ELECTROSTATIC MEASUREMENT OF ELECTRODE POTENTIALS.

BY ARTHUR W. EWELL.

THE determination of the difference of electrical potential of two electrodes dipping in a common electrolyte is simple and can be accomplished with a high degree of accuracy by several well-known methods. Measurement of the absolute potential difference between a single electrode and the electrolyte is difficult and the various methods which have been employed have yielded widely differing results.[1] Excellent bibliographies of this entire subject are accessible[2] and will not be repeated here. The papers of Borelius and Guyot referred to later are the only important memoirs which have appeared since these compilations.

HISTORICAL.

The different experimental methods for determining electrode potentials may be classified respectively as electro-capillary, endosmotic, capacity and electrostatic.

Mercury is naturally the electrode which has been employed for electrocapillary methods. Assuming that the absolute potential difference between mercury and an electrolyte results in the formation of a Helmholtz "double layer" which reduces the surface tension, Ostwald and others have concluded that when mercury in a capillary tube shows maximum surface tension the double layer is absent and that therefore the applied potential required to give the maximum surface tension is equal and opposite to the natural potential difference between mercury and the electrolyte. By somewhat similar reasoning mercury breaking into fine drops at the surface of the electrolyte was assumed to come to the same potential as the electrolyte and therefore the difference of potential between the reservoir supplying the drops and the mercury collecting at the bottom of the electrolyte was the absolute potential sought. The results by the two methods agree closely and give for the

[1] "Wir gegenwartig über die Komponenten der electromotorischen Kraft eines Elementes einfach gar Nichts wissen" (Chwolson).

[2] Palmaer, Zeit. f. phys. Chem., 59, 129, 1907. Potentialkommission d. deutsch. Bunsen Gess., Zeit. f. Electrochemie, 50, 818, 1908. Chwolson, Lehrbuch d. Physik, IV., I., 228, 1908.

absolute potential, if the solution contains normal concentration of mercury ions, about 1.05 volts, or when combined[1] with a "normal calomel electrode" give for the absolute potential of the latter 0.593 volts, the mercury of the electrode being positive with reference to the solution.[2]

Endosmotic methods have been chiefly developed by Billitzer.[3] He observed the motion of fine wires suspended in an electrolyte between parallel plate electrodes and also the motion of colloidal particles which dropped between the plates. The concentration of the electrolyte was varied until a difference of potential applied to the plates produced no motion of the wires or the particles and he concluded that they were then at the same potential as the solution. These experiments, with others of a similar nature, gave for the absolute potential of the tenth normal calomel electrode $-.125$ volt, the negative sign signifying that the mercury was at a lower potential than the calomel solution. Billitzer also obtained approximately the same results by methods depending upon the change of concentration in the vicinity of a dropping electrode, motion of a mercury meniscus, and motion of the electrolyte.

The results of Billitzer differed so greatly from the values given by capillary and dropping electrodes that portions of his work were repeated by Whitney and Blake,[4] and Goodwin and Sosman.[5]

These investigators either failed to obtain his results or interpreted them differently. Later Freundlich and Mäkelt[6] succeeded in duplicating certain of Billitzer's determinations, but failed to obtain his values when the conditions were somewhat varied. Billitzer answered these criticisms with explanations of their failures and arguments for the validity of his original results. He ascribed the difference between his values and those obtained by capillary electrodes to direct or indirect dependence of the surface tension upon the applied potential resulting in the maximum surface tension appearing not when electrode and electrolyte are at the same potential but when the electrode is at about 0.7 lower potential.[7]

The third method for evaluating absolute electrode potentials is also due to Billitzer,[8] and is based upon the assumption that changes in the

[1] If one single electrode potential is determined absolutely with reference to a particular electrolyte any other electrode may also be inserted in the electrolyte and its potential determined from the absolute potential of the first and the difference of potential of the two.

[2] Palmaer, Zeit. f. phys. Chem., 59, 129, 1907.

[3] Drude's Ann., II., 902, 1903. Zeit. f. phys. Chemie, 48, 513, 542, 1904; 48, 624, 1908.

[4] Jour. Am. Chem. Soc., 26, 1339, 1904.

[5] PHYS. REV., 21, 129, 1905.

[6] Zeit. f. Electrochemie, 15, 161, 1909.

[7] Zeit. f. phys. Chemie, 51, 167, 1905. Zeit. f. Electrochemie, 12, 281, 1906; 14, 624, 1908; 15, 439, 1909.

[8] Zeit. f. phys. Chemie, 51, 167, 1905.

potential difference between the two elements of the electrode-electrolyte interface will produce changes in the distance between the two oppositely charged layers and consequently changes in the capacity. Billitzer found evidence in the works of Scott[1] and Kruger[2] of marked abnormality in the capacity at the potential which he had determined as the absolute potential by endosmotic methods. The writer, however, after careful study of the original observations is not convinced that these abnormalities are demonstrated beyond the limits of experimental errors.

The fourth method of determining absolute electrode potentials consists in direct electrostatic measurement. A large amount of work was done by this method previous to 1890, references to which may be found in the bibliography in Chwolson.

The observations of Exner and Tuma[3] were the only ones which were reproduceable and fairly consistent, *i. e.*, which gave for two different electrodes values of the absolute potentials whose algebraic difference was their known potential difference. Their method was similar to Kelvin's water dropper with the water replaced by mercury and the cylinder lined inside by filter paper saturated with the electrolyte which was connected by a wick with the electrolyte in which the electrode dipped. Their results were in rough agreement with those of Billitzer. Certain assumptions in their method may however involve serious systematic errors, which are about to be investigated in this laboratory. The only recent electrostatic work known to the writer is a paper by Borelius describing measurements of the relative, not absolute, potentials in the vicinity of an electrode and its electrolyte.[4]

This uncertainty in the absolute values of electrode potentials led the writer to begin several years ago an attempt to obtain accurate and reliable measurements by electrostatic methods. The final apparatus alone will be described and only the observations made during the past eight months will be presented.

APPARATUS.

Fig. 1 is a schematic sketch of the final apparatus. The electrolyte was usually contained in a flask A, 50 to 150 cm.^{3} capacity mounted on a platform supported by legs a of fused quartz. The outside of the flask except the neck was coated with a thin metallic film to which connection was made by the wire b. The latter could either be connected by the movable wire c to the Dolezalek electrometer C or, by the movable wire d with the wire e which could be connected to the earth or to a

[1] Wied. Ann., 67, 388, 1899.

[2] Zeit. f. phys. Chemie, 45, I., 1903.

[3] Wien. Akad. Sitz. Berich., 97, 917, 1889.

[4] Ann. d. Physik, 42, 1129, 1913.

source of known potential. The portions f of the threads by which c and d were raised and lowered were of fused quartz. The entire apparatus including the water battery g for charging the electrometer needle was surrounded by grounded wire netting. The electrode B (about 1 mm. in diameter) could be moved up and down and was usually grounded.

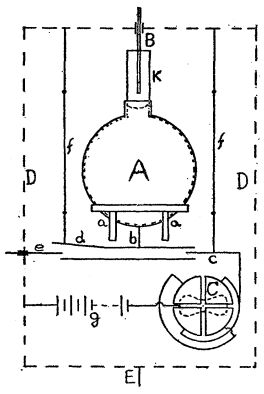

Fig. 1.

The theory of the method was as follows: If the electrolyte was initially at zero potential, upon introduction of the earthed electrode B it would acquire a potential equal to its natural absolute potential with reference to the particular electrode. A charge at somewhat different potential would be induced upon the metal film upon the outside of A, the deflection of the electrometer would be proportional to this potential, and, by a calibration described later, the potential of the electrolyte could be ascertained.

The procedure of an observation was as follows: The electrometer and the outside of the flask were earthed by the wires b, c, d and e, the latter being connected to earth. The electrolyte was poured into A. The neck k and the legs a were then cleansed with dilute alcohol and heated with a Bunsen burner to remove any moisture. The earthed electrode B was then lowered until it dipped in the electrolyte and immediately withdrawn. No readings were taken because the introduction of the electrolyte and the heating of the neck often produced static charges of many volts potential. After standing undisturbed several hours d was disconnected from e, and the electrometer reading was observed on a scale 160 cm. from the mirror. The earthed electrode B was then lowered until it dipped in the electrolyte and the accompanying deflection of the electrometer was observed from which, as explained later, the absolute potential of the electrolyte was calculated.

The following readings are those of a typical experiment.

Oct. 5, 1914. Flask e^1. Normal $ZnSO_4$ solution.

Electrometer Readings.

After heating neck and legs	49.5
Outside film and needle earthed	48.1
Outside film and needle insulated.	
Earthed zinc electrode dipped in electrolyte	39.9
One minute later	40.0
Fourteen minutes later	40.2
Thirty-two minutes later	41.0

[1] See below.

SOURCES OF ERROR.

1. *Poor Insulation.*—The loss of charge rarely exceeded 2 per cent. per minute. Since the complete period of the electrometer needle was about four seconds and its motion was considerably damped, a reading required only a small fraction of a minute. Occasionally the leakage was excessive and the observation was rejected. If the metal film on the outside was different from the electrode and the electrolyte had stood for some days in a glass flask there was occasionally evidence of conduction through the glass. When such conductivity was present the electrometer would not at once come to a definite reading when the earthed electrode was introduced but slowly drifted, and the final resting point of the needle when the electrode was left in the electrolyte differed from the zero position. Also there was a slow drift to this latter position if the needle was momentarily earthed and then insulated, the electrode remaining in the electrolyte. Quartz flasks never showed such conductivity. In particularly cold, dry weather surface leakage was inappreciable, but such static charges appeared when any part of the apparatus was disturbed that observations were impossible.

2. *Volta Effects.*—We are seeking the absolute difference of potential between an electrode and the surrounding electrolyte. The writer believes that the apparatus and procedure outlined above eliminates so-called Volta potentials or effects due to possible differences in potential in the air immediately surrounding electrode and electrolyte. As proof of the correctness of his belief, the electrolyte was successively replaced by mercury in each of the flasks employed and the deflections of the electrometer were observed when earthed wires of different metals (Cu, Ag, Zn, Ni, Fe) were dipped into the mercury. In every case the potential observed was less than 0.1 volt and usually it was inappreciable.

3. *Initial Static Charges on Electrolyte.*—As mentioned above, such charges were usually observed when the flask was first filled and the neck of the flask was heated. It was assumed that after several hours these static charges largely disappeared and that the potential of the electrolyte differed little from zero (the potential of the cage). The deviations in the observations are probably largely attributable to this cause. It was not possible to further reduce errors from this source by delaying observations because errors of the first type usually began to appear. The fact that mercury in the different flasks and with different electrodes showed practically no potential is further evidence against this source of error being serious.

4. *Influence of Material of Flask and Metal Film.*—To eliminate any such specific influence different materials were used which are designated as follows in subsequent tables.

a = quartz flask No. 1 with outside film of silver.[1]
b = quartz flask No. 1 with outside film of aluminum.[2]
c = quartz flask No. 2 with outside film of silver.
d = quartz flask No. 2 with outside film of aluminum.
e = glass flask No. 1 with outside film of silver.
f = glass flask No. 1 with outside film of aluminum.
g = glass flask No. 2 with outside film of silver.
h = glass flask No. 2 with outside film of aluminum.

Observations with paraffin coated vessels and vessels of other shapes are described later.

EXPERIMENTAL RESULTS.

The following table gives all the observations made during the past months with narrow neck flasks with the final form of apparatus except a few observations which were discarded because of evidence of errors of the first type mentioned above. At the foot of each column is stated the mean with its probable error, except for Cu — $CuSO_4$ where the variation in the readings is so great that little quantitative importance can be given the results.

CALIBRATION.

The algebraic difference in the mean deflections for zinc and silver is 11.67. The difference of potential of zinc and silver electrodes, each in a normal solution is 1.541 volts.[3] Dividing one by the other gives 7.50 divisions per volt as the calibration constant of the system. This constant was checked by substituting mercury for the electrolyte and observing the electrometer deflection due to the charge induced on the outside of the flask when the potential of the mercury was changed by known steps by means of the electrode B.

This method of calibration gave values for this constant, which for narrow neck vessels were often as much as 15 per cent. greater than the values calculated as just described while for wide necked vessels (see below) both methods of calibration gave almost identical results. This difference was to be expected since the outside metallic coating was nearer the wire when the neck was narrow and this wire had a like charge in the direct calibration with mercury and a charge of opposite sign in the method of calibration by known differences of potential, and in all the actual experiments. The mercury calibration proved that the deflection of the electrometer was proportional to the potential within 0.2 per cent. up to 1.43 volts and that there was no appreciable asymmetry in the deflections on the two sides.

[1] Chemically deposited upon flask.

[2] Aluminum foil attached by a very thin film of shellac.

[3] Wilsmore's Tables, Winkelmann's Handbuch, IV., I., p. 856.

TABLE I.

Zn $n ZnSO_4$	Ag $n AgNO_3$	Cu $n CuSO_4$	Zn $n/2 H_2SO_4$	Cu $n/2 H_2SO_4$
a +7.8	*a* −2.0	*a* 0.0	*a* +9.2	
" 6.3	" .5	" +2.3	" 7.0	*a* +2.2
" 6.0	" 3.5	" + .8	" 8.7	" 0.0
" 8.8	" 3.5	*e* +3.0	" 8.3	" +3.5
" 9.1	" 4.3	*g* + .3	*e* 9.7	" +2.1
" 7.3	" 3.6	" +1.1	" 9.3	" +1.1
b 8.0	" 3.0	*f* −2.9	" 9.2	" − .8
" 7.9	" 2.8	" −2.3	" 8.8	" − .3
" 8.4	" 2.8	" − .5	" 7.9	" + .2
c 7.0	" 2.4	*c* − .3	*f* 7.6	*e* +1.0
" 7.4	*b* 2.0		" 7.7	" +1.1
" 6.5	" .7		" 7.6	" +1.2
g 8.2	" 3.2		*g* 8.8	" + .6
f 10.6	" 3.5		" 8.7	" + .7
" 6.9	" 3.0		" 8.7	*f* − .8
g 8.5	" 4.7		" 11.6	" − .8
" 9.6	" 4.4		" 10.9	" − .7
" 9.0	" 3.3		" 8.1	*g* + .5
" 8.0	*e* 5.4		" 7.1	" + .4
" 9.2	" 4.9		" 10.2	" + .4
f 7.7	" 4.8		" 9.2	" +3.1
" 6.3	*f* 3.1		" 9.3	" +2.9
c 7.2	" 8.3		" 9.6	" +1.3
	h 2.4		*f* 6.5	" +1.0
	g 1.8		" 7.3	" +1.4
	f 6.8		" 8.7	" +2.5
	" 7.3		" 5.5	" +1.8
	" 4.6		" 5.4	" +2.3
	c 4.1		" 5.7	*f* −1.5
			" 5.7	" − .7
			" 7.3	" −2.1
			" 7.2	" −2.5
				" −2.3
				" −1.9
				" −2.0
				" − .3
				" − .2
+7.90±.16	−3.67±.19	+0.18	+7.84±.20	+0.37±.19

FINAL RESULTS.

Dividing the mean deflection by this constant 7.50 we find for the potential of zinc in normal zinc sulphate solution − 1.05 ± .02 volts, and for zinc in half normal sulphuric acid solution − 1.04 volts. For silver in normal silver nitrate solution we find + .49 ± .03 volt and for

copper in normal copper sulphate solution — .02 volt and in half normal sulphuric acid solution — .05 volt.[1]

Observe that these results are mutually consistent. The respective potentials of zinc and copper are very nearly the same in both electrolytes, as would be expected. The differences of potential of copper and zinc are 1.07 and 1.09 volts respectively which compare well with the difference of 1.099 in Wilsmore's table.

WIDE NECK VESSELS.

To make certain that the results were not influenced by the degree to which the outside metal film approached a "closed" conductor, observations were made both with test-tubes 2.5 cm. in diameter 20.5 cm.

TABLE II.

Test-tube.	Beaker.	Test-tube Covered Inside with Paraffin.
Ag. — 4n $AgNO_3$		Ag — n $AgNO_3$
3.1	3.8	4.0
3.6	3.6	5.0
3.2	4.0	4.3
3.6	3.2	3.4
3.4	3.3	3.9
3.3	3.0	4.1
3.3	——	3.4
3.6	Mean, 3.48	2.7
4.2	(0.40 volts)	——
3.2		3.85
——		(0.50 volts)
Mean, 3.47		
(.38 volts)		
Zn — 2.5n $ZnSO_4$		Zn — n $ZnSO_4$
9.9	11.6	8.1
10.8	9.9	7.9
11.1	8.8	8.2
11.1	——	——
10.6	Mean, 10.1	Mean, 8.1
10.1	(1.15 volts)	(1.05 volts)
10.1		
10.4		
11.0		
——		
Mean, 10.5		
(1.16 volts)		

[1] The signs in Table I. apply to the electrolyte since its potential rather than that of the electrode was under observation. The electrode potential will obviously have the opposite sign.

long, covered with an outside silver film for 7.5 cm. from the closed end, and with a beaker about 7 cm. high, 4 cm. in diameter at the top and 3 cm. in diameter at the bottom with an outside silver coating extending to within about 3.5 cm. of the top. One test-tube was covered upon the inside with paraffin to secure further evidence that the results were independent of the insulating medium. The electrometer readings are given in Table II.

The potentials stated in parentheses were calculated as explained above. Allowing for the difference in concentration, they agree closely with the previous results and show that the values obtained are independent of the shape of the vessel. The results in the last column show that a coating of paraffin inside the vessel does not affect the potential. Similar observations were made with a number of other test-tubes with like results. Further experimental confirmation of certain of the above figures will be found when considering the effect of concentration. Table III. gives a comparison of the writer's results

TABLE III.

	n/10 Calomel Electrode.	Silver.	Zinc.
Wilsmore and Palmaer	+.573	+1.008	− .533
Ewell	(+.06)	+ .49	−1.05

with the values commonly found in tables (Wilsmore's) except that the latter are decreased by .04 volt to correspond to Palmaer's more recent value of the potential of the tenth normal calomel electrode (.573 volt in place of Wilsmore's value of .613).

INFLUENCE OF CONCENTRATION OF ELECTROLYTE.

The final form of apparatus is illustrated in Fig. 2. The glass flasks A and A' contained two concentrations of the same electrolyte. The silver film on the outside of one flask was connected to one pair of quadrants of the electrometer and the other film to the other pair of quadrants. The wires b, b' permitted grounding of the films and quadrants. An observation was preceded by preliminary steps similar to those previously described. The deflection of the electrometer was observed when one earthed electrode B was dipped into the electrolyte and

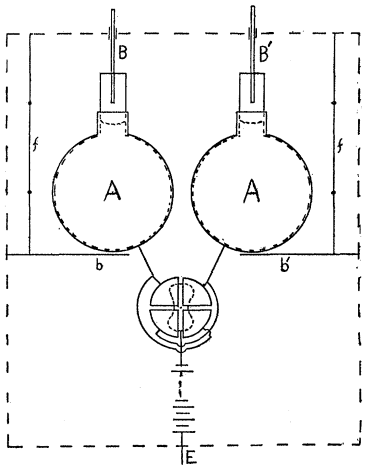

Fig. 2.

then when the other electrode B' was also dipped into the other electrolyte. From the deflection with both earthed electrodes in their respective solutions the difference of potential of the two electrolytes was determined. Lack of symmetry was eliminated by changing the order of introduction of the electrodes and by exchanging the two concentrations of the solution between the two flasks. Table IV. gives the final readings with silver nitrate and zinc sulphate.

TABLE IV.

Electrode.	Electrolyte.	Deflection of Electrometer upon Dipping Earthed Electrode into Flask Connected with		Both Electrodes in their Respective Solutions.
		First Pair of Quadrants.[1]	Second Pair of Quadrants.	
Ag.....	$4n$ $AgNO_3$ in first flask.....	−3.1	+4.4	+1.3
		−2.2	+2.7	+ .5
	$n/250$ $AgNO_3$ in second flask.....	−2.5	+4.3	+1.8
		−3.2	+3.6	+ .4
		−2.6	+3.2	+ .6
		−2.6	+2.8	+ .2
		−1.8	+2.9	+1.1
	$n/250$ $AgNO_3$ in first flask.....	−2.9	+ .8	−2.1
		−2.7	+1.7	−1.0
	$4n$ $AgNO_3$ in second flask.....	−2.1	+1.4	− .7
		−3.0	+2.5	− .5
		−1.7	+ .9	− .8
		−3.6	+2.9	− .7
Zn.....	$2n$ $ZnSO_4$ in first flask.....	+4.7	−3.4	+1.3
		+5.2	−4.0	+1.2
	$n/500$ $ZnSO_4$ in second flask.....	+5.1	−4.0	+ .9
		+5.7	−4.5	+1.2
		+5.0	−3.9	+1.1
		+5.4	−4.6	+ .8
	$n/500$ $ZnSO_4$ in first flask.....	+3.7	−5.0	−1.3
		+4.4	−5.0	− .6
	$2n$ $ZnSO_4$ in second flask.....	+4.0	−4.8	− .8
		+3.8	−4.9	−1.1
		+2.9	−4.4	−1.5

[1] The first pair of quadrants is the pair to which the flask was connected in the work described earlier, and the first flask is the flask connected to these quadrants.

The lower concentration of silver nitrate gives the greater deflection the mean excess being 0.90 which divided by 7.50 gives 0.12 volt. The sign of the deflection shows that the weaker solution is at a lower potential, and therefore a silver electrode in $4n$ $AgNO_3$ solution in a glass

vessel is about 0.1 volt lower potential than a silver electrode in $n/250$ $AgNO_3$ solution.

A concentration cell

$$Ag - 4n\ AgNO_3 - n/250\ AgNO_3 - Ag$$

gave by potentiometer measurement an E.M.F. of 0.13 volt, the silver in the *stronger* solution being at the higher potential, while by Nernst's theory this electrode should have an excess potential of 0.16 volt.

The electrode in the stronger $ZnSO_4$ solution shows a mean excess deflection of 1.07 divisions. A zinc electrode in $2n$ $ZnSO_4$ solution in a glass vessel is therefore about 0.14 volt more negative than a similar zinc electrode in $n/500$ $ZnSO_4$ solution. Borelius observations referred to earlier, gave approximately 0.17 difference in the potentials induced in a conductor upon approaching successively solutions of zinc nitrate containing earthed zinc electrodes when the concentration ratio was 1,000, and the sign of the induced potential indicated that the stronger solution (or the region about it) was more negative. In the opinion of the writer it is not however possible to differentiate in Borelius observations between Volta potentials and the true electrolytic potentials which we are here investigating.

For these observations upon the influence of concentration, it was necessary to keep the electrolyte in the flasks for considerable lengths of time and the possibility of some electrolytic conduction through the glass reduces somewhat the dependence which may be given the results. However, although there is a wide variation in the above small differences, taken as a whole, they indicate that when a single electrode dips in a homogeneous electrolyte containing ions of the metal in a glass vessel, the potential of the metal decreases as the concentration of the solution increases. This is opposite to the theory of Nernst, which has often been approximately substantiated for the quite different cases of *two* electrodes, either both dipping in a non-homogeneous solution, or one dipping in the solution and the other separated from the solution by ionized air.[1]

If from an external source the film on the outside of one flask was raised to a known potential, the other flask and its quadrants being insulated, the deflection was 0.59 of the deflection when this pair of quadrants was earthed. The mean deflection with $4n$ AgNO was

$$2.17 = \frac{2.17}{.59 \times 7.50} = -.49 \text{ volt.}$$

The mean deflection with $2n$ ZnSO = 5.02 = 1.11 volts. Both of these potentials are seen to be in fair agreement with the results of direct measurement.

[1] Guyot, C. R., 153, 867, 1911.

CONCLUSIONS.

A new method for measuring absolutely single electrode potentials has been developed. The results obtained indicate that the potential of a metal in a homogeneous normal solution of one of its salts is about 0.5 volt more negative than the potential deduced from electrocapillary phenomena and usually found in tables. Increasing the concentration of a salt solution contained in a glass vessel appears to lower the potential of an electrode of the metal of the salt.[1]

The writer wishes to express his indebtedness to Mr. C. G. Cummings for assistance in the preliminary observations.

WORCESTER POLYTECHNIC INSTITUTE,
April 24, 1915.

[1] After this paper had been sent to the editors, a second paper of Borelius (Ann., 22, p. 927, 1914) came to the writer's attention, in which the experiments described in the earlier paper were repeated with electrolytes contained in paraffin-coated flasks connected with a calomel electrode by a syphon. In contrast to the previous results, these later observations gave values for the potentials outside the glass vessels which were in accord with Nernst's theory. The writer, with the assistance of Mr. A. G. Aldrin, has repeated the concentration observations described above using vessels of various shapes of clean glass, glass vessels covered inside with paraffin, and glass vessels covered with shellac. The results with clean glass have been similar to those described above, *i. e.*, opposite to Nernst's theory. A limited number of observations with coated glass have usually given qualitative agreement with the theory. Further investigation is in progress.