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On the Nature of Electrocapillary Phenomena. I. Their Relation to the Potential Differences between Solutions

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II. *On the Nature of Electrocapillary Phenomena.*—I. *Their Relation to the Potential Differences between Solutions.*

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INTRODUCTION.

THE phenomenon of surface tension exhibited at the surface of separation between two homogeneous liquids may be regarded as arising from such a variation in the distribution of the matter composing each of the liquids, in the immediate neighbourhood of the surface of separation, that the energy of given quantities of the two liquids is greater when these are in the neighbourhood of the surface than when each is in the homogeneous interior of its corresponding liquid.

On such a view, the tension per unit length in the surface will be equal to $d\mathrm{E}/d\mathrm{S}$, where $d\mathrm{E}$ is the increase in the potential energy of the system of two liquids, resulting from an increase, $d\mathrm{S}$, of the surface of separation between them. The distribution of energy here referred to may be considered independent of possible electrostatic effects at the surface of separation.

There is little doubt, however, that there is frequently a potential difference of considerable amount at the surface separating two such liquids as mercury and a solution of a salt in water. There must, therefore, be a corresponding separation of electricities of opposite sign at the surface, and we may regard these as forming a condenser-like "double-layer." This double-layer will give rise to an electrostatic surface energy, whose value we may write as $\mathrm{E}' = \frac{1}{2}c\mathrm{S}\pi^2$, where c is the capacity of the double-layer per unit surface and π is the potential difference across it. S is, as before, the area of the surface separating the two liquids. Now, if a small change of this surface, $d\mathrm{S}$, be supposed to take place while the potential difference across the double-layer is kept constant by an external electromotive force, we get

$$d\mathrm{E}'/d\mathrm{S} = \tfrac{1}{2}c\pi^2.$$

This increase in the potential energy of the system, with increase in the surface of separation between the two components, will be an effect that tends to take place under the influence of the external electromotive force, and will be equivalent to a force per unit length tending to *increase* the surface of separation between the two liquids.

The observed surface tension will thus be

$$\gamma = d\mathrm{E}/d\mathrm{S} - d\mathrm{E}'/d\mathrm{S} = \gamma_0 - \tfrac{1}{2}c\pi^2,$$

where γ_0 is the surface tension arising from the non-electrical distribution of energy first mentioned. The equation will give the relation between the observable surface tension and the potential difference at the mercury surface.

The above may be regarded as the Helmholtz theory of electro-capillary phenomena. LIPPMANN found that the curve showing the relation between the surface tension and the E.M.F. applied between the terminals of a capillary electrometer was (for a particular solution of sulphuric acid) approximately parabolic through a considerable portion of its course, and it appeared from this that c was a constant and that γ_0 was independent of π.

It is not a necessary consequence of considerations such as the above, that c should be constant; but if the only effect of the potential difference is to produce an electrostatic surface energy represented by $\frac{1}{2}c\pi^2$ per unit surface, then the observed surface tension should have a maximum value when $\pi = 0$, even although c may be variable. The assumption, that the maximum surface tension corresponds to zero potential difference between the mercury and the solution, has been much employed in recent years in the deduction of values for the contact potential difference between various electrodes and electrolytes. It must be remembered, however, that the observed variation in the surface tension need not be due solely to variation in the quantity $\frac{1}{2}c\pi^2$. The non-electrical surface energy, represented by γ_0, may vary with the potential difference. A variation in the potential difference at the surface of separation between the mercury and the solution may be accompanied not only by a variation in the electrostatic surface energy, but also by a variation in the distribution of the matter in the neighbourhood of the surface.

If a variation of the kind just mentioned can be traced, it is clear that we cannot consider the phenomena as if they were due to a certain non-electrical distribution upon which is superposed an electrostatic double-layer, producing no other effect than that represented by its electrical energy. Hence it need not happen that the maximum surface tension corresponds to zero potential difference, for the maximum surface tension may arise from the fact that non-electrical effects, accompanying the change in the potential difference and tending to reduce the surface tension, pass through a minimum value as the potential difference changes. This minimum value need not necessarily correspond to zero potential difference. The possible nature of non-electrical effects which may accompany changes in the potential difference is discussed later. The first part of the paper contains an experimental analysis of the Lippmann-Helmholtz theory.

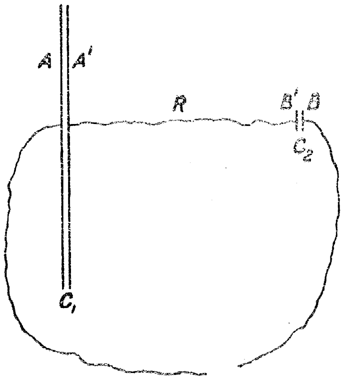
THE LIPPMANN-HELMHOLTZ THEORY OF ELECTROCAPILLARY PHENOMENA.

In the Lippmann-Helmholtz theory of the capillary electrometer there are in reality two distinct hypotheses, either of which may be separately justifiable. The first concerns the manner in which the potential difference at the capillary varies with the electromotive force applied between the terminals of the electrometer. The second deals with the relation between the above potential difference and the tension of the surface separating the mercury and the solution.

The First Hypothesis of the Lippmann-Helmholtz Theory.

The first hypothesis would apply to any electrolytic cell consisting of two polarizable electrodes placed in a conducting solution. When an E.M.F. (of which the value is kept within certain limits depending on the nature of the electrodes and of the solution) is applied to such a cell there may be a considerable current for a very short time; but the system almost at once assumes a practically steady state in which there is only a very feeble continuous current through the cell. The value of this current can in general be neglected in comparison with the current value found by dividing the E.M.F. applied by the calculable resistance of the electrolyte. It is therefore considered that the potential fall within the liquid can be neglected in comparison with the sum of the potential changes in the neighbourhood of the electrodes, and that this sum is equal in value to the applied E.M.F. The system is, in fact, considered equivalent to a pair of condensers (supposed existent at the surfaces of separation between electrode and solution) connected in series by a resistance (represented by the resistance of the electrolyte). For electrodes of the same nature in the same solution the respective capacities are taken to be proportional to the areas of the surfaces in contact with the solution. In the capillary electrometer, therefore, the capacity of one electrode would in general be indefinitely small compared with that of the other.

Let AA′ and BB′ represent condensers (of capacities C_1 and C_2) of which the plates A′ and B′ are connected by a resistance R, and of which the "external" plates A and B are at first also connected.



Suppose the condensers are charged, and let A and B be at zero potential while A′ and B′ are at the potential $-\pi_n$. Let now an E.M.F. π_e be introduced in the external circuit connecting A and B, and let the resistance of this circuit be R′. Let π, π' and π'' be the final potentials of A, A′ and B′ respectively, — B being supposed kept at zero potential. Then it is easy to show that

$$\pi_e = \left(\frac{1}{c_1} + \frac{1}{c_2}\right) \int_0^{\tau} \iota \, dt,$$

in which the integral represents the quantity of electricity that has passed in the circuit during the time τ taken by the system to acquire its steady state. Also

$$\pi = \pi_e$$

$$\pi' = (\pi_e - \pi_n) - \frac{1}{c_1}\int_0^\tau \iota\, dt$$

and

$$\pi'' = \frac{1}{c_2}\int_0^\tau \iota\, dt - \pi_n = \pi'.$$

Now if the condenser AA′ is very large compared with the condenser BB′, we may neglect $\frac{1}{c_1}$ in comparison with $\frac{1}{c_2}$, so that we get

$$\pi'' = \pi_e - \pi_n$$

and

$$\pi - \pi' = \pi_n.$$

Thus the effect of introducing the E.M.F. π_e is that the potential difference at the small condenser is changed from $-\pi_n$ to $\pi_e - \pi_n$, while the change at the large condenser is negligible.

If the supposed analogy were complete, we should, therefore, have the result that in the capillary electrometer the variation of the potential difference at the capillary electrode is the same as the variation of the E.M.F. applied between the terminals. The analogy between the condenser system and the electrolytic cell cannot, however, be complete. In the latter case the original potential difference (corresponding to $-\pi_n$) is not arbitrary, but represents one of the conditions of the equilibrium at the electrode. Any cause which tends to alter the "natural" potential difference $-\pi_n$ at the small electrode—the nature of the solution in the neighbourhood of the electrode remaining sensibly constant—must in general be accompanied by a "depolarization" current representing the continual tendency of the "polarized" electrode to revert to the original potential difference. We cannot, therefore, have $\iota = 0$ in the final steady state as in the condenser system.

The Effect of Depolarization.

If we assume, however, that the effect of the depolarization is to produce a fall of potential within the electrolyte according to Ohm's law, the nature and magnitude of the effect can be readily specified. Thus, taking the symbols as above to be applicable to the capillary electrometer, we shall have

$$\pi_e - \pi = \mathrm{R}' . f(\pi'')$$

and

$$\pi' - \pi'' = \mathrm{R} . f(\pi''),$$

in which the continuous depolarization current is written as a function of π'', because of the assumption that if the area of the capillary electrode is kept constant, the magnitude of the current will depend only on the potential fall at that electrode. It is not to be expected that the depolarization current will remain constant for an indefinite time. Owing to the variation of the concentration of the solution in the neighbourhood of the electrode, which must necessarily accompany the passage of the current through the electrolyte, the relation between π'' and the depolarization current will alter; but an effect of this kind will be gradual, and we may consider the depolarization current to be constant for some time after the introduction of π_e. In like manner, the accumulated effect of the continuous current upon the potential fall at the large electrode will only be gradually perceptible.

Adding the two above equations, and putting $\pi - \pi' = \pi_n$, we get

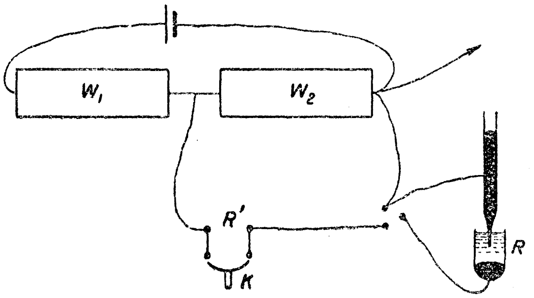
$$\pi'' + (\mathrm{R} + \mathrm{R}') f(\pi'') = \pi_e - \pi_n.$$

It therefore follows (as is otherwise obvious), that the effect of depolarization would be to cause the potential difference at the small electrode to change less rapidly than the applied E.M.F. Hence, before one can proceed beyond the first hypothesis to examine quantitatively whether the second hypothesis, concerning the relation between the potential difference and the surface tension, is true, it is necessary to determine whether the effect of the depolarization can under any circumstances become appreciable.

The magnitude of the effect will depend upon the value of $(\mathrm{R} + \mathrm{R}') f(\pi'')$. The internal resistance, R, will, of course, depend upon the nature of the electrolyte employed, upon the internal cross-section of the capillary tube and upon the distance between the mercury meniscus and the point of the capillary tube. Its value may range from something like 50,000 or 100,000 ohms to a million ohms or more. So that, under usual circumstances, the external resistance, R′, can be neglected in comparison with R. The value of $f(\pi'')$ will depend upon the area of the mercury meniscus. It will, therefore, be possible in a given electrometer to vary the value of $\mathrm{R}f(\pi'')$ for a given solution, and (by comparison of the curves for two different positions of the meniscus) to determine whether the form of the curve is appreciably affected by the change. On the other hand, the effect may be rendered directly evident and measurable by interposing a very high resistance in the external circuit, so that, although $f(\pi'')$, and even $\mathrm{R}f(\pi'')$, may be very small, $\mathrm{R}'f(\pi'')$ will have an easily observable magnitude.

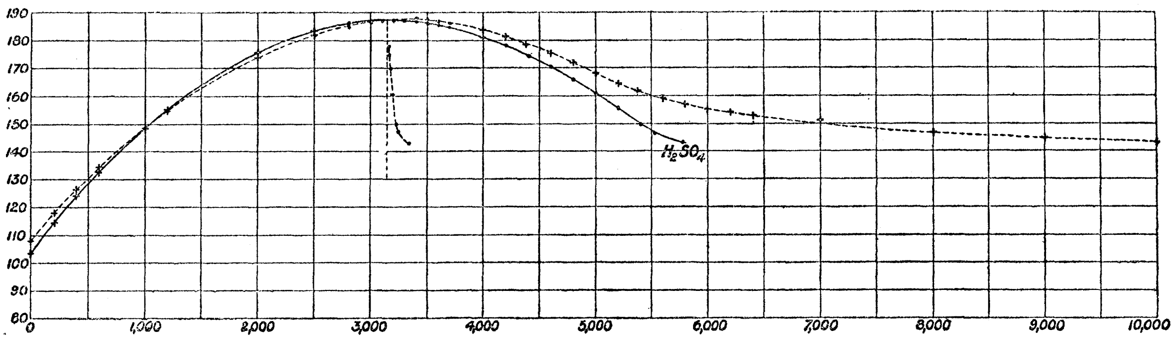
Experimental Determination of the Magnitude of the Depolarization Effect.

I have used this latter method, and the following experiments may be given in illustration of it. The high resistance consisted of graphite rulings upon ebonite, and in the experiments in question had an approximate value of 10 megohms. The arrangement was as in the diagram :—



The graphite resistance could be cut out of the circuit by means of the key K. For each E.M.F. applied, the direct reading with R′ cut out of the circuit (as in the ordinary method of determining capillary curves), was taken ; the "indirect" reading with R′ in the circuit was then observed. The results for a solution of sulphuric acid are shown in fig. 1. The ordinates are the scale readings of the summit of the mercury column of the electrometer, and the abscissæ denote the values of the resistances unplugged in the resistance box W_2. 1000 ohms correspond approximately to 0·28 volt. These depolarization experiments were made in June, 1896, with an electrometer slightly different from that described later in the paper.*

Fig. 1.



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* These experiments were described in a Dissertation presented at Trinity College, Cambridge, in August, 1896. I have since found that WIEDEBURG has also indicated, *theoretically*, the effect of depolarization. 'Wied. Ann.,' 59, 1896 (October). WIEDEBURG'S conclusion concerning the *possible* magnitude of the depolarization effect is not supported by the experimental results contained in this paper. For example, when the surface tension has its maximum value at the capillary electrode in an electrometer containing a normal solution of potassium iodide, he suggests a possible potential fall of about 0·25 volt within the electrometer solution (due to a depolarization current) as a means of reconciling certain results, mentioned later, with the ordinary Lippmann-Helmholtz theory. The actually observed depolarization current for a KI solution is far smaller than that required to substantiate WIEDEBURG'S suggestion, and, apart from this, the relations established later are at variance with his view.

The method of taking the electrometer curves and their degree of accuracy is discussed later.

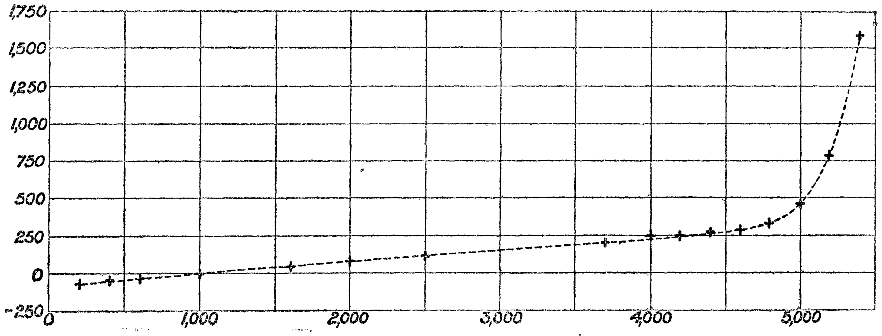
The dotted curve represents the indirect curve, while the continuous one represents the ordinary capillary curve. In this particular experiment it apparently happened that for some accidental reason (such as difference in purity of the mercury of the large and small electrodes) the "natural" potential difference at the small electrode was appreciably different from that at the large. In consequence of this, the surface tension of the small electrode began to increase immediately the connection between it and the large electrode was broken. As I have subsequently observed, this is an effect which can be obviated when due care is taken, with pure mercury and a solution of uniform concentration. The phenomenon does not affect the conclusions in the present case, but in fact rather increases the interest attaching to the observations. When the electrodes were joined by a short wire, the surface tension was different from what it was when they were joined by the graphite resistance. The reading in the latter case was not appreciably affected by reversing the resistance, so it could be assumed that the graphite did not introduce any appreciable E.M.F. into the circuit.

At first the indirect readings for a given external E.M.F. give higher values for the surface tension than the direct. The curves cut one another at an E.M.F. corresponding to about 0·28 volt, so that for this E.M.F., the surface tension assumed by the mercury is the same whether the E.M.F. is applied directly or through a very high resistance. Hence, when the surface tension at the capillary has this particular value, there can be no appreciable continuous current through the electrometer. It was found that the surface tension in question was practically identical with that assumed by the capillary, when the electrometer was disconnected from the rest of the apparatus—the electrodes being also unconnected. From this it is highly probable that this surface tension corresponded to the natural potential difference at the small electrode, and the significance of the disappearance of the depolarization current becomes immediately clear.

The horizontal distance between two points corresponding to the same surface tension, one on each curve, is a measure of the depolarization at the small electrode when the potential difference there has the value corresponding to the given surface tension. The actual value of the current is equal to the above horizontal distance (expressed in volts), divided by the value of the graphite resistance in ohms.

The curve in fig. 2 shows how the depolarization current varies with the externally applied E.M.F. The depolarization, apparently for a considerable range, is nearly proportional to the extent by which the potential difference at the small electrode has been displaced from its natural value. The ordinate of any point on this curve is the horizontal distance between a given point on the direct curve and the corresponding point on the indirect curve; the abscissa is the same as that of the given point on the direct curve. Since each of the curves has a maximum ordinate, they cross one another a second time. In the neighbourhood of the maxima the horizontal distances between the curves are not very accurately determinable; but the general nature of the depolarization curve is obvious.

Fig. 2.



The vertical dotted line in fig. 1 is drawn as nearly as possible through the highest point of the capillary curve. Immediately to the right of this line there is a dotted curve. The points required to determine this curve were obtained by bisecting the horizontal lines drawn between points on the direct curve corresponding to the same surface tension. Considering any horizontal line, therefore, the intercept made on it between the vertical line and the above dotted curve represents the extent by which a point on the descending branch departs from symmetry with the corresponding point on the ascending branch, with respect to the vertical axis. The whole curve, therefore, represents the manner in which the descending branch of the capillary curve departs from symmetry with the ascending branch, with respect to a vertical axis through the point of maximum surface tension. The internal resistance of the electrometer used in the experiment above described was certainly less than 100,000 ohms, and probably not much above 50,000 ohms. Hence the depolarization effect upon the form of the curve, due to the internal resistance of the electrometer, lay between 0·5 per cent. and 1 per cent. of the corresponding effect due to the external resistance of 10,000,000 ohms. From an examination of the horizontal distance between the ascending branches of the direct and indirect curves we therefore see that the depolarization effect (due to the internal resistance) upon the ascending branch of the direct curve is negligible within the limits of observation.

The ascending branch of the curve can, therefore, be taken to be sensibly independent of the depolarization. It is seen from the indirect curve, however, that the depolarization current continues to increase after the maximum is passed, and that, eventually, the rate of increase becomes very rapid. It is also evident from the curves that the rate at which the descending branch of the direct curve departs from symmetry with the ascending branch is very similar to the rate at which the depolarization current increases. The departure from symmetry might, therefore, be very well due to the depolarization.

In order to determine whether the depolarization is the sole cause of the observed flattening of the direct curve, an accurate knowledge of the relation between the graphite resistance and the internal resistance of the electrometer would be necessary. But an approximate knowledge of this relation is quite sufficient to show that the depolarization must soon affect the form of the curve. Thus, to take an example, the horizontal distance between the direct and indirect descending branches for a surface tension corresponding to 150 is not less than 64 horizontal divisions (see fig. 1), equivalent to a potential difference of 1600 (= 1·6 × ·28 volt), and even if the electrometer resistance is not above 50,000 ohms, the effect of the latter will be a displacement of the direct curve to the right to the extent of one-third of a horizontal division—a quite perceptible amount—due to the potential fall within the electrometer. As the actually observed displacement is considerably greater than the above, it seems probable that the flattening in the upper portion of the curve is not due to depolarization alone. This is rendered still more probable when the curve for such a substance as hydrochloric acid (in which the ascending branch is very much steeper than the descending) is considered.

Fig. 3.

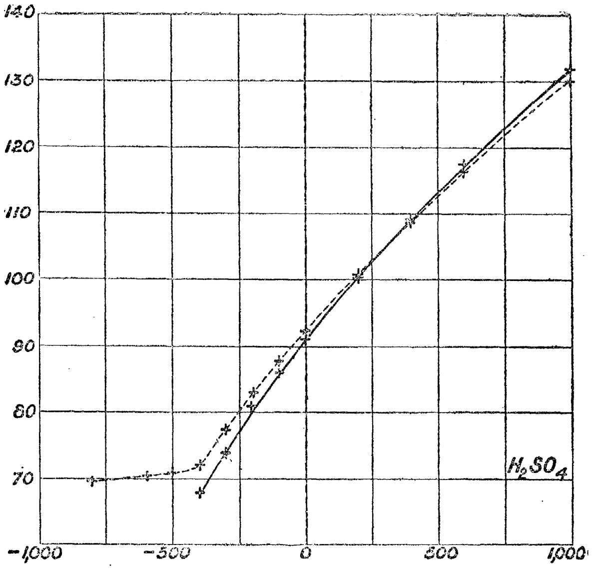
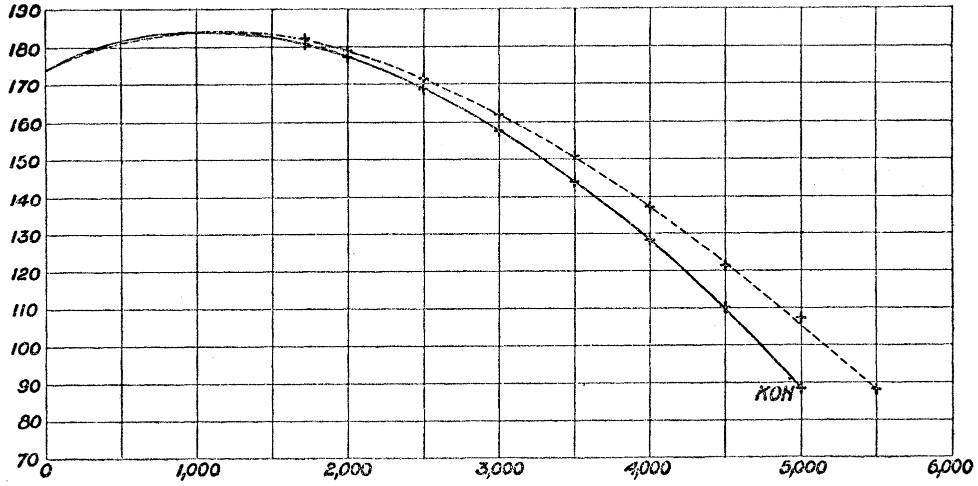


Fig. 3 gives a portion of another pair of direct and indirect curves, showing how the depolarization increases when the potential difference applied between the terminals of the electrometer is reversed in sign.

In order to show how the depolarization for kathodic polarization of the small electrode varies with the nature of the kation, curves (corresponding to those above described) are given for a dilute solution of caustic potash (fig. 4).

The curves show that in this case, for a given surface tension, the depolarization is very much less than when the kation is hydrogen of the same order of concentration. As is well known, the magnitude of the depolarization in an electrolytic cell depends not only upon the chemical nature of the ions, but also upon their concentration in the solution. This can be readily rendered obvious by the above method.

Fig. 4.



For the above solution of potash it is clear that within the range of the experiment the effect of depolarization upon the direct curve can be considered negligible. The same can be said of most of the solutions considered later.

The Second Hypothesis of the Lippmann-Helmholtz Theory.

The second hypothesis in the Helmholtz explanation of electro-capillary curves is that the electrical effect upon the surface tension is a purely electrostatic effect depending at a given potential difference upon the capacity of the electrode per unit area. It supposes that, in general, the capacity per unit area is independent of the chemical nature of the solution employed in the electrometer. From the approximately parabolic nature of some of the curves through a considerable portion of their course, the Helmholtz theory leads not only to the view that through the range considered the capacity per unit area is constant, but also makes it possible for the value of this capacity to be calculated. Assuming the inductive capacity of the dielectric of the double layer to be unity, the theory further allows an estimate to be formed of the distance between the parallel charges forming the double layer. That the distance so calculated is of the same order of magnitude as molecular distances calculated in other ways is, however, no proof of the validity of the Helmholtz view. For the distance between the layers, as so calculated, might have amounted to something very much larger without standing in opposition to other known data concerning molecular distances. In other words, there is no *à priori* objection to a view which supposes that the capacity per unit area of the common surface may really be much smaller than the Helmholtz view requires.* If such a view as this were true, the electrostatic effect would be insufficient to account for the observed variation in the surface tension. Assuming the potential difference, the existence of the electrostatic effect is scarcely open to doubt, it is only the relative importance of the effect that may be questioned. The electrostatic effect apart, the Helmholtz view assumes that the nature of the transition from the solution to the mercury is (through a considerable range) independent of the potential difference and of the nature of the solution.

Several published observations show that there are cases for which this assumption cannot be true. There are many facts in favour of the view that for a given potential difference there is a corresponding condition (of the partly physical, partly chemical kind, pictured by WARBURG) of the space bounded on the one side by the mercury, and on the other by the sensibly homogeneous solution. Obviously the surface tension will depend upon the nature of the transition through the surface layer. The mode of transition may depend only on the chemical nature of the solution and the potential difference across the space in which the transition takes place. On this view the electrostatic effect and the mode of transition for a given solution will be determined by the potential difference, and therefore the surface tension will be fixed by the potential difference. It remains to determine how the relation between the surface tension and the potential difference depends upon the chemical nature and concentration of the solution.

It is scarcely necessary now to set forth the arguments against the second hypothesis of the Helmholtz theory of the electrometer; but I shall endeavour to show by consideration of observations of the type held to throw greatest doubt upon the theory, that the first hypothesis gives results in close accord with the facts, and need not therefore be abandoned, even if the second should be proved untenable.

RELATION BETWEEN THE LIPPMANN-HELMHOLTZ THEORY AND OTHER THEORIES OF ELECTROCAPILLARY PHENOMENA.

It may be well to point out the relation such results bear to the theory of WARBURG, which is, perhaps, the most strongly advocated in opposition to the Helmholtz theory. Strictly speaking, the Warburg theory deals only with the ascending branch of the curve. It ascribes the increase in surface tension to the diminution in the concentration of a mercury salt in the neighbourhood of the capillary meniscus. According to WARBURG the effect of an E.M.F. established between the terminals of the electrometer is to convert the latter into a kind of concentration cell. Part of the E.M.F. of this cell will presumably be due to a potential difference within the electrolyte. The conclusions drawn later depend upon observations of the descending portions of capillary curves, which are usually much

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* *Cf.* WARBURG, 'Wied. Ann.,' 1890, vol 41.

more definite and more accurately measurable than the ascending portions; but unless the concentration E.M.F. within the electrolyte is supposed to be the same for quite different liquids subjected to very different degrees of polarization, there does not seem to be any simple method of reconciling the results with the Warburg theory. G. MEYER* has attempted to complete WARBURG'S theory of the phenomena by supposing that the descending portions of the curves are produced by formation of an amalgam between the mercury and the element forming the kation of the solution, while LUGGIN † has endeavoured to show that the descending branch of the curve is absent when the solution does not contain hydrogen. The experimental evidence adduced in favour of these views is mainly qualitative in nature. An extended examination of the quantitative relation between the capillary curves for differently concentrated solutions of the same salt shows that difficulties arise in the quantitative application of the idea that the surface tension in the descending branch depends only upon the concentration of the amalgam upon the electrode surface.

While it is unnecessary to deal with the nature of these difficulties at present, since they do not immediately concern the experiments first discussed, it may be pointed out that if the first hypothesis of the Helmholtz theory be true, it is possible to trace (by means of the capillary curves) the relation between the variation of the potential difference at the capillary electrode, the surface tension and the nature and concentration of the electrolyte. Probably it is only by the investigation of the relation between these quantities that the value of the capillary curves, as a method of determining "single potential differences" in voltaic phenomena, can be definitely fixed.

THE DISCREPANCY BETWEEN THE LIPPMANN-HELMHOLTZ THEORY AND THE NERNST-PLANCK THEORY OF THE POTENTIAL DIFFERENCE BETWEEN SOLUTIONS.

The result, derived from the Helmholtz theory, that the E.M.F. which must be applied between the terminals of the electrometer to cause the capillary electrode to assume its maximum surface tension, is equal to the natural potential difference between the large electrode and the solution, is so important, if true, that this E.M.F. has been observed for a large number of solutions. It is, however, impossible to test directly the validity of the numbers so found, since no other independent means of determining single potential differences has, up to the present, been discovered—if we except the dropping electrode method (which will be referred to later).

We may set up and measure the E.M.F. of a cell of the type

$$\mathrm{Hg} \mid \mathrm{M_1X_1} \mathrel{\vdots} \mathrm{M_2X_2} \mid \mathrm{Hg},$$

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* MEYER, 'Wied. Ann.,' 45, 1892.

† LUGGIN, 'Zeits. f. Physik. Chemie.,' 16, 1896.

where M_1X_1 and M_2X_2 signify two solutions which have been examined in the capillary electrometer; but the E.M.F. found cannot be applied to test the Helmholtz theory of the electrometer unless we know the value of the potential difference between the two solutions.

The state of our knowledge of the potential differences between liquids is not satisfactory. Within recent years, however, NERNST,* starting from the dissociation hypothesis, has given a theoretical investigation for the case in which the two liquids are solutions of the same salt, but of unequal concentration. PLANCK† has extended the investigation to the case in which the liquids are solutions of different salts. In many cases the values found experimentally agree very closely with those calculated; but it must be borne in mind that in the experiments the potential difference between the liquids only formed part of the E.M.F. actually measured. For example, in testing the formula as applied to two solutions of potassium chloride of different concentrations, it is necessary to introduce a fresh hypothesis in order to calculate the difference between the potential difference between mercury, covered with calomel, and the stronger solution, and the potential difference between mercury, covered with calomel, and the weaker solution.‡ In order to show the nature of the agreement between the calculated values and those found experimentally, some results for KCl solutions are given below. In the first column are given the concentrations in gram equivalents per litre; in the second the observed E.M.F.s of cells of the type;

$$\mathrm{Hg}\;\Big|\;\underset{\text{dilute}}{\mathrm{HgCl}\quad\mathrm{KCl}}\;\Big\vdots\;\underset{\text{concentrated}}{\mathrm{KCl}\quad\mathrm{HgCl}}\;\Big|\;\mathrm{Hg},$$

and in the third the calculated values of these E.M.F.s.

Concentrations. Gram equivalents per litre.	Observed E.M.F.	Calculated E.M.F.
	volts.	volts.
3·0 and 0·5	·0443	·0402
1·0 ,, 0·1	·0533	·0525
0·5 ,, 0·1	·0359	·0367
0·1 ,, 0·05	·0162	·0162
0·1 ,, 0·02	·0387	·0380
0·1 ,, 0·01	·0545	·0548
0·05 ,, 0·01	·0387	·0384

These observations form part of a series of experiments which will be described later.

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* NERNST, 'Zeits. f. Physik. Chemie,' 4, 1889.

† PLANCK, 'Wied. Ann.,' 39, 1890, and 40, 1890; *cf.* also NEGBAUR, 'Wied. Ann.,' 44, 1891.

‡ NERNST, 'Zeits. f. Physik. Chemie,' 4, 1889.

In a cell of the type

$$\mathrm{Hg} \,\Big|\, M_1X_1 \;\vdots\; M_2X_2 \,\Big|\, \mathrm{Hg}$$

let π_{n_1} and π_{n_2} be the respective potential differences between mercury and the solutions (calculated on the Helmholtz theory of the capillary electrometer), and let π_{12} be the potential difference between the liquids and π_e the observed E.M.F. of the cell, then we should have

$$\pi_e = \pi_{n_1} - \pi_{n_2} + \pi_{12}.$$

Rothmund has made observations upon cells of this type and has found values for π_e, π_{n_1} and π_{n_2} for a number of different solutions. The following table gives the results of some of his experiments :—

M_1X_1.	M_2X_2.	π_e.	π_{n_1}.	π_{n_2}.	$\pi_e - (\pi_{n_1} - \pi_{n_2})$.
nKCl	nKI	·349	·560	·437	·226
nKCl	nKCNS	·172	·560	·534	·146
$n\mathrm{Na_2S}$	nKCl	1·006	·560	— ·030	·416

He estimates the possible error in the determination of π_{n_1} and π_{n_2} from the curves to be not greater than 0·01 volt.*

Referring to such experiments, Nernst says :—"While, therefore, the Helmholtz hypothesis concerning electrocapillarity is found to be in good agreement with the osmotic theory . . . as far as the qualitative side of the phenomena goes, we come upon serious contradictions so soon as we proceed to a quantitative comparison. As results of the electrocapillary method of measuring contact potentials, we obtain the following table :—

$\mathrm{HCl} \mid \mathrm{H_2SO_4}$	·025	·010
$\mathrm{KCl} \mid \mathrm{HCl}$	·022	·028
$\mathrm{KCl} \mid \mathrm{KCNS}$	·161	·000
$\mathrm{KCl} \mid \mathrm{KI}$	·247	·000
$\mathrm{KCl} \mid \mathrm{Na_2S}$	·419	·000

Column 1 gives the symbols of the solutions examined ; column 2 contains the values of the potential differences between them deduced from the Helmholtz theory of the electrometer ; and column 3 gives the values of the same potential differences calculated according to the osmotic theory. The differences are great, and not explicable as errors of observation."†

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* Rothmund, 'Zeits. f. Physik. Chemie,' 15.

† Nernst, 'Wied. Ann.,' 58, Beilage, 1896.

SOLUTIONS OF POTASSIUM CHLORIDE AND POTASSIUM IODIDE.

1. *The Potential Difference between Equally-concentrated Solutions.*

The experiments show that the Helmholtz theory of the electrometer and the Nernst-Planck calculations of the potential differences between solutions cannot both be true. While there are many facts in favour of the view that the Nernst-Planck hypothesis gives the quantitative expression for the potential difference between two solutions, there is one result calculated from the hypothesis which seems to possess greater weight than any of the others, since it would seem to be a consequence of almost any form of diffusion hypothesis. This is the result that the potential difference between equally-concentrated solutions of potassium chloride and potassium iodide is so small that in measurements of the type with which we are concerned it can be taken to be zero.

KOHLRAUSCH has investigated the electrolytic conductivity of solutions of KCl and KI for different degrees of dilution, and an examination of his numbers shows the relative amount of ionization in equally-concentrated solutions of the two salts may be considered identical when the solutions do not contain more than 0·01 gramme molecule per litre ($\frac{1}{100}$th normal). Even when the strengths correspond to a gramme molecule in 2 litres ($\frac{1}{2}$ normal) the coefficients of ionization only differ by about two per cent.* Again, according to the most recent values, the ionic velocities of chlorine and iodine are practically identical.† When, therefore, dilute solutions of KCl and KI of equal strength are brought into contact there can be no tendency of the potassium ions to diffuse, while the chlorine and iodine ions will tend to diffuse with equal velocities across the common surface. Granting the ionic hypothesis we may, therefore, safely assume that no forces which tend to alter the quantity of electricity in the unit of volume act across the surface of separation between the liquids, and that, therefore, no potential difference will arise between the liquids.

2. *The Nature of the Electrocapillary Curves for the same Solutions.*

For the reason given above I have carefully examined the relation between the capillary curves for KCl and KI in order to determine further the result of the hypothesis that the potential difference between equally-concentrated solutions of KCl and KI is zero.

(a.) *General character of electrocapillary curves.*

The behaviour of the meniscus in the capillary electrometer is in general very different in the "ascending" portion of the curve from what it is in the "descending"

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* KOHLRAUSCH, 'Wied. Ann.,' vol. 26, 1885.

† KOHLRAUSCH, 'Wied. Ann.,' vol. 50, 1893.

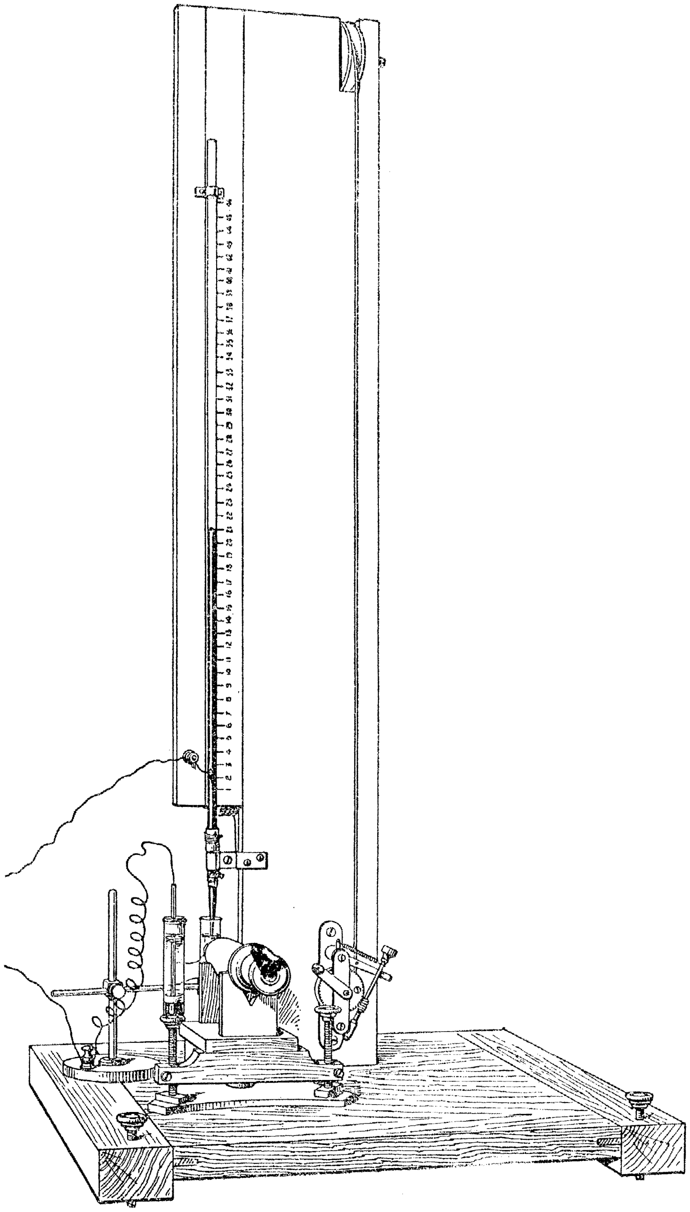
portion. In the ascending portion the mercury is often apparently sluggish, and the surface tension becomes difficult to measure. Further, the surface tension may take up a certain value immediately after a given potential difference is established between the terminals of the electrometer, and then fall gradually as the time of contact continues. In contrast with this, the surface tension in the descending portion of the curve is almost always very definite. Moreover, while the form of the ascending portion is widely different for solutions with chemically different anions, and even noticeably different for unequally concentrated solutions of the same salt, the form of the descending portion, for a considerable part of its course, is the same (within the limits of experimental error) for equally-concentrated solutions of quite different salts, and only varies very slightly for unequally concentrated solutions of a given salt.

(b.) *Definite nature of the descending branches.*

While therefore both the ascending and descending branches have been observed, the first conclusions are based upon observation of the descending portions of the curves. These were definite and amenable to quantitative treatment.

(c.) *Method adopted in examining the electrocapillary curves, and discussion of the degree of accuracy attainable in the experiments.*

The form of electrometer that I have used has a movable mercury reservoir in direct communication with the mercury column supported by the surface-tension effect at the capillary electrode. The mercury reservoir can be raised or lowered by means of a flexible cord, wound upon a bobbin, having a tangent-screw fine adjustment. By means of this arrangement the small electrode can be maintained at a constant position in the capillary tube. The diameter of the capillary—the same one was used in determining the curves for a large number of solutions—was about 0·003 centim., and the usual length of the column of solution between the meniscus and the point of the capillary was 0·057 centim. The resistance of such a column (supposed cylindrical) would, if the solution were normal KCl at 18°, be approximately 83,000 ohms. The position of the capillary meniscus was fixed by means of a scale within the microscope. The apparent magnitude of a division of this scale is about 1·5 millim. Every tenth division of the scale is marked. When the position of the microscope is so adjusted that the zero of the micrometer scale coincides with the end of the capillary, the fortieth division (marked 4) of the scale is practically in the centre of the field. The meniscus was always made to coincide as nearly as possible with the central division of the scale. The height of the mercury column, supported by the capillary electrode, when possessing its maximum surface tension in such a solution as dilute sulphuric acid, was about 440 millims. The variation of the surface tension was observed by means of a scale divided into millimetres placed directly behind the mercury column. The greatest error in the scale division was about 1 part in 500. The conclusions first drawn from the curves are practically independent of the accuracy of the division of the scale. The zero of this scale was about 12·4 centims. above the capillary point, so that the reading corresponding to the maximum surface tension, in dilute sulphuric acid, was about 31·6 centims. The position of the summit of the mercury column relative to the scale could be determined to within about a tenth of a millimetre. It would not be difficult to arrange for a greater degree of accuracy in this measurement; but, apart from the increase in the time occupied by the observations, which more delicate determination would involve, the above error does not exceed that introduced from other causes. Usually the solution to be examined was placed in a Clark cell tube of the Rayleigh H form.



The mercury forming the large electrode was placed at the bottom of one limb; the capillary electrode dipped into the other limb. In order that the definition of the capillary meniscus might be as good as possible, the capillary was placed close to the side of the limb that received it. After the curve for the solution had been determined, the H tube, containing it, was removed and replaced by another containing a different solution. It would have been very inconvenient to have worked always with the same H tube, as in many cases it was desirable to allow the solution to stand some considerable time over mercury before examining it in the electrometer. A number of H tubes were used, and naturally these were not precisely similar. In every case the definition of the capillary meniscus, when at the fortieth division of the scale, was made as good as possible; but it did not always happen that the definition of the capillary point was then correspondingly good. However, the maximum error in the setting of the capillary point was not greater than about one of the small scale divisions, while it could usually be set at the zero within two-tenths of a small scale division. The capillary meniscus could be readily set at the fortieth division with an error of less than one-tenth. An error of a scale division in the setting of the meniscus produced a maximum error of about ·4 millim. in the reading of the summit of the mercury column. Under ordinary circumstances, therefore, the error introduced into the surface tension observations by the necessary replacement of one H tube by another was not greater than ·08 millim.

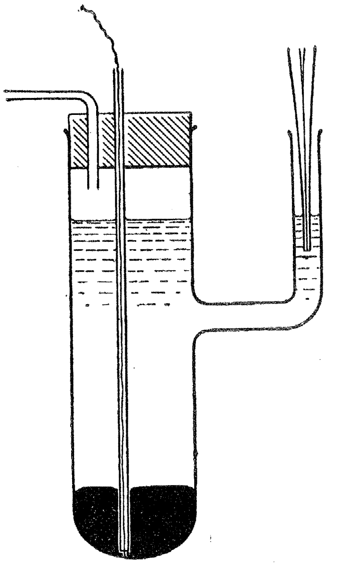
In order to remove one solution from the interior of the capillary tube before the introduction of the succeeding one, the following method of procedure was adopted. The capillary tube was immersed in a beaker of distilled water, and by alternately lowering and raising the mercury reservoir, the water could be drawn into the tube and then again expelled along with a little mercury. This process was repeated several times, the excursions of the meniscus in each case being very much longer than any that occurred during the experiments, as the result of electrical effects. The beaker was then withdrawn, and as much of the water as possible was removed from the capillary. A similar process was then adopted in order to fill the capillary with the solution next to be examined. To test the sufficiency of this treatment, a second set of observations upon a given liquid was made, several other solutions having been used in the electrometer during the interval. The first and second sets were found to agree within the limits of experimental error. In a case where one solution was followed by a more concentrated one of the same salt, the intermediate operation with distilled water was, of course, unnecessary.

The potential difference between the terminals of the electrometer was varied by means of an ordinary potentiometer arrangement. The potentiometer circuit consisted usually of a secondary cell (E.M.F. about 2·03 volts) and two resistance boxes in series. The sum of the resistances introduced into the circuit by these boxes always amounted to 10,000 ohms. Usually the resistance in each box was altered by 500 ohms at a time, so that the corresponding change in the potential difference applied between the electrometer terminals was about a tenth of a volt. The probable error of each of the box resistances was less than a tenth per cent., and the constancy of the potentiometer current was tested by means of a standard Clark cell, of which the E.M.F. at 15° was known to be within one-tenth per cent. of 1·434 volts. The accuracy of the potential measurement was therefore considerably greater than that which could be conveniently given to the surface tension observations.

(d.) *The Electrocapillary Curves for* KCl *and* KI.

1. *Preliminary Experiment.*—Before proceeding to the experiments of the ordinary capillary electrometer type, mention may be made of a simple means by which very suggestive results as to the relation between capillary curves may be obtained.

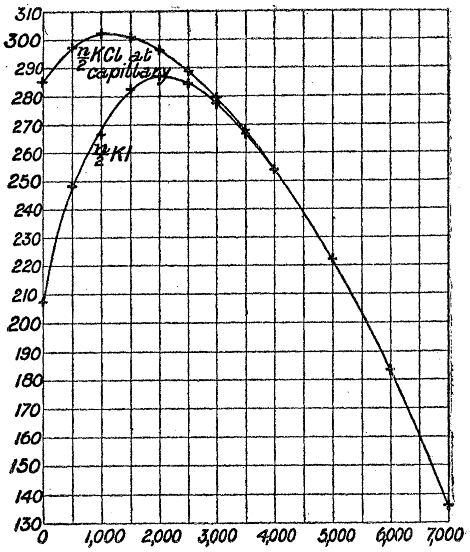
A vessel for containing the solution is constructed of the shape shown in the figure.



The mercury forming the large electrode is placed at the bottom of the main tube. The point of the capillary is brought within the smaller tube. The vessel is first filled with a solution of one of the salts (say $\frac{1}{2}n$ KI), and the capillary curve is determined. Withdrawing air from the apparatus by means of the side tube at the top of the main tube, the liquid rises in the latter and falls in the narrow tube. After the small tube has been nearly emptied, it is filled to the level of the liquid in the main tube with a solution of the other salt (say $\frac{1}{2}n$ KCl), and the capillary curve is again taken.

Fig. 5 shows the forms of the resulting curves for the solutions in question. The numbers from which the curves were constructed are as follow :—

Fig. 5.



Applied E.M.F.	$\frac{1}{2}n$ KI.	$\frac{1}{2}n$ KI with capillary in $\frac{1}{2}n$ KCl.
0	20·75	28·5 ?
500	24·9	29·75
1000	26·69	30·23
1500	28·3	30·1
2000	28·71	29·69
2500	28·47	28·88
3000	27·73	27·88
3500	26·65	26·7
4000	25·39	25·38
5000	22·2	22·2
6000	18·3	18·3
7000	13·52	13·55

The surface tensions in the ascending branches of the curves were somewhat uncertain and difficult to measure. The descending branches, however, were quite definite. It is seen that when the E.M.F. exceeded a value corresponding to the abscissa 4000 (= about ·8 volt) the curves were identical. This result can be very readily explained on the double layer view of polarization in an electrolytic cell considered at the beginning of the paper, if we assume that the potential difference between $\frac{1}{2}n$ KI and $\frac{1}{2}n$ KCl can be neglected, and that there is no appreciable concentration E.M.F. within the liquid. Since the potential difference at the large electrode has not been altered between the two sets of experiments, the potential difference $(\pi_e - \pi_n)$ at the small electrode for a given applied E.M.F. will be the same for both curves. When the applied E.M.F. is less than ·8 volt., the surface tension does not depend merely upon the potential difference at the small electrode, but also upon the chemical nature of the solution. Now the solutions are the same in every respect except that the anion in one is iodine, and in the other chlorine. Until the potential difference reckoned from the solution to the electrode reaches a certain value the effect of the anion upon the surface tension (*i.e.*, in determining the mode of transition from the solution to the mercury) is appreciable; but this effect gradually diminishes and finally disappears, as is shown by the fact that the form of the curve (beyond 4000) is independent of the nature of the anion.

From this point of view it is obviously futile to consider that the highest point of the iodide curve corresponds of necessity to zero potential difference between the KI solution and the mercury electrode, since it might equally well be argued that the highest point of the curve obtained with KCl at the capillary corresponded to zero potential difference between the mercury and the KCl. If there is no appreciable potential difference between the KI and the KCl both results cannot be true. The potential differences in the two cases (maximum surface tension) must differ by about 0·2 volt, or else the potential difference between $\frac{1}{2}n$ KI and $\frac{1}{2}n$ KCl must be about 0·2 volt.

In the face of evidence that there is a chemical effect of the anion upon the surface tension, and that this effect increases as the potential of the liquid with respect to the electrode decreases, it does not seem advisable to say more than that the potential difference (reckoned from the solution to the electrode) is considerably less at the maximum surface tension when the solution is KCl than when it is KI. The marked depression of the maximum value of the surface tension observable in the case of potassium iodide solutions is one of the characteristic features of the curves dealt with by ROTHMUND—the actual fact of the depression was apparently first noticed by GOUY;* but the depression is really a perfectly general phenomenon. The amount of depression depends upon the concentration of the solution as well as upon its chemical nature. The depression for concentrated solutions of chlorides is very pronounced, and for dilute solutions it can readily be observed that the maximum value of the surface tension rises as the concentration diminishes. It is obviously an effect which does not depend upon the density of the solution. For example, a saturated solution of caustic potash (which is soluble in about half its weight of water) has as high a maximum surface tension as a half-normal solution of potassium chloride. The effect of the ions (apart from the electrostatic effect) upon the surface tension would appear to depend, for a given potential difference, upon their nature and concentration in the solution. Whether the surface tension in the neighbourhood of the maximum is ever controlled by the electrostatic effect alone, depends (on this view) upon whether, when the potential difference between the solution and the electrode is small, the nature and concentration of the ions is such that their non-electrical effect upon the surface tension can be neglected.

In the case above considered the curves are identical when the applied E.M.F. exceeds 0·8 volt. The subsequent variation of the surface tension is therefore

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* 'Comptes Rendus,' vol. 114, 1892.

presumably independent of the nature of the anion; but it is obvious that we obtain no information from the curves as to whether their subsequent course is free from any non-electrostatic influence depending upon the kation. For the kation is the same and of the same concentration in the two solutions. It is, however, easy to extend the above observations so as to show that (granting the Nernst calculation gives at least approximately the potential difference between unequally concentrated solutions of the same salt), although the *form* of the lower portion of the descending curve varies very little with the strength of the solution, yet the surface tension for a given potential difference depends upon the strength of the solution. From this it would appear that the surface tension does not depend upon the electrostatic effect alone even when the anion effect has presumably disappeared; but that, in fact, there is also a kation effect which becomes evident as the solution becomes increasingly positive with regard to the electrode.

2. *Final experiments showing the agreement of the first hypothesis of the Lippmann-Helmholtz theory with the Nernst-Planck theory of the potential difference between* KCl *and* KI.—We may, however, first apply to the ordinary electro-capillary curves for equally concentrated solutions of KI and KCl, the result suggested by the curves already given, that ultimately the descending branch of either curve is practically unaffected by the nature of the anion, and that if it is then influenced by the kation, the nature of the influence is such that, in equally concentrated solutions of salts possessing the same kation, the potential difference for a given surface tension is the same in both solutions. It is found that the descending branches eventually approximate very closely to parallelism. Considering the parallel portions, let π_e be the E.M.F. required to be applied between the terminals to produce a given surface tension for the KCl solution, and let π_e' be the E.M.F. required to produce the same surface tension for the KI solution. Then $\pi_e - \pi_e'$ is very approximately constant. Let $-\pi_n$ be the natural potential difference between the KCl solution and mercury (the electrode being considered positive to the solution), and let $-\pi_n'$ be the corresponding quantity for the KI solution. Then on the first hypothesis of the ordinary electrometer theory (applicable to any electrolytic cell), the potential differences between the solution and the capillary for the two points of equal surface tension (one on each curve) are

$$\pi_e - \pi_n \qquad \text{and} \qquad \pi_e' - \pi_n'$$

respectively. Now if we suppose the potential difference is the same in the two cases because the surface tension is the same, we get

$$\pi_e - \pi_n = \pi_e' - \pi_n'$$

or

$$\pi_n - \pi_n' = \pi_e - \pi_e' = a,$$

where a, an observable quantity, is represented by the horizontal distance between the parallel portions of the curves. Let now a cell be constructed of the form

$$\mathrm{Hg}\;\Big|\;\mathrm{KCl}\;\vdots\;\mathrm{KI}\;\Big|\;\mathrm{Hg}$$

and let its observed E.M.F. be b, and suppose π_l is the potential fall from the KCl to the KI solution. Then

$$\pi_n - \pi_n' + \pi_l = b.$$

If $\pi_l = 0$, we must have

$$a = b.$$

The following experiments show the observed relation between a and b.

E.M.F. applied to electrometer [1000 = ·202 volt].	Surface tension readings.		Horizontal distance between parallel portions of curves. (a.)	Calculated E.M.F. of cell $\mathrm{Hg}\vert\mathrm{KCl}\vdots\mathrm{KI}\vert\mathrm{Hg}$ assuming P.D. between KCl and KI negligible.	Observed E.M.F. of cell $\mathrm{Hg}\vert\mathrm{KCl}\vdots\mathrm{KI}\vert\mathrm{Hg}$. (b.)
	$\frac{n}{2}$ KCl.	$\frac{n}{2}$ KI.		volt.	
0	23·5	20·39	1975 ± 6	·3990 ± ·0012	1950 (max.) = ·3940 volt.
500	26·0	24·8			
1000	28·0	27·1			
1500	29·21	28·29			
2000	30·0	28·71			
2500	30·49	28·5			
3000	30·6	27·81			
3500	30·29	26·78			
4000	29·69	25·48			
4500	28·90	24·0			
5000	27·9	22·35			
5500	26·75	20·51			
6000	25·41	18·55			
6500	23·95				
7000	22·29				
				Calculated E.M.F. on ordinary Helmholtz theory, assuming P.D. between KCl and KI to be zero.	
				·162 volt (approx.)	

E.M.F. applied to electrometer [1000 = ·2027 volt].	Surface tension readings.		Horizontal distance between parallel portions of curves. (*a.*)	Calculated E.M.F. of cell Hg | KCl ⋮ KI | Hg assuming P.D. between KCl and KI to be negligible.	Observed E.M.F. of cell Hg | KCl ⋮ KI | Hg. (*b.*)
	$\frac{n}{10}$ KCl.	$\frac{n}{10}$ KI.			
				volt.	
0	24·78	19·9 ?			
500	27·40	25·6			
1000	29·0	28·34			
1500	30·2	29·73			
2000	30·65 ?	30·3			
2500	31·33	30·2			
3000	31·41	29·57	1725 ± 6		1729 ± ·5 = ·3503 volt.
3500	31·2	28·6			
4000	30·7	27·49		·3496 ± ·0012	
4500	29·99	26·13			
5000	29·1	24·65			
5500	28·0	22·99			
6000	26·72	21·11			
6500	25·33	19·13			
7000	23·79	16·9			
7500	22·0	14·43			
8000	20·01	11·73			
8500	17·9				
9000	15·6				
	E.M.F. for maximum surface tension			Calculated E.M.F. of cell assuming P.D. between KI and KCl zero, on ordinary Helmholtz theory	
	$\frac{n}{10}$ KCl.	$\frac{n}{10}$ KI.			
	2800 ± 50	2200 ± 50		·122 (approx.)	

<table>
<tr><th rowspan="2">E.M.F. applied to electrometer [1000 = ·2027 volt].</th><th colspan="2">Surface tension readings.</th><th rowspan="2">Horizontal distance between parallel portions of curves.
(a.)</th><th rowspan="2">Calculated E.M.F. of cell Hg | KCl ⋮ KI | Hg assuming P.D. between KI and KCl zero.</th><th rowspan="2">Observed E.M.F. of cell Hg | KCl ⋮ KI | Hg.
(b.)</th></tr>
<tr><th>$\frac{n}{20}$ KCl.</th><th>$\frac{n}{20}$ KI.</th></tr>
<tr><td></td><td></td><td></td><td></td><td>volt.</td><td></td></tr>
<tr><td>0</td><td>25·1 ?</td><td>19·95 ?</td><td></td><td></td><td></td></tr>
<tr><td>500</td><td>27·4 ?</td><td>25·3</td><td></td><td></td><td></td></tr>
<tr><td>1000</td><td>29·0 ?</td><td>28·35</td><td></td><td></td><td></td></tr>
<tr><td>1500</td><td>30·18</td><td>29·92</td><td></td><td></td><td></td></tr>
<tr><td>2000</td><td>30·99</td><td>30·57</td><td></td><td></td><td></td></tr>
<tr><td>2500</td><td>31·45</td><td>30·49</td><td>1663 ± 6</td><td></td><td>1668 ± 0·5</td></tr>
<tr><td>3000</td><td>31·5</td><td>29·9</td><td></td><td></td><td>=</td></tr>
<tr><td>3500</td><td>31·3</td><td>29·0</td><td></td><td></td><td></td></tr>
<tr><td>4000</td><td>30·85</td><td>27·98</td><td></td><td>·3371</td><td>·3381 volt.</td></tr>
<tr><td>4500</td><td>30·2</td><td>26·72</td><td></td><td>± ·0012</td><td></td></tr>
<tr><td>5000</td><td>29·38</td><td>25·31</td><td></td><td></td><td></td></tr>
<tr><td>5500</td><td>28·32</td><td>23·78</td><td></td><td></td><td></td></tr>
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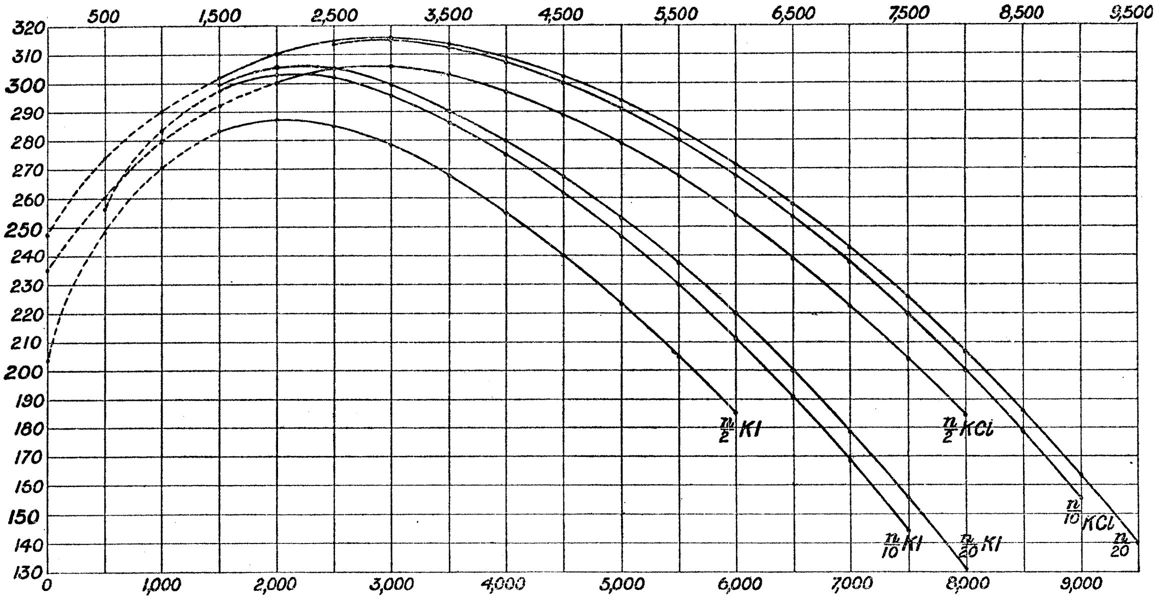
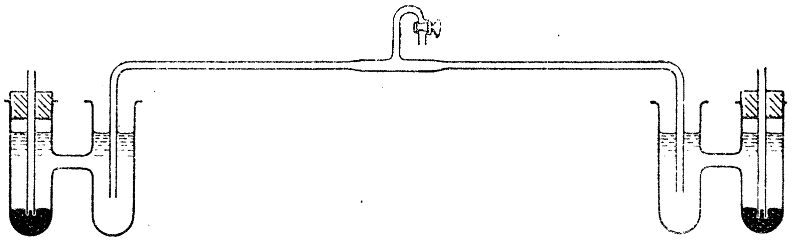
<tr><td>6500</td><td>25·79</td><td>20·0</td><td></td><td></td><td></td></tr>
<tr><td>7000</td><td>24·28</td><td>17·9</td><td></td><td></td><td></td></tr>
<tr><td>7500</td><td>22·6</td><td>15·6</td><td></td><td></td><td></td></tr>
<tr><td>8000</td><td>20·7</td><td>13·1</td><td></td><td></td><td></td></tr>
<tr><td>8500</td><td>18·62</td><td></td><td></td><td></td><td></td></tr>
<tr><td>9000</td><td>16·4</td><td></td><td></td><td></td><td></td></tr>
<tr><td>9500</td><td>14·0</td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="2">E.M.F. corresponding to maximum surface tension.</td><td></td><td rowspan="2">Calculated E.M.F. on ordinary Helmholtz theory, assuming P.D. between KCl and KI negligible.</td><td></td></tr>
<tr><td></td><td>$\frac{n}{20}$ KCl.</td><td>$\frac{n}{20}$ KI.</td><td></td><td></td></tr>
<tr><td></td><td>2950 ± 50</td><td>2150 ± 50</td><td></td><td>·162 (approx.)</td><td></td></tr>
</table>

The corresponding curves are shown in fig. 6. In order to find *a*, the horizontal distances were measured directly from the curves, as it was more convenient to do this than to observe the difference between the E.M.F.s required to produce the same surface tension in the different solutions. The E.M.F. of the cell was determined immediately after the corresponding curves had been observed. The same potentiometer circuit was used in the determination of the curves and of the cell E.M.F. The constancy of this circuit was checked by means of a standard cell.

The curves for the half normal solutions are not strictly comparable with the others; they were taken (with the same electrometer) about a year before the latter, under slightly different conditions. Although in the case of the later KCl solutions the mercury was covered with a layer of calomel, it was not necessary to add a "depolariser."* When any one of the above solutions has stood for several hours over mercury, the electro-capillary curve determined from it can be treated as independent of the time, since it remains constant for a much longer period than a complete set of observations occupies. The E.M.F. of the Hg | KCl ⋮ KI | Hg cell was determined by fixing the pair of H cells at a suitable distance apart, and adjusting so that the solutions in the cells were at the same level. The tubes were then joined across by a capillary siphon (about 1 sq. millim. in cross-section) of which the total length was about 60 centims. Contact within the cell was made by carefully drawing the solutions to the centre of the siphon. Care was further taken to avoid any considerable shaking of the mercury surfaces. The diagram following represents the cell.

Fig. 6.





The numbers given show that, for dilute solutions at any rate, the double-layer theory gives results in complete accord with the Nernst-Planck view of the potential difference between KCl and KI. If it be considered that the former is *à priori* the more probable of the two hypotheses, the results may be taken to corroborate the

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* *Cf.* NERNST, 'Zeits. f. Physik. Chemie,' 4, 1889.

views of Nernst, and the method may be further employed to test directly the potential differences between equally concentrated salts of the same metal. It will be shown below that there are apparently cases in which the method can still be applied even when the metals of the solutions are different.

The agreement for the half-normal solutions is less complete than for the more dilute solutions. This may be partly due to the fact that the observed E.M.F. of the cell was more uncertain in this case than in the others; but a much more probable explanation lies in the fact that the difference between the coefficients of ionization for KI and KCl respectively becomes appreciable when the solutions are not dilute. Before examining the effect of such a difference further, I will give the results of experiments upon some of the other solutions mentioned by Nernst.

Examination of other known Discrepancies between the Lippmann-Helmholtz Theory and the Nernst-Planck Theory of the Potential Differences between Solutions.

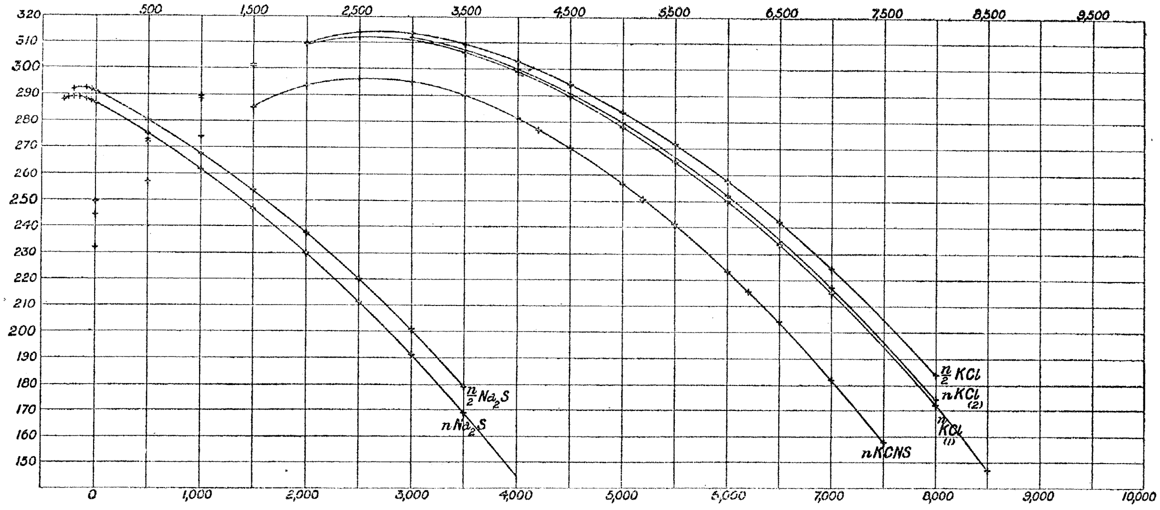
The tables which follow give the results of experiments conducted in a similar way to those already described.

E.M.F. applied to electrometer [1000 = ·2037 volt].	Surface tension Readings.		Mean horizontal distance between curves. (*a*.)	Calculated E.M.F. of Hg | KCl ⋮ KCNS | Hg assuming P.D. between KCl and KCNS to be negligible.	Observed E.M.F. of cell Hg | KCl ⋮ KCNS | Hg. (*b*.)
	n KCl.	*n* KCNS.			
0	24·75	23·2		volt.	
500		25·7			
1000	28·92	27·4			
1500		28·59			
2000	30·92	29·34			
2500		29·62			
3000	31·2	29·5			
3500		29·0			
4000	30·01	28·14			
4500		27·02			
5000	27·99	25·66	830 ± 6		820 ± 10
5500		24·1			=
6000	25·2	22·33		·1691	·1670 volt.
6500		20·4		± ·0012	± ·0020
7000	21·7	18·2			
7500		13·2			
8000	17·4	10·39			
8500					
9000		7·3			
4200		27·7			
5200		25·05			
6200		21·57			

E.M.F. applied to electrometer [1000 = ·204 volt].	Surface tension readings.		Mean horizontal distance between curves. (*a.*)	Calculated E.M.F. of $\mathrm{Hg} \mid \mathrm{KCl} \,\vdots\, \mathrm{Na_2S} \mid \mathrm{Hg}$ assuming P.D. between KCl and Na_2S to be negligible.	Observed E.M.F. of cell. $\mathrm{Hg} \mid \mathrm{KCl} \,\vdots\, \mathrm{Na_2S} \mid \mathrm{Hg}$ (*b.*)
	n KCl.	*n* Na_2S.		volt.	
− 300		28·8 ?			
− 250		28·89			
− 200		28·91			
− 150		28·9			
− 100		28·84			
− 50		28·78			
0	24·94	28·69			
500	27·3	27·5			
1000	28·95	26·18			
1500	30·1	24·68	4600 ± 20		4700 (max.)
2000	30·85	23·01			=
2500	31·21	21·15		·9384	·9588 volt.
3000	31·11	19·15		± ·0041	
3500	30·63	16·89			
4000	29·9	14·4			
4500	28·97	11·75			
5000	27·81			Calculated E.M.F. of cell, on ordinary Helmholtz theory, assuming P.D. between liquids zero	
5500	26·5				
6000	25·01				
6500	23·39				
7000	21·5				
7500	19·41				
8000	17·19				
8500	14·7			·581 (approx.)	
9000	12·0				

E.M.F. applied to electrometer [1000 = ·204 volt].	Surface tension readings.		Mean horizontal distance between curves. (a.)	Calculated E.M.F. of Hg │ KCl ⋮ Na_2S │ Hg assuming P.D. between KCl and Na_2S to be negligible.	Observed E.M.F. of cell. Hg │ KCl ⋮ Na_2S │ Hg (b.)
	$\frac{n}{2}$ KCl.	$\frac{n}{2}$ Na_2S.			
				volt.	
− 200		29·19			
− 100		29·23			
0	24·43	29·1			
500	27·2	28·02			
1000	28·89	26·79			
1500	30·1	25·39			
2000	30·96	23·8	4625 ± 25		4695
2500	31·4	22·0			=
3000	31·33	20·08		·9435	·9578 volt.
3500	30·95	17·91		± ·0051	
4000	30·29	15·59 ?			
4500	29·41				
5000	28·39			Calculated E.M.F. of cell on Helmholtz theory, assuming P.D. between KCl and Na_2S zero.	
5500	27·18				
6000	25·78				
6500	24·2				
7000	22·43				
7500					
8000	18·37				
8500					
9000	13·41			·581 (approx.)	

Fig. 7.



The corresponding curves are given in fig. 7. In the case of the curves for potassium sulphocyanide and chloride it is clear that the results again agree with the hypothesis that in these solutions, when the potential difference between the solution and the meniscus exceeds a certain value, the surface tensions are the same when the potential differences are equal. Conductivity data for KCNS are not available, so that it is impossible to say whether the ionic concentration is strictly the same for the two solutions; but if we may argue from the values for corresponding solutions of HCl and HCNS,* it would appear probable that the degree of dissociation of equally concentrated solutions of the salts is practically the same. The ionic velocities of the anions would also seem to be about the same.

THE RELATION BETWEEN THE NATURE OF THE KATION OF THE SOLUTION AND THE FORM OF THE ELECTROCAPILLARY CURVE.

Before the argument previously employed can be applied in the case of salts like KCl and Na_2S possessing different kations, it is necessary to assume that the effect of the kation upon the electro-capillary curve is independent of its chemical nature. The observations upon KCl, NaCl and HCl described below show that this is probably true. But apart from this there are uncertainties in the above experiments with sodium sulphide from which the others are free. It is difficult to prepare a standard solution of sodium sulphide. The solutions used were only approximately normal and half-normal. But besides this, the degree of dissociation of a normal sodium sulphide solution is probably considerably less than that of a normal potassium chloride solution. Hence the potential difference between the solutions is uncertain. Further, if the Na_2S solution is less concentrated than the corresponding KCl solution, the Na_2S descending curve will be relatively nearer the KCl descending curve than it would be if the ionic concentrations were equal (see below). This in itself might suffice to explain why the horizontal distance between the curves is less than that corresponding to the observed E.M.F. of the cell.

While it seems reasonable to suppose that if the uncertainity concerning the sodium sulphide were eliminated, the agreement would be as close as in the other cases, the experiments seem to leave little doubt as to which of the numbers quoted by NERNST (0·416 volt and zero) is nearer the true value of the potential difference between equally concentrated solutions of KCl and Na_2S.

Experiments with equally concentrated Solutions of Potassium and Sodium Chlorides.

The following experiments show the probability that for equally concentrated solutions of potassium and sodium salts the kation produces the same effect upon the surface tension.

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* OSTWALD, 'Journ. f. Prakt. Chemie,' 32, 1885.

E.M.F. applied.	Surface tension readings.					
	$\frac{n}{2}$ KCl.	$\frac{n}{2}$ NaCl.	$\frac{n}{10}$ KCl.	$\frac{n}{10}$ NaCl.	$\frac{n}{20}$ KCl.	$\frac{n}{20}$ NaCl.
0	24·09	24·31	24·78 ?	24·99	25·1 ?	25·22
500	26·99	27·08	27·4	27·42	27·4 ?	27·36 ?
1000	28·71	28·76	29·0	29·0	29·0 ?	28·9 ?
1500	29·95	30·01	30·2	30·21	30·18	30·1
2000	30·85 ?	30·89	30·65	31·0	30·99	30·95
2500	31·25	31·31	31·33	31·44	31·45	31·41
3000	31·25	31·3	31·41	31·47	31·5	31·5
3500	30·9	30·93	31·2	31·2	31·3	31·27
4000	30·28	30·31	30·7	30·7	30·85	30·81
4500	29·42	29·5	29·99	30·0	30·2	30·19
5000	28·41	28·5	29·1	29·11	29·38	29·38
5500	27·27	27·3	28·0	28·10	28·32	28·35
6000	25·9	25·95	26·72	26·83	27·13	27·18
6500	24·32	24·4	25·33	25·43	25·79	25·83
7000	22·62	22·7	23·79	23·89	24·28	24·31
7500	20·7	20·82	22·0	22·15	22·6	22·7
8000	18·6	18·7	20·01	20·22	20·7	20·81
8500	16·33	16·5	17·9	18·15	18·62	18·79
9000	13·80	14·01	15·6	15·89	16·4	16·59
9500	...	...	...	...	14·0	14·2
Mean temperature.	17°	16°	17°	17°	16·7°	17°

Fig. 8 shows the electro-capillary curves for half-normal, one-tenth normal, and one-twentieth normal solutions of potassium and sodium chlorides. In every case the mercury of the large electrode was covered with a layer of calomel before the introduction of the solution into the electrometer cell. The appreciable departure of the curves from one another at the lower surface tensions may be partly due to the appreciable effects of depolarization, since the conductivity of a KCl solution is about 20 per cent. greater than that of the corresponding NaCl solution. Apart from this departure at lower surface tensions, it is seen that the curves for corresponding solutions coincide within the limits of experimental error.

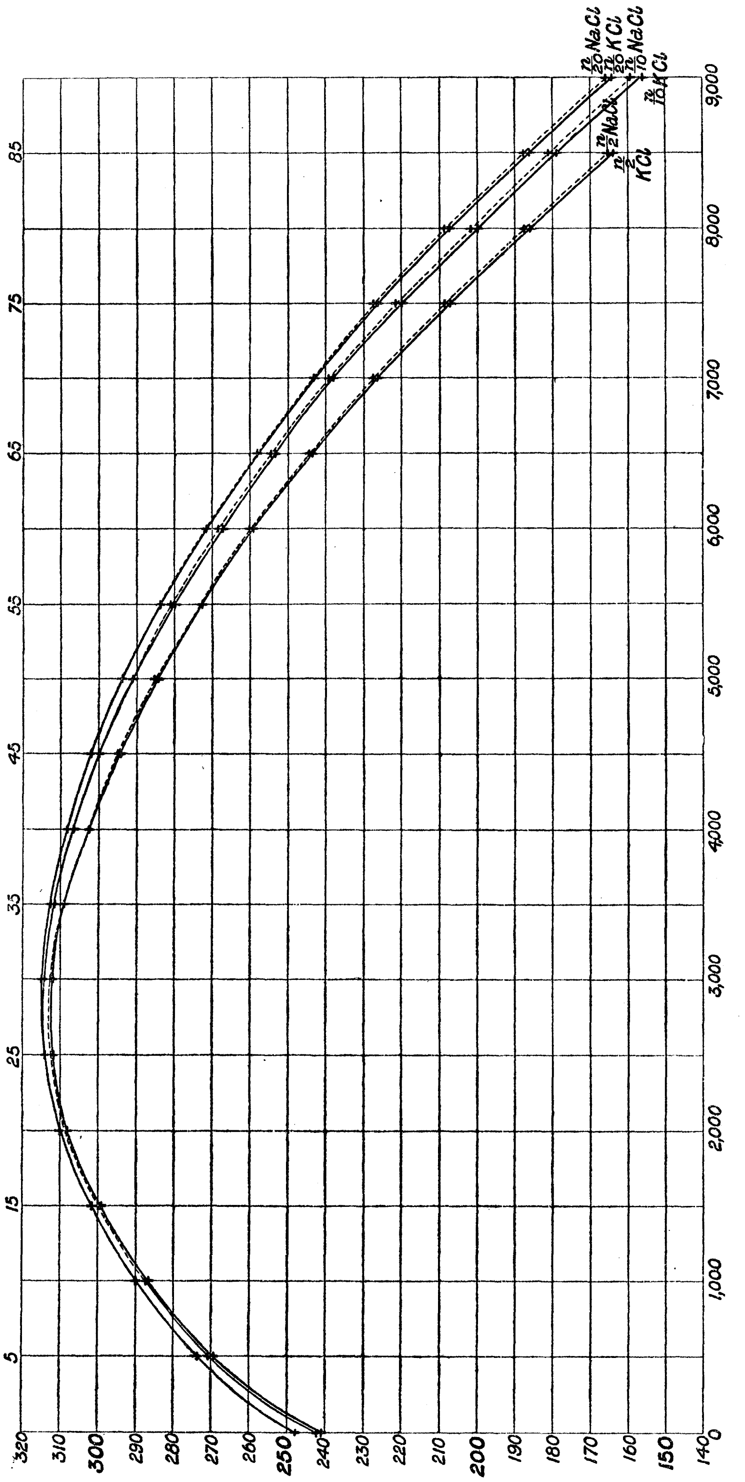
If we are to assume that the kations K and Na affect the surface tension in the same way, the E.M.F. of the cell of the type

$$\begin{array}{c|cc:cc|c} & & \mathrm{NaCl} & \mathrm{KCl} & & \\ \mathrm{Hg} & \mathrm{HgCl} & & & \mathrm{HgCl} & \mathrm{Hg} \end{array}$$

should be merely the potential difference between the solutions.

The following are the calculated potential differences between the solutions and the observed E.M.F.s of the cells:—

Fig. 8.



$\frac{n}{20}$ NaCl
$\frac{n}{20}$ KCl
$\frac{n}{10}$ NaCl
$\frac{n}{10}$ KCl
$\frac{n}{2}$ NaCl
$\frac{n}{2}$ KCl
5
15
25
35
45
55
65
75
85
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
0
1,000
2,000
3,000
4,000
5,000
6,000
7,000
8,000
9,000

		Observed.	Calculated.
$\frac{n}{10}$ NaCl	$\frac{n}{10}$ KCl	·0050	·0045
$\frac{n}{20}$ NaCl	$\frac{n}{20}$ KCl	·0045	·0045

From these results we see that, assuming the potential difference between the liquids is as calculated, the respective effects of Na and K on the electro-capillary curves are practically identical. To examine the effect when hydrogen is the kation, I have also performed similar experiments with hydrochloric acid of different strengths. The curves are practically the same as those for NaCl and KCl, with the exception that the hydrochloric acid curves eventually flatten out in a similar way to the sulphuric acid curve described earlier, and doubtless for a similar reason. Subsequently I hope to describe how the surface tension for a given potential difference depends upon the nature and concentration of the kation in the general case.

Relation between the Surface Tension for a Given Potential Difference and the Concentration of the Solution Employed in the Electrometer.

Following the same hypotheses as have been adopted above, it is easy to see, from the curves just given, the nature of the effect of the kation upon the surface tension. The surface tension for a given potential difference would seem to increase as the concentration of the solution diminishes, or conversely, for a given surface tension the potential fall from the solution to the electrode would seem to increase with diminishing concentration. Thus, to take the potassium chloride curves, suppose π_{n_2}, $\pi_{n_{10}}$, and $\pi_{n_{20}}$ are the natural potential differences between the large electrode and the solution (reckoned from the electrode to the solution) in the $\frac{n}{2}$, $\frac{n}{10}$, and $\frac{n}{20}$ solutions respectively. Considering the parallel portions of the curves, let π_{e_2}, $\pi_{e_{10}}$, and $\pi_{e_{20}}$ be the E.M.F.s required to be applied between the terminals in the respective cases, in order to produce a given surface tension. If the surface tension depends only on the electrostatic effect we should have

$$\pi_{e_2} - \pi_{n_2} = \pi_{e_{10}} - \pi_{n_{10}} = \pi_{e_{20}} - \pi_{n_{20}},$$

assuming, as in the previous cases, that there are no appreciable potential falls within the solutions, or that, if present, they are the same for all.

Suppose, now, that we measure the E.M.F.s of the cells

$$\mathrm{Hg} \,\Big|\, \mathrm{HgCl}\ \frac{n}{20}\ \mathrm{KCl} \,\vdots\, \frac{n}{10}\ \mathrm{KClHgCl} \,\Big|\, \mathrm{Hg}$$

and

$$\mathrm{Hg} \,\Big|\, \mathrm{HgCl}\ \frac{n}{10}\ \mathrm{KCl} \,\vdots\, \frac{n}{2}\ \mathrm{KClHgCl} \,\Big|\, \mathrm{Hg}$$

and find them to be π_2 and π_1 respectively. Then

$$\pi_2 = \pi_{n_{20}} - \pi_{n_{10}} + \pi_{21},$$

and

$$\pi_1 = \pi_{n_{10}} - \pi_{n_2} + \pi_{51},$$

where π_{21} and π_{51} are the potential differences between the unequally-concentrated solutions of KCl. Calculating the values of these by NERNST'S formula we get

$$\pi_{21} = -\cdot 0003 \text{ and } \pi_{51} = -\cdot 0007.$$

The observed E.M.F.s of the cells were

$$\pi_2 = \cdot 0162 \text{ and } \pi_1 = \cdot 0359,$$

from which we see that (assuming NERNST'S formula)

$$\pi_{n_{20}} - \pi_{n_{10}} = \cdot 0165,$$

and

$$\pi_{n_{10}} - \pi_{n_2} = \cdot 0366.$$

Now, from the curves

$$\pi_{e_{20}} - \pi_{e_{10}} = \cdot 0331\ (\pm \cdot 0006)$$

and

$$\pi_{e_{10}} - \pi_{e_2} = \cdot 0670\ (\pm \cdot 0006).$$

Hence, subtracting corresponding equations,

$$(\pi_{e_{20}} - \pi_{n_{20}}) - (\pi_{e_{10}} - \pi_{n_{10}}) = \cdot 0166$$

and

$$(\pi_{e_{10}} - \pi_{n_{10}}) - (\pi_{e_2} - \pi_{n_2}) = \cdot 0304,$$

whereas, if the surface tension variation had been due to a purely electrostatic effect,* we should have expected

$$(\pi_{e_{20}} - \pi_{n_{20}}) - (\pi_{e_{10}} - \pi_{n_{10}}) = 0$$

and

$$(\pi_{e_{10}} - \pi_{n_{10}}) - (\pi_{e_2} - \pi_{n_2}) = 0.$$

Disagreements of a similar kind are found when solutions of other strengths are examined. The same result can be very easily illustrated by means of the apparatus

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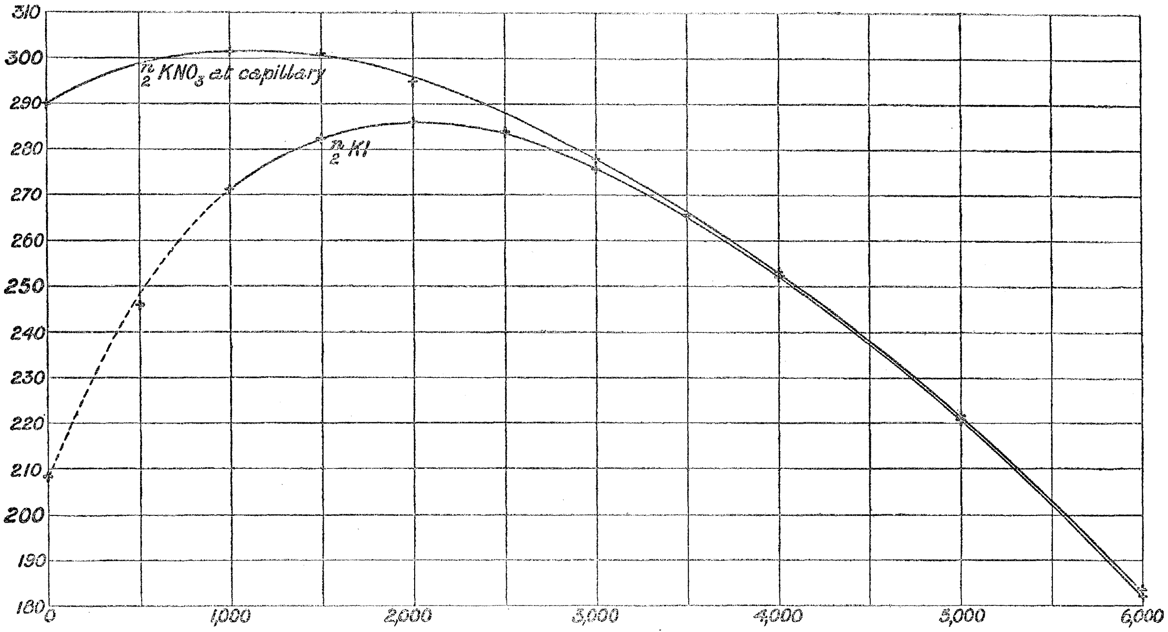
* It can also be shown from the above and similar experiments that the surface tension variation in the descending branch cannot, in general, be a purely amalgam effect.

first described. Fig. 9 shows a curve for $\frac{1}{2}n$ KI, and another for the same solution, with the exception that the $\frac{1}{2}n$ KI, in which the capillary was first immersed, was replaced by $\frac{1}{2}n$ KNO_3, the degree of dissociation of which is 16 per cent. less than that of $\frac{1}{2}n$ KI. The calculated potential difference between $\frac{1}{2}n$ KNO_3 and $\frac{1}{2}n$ KI is rather less than ·001 volt—an amount which would be barely perceptible on the scale to which the curves are drawn—so that the appreciable separation between the parallel portions of the curves is most probably due in part to the effect of the different concentrations of the potassium ions upon the surface tension.

Fig. 9.



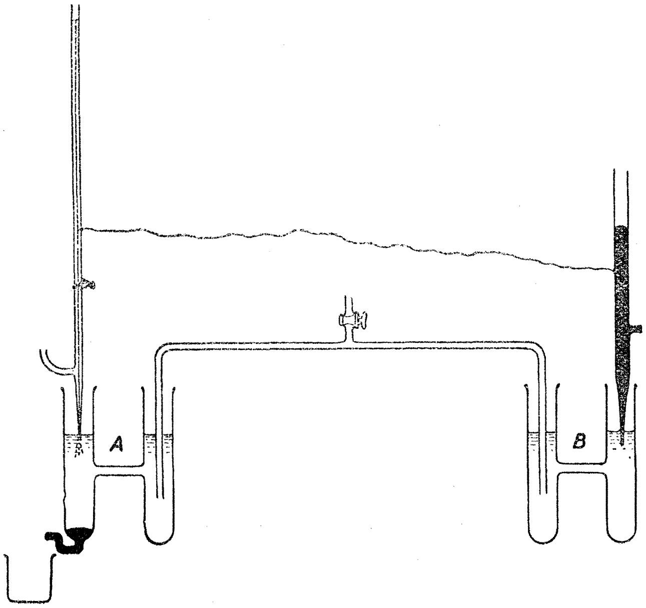
Since it is beyond the purpose of the present paper to deal with the quantitative nature of the possible ion effects upon the surface tension, it will be unnecessary to give further instances which show that the observed surface tension is, in general, partly determined by the chemical nature of the solution. It may, however, be remarked that there is nothing unusual in the supposition that as the potential difference reckoned from the solution to the electrode increases, the kation effect becomes pronounced, while conversely, when it diminishes, the anion effect becomes increasingly evident. For if the potential difference be altered in the above sense, through a sufficient range, we get an obvious combination of the mercury with the anion (and not simply a molecular layer of the compound) on the one hand, and with the kation (amalgam) on the other. Whether the formation of these compounds proceeds suddenly when the potential differences between the solution and the electrode reach certain amounts, or whether they are gradually led up to through intermediate stages in which the surface films contain only molecular quantities of the compounds, of gradually-increasing concentration, is a question concerning the answer to which we have imperfect knowledge.

Relation between the Electrocapillary Curves for KCl and KI and Dropping Electrode Measurements for Solutions of these Salts.

There is a point in connection with the explanation of dropping electrode phenomena which, as it is closely connected with the question of the potential difference between KCl and KI, may perhaps be mentioned here. If it be granted that the potential difference between $\frac{1}{2}n$ KCl and $\frac{1}{2}n$ KI can be considered negligible, it follows from the experiments described below that the potential difference between dropping mercury and KCl (under the conditions described by Paschen) is very different from that between dropping mercury and KI. And, at the same time, it follows that if the potential difference between a KCl solution and mercury is zero when the surface tension is a maximum, then, when the latter is a maximum in KI solution, the potential difference from the solution to the electrode has a considerable magnitude.

The result obtained by Paschen* (following up the experiments of Ostwald†) for chlorides and iodides, among other salts, that the E.M.F. required to produce the maximum surface tension for a given solution is practically identical with the E.M.F. of a cell containing the same solution and having as electrodes a similar large mercury electrode to that used in the electrometer, and a dropping electrode of which the jet becomes discontinuous in the surface of the solution seems, at first sight, a striking confirmation of the Helmholtz theory of the electrometer. But, in fact, it is sufficient for this result that the potential difference between mercury and the solution when the surface tension is a maximum is the same as the potential difference between the dropping electrode (of the Paschen type) and the solution.

A dropping electrode and a capillary electrode were connected up as in the diagram.



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* Paschen, 'Wied. Ann.,' 41, 1890.

† *Cf.* Ostwald, 'Lehrbuch,' 2, 938.

The mercury of the dropping electrode fell into the tube A, which had a vertical fine adjustment attached, so that the position of the liquid in it could be varied with respect to the point of the dropping electrode. The capillary electrode was immersed in the liquid of the vessel B. The two electrodes were directly connected by a wire, and A and B were connected by a siphon tube.

The surface tension of the capillary electrode was measured under four different conditions, viz., when—

1. A and B were filled with $\frac{1}{2}n$ KCl.
2. A and B were filled with $\frac{1}{2}n$ KI.
3. A was filled with $\frac{1}{2}n$ KCl and B with $\frac{1}{2}n$ KI.
4. A was filled with $\frac{1}{2}n$ KI and B with $\frac{1}{2}n$ KCl.

The capillary electrode formed part of the electrometer previously described, and the curves which it gave for the $\frac{1}{2}n$ KI and the $\frac{1}{2}n$ KCl respectively were first determined.

From the behaviour of the capillary meniscus it was easy to observe when the dropping electrode jet broke in the surface of the solution in B. If the jet were completely immersed in the liquid and if, then, the latter were gradually lowered, the surface tension of the capillary electrode in general increased correspondingly to a maximum value and then changed in the same way as it did when the dropping electrode was absent—showing that the communication between the electrodes had then ceased.

In cases 1 and 2 the mercury in the capillary electrode assumed (within the limits of experimental error) its maximum surface tension when the dropping electrode broke in the surface of the liquid in A. Thus, for $\frac{1}{2}n$ KCl the readings lay between 31·3 and 31·35; for $\frac{1}{2}n$ KI the reading for several observations was 29·41. The corresponding readings of maximum surface tension for the electro-capillary curves were 31·4 and 29·43.

In case 3 the capillary surface tension lay between 26·38 and 26·31, and from the behaviour of the capillary meniscus when the drop electrode jet broke above the liquid surface—the surface tension gradually decreased—it was evident that this corresponded to a point on the ascending portion of the $\frac{1}{2}n$ KI curve. The horizontal distance between surface tensions of 29·43 and 26·35 on the $\frac{1}{2}n$ KI curve corresponds to a difference in the applied E.M.F. of about ·28 volt. So that, if the potential difference between $\frac{1}{2}n$ KI and $\frac{1}{2}n$ KCl can be neglected, the conclusion from the above observations is that the potential difference between a Paschen electrode and the solution (reckoned from the latter to the former) is about ·28 volt. greater when the solution is $\frac{1}{2}n$ KI than when it is $\frac{1}{2}n$ KCl.

The observation in case 3 is corroborated by that in case 4. In this case, when the electric contact between the dropping electrode and the solution was on the point of breaking, the observed surface tension of the capillary lay between 30·48 and 30·5;

but the surface tension increased when the contact broke, showing that the number given corresponded to a point on the descending branch of the KCl curve. The horizontal distance between the maximum and 30·5 on the KCl curve is approximately the same as in the former case. It corresponds to a potential difference of about ·24 volt. Both results are somewhat uncertain, partly owing to the difficulty of determining the exact points of maximum surface tension on the capillary curves; but as the effects observed are so considerable, and as they are further corroborated by the results described below, there can be little doubt concerning their significance. The results can be further tested by experiments similar to PASÇHEN's by measuring the E.M.F.s of cells of the type

$$\text{Hg} \;\Big|\; \text{KI} \;\vdots\; \text{KCl} \;\Big|\!\!\downarrow ,$$

in which the vertical arrow signifies the dropping electrode. The following approximate results were obtained;—

$$\overset{+}{\text{Hg}} \;\Big|\; \frac{n}{2}\text{KCl} \;\vdots\; \frac{n}{2}\text{KCl} \;\Big|\!\!\downarrow^{-} \quad = \cdot 522 \text{ volt.}$$

$$\text{Hg} \;\Big|\; \frac{n}{2}\text{KCl} \;\vdots\; \frac{n}{2}\text{KI} \;\Big|\!\!\downarrow \quad = \cdot 784 \text{ ,,}$$

$$\text{Hg} \;\Big|\; \frac{n}{2}\text{KI} \;\vdots\; \frac{n}{2}\text{KI} \;\Big|\!\!\downarrow \quad = \cdot 383 \text{ ,,}$$

$$\text{Hg} \;\Big|\; \frac{n}{2}\text{KI} \;\vdots\; \frac{n}{2}\text{KCl} \;\Big|\!\!\downarrow \quad = \cdot 127 \text{ ,,}$$

The first and second results give ·262 volt and the third and fourth give ·256 volt as the difference between the potentials

$$\frac{n}{2}\text{KI} \;\Big|\!\!\downarrow \quad \text{and} \quad \frac{n}{2}\text{KCl} \;\Big|\!\!\downarrow .^{*}$$

The difference between the chemical effects during the dropping of mercury into

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[*] I have found, since this was written, that G. MEYER ('Wied. Ann.,' vol. 56, 1895) measured the E.M.F. of a cell of the type $\Big|\!\!\downarrow n\text{KCl} \;\vdots\; n\text{KI} \;\Big|\!\!\downarrow$ and found it to be ·284 volt. The observations described above are in accord with this result.

KI and KCl respectively is rendered evident if a drop of phenol phthalein solution is added to the solution in each experiment. The solution turns pink very much more rapidly in the case of the KI than in the case of the KCl, showing apparently that the combination of the mercury with the iodine is very much more rapid than with the chlorine, of the solution into which it is dropped, under the conditions described.

Summary.

1. The Lippmann-Helmholtz theory of the capillary electrometer contains two assumptions.

2. The first assumption would apply to any electrolytic cell. A deduction from it, which would apply to any cell having a large and a small electrode, is that the variation of the potential difference at the capillary electrode of an electrometer is the same as that of the applied electromotive force.

In order to trace the relation between surface tension and potential difference on the view that this first assumption is correct, it is necessary to eliminate the possible effect of depolarization upon the form of the electrocapillary curve—*i.e.*, the curve which shows the relation between the surface tension and the applied electromotive force. A direct method of examining the depolarization current is described and applied. An estimate of the magnitude of the depolarization effect is given, and the circumstances under which the effect may become appreciable are discussed.

3. The second assumption of the Lippmann-Helmholtz theory, that the electrocapillary phenomena are controlled by a simple variation of the electrostatic surface energy, leads to two conclusions, each of which is beset with difficulties.

(*a.*) The form of the electrocapillary curve is remarkably dependent upon the nature and concentration of the electrolyte, and depolarization is quite insufficient to account for the dependence.

(*b.*) The conclusion that the potential difference between the solution and the capillary electrode is zero when the surface tension has its maximum value, leads to the necessity for assuming large potential differences between certain solutions.

4. The hypothesis that the potential difference between equally concentrated solutions of potassium chloride and iodide is negligible possesses a high degree of probability. It has been shown by previous observers that if this hypothesis be true the points of maximum surface tension on the electrocapillary curves for the above solutions cannot have the significance which HELMHOLTZ's theory gives them.

It is shown in the paper that the first hypothesis of the Lippmann-Helmholtz theory is in striking accord with this hypothesis concerning the potential difference between KCl and KI when the very definite "descending" branches of the electrocapillary curves are considered.

5. If both the hypotheses just mentioned be true, we get the result that the surface tension of mercury (for a certain range of potential differences) in two solutions

is the same for a given potential difference between the mercury and the respective solutions, if the solutions are equally concentrated and possess the same kation.

6. An extension of this result shows that it is indifferent whether the kation be K, Na, or H.

7. The relation found for the KCl and KI curves can be extended to the other known cases in which the electrometer curves and liquid potential difference calculations seem to be contradictory, in such a way as to account for the apparent contradiction. Several of the cases are examined.

8. The results in 4, 5, and 6 would give a direct and accurate method of finding the potential differences between equally concentrated solutions, and could be extended to the case of solutions of different concentrations.

9. The probability that the electrocapillary curves are never completely free from influences other than electrostatic is shown by an examination of the relations between the curves for unequally concentrated solutions of the same salt.

10. In confirmation of results obtained by G. MEYER, in a slightly different way, it is shown that if the potential difference between KCl and KI is very small, the potential fall from a half-normal solution of KI to a dropping electrode of the Paschen type is about a quarter of a volt greater than that from a half-normal solution of KCl to the same electrode.

In the same way the potential fall from KI to mercury when the surface tension is a maximum is about a quarter of a volt greater than that from KCl to mercury when the tension of the surface separating the solution from the mercury is a maximum.

These results follow from direct observations with dropping electrodes, and give further support to the view that the first assumption of the Lippmann-Helmholtz theory is true and that the second is not.