apparatus. Here belong, among others, the well-known phenomena of electrified jets and drops, investigated by Bose,[1] Nollet,[1] Beccaria,[2] Carmoy,[3] Singer,[4] Faraday,[5] Magnus,[6] Tate,[7] Beetz,[8] and Rayleigh;[9] the phenomena of electrified liquid

[1] Nollet, Reserches sur les causes des phénomènes électrique, 1749, seq. 327; Fischer, Geschicté der Physik, 5, 545 et seq.

[2] Beccaria, Dell. elletricismo artificiale, 1772.

[3] Carmoy, Obs. sur la Physique, sur l'Histoire Nat. et les Arts, 33, 340, 1788.

[4] Singer, Elements of Elec. and Electrochemistry, 1814.

[5] Faraday, Exp. Res., Art 1571, et seq.

[6] Magnus, Pogg. Ann. 106, 27, 1859.

[7] Tate, Phil. Mag. (4) 21, 452, 1861.

[8] Beetz, Pog. Ann. 144, 443, 1872.

[9] Rayleigh, Proc. R. S. L. 28, 406, 1879, et al.

films, observed by Van der Mensbrügghe,[1] Boys,[2] Kaiser,[3] and others; some of the effects attained by Herwig[4] with electrified mercury; and the phenomena of electrified falling drops, studied by Nichols and Clark.[5]

II. In the second group belong a great number of phenomena which are now known to be due principally to the presence of products of chemical change brought about by electrical action, and not primarily to this action itself. Many of these were once believed[6] to indicate a true effect of electrification upon surface tension, but their electrolytic nature is now established beyond doubt. Here are to be included the effects observed at the bounding surface between a liquid metal and electrolyte, when an external e. m. f., greater than their maximum e. m. f. of polarization is applied to them; and, if the views of one school of physicists are accepted (Cf. Group III), when any e. m. f., however small, is so applied. Effects of this kind were first observed by W. Henry[7] and by Gerboin;[8] later, by Hellwig,[9] Erman,[10] Draper,[11] and many others, including all who have worked on mercury-electrolyte potential relations with higher e. m. f.'s than the maximum previously mentioned. To this group belong also some of the effects obtained by Herwig.[12]

III. In the third and last group are included the phenomena with which we are here particularly concerned; those, namely, which are supposed to be caused by an actual change in the surface tension, due to the presence of an electric charge. By far the best known experiments dealing with this matter are those upon the capillary electrometer at low e. m. f.'s, and others the same in essential nature. It is well known that scientific opinion in regard to the nature of the phenomena here exhibited is divided between two theories and com-

[1] Van der Mensbrügghe, Pogg. Ann. 141, 287, 1870.
[2] Boys, Phil. Mag. (5) 25, 410, 417, 1888.
[3] Kaiser, Wied. Ann. 53, 671, 1894.
[4] Herwig, Pog. Ann. 159, 489, 1876; Wied Ann. 1, 73, 1877.
[5] Nichols and Clark, PHYSICAL REVIEW, 4, 375, 1897.
[6] Cf. Wied. Electricität, II., § 943, p. 737.
[7] W. Henry, Nichols. J. 4, 223; Gilb. Ann. 6, 370; 1800.
[8] Gerboin, Ann. de Chim. 41, 196; Gilb. Ann. 11, 340; 1801.
[9] Hellwig, Gilb. Ann. 32, 289, 1809.
[10] Erman, Gilb. Ann. 32, 261, 1809.
[11] Draper, Phil. Mag. (3) 26, 185, 1845.
[12] Herwig, loc. cit. ante.

binations of the two: the "Ladungsstromtheorie" of Helmholtz[1] and Lippmann,[2] and the "Leitungsstromtheorie" of Warburg[3] and Meyer.[4] If the latter theory, according to which the phenomena are wholly of an electrolytic nature, is correct, these phenomena must all be relegated to the second group above. But this theory, while it has gained considerable ground in recent years, has met with by no means general acceptance. The "Ladungsstromtheorie," according to which the phenomena are due wholly to electrostatic action, is still supported by very powerful names, including that of Ostwald[5] and that of Burch,[6] whose experiments, made with applied e. m. f.'s not greater than 0.5 volt, it seems impossible to explain by any form of electrolytic theory. An outline of the Ladungsstromtheorie is given by Meyer as follows:[7] "Nach. Hrn. v. Helmholtz wird die Polarisation des Meniscus im Capillarelectrometer als ein Ladungsphänomen aufgefasst. Zwischen Quecksilber und Electrolyt besteht ein Contactpotential-differentz, welche zur Entstehung einer electrischen Doppelschicht Anlass gibt, deren positiver Theil im Quecksilber liegt. Wird das Quecksilber kathodisch polarisirt, so vermindet sich die positive Ladung und die Oberflächenspannung nimmt zu, bis Gleichheit des Potentials zwischen Metall und Electrolyt besteht. Eine Polarisaation mit stärkeren Kräften ruft dann wieder durch die electrostatische Wirkung der in dem Meniscus vorhandenen negativen Ladung Verminderung der Oberflächenspannung hervor." This "electrostatische Wirkung" is described in the following words by Helmholtz himself:[8] "Jede elementare Elektricitätsmenge in einer solchen Doppelschicht wird abgestossen von den benachbarten gleichnamigen Mengen derselben Schicht, angezogen durch die entgegengesetzten der anderen Schicht. Da aber die Theile der

[1] Helmholtz, Berl. Monatsber., 945, 1881; Wied. Ann. 16, 30, 1882; Wiss. Abh. I, 925, 1882.

[2] Lippmann, Ann. de Chim. et de Phys. (5) 5, 515, 1875; et al.

[3] Warburg, Wied. Ann., 38, 321, 336, 1889.

[4] Meyer, Wied. Ann. 45, 508, 1892; 53, 845, 1894; 56.

[5] Ostwald, Allg. Chemie, 2 Aufl., II., 1, seq. 927, 1893; et al.

[6] Burch, Proc. R. S. L. 50, 172, 1891; Phil. Trans. 183 A, 104, 1892; and especially London Electrician, July 17–Aug. 21, 1896; and Proc. R. S. L. 60, 329–335, 1896.

[7] Meyer, Wied. Ann. 53, 867–868, 1894.

[8] Helmholtz, Wiss. Abh., I., 931 et. al. loc. cit.

eigenen Schicht näher sind, als die gleich grossen der entgegengesetzten, und näher den tangentialen Richtungen in der Fläche liegen, so wird die Abstossung in Richtung der Fläche die Anziehung überwiegen und in jeder mit einer Doppelschicht belegten Fläche muss die elektrostatische Kraft eine Dehnung der Fläche hervorzubringen streben. Wenn also die elektrisirte Fläche eine capillare Contractionskraft von gewisser Grösse hat, so wird die mit einer Doppelschicht beladene Fläche eine Verminderung der capillaren Spannung zeigen müssen. Es wäre also unter diesen Umständen zu erwarten, dass die capillare Spannung der Fläche im unbeladenen Zustande ein Maximum sein müsste." Whether the phenomena for which Helmholtz developed this theory are of electrostatic origin, as here conceived, or not, the reasoning on which the theory is based seems thoroughly sound when it is applied to the case of a liquid surface actually known to possess a static charge. The presence of the "Doppelschicht" and contact potential difference, which we have in the case of a metallic liquid and electrolyte, is not essential; an intense electrostatic field, however produced, effecting the same results. An immediate corollary of Helmholtz's theory is that the diminution of surface tension will be independent of the sign of the electric charge, and thus an even function of the electric surface density. Three investigations with reference to this effect have hitherto been made on surfaces statically charged to high potentials and must here be briefly discussed.

Herwig[1] in 1876 and 1877 described many experiments upon mercury surfaces. Among other results he found that a drop of mercury upon a surface of glass, ebonite, or other substance, became more flattened when highly electrified; that the liquid in a conical glass tube open at both ends and wider at the top, though supported by capillarity when unelectrified, fell through when charged; and that the depression of the mercury meniscus in a capillary tube of glass diminished considerably with electrification, the diminution being greater for positive than for negative charges. When the capillary tube, which was one branch of a U tube, was of iron, however, he observed no motion of the meniscus whatever, either for positive or negative charges, even when the meniscus

[1] Herwig, loc. cit. ante.

reached the end of the tube; while in similar experiments with glass tubes the mercury, when electrified, flowed out the end of the capillary branch. The experiments upon drops were repeated with various insulating and conducting substances as supporting surfaces, and under different conditions of the surface with respect to temperature and moisture. The experiments on glass tubes also were performed with the air above the meniscus in the capillary in various conditions; and in one set of experiments the tube was closed and was filled with pure hydrogen. From a study of all the phenomena observed Herwig concluded that the effects were due to several causes: (1) a diminution of the cohesion of mercury, (2) a change in the adhesion between mercury and glass, (3) oxydation of the mercury surface under the action of the positive charge, (4) a reducing effect of the negative charge, and (5) actual dissociation of the glass in contact with the charged mercury. The fact, however, that no effect was obtained with the capillary tube of iron, where chemical action, which in the glass capillaries and on the glass surfaces made itself manifest by a marked deposit, was prevented, would indicate that only an imperceptible change took place in the surface tension of pure mercury. Also, a consideration of the distribution of the Faraday tubes over the electrified surfaces of the mercury in the form of drops and in the conical tube shows that a part at least of the effects observed in these cases must have been due to ordinary electrostatic action.

In 1890 C. M. Smith,[1] at Edinburgh, applied the method of ripples to a study of the surface tension of mercury, making his measurements on photographs of the ripple-covered surface. The mean value of the tension of the unelectrified surface he found to be 529 dynes per cm. Two photographs were taken with the surface highly electrified with an induction machine, though no measurements of the electrification are given. The results were accordant and gave as the apparent[2] tension of the electrified surface only 421 dynes per cm. In view of experiments to be described later this diminution is extremely large, and great doubt is cast upon the result. If, as seems highly improbable, the effect was truly electrical the potential of the surface must have been enormous.

[1] C. M. Smith, Proc. R. S. E. 17, 115, 1890.

[2] Smith conceived that the effect *might* be purely mechanical.

The last of the three investigations on this subject, in which the method of falling drops was employed, was published by Nichols and Clark[1] in 1897. With a given dropping tube the surface tension is proportional to the weight of a drop, provided cohesive and gravitational forces only act. When the falling drops and the apparatus are electrified, however, the mutual repulsion between the "elementary electric charges" of the surface, which may be included in the cohesive forces, as it is related in its effect with these only, is wholly obscured by the electrostatic repulsion between the various parts of the liquid drop and the tube; and the method is, therefore, incapable of giving determinations of the true surface tension effect.[2]

From the foregoing discussion of previous work it is obvious that to secure reliable measurements of this effect some method of investigating the surface tension must be adopted in the practice of which both electrolytic action and electrostatic disturbances—including all electrostatic action except that between the "elementary electric charges" at the surface—are excluded. Professor Nichols therefore suggested to me some months ago the investigation of this matter by a method which, though by no means completely excluding electrostatic disturbances, has proved more satisfactory for the purpose than those hitherto employed—the method of ripples in its latest and most nearly perfect form. That the sources of error mentioned are much reduced in importance through the use of this method will appear farther on.

The method of measuring surface tension now known as the method of ripples originated with a suggestion of Tait[3] in 1875 that Kelvin's[4] formula for the velocity of propagation over the surface of a perfect liquid of a train of plane sine waves of infinitely small amplitude might be utilized, since it contains the surface tension as an important factor, in the accurate determination of this constant. This formula has now been experimentally tested by a number of

[1] Nichols and Clark, loc. cit. ante.

[2] Cf. London Electrical Review, 40, 522, 1897; Houllevigue, Journal de Physique, 3, 6, 325, 1897.

[3] Tait, Proc. R. S. E. 8, 485, 1875.

[4] W. Thomson, Phil. Mag. (4), 42, 375, 1871.

investigators, including Matthiessen,[1] Rayleigh,[2] Dorsey,[3] and others; and the method based on it has been shown to be capable of giving extremely accurate results in close agreement with the best of those obtained by other means. The great advantages of this method over others, so far as the determination of the tension of unelectrified surfaces is concerned, lie in the fact that with it the measurements are all made upon the liquid surface only and are thus independent of all contacts and contact angles between liquid and solids, and in the means it affords of using surfaces of the highest degree of purity. For the detailed history of the method and the discussion of the effects of viscosity, finite amplitude, floating dust particles, etc.—causes of deviation from the conditions of Kelvin's formula—reference must here be made to the papers of previous investigators.[4]

If[5] we denote by g the acceleration of gravity, ρ the density of the liquid, h its depth, λ the wave-length, n the wave frequency, T the surface tension, and V the velocity of propagation of the waves, Kelvin's equation is

$$V^2 = n^2\lambda^2 = \left(\frac{g\lambda}{2\pi} + \frac{2\pi T}{\rho\lambda}\right) \tanh \frac{2\pi h}{\lambda};$$

whence

$$T = \rho\left(\frac{\lambda^3 n^2}{2\pi} \coth \frac{2\pi h}{\lambda} - \frac{g\lambda^2}{4\pi^2}\right).$$

The quantity $\coth \frac{2\pi h}{\lambda}$ was in these experiments sensibly equal to unity. Even with λ so large as 0.5 cm. and h so small as 0.3 cm., which limits were not reached, $\coth \frac{2\pi h}{\lambda}$ differs from unity by only one part in about 1900; for $h = 0.4$ cm. and λ the same as before, by less than one part in 23,000. The determination of T in absolute measure is thus reduced to the measurement of λ, ρ, n, and g.

Kelvin's formula postulates, however, that the only forces acting are cohesion and gravitation; and it cannot therefore be used, with-

[1] Matthiessen, Wied. Ann. 38, 118, 1889.

[2] Rayleigh, Phil. Mag. (5) 30, 386, 1890.

[3] Dorsey, PHYSICAL REVIEW, 5, 170 and 182, 1897.

[4] Cf. especially the papers of Rayleigh and Dorsey, loc. cit. ante, and Tait, Proc R. S. E. 17, 110, 1890.

[5] Cf. Rayleigh, loc. cit. ante.

out modification, to find the *true* surface tension of an *electrified* surface, but will give only the *apparent* surface tension, determined from the wave-length and the constants of the equation. The wave-length, however, is affected not only by the change (if any) in the cohesion due to electrostatic induction over the surface, but also by the other kinds of electrostatic action present. All but one of these disturbances may be safely neglected as affecting the wave-length by only insensible amounts. One of them, however, can be by no means disregarded: The effect of the electrostatic field is to diminish the potential energy of the deformation of the surface due to the wave motion, and thus to diminish the velocity of the waves, corresponding to a given frequency or to diminish the wave-length—an effect in the same direction as that due to a diminution of surface tension. The *true* surface tension, at any state of electrification, will therefore be found from the formula by adding to the second member, which gives the *apparent* surface tension, an intrinsically positive function of the square of the electric surface density:

$$T = \rho\left(\frac{\lambda^3 n^2}{2\pi}\coth\frac{2\pi h}{\lambda} - \frac{g\lambda^2}{4\pi^2}\right) + F(\sigma^2).$$

F is an even function of the surface density (σ) since the electrostatic effect it represents must be independent of the sign of the charge. The function vanishes with σ. This formula will be returned to later.

For the production and measurement of ripples, Lord Rayleigh's[1] experimental method was adopted nearly in the elegantly modified form used by Dorsey.[2] Rayleigh's method consists essentially in the production of waves satisfying as nearly as is practicable the conditions of Kelvin's formula; and in the measurement of their wave-length by the aid of light made intermittent in the period of the waves and by the employment of Foucault's optical method for rendering visible small departures from truth in plane or spherical reflecting surfaces.[3] While Dorsey's disposition of apparatus has been in general followed, some improvements have been made, as

[1] Rayleigh, loc. cit. ante.

[2] Dorsey, loc. cit. ante.

[3] Cf. Rayleigh, Theory of Sound, II., 345.

well as alterations better adapting the apparatus to the requirements of the present work. For the sake of completeness and of these modifications a description will now be given.

The liquid to be experimented upon was contained in a shallow vessel N (Fig. 1), which was supported on the massive stone slab X. On this slab was also carried, at a height of about 20 cm., and in adjustable mountings, the large König fork F_2, supplied with sliding weights, etc. To its lower prong was clamped by means of a "counter weight" the dipper D, which generated the ripples on the surface of the liquid, into which its glass plate lightly dipped. Several dippers were used during the investigation; the construction of the one used in the principal experiments is shown in Fig. 2. G was a wedge-shaped glass plate of the dimensions indicated, connected by the slender hard rubber rod R, fastened with shellac at both ends, to the stiff aluminium strip A, which was clamped directly to the fork. In the experiments on water the portion P of the plate G was coated with paraffine, and in those on mercury, was left uncoated. The rest of the plate was coated with shellac, both this and the paraffine being used to prevent creeping of the charge. The ripple fork F_2 (Fig. 1) was driven electro-magnetically by a shunt circuit from the terminals of the similar fork F_1, with which it was tuned into unison and which was also driven electro-magnetically (platinum contact). The frequency of F_1 was determined by an arrangement similar to Lissajous' "mirror vibroscope" but simpler. The horizontal motion of a polished steel ball attached to one prong of F_1 near B and illuminated by the lamp I_2, combined with the motion, at right angles to that of the ball, of the mirror M_3 of the massive standard fork F_3, gave a Lissajous' figure in the focal plane of the telescope T_2. The temperature coefficient of the frequency of F_3 was known. This apparatus was set up early in the course of the work when large effects were expected and some absolute measurements contemplated. In view of the small effects actually observed the frequency of F_1 could probably have been obtained with sufficient accuracy by a moderately good ear without comparison with F_3. The frequency of F_1, in use, was 64.4.

The ripples were illuminated by the 20 c. p. incandescent lamp I_1, the image of whose *thick* filament was formed by the lens L_1

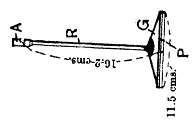

Fig. 2.

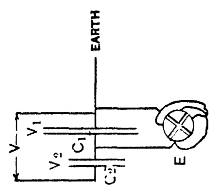

Fig. 3.

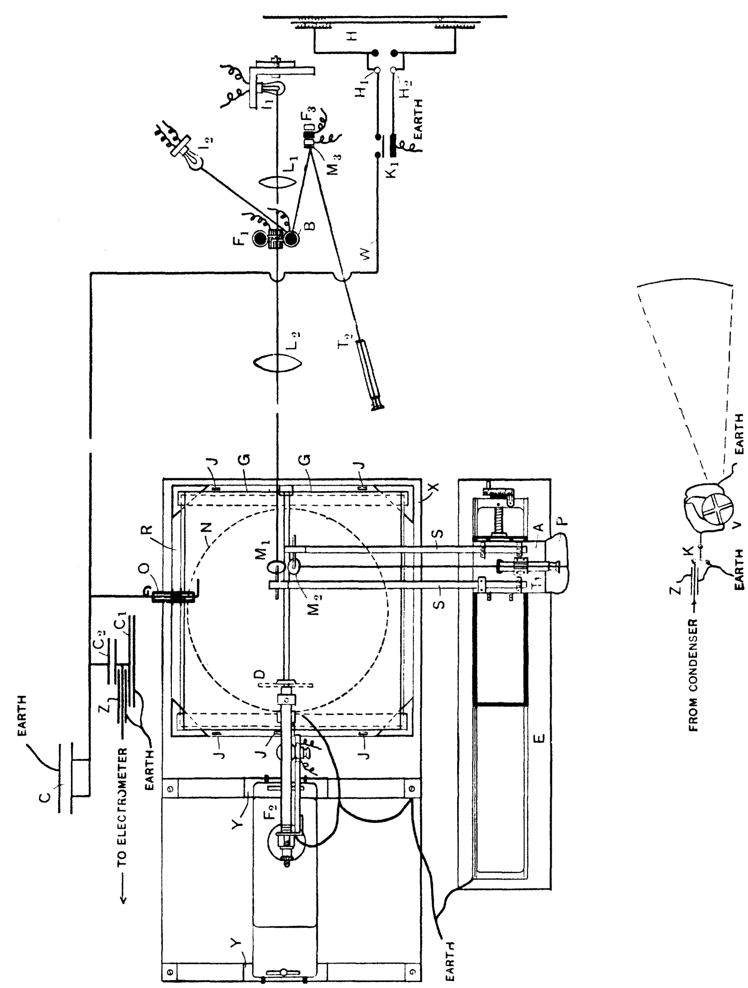

Fig. 1.

upon two stiff aluminum vanes clamped firmly by the counter-weights to the prongs of F_1. They overlapped between the prongs and were pierced by a very small circular hole, through which the light converged by L_1 passed when the prongs were in their mean positions. The hole was at the principal focus of a second lens L_2, after passing through which the light formed a parallel beam. At a distance of more than a meter from L_2 the light struck the mirror M_1, was reflected by it to the liquid surface, thence to a second mirror M_2, and after a third reflection passed into the observing telescope T_1. M_1 and M_2 were large König fork mirrors with plain metallic faces and were so attached to the heavy glass tubes SS that each could be rotated about one axis perpendicular to its supporting tube, and could be moved for a few centimeters in the direction of this axis. The tubes SS (over 60 cm. long) were clamped to the wooden block A, and they also could be rotated about their axes and moved in the directions of their lengths. The telescope T_1, provided with adjusting screws, and the counter-balancing weight P of sheet lead were also mounted upon the block A. The cross hairs of the telescope and the centers of the two mirrors were nearly in the vertical plane passing through the direction of the waves. The wooden block was rigidly clamped to the carriage of the dividing engine E. The engine was provided with levelling screws and supported on one end of a firm table resting squarely on the cement basement floor and projecting underneath and beyond the stone slab X.

With[1] the apparatus in proper working order and in action the field of the telescope focused for the crests of the waves reveals a series of bright bands, one coming from each crest by Foucault's process. They appear stationary, since the period of the ripple fork is identical with that of the fork which renders the light intermittent, being driven by it even when not tuned in unison. The bands are separated by distances corresponding approximately to half a wave-length, since the light is intermittent with twice the frequency of the forks. The waves are not perfectly symmetrical in their two halves, or the crests would appear exactly half a wave-length apart. The forks were tuned to unison by moving the slid-

[1] Cf. Dorsey, loc. cit. ante.

ing weights on F_2 until the bands in the field remained stationary when the circuit driving F_2 was broken. This insured the stationary appearance even when the platinum wire failed to make perfectly regular contact. To measure the wave-length the cross hairs of the telescope were set upon one or more crests by means of the screw of the engine and then upon one or more a whole number of wave-lengths nearer the fork. From the readings of the screw and the number of waves passed over the wave-length at once follows.

That measurements by this method be reliable, it is necessary, first of all, that the wave pattern be steady and that the waves be straight and parallel. The first condition was satisfied by mounting the tuning fork F_2 and the vessel containing the liquid upon rubber tubing in the manner of Rayleigh, and by a method of suspension somewhat improved over one which has been in use here for a number of years[1] and which is similar to that used by Dorsey. The heavy stone slab X was used, and was mounted on a slightly larger wooden panel suspended from the ceiling by twisted cords attached at three points and very roughly parallel. The cords were previously soaked in melted paraffine to prevent changes in length, due to variations in the hygrometric state of the atmosphere. When the apparatus hung freely no extraneous vibrations appeared to affect the surface except those due to walking on the floor overhead. During the electrical experiments a few tufts of cotton waste were placed loosely between the wooden panel and the table to prevent any possible motion due to static charges, but extraneous disturbances, again excepting walking overhead, gave practically no trouble. As to the second point, the form of dipper used insures sufficiently straight waves when it is clean and the surface is in proper condition. It is easily cleaned, when the waves have ceased to be straight and parallel, by rubbing the paraffine with clean filter paper, and treating the glass surface—when it is used—by ordinary processes of cleansing. It is not necessary that the dipper be wetted by the liquid, but only that the part of it coming in contact with the surface be uniform throughout and free from anything which can alter the surface. It should be remarked here also that the deviation of the waves from sine form, before referred to, and from infinitely small amplitude,

[1] Due to O. M. Stewart and described by him in THIS JOURNAL, 4, 442, 1897.

do not appreciably affect the wave-length when the amplitude is very small. That this statement is correct, at least when relative measurements are concerned, there is abundant evidence, both from experiments made by Dorsey and from some performed during this investigation. The amptitudes here used were so small that the ripples could be seen only by some stroboscopic means.

Several other conditions must be satisfied:[1] (1) The mountings of the mirrors, etc., must be rigid—which is easily secured. (2) The screw of the engine and its ways in the parts used must be sensibly correct; the screw was assumed to be without sensible error from a knowledge of the general excellence of the engine, and the ways were tested by Dorsey's second and more accurate method, without discovery of any irregularities. (3) The light must issue from L_2 in a beam which is parallel at least vertically; the position of F_1 was adjusted until the vertical diameter of the beam was the same (5.5 cm.) just beyond L_2 and at a point a meter and a half further on. It is not necessary that the beam be horizontal or parallel to the ways of the engine provided it is of sufficient cross-section otherwise to illuminate M_1 in all its positions. (4) In the case of absolute measurements the ways of the engine must be parallel to the liquid surface and perpendicular to the vertical plane through the direction of the ripples. Both conditions are easily satisfied, as the engine and ripple fork being in adjustable mountings; though in the case of relative measurements neither adjustment is of importance. (5) To avoid error due to the viscosity of the liquid and consequent damping of the waves, the light producing a band in the field of the telescope should come from as small a strip as practicable in the immediate neighborhood of a crest, and the light should be thrown symmetrically by M_1 on both sides of the crest. This was practically effected by the arrangement of telescope and mirrors described.

The electrical part of the apparatus is also shown diagrammatically in Fig. 1. In default of the ideal instrument, a high potential battery, a Holtz machine H, driven by an electric motor, was used to produce electrification. Contact with the liquid, the steadying capacity C, consisting of a few Leyden jars, and the condenser C_2,

[1] Cf. Dorsey, loc. cit. ante.

which formed part of the electrometer arrangement yet to be described, was made through the key K_1 by the large smooth copper wire W, carried from the machine on rubber rod supports. One pole of the Holtz machine, one coating of the condenser C, the dividing engine, the ripple fork, and the stone slab X were grounded. The vessel containing the liquid was insulated from X by an abundant supply of glass. In the experiments upon water it was a circular copper dish 51 cm. in diameter and not over 1.3 cm. deep; in those upon mercury, a rectangular box of wood of inside dimensions 37 by 44 by 1.5 cm. The Holtz machine and key K_1, were separated from the ripple apparatus and electrometer by the wall of a small room in which they were kept. When the key was placed near the ripple surface even the slight mechanical disturbance due to its operation was communicated by the wire to the surface and injured the observations.

According to the results of previous investigators the diminution of surface tension due to electrification is so large that it would be easily possible, without the use of a measuring instrument, to detect, with the aid merely of stroboscopic vision, the corresponding alteration in the length of the waves. This was tested as follows: A dipper was constructed with its glass plate so long as to produce waves parallel and straight for a length of 16 cm. or more. The copper dish was nearly filled with water and so placed that one end of the dipper was near its edge. The straight portions of the waves then extended from near the edge to near the center of the vessel—a range over which the electric density of the charged surface varied greatly. The surface was illuminated by a window and observed through the openings of a rotating disk driven by a motor with such speed that the wave pattern was steady enough to be clearly seen. If the effect sought were large the wave-length would be seen to diminish under electrification and the waves would cease to be parallel, the diminution being greater near the edge than near the center of the surface. On electrifying the liquid to a potential of about 12,000 volts no change whatever was detected.

A series of accurate measurements of the wave-length on surfaces of both water and mercury was then begun. Four successive crests were usually set upon at a distance of about 15 cm. from the dipper and four more 20 wave-lengths nearer, thus giving four independent determinations of the wave-length for one complete observation. One or more such observations were made with the surface uncharged, the time of each being noted, then one or more in precisely similar manner with the surface charged to a potential usually in the neighborhood of 25,000 volts. The process was repeated a number of times for each surface examined. Several specimens of mercury and one of water were examined in this way, and the results are exhibited in the curves of Fig. 4 with wave-lengths as ordinates and times as abscissæ. The average acci-

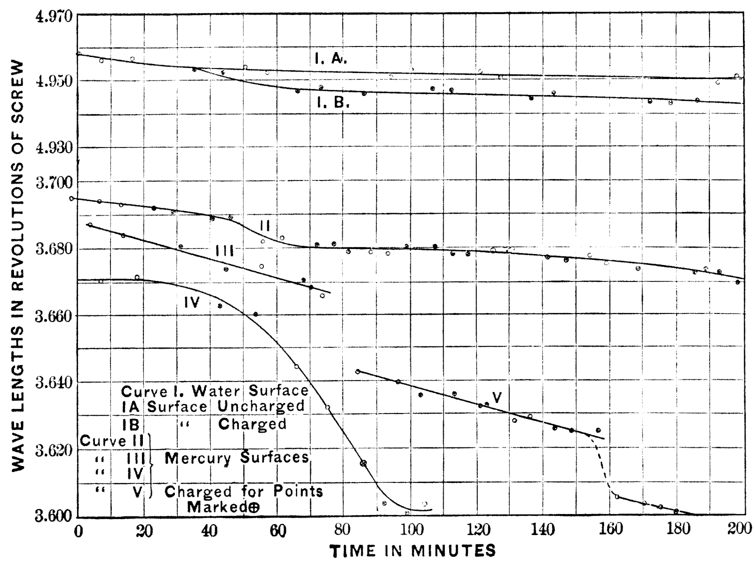

Fig. 4.

dental error in measuring the wave-length was less than one part in 4,000 in the case of mercury, and less than one part in 6,000 in the case of water. The crosses in circles and circles denote measurements upon charged and uncharged surfaces respectively. No change in the case of mercury was detected, indicating that the change in the apparent tension was not so great as three parts in 4,000 $\left(\frac{\Delta T}{T} = \text{approx. } 3\frac{\Delta\lambda}{\lambda}\right)$. In the case of water, however, there was a distinct, though very small, effect, the time curve splitting up into two and indicating a diminution of the wave-length due to electrification. The gradual diminution of wave-length with time must be attributed to changes of temperature, contamination of surface, etc. Some of the mercury surfaces were good, others poor, the better giving always the greater wave-length. The tension of mercury, as the curves show, is subject at times to very rapid alterations; probably due in these cases to rapid contamination.

From these experiments it is evident that to obtain effects measurable with any accuracy much greater intensity of electric field over the surface must be produced. This field must also be as nearly uniform as possible. The following way of effecting both these results was adopted: The liquid surface was made the lower coating of a horizontal parallel plate air condenser. The other coating, which was grounded, was of tin foil fastened smoothly with shellac to the under surfaces of two heavy plane plates of glass *GG* (Fig. 1). These plates rested on narrow plane glass supports mounted by means of glass corner pieces upon two sides of the rigid, plane, rectangular wooden frame *R*. The plates *GG* were adjusted to a distance of from 8.5 to 10 or 11 mm. apart, and their inner edges, over which the tin foil continued, were made parallel to the ways of the engine. The narrow slit thus formed admitted the dipper rod *R* (Fig. 2), and also permitted the passage of all necessary light. The area of the tin foil was somewhat greater than that of the liquid surface. A glass tube *O* (Fig. 1) admitted the wire from the Holtz machine. The frame was provided with leveling and supporting screws *JJJJJ*. By means of these screws and a spirit level mounted on one of the plates *G*, whose thickness was uniform, the two surfaces, liquid and tin foil, were rendered parallel and kept so. The distance between them was measured with a micrometer constructed for the purpose and consisting of a long screw turned to a point at one end and passing perpendicularly through a plane brass plate. To perform the measurement the plate was placed at the edge of the slit, with the pointed end of the screw projecting toward the liquid, and the screw was turned until the point and its image in the surface came in contact. The distance from the point to the brass plate was then measured, and the distance between the condenser plates obtained from this by substracting the thickness of the glass plate and foil. As the waves measured extended over a distance always less than 12 cm. in the central portion of the surface, while the distance between the liquid surface and the tin foil was always less than 4.1 cm., practical uniformity of electric field was secured. The effect of the width of the slit was considered negligible.

The only measurement now remaining to be discussed is that of potentials. As high potentials were of necessity employed and no reliable high potential instrument was on hand, it was necessary either to construct such an instrument or to devise some means by which a low potential electrometer could be used to measure very high potentials. The latter course was chosen and some methods devised by which the range of an electrometer or ballistic galvanometer may be almost indefinitely extended. The first method which suggested itself is an inversion of Faraday's well-known method of comparing capacities. The ratio of capacities being known, the initial potential can be computed from the measurement of the final, which may be made as low as desired by suitably selecting or adjusting the condensers to be used. The second method, which was used in the investigation, consists in applying the whole potential difference to the terminals of two condensers arranged in series and measuring the potential difference between the plates of one of them. From this and the known ratio of capacities the whole potential difference follows. Let C_1 and C_2 (Fig. 3) denote two condensers and their capacities connected in series and having the joint capacity C. Let the electrometer E be connected to the coats of C_1, the terminal coat of which is earthed. Let V be the whole fall of potential through the series and V_1 that through C_1. Then we have, including in C_1 the capacity of the electrometer,

$$CV = C_1 V_1 = \frac{C_1 C_2}{C_1 + C_2} V; \text{ whence } V = V_1 \frac{C_1 + C_2}{C_2}.$$

By suitably adjusting the ratio $\frac{C_1 + C_2}{C_2}$ an electrometer (or ballistic galvanometer) of any convenient range may be used to measure any potential within its range or higher—except in so far as leakage, absorption, etc., make the indications of the instrument unreliable. In the first described method these difficulties are wholly or almost wholly avoided. From the above equation we have, solving for the ratio of capacities,

$$\frac{C_1}{C_2} = \frac{V - V_1}{V_1}.$$

Thus by measuring both V and V_1, which may easily be done with the same electrometer when a constant battery is used, capacities may be very accurately and expeditiously compared.

The electrometer arrangement actually used is shown in Fig. 1. The electrometer V was a Thomson quadrant, used idiostatically, and read up to 400 volts. The quadrants were adjusted to accurate symmetry, and the same deflections were obtained for positive and negative charges of the needle. The jar was connected in and the case, induction plate, and its pair of quadrants grounded. The other pair of quadrants was connected to the insulated coating of C_1, through the key K, by an insulated wire running through the grounded leaden tube Z for protection from static disturbances. C_1 was a mica condenser, and C_2 a pair of leyden jars in multiple. The jars were insulated on glass varnished with shellac, and connections were made as shown in the diagram. The ratio of capacities $\frac{C_1 + C_2}{C_2}$ was 75 to 1. The capacities were determined by the method above indicated, comparisons being made with a Nalder standard. The capacities of the electrometer and connecting tube were negligible in the above ratio. In actual practice with high potentials the leakage and absorption of the condensers are very troublesome. That the electrometer may give reliable indications, the ratio of capacities, including the absorption and leakage, must remain the same during the observations as the ratio of calibration. This, with the condensers used, was not the case except when the condensers and electrometer—which will together be referred to as the condenser electrometer—were charged rapidly. It was then approximately true as the following test shows: The condenser series was short circuited, and the electrometer as quickly as possible thereafter insulated by means of the key K. The spot of light came to rest sometimes at the zero of the scale and sometimes a few divisions from zero. This test was made repeatedly and indicated that the readings averaged a few per cent. too low. That they were too low and not too high, follows from the fact that the charge remaining after short circuiting was always of sign opposite to that of the original charge. Whether this method of measuring potentials is new or not I do not know, but I have not succeeded in finding any account of it published. Since it occurred to me, however, I have found that it had previously occurred also to other members of this laboratory, and its simplicity is so great that it can hardly fail to have occurred to others elsewhere. In addition to the two condenser methods here given for measuring potentials, any electrometer method of measuring capacities may be inverted for the same purpose.

As a desirable check upon the indications of the condenser electrometer, it was used to measure the potentials corresponding to a number of spark lengths between polished brass spheres 3 cm. in diameter. The mean values of the spark lengths and electrometer potentials are given in Table I., together with Baille's[1] potentials for the same spark lengths between spheres of the same diameter. The measurements of spark lengths were only rough. In Fig. 5 the results of the comparison are shown graphically. The most reliable determinations with the condenser electrometer were the last two, which agree closely with Baille's results. If the agreement were exact the continuous and broken lines would coincide.

With the apparatus as now described an extended series of observations was made upon surfaces of water and mercury. Since the indications of the electrometer, as before stated, were reliable only when the instrument was rapidly charged, the following method of procedure was adopted: With the surface unelectrified and all the condensers discharged, two crests A and B, a known number of wave-lengths apart and equidistant from the center of the surface, were chosen and the position of one of them, say A, accurately determined by several settings of the cross hairs of the telescope. Through the key K_1 connection was then made with the Holtz machine. The electrification—the sign of which was readily determined by observation of the brushes given off at the discharging

[1] Baille, Ann. de Chim. et de Phys. (5) 25, 531, 1882.

TABLE I.

Electrometer Test.

Spark length in cms.	Potential in volts; Baille's values.	Potential in volts as measured with condenser electrometer.	No. of observations with condenser electrometer.
0.2	7,800	6,200	2
0.42	14,530	12,800	4
0.50	16,500	15,200[1]	—
0.67	21,450	20,400	10
0.82	25,910	26,200	3
0.93	29,290	29,400	3

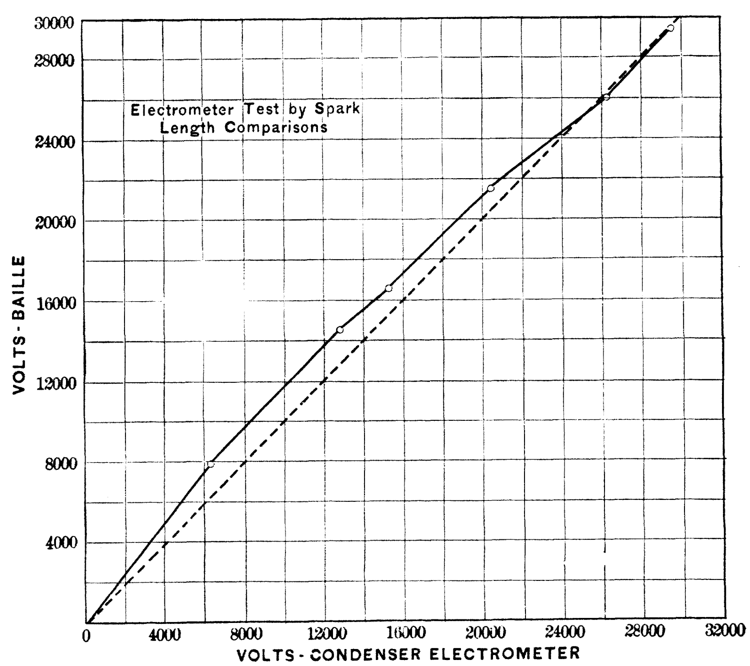

Fig. 5.

points to the plate of the machine—rose and the crest moved toward the fork F_2. The cross hairs were again set upon it and the deflection on the scale of the electrometer—which was so placed

[1] This value was obtained by interpolation.

that the observer at the telescope could read it by merely turning his head—at once noted. The reading of the screw of the engine was then taken and the process rapidly repeated until the electrometer indication began to fall, showing that it was not safe to proceed farther. The process of electrification was very often made so rapid that only one or two observations could be taken in a set. The condenser electrometer then ceased to have any advantage over the electrometer based on Faraday's method of comparing capacities—was in fact at a disadvantage owing to the presence of absorption and leakage. After each set the condensers, including the liquid surface and tin foil, were all discharged through the key K_1. The two condensers, C_1 and electrometer, and C_2 were by this put in multiple and, still retaining a charge on account of absorption, etc., were then discharged. The whole process was then repeated once or more and the crest B observed in the same manner. The sign of the electrification was changed at will by interchanging the connections at the terminals H_1 and H_2 of the induction machine. Until it was certain that experimental conditions could be kept practically constant, the interchange of the signs of the electrification, and of the crests whose motion was measured, was frequent.

To avoid dampness in the air and consequent poor insulation, the experiments were performed at the high temperature of 22°–23° C.

In the experiments upon water clean tap water was used and the observations were made upon two surfaces. Conditions were kept so nearly constant that the wave-length for the unelectrified surface changed during the first set only from 4.959 R to 4.954 R, and during the second set from 4.952 R to 4.958 R—R being a revolution of the screw and equal to one mm. The distance δ between the surface of the liquid and that of the metal plates above was 4.09 cm. and the width of the slit between the plates was 10–11 mm. The distance between the crests A and B was twenty wave-lengths.

The experiments upon mercury were all made upon one fine, clean surface of pure distilled mercury, which retained its character well throughout the observations. It was protected from dust, etc., by the wooden frame R (Fig. 1), the condenser plates GG, and by paper, which was tacked about the frame and closed up the liquid almost completely. The distance δ between the surface and the plates above was 3.41 cm., and the width of the slit 9 mm. The wave-length for the uncharged surface changed during the observations from 3.699 *R* to 3.679 *R*. The distance between the crests *A* and *B* was thirty wave-lengths.

The mean results of the observations, averaged according to agreement of potentials, are contained in Tables II. and III., and exhibited graphically in Figs. 6 and 7. The circles represent positive, and the crosses negative electrifications.

The effect on the wave-length is seen to be independent of the sign of the charge; and much greater in the case of water than in the case of mercury, as would be expected from the relative densities and tensions of the two. The motion of crest *A* is approximately twice that of *B* for the reason that its distance from the dipper was about twice as great—some 20 cms. Sometimes, with the water,

TABLE II.

Water. Positive Charges.						Water. Negative Charges.					
$10^{-3}\times$ Potential in volts.	Motion of crest *A* in revs. of screw.	No. of observations	$10^{-3}\times$ Potential in volts.	Motion of crest *B* in revs. of screw.	No. of observations	$10^{-3}\times$ Potential in volts.	Motion of crest *A* in revs. of screw.	No. of observations	$10^{-3}\times$ Potential in volts.	Motion of crest *B* in revs. of screw.	No. of observations
8.9	0.25	6	10.7	0.16	6	8.9	0.28	6	8.0	0.12	6
11.1	0.34	..	13.1	0.26	..	11.0	0.39	..	11.6	0.22	..
12.6	0.49	..	16.1	0.39	..	12.7	0.41	..	14.0	0.28	..
14.2	0.62	..	18.8	0.56	..	14.6	0.62	..	16.1	0.40	..
16.2	0.82	..	20.1	0.68	..	15.6	0.75	..	17.6	0.44	..
17.4	0.98	..	22.0	0.75	..	16.7	0.82	..	18.4	0.55	..
18.6	1.23	..	23.7	0.96	..	18.3	1.05	..	19.4	0.55	..
19.4	1.34	..	25.4	1.07	..	19.8	1.32	..	20.4	0.75	..
20.8	1.41	..	26.9	1.05	4	20.3	1.42	..	21.5	0.73	..
22.0	1.68	..				21.2	1.52	..	22.0	0.81	..
23.3	1.78	..				22.0	1.74	..	23.2	0.96	..
24.1	2.08	..				22.7	1.80	..	23.8	0.95	..
24.9	2.18	..				23.3	1.85	..	24.6	0.96	..
25.5	2.36	..				24.4	1.98	..	25.4	1.08	..
26.6	2.42	4				25.6	2.32	..	26.0	1.07	..
						26.0	2.10	..	26.6	1.12	..
						26.3	2.18	..	27.1	1.12	2
						26.8	2.30	..			
						27.1	2.55	4			

$\lambda = 4.96$ revolutions of screw.
Distance from liquid surface to metal plate above $= \delta =$ 4.09 cm.
B is the crest nearer the dipper; *A*, 20λ farther away.

TABLE III.

Mercury. Positive Charges.						Mercury. Negative Charges.					
$10^{-3}\times$ Potential in volts.	Motion of crest *A* in revs. of screw.	No. of observations	$10^{-3}\times$ Potential in volts.	Motion of crest *B* in revs. of screw.	No. of observations	$10^{-3}\times$ Potential in volts.	Motion of crest *A* in revs. of screw.	No. of observations	$10^{-3}\times$ Potential in volts.	Motion of crest *B* in revs. of screw.	No. of observations
11.1	0.10	4	11.6	0.06	4	10.7	0.09	4	12.5	0.06	4
15.2	0.17	..	16.6	0.11	..	13.3	0.11	..	16.7	0.08	..
16.5	0.15	..	18.5	0.14	..	14.7	0.16	..	21.0	0.14	..
19.0	0.29	..	20.9	0.16	..	18.1	0.24	..	22.8	0.15	..
20.2	0.24	..	23.0	0.19	..	18.8	0.22	..	23.5	0.16	..
20.8	0.30	..	24.8	0.20	..	19.7	0.24	..	24.1	0.19	..
22.0	0.38	..	26.0	0.21	..	20.3	0.27	..	24.8	0.14	..
23.6	0.41	..	27.1	0.26	..	21.0	0.31	..	25.9	0.18	..
24.9	0.45	..	27.7	0.28	..	21.8	0.32	..			
26.8	0.48	..	28.4	0.30	..	22.9	0.40	..			
27.4	0.54	..				23.2	0.39	..			
28.5	0.57	5				23.8	0.42	..			
						24.3	0.42	..			
						25.4	0.49	..			

$\lambda = 3.69$ revolutions of screw.
Distance from liquid surface to metal plate above $= \delta = 3.41$ cm.
B is the crest nearer the dipper; *A*, 30 λ farther away.

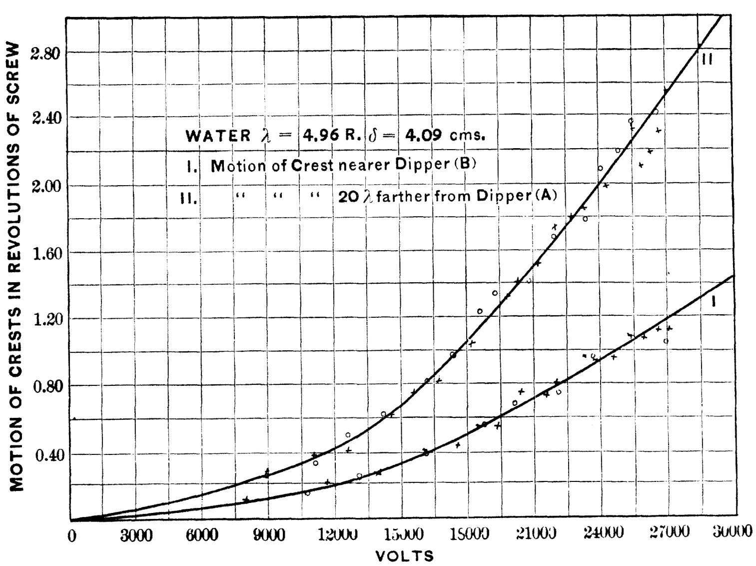

Fig. 6.

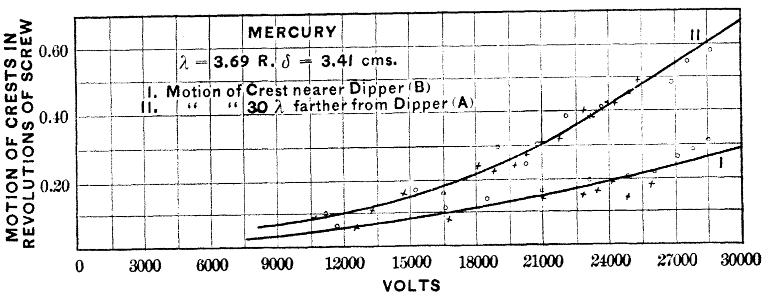

Fig 7.

the amplitude of the fork was increased while the motion of A was being measured, and then diminished again for B, in order to make the definition of both as good as possible. This was regularly done in the experiments on mercury, as the small effect on its wave-length made every help to accurate measurement indispensable.

From the curves in Figs. 6 and 7 and the values of λ (wave-length) already given were obtained the first five columns of Table IV., and the first three of Table V. σ (electric surface density) and σ^2 were computed from the formula for parallel plate condensers— $\sigma = \frac{V}{4\pi\delta}$, where δ if the distance between the plates and V is their potential difference in electrostatic units. T is the apparent surface tension (= true surface tension $- F(\sigma^2)$), given in percentage of its value for no electrification, and was obtained by the aid of Kelvin's formula. We have for an infinitesimal variation of λ, caused by a variation of the electrification

$$\frac{dT}{T} = 3\frac{d\lambda}{\lambda}\left\{\frac{1 - \dfrac{g}{3\pi\lambda^2 n^2}}{1 - \dfrac{g}{2\pi\lambda n^2}}\right\}.$$

The quantity in the parentheses is sensibly constant for such small variations of λ as occur in these experiments. In the case of mercury the maximum change in λ is so small—0.3 per cent.—that we may at once write, throughout the range of actual variation of λ,

$$T_0 - \Delta T = T_0\left(1 - 2.73\frac{\Delta\lambda}{\lambda}\right) = T.$$

In the case of water the diminution of λ reaches 1.35 per cent., and more accurate results are obtained by applying this formula in succession to each value of T. Thus

$$T_1 = T_0 - \Delta T_0 = T_0\left(1 - 2.92\frac{\Delta\lambda_1}{\lambda_0}\right),$$

$$T_2 = T_1\left(1 - 2.92\frac{\Delta\lambda_2 - \Delta\lambda_1}{\lambda_1}\right), \text{ etc.}$$

In this way the values of T, given in the final columns of the tables, were computed, with T_0 put equal to 100. In the curves of Figs. 8 and 9 the results contained in the tables are shown graphically. The apparent surface tension is given both as a function of the surface density of the electric charge and as a function of its square. The relation between the tension and the density of the charge is seen to be nearly parabolic, especially in the case of water.

Some rough measurements were also made upon a dense solution of sodium chloride and a similar change in its apparent surface tension observed.

A similar diminution of the apparent tension of water was observed with alternating charges. One terminal of the secondary of a large induction coil was connected to earth and the other to the liquid, and

Table IV.

Water.

Potential in volts.	$20 \times \Delta\lambda$.	$\Delta\lambda$.	$\Delta\lambda_{n+1} - \Delta\lambda_n$.	λ	σ	σ^2	T
0	0.000	0.0000	0.0000	4.96	0.00	0.00	100.00
9000	0.132	0.0066	0.0066	4.96	0.58	0.34	99.61
12000	0.240	0.0120	0.0054	4.95	0.77	0.59	99.29
15000	0.348	0.0174	0.0054	4.95	0.97	0.94	98.98
18000	0.554	0.0277	0.0103	4.94	0.17	1.37	98.37
21000	0.788	0.0394	0.0117	4.93	1.36	1.85	97.69
24000	1.046	0.0523	0.0129	4.92	1.56	2.43	96.94
27000	1.330	0.0665	0.0142	4.91	1.74	3.03	96.13

λ, $\Delta\lambda$, etc., in revolutions of screw.
Frequency of ripples = 64.4.

TABLE V.

Mercury.					
Potential in volts.	30 × Δλ.	Δλ	σ	σ^2	*T*
0	0.000	0.00000	0.00	0.00	100.00
9000	0.034	0.00113	0.70	0.49	99.92
12000	0.048	0.00158	0.93	0.86	99.88
15000	0.068	0.00227	1.17	1.37	99.83
18000	0.101	0.00337	1.39	1.93	99.75
21000	0.160	0.00533	1.63	2.66	99.61
24000	0.229	0.00763	1.87	3.50	99.44
27000	0.304	0.0101	2.09	4.37	99.25
30000	0.374	0.0125	2.33	5.43	99.08

$\lambda = 3.69$. λ and Δλ in revolutions of screw.
requency of ripples = 64.4.

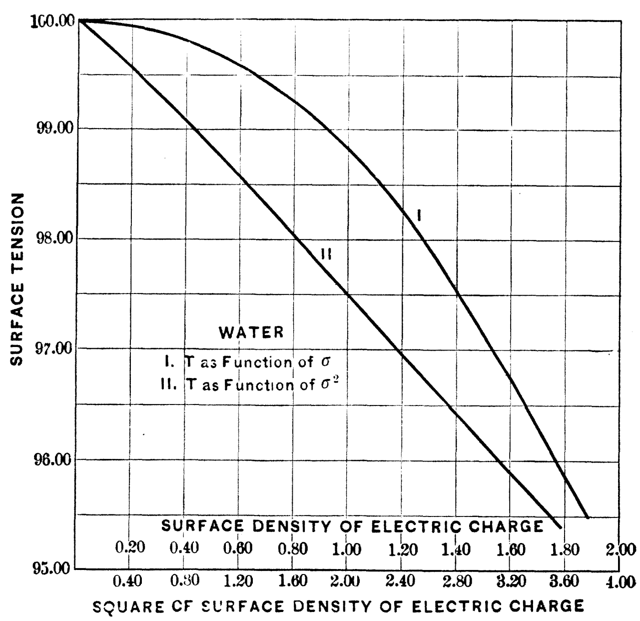

Fig. 8. The ordinate is the "apparent" surface tension.

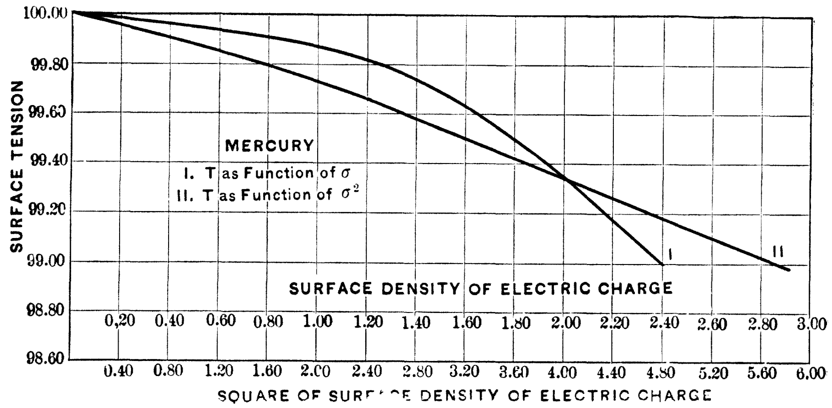

Fig. 9. The ordinate is the "apparent" surface tension.

the primary fed by an alternating current. In these circumstances the appearance in the telescope depends, as would be expected, on the phase relation between the charging of the surface and the intermittence of the light. This frequency of intermittence is twice the frequency of the forks, and the frequency of charging is twice the frequency of the alternator furnishing current, since positive and negative charges produce the same effect. The displacement of the crests varies from zero, when illumination takes place at the time of zero charge, to a maximum when illumination occurs at the time of maximum charge, either positive or negative. Of course, as the frequency of illumination is 128.8, only summational effects can be observed. With a frequency almost exactly double that of the intermittence of the light slow "beats" between the illumination and the charge were at one time observed, the bands moving to and fro in the field of the telescope. The rest of the time the crests appeared perfectly steady. With a frequency of charging of 110 the bands periodically underwent a rapid series of changes; breaking up into a number of similar bands moving in the field, then uniting in their original positions, only to break up again, the whole process repeating itself indefinitely. The explanation of these phenomena is obvious from what has been already said.

The results of this investigation, so far as they go, are in accord with the theory of Helmholtz given above. While the air above the liquid surface is doubtless in a highly polarized state, such as obtains in Helmholtz's "Doppelschichten," all possibility of an electrolytic explanation of the effects observed seems excluded. The fact that the surface tension of the uncharged surface remains practically constant for hours, within which it has been repeatedly charged and discharged; the instantaneous nature of the effect, both in the case of steady potentials and in that of alternating potentials; and the identity of the results produced by positive and negative charges, all strongly negative any interpretation of the phenomena as other than electrostatic in origin. It is certain, however, that the diminution of wave-length observed on electrifying the surface is at least partially accounted for by the kind of electrostatic action whose effect is denoted by $F(\sigma^2)$ in the modified form of Kelvin's equation given above; and as this function has not yet been determined, it is possible that the whole effect observed is due to this cause, and no part of it to the forces tangential to the surface acting between the "elementary electric charges." If an effect of the latter kind exists, the results given above show that it must be much smaller than has hitherto been supposed; but, within experimental errors, the same for positive and negative charges. If this effect does not exist, the phenomena here described must be relegated to Group I. of the summary in the early part of this paper. It is remarkable in how many cases a diminution of surface tension would go to produce effects of the same kind as those actually produced by electrostatic and electrolytic causes.

To Professors Nichols and Merritt and to Mr. Homer J. Hotchkiss I am indebted for the effective interest which they have taken in this investigation throughout its progress, especially for their valuable suggestions.

THE PHYSICAL LABORATORY OF CORNELL UNIVERSITY
March, 1898.