

THE ABSOLUTE VALUE OF AN
ELECTRODE POTENTIAL.

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HISTORICAL AND INTRODUCTORY.

The method of determining the difference of potential between two electrodes dipping into a common electrolyte is a relatively simple and an extremely accurate one. When, however, attempts have been made to determine the difference of potential existing between a single electrode and an electrolyte, difficulties were encountered, and the results which were obtained were far from concordant.

There are four principal lines of attack on the problem of determining the absolute value of an electrode potential, namely, the dropping electrode, the capillary electrometer, endosmosis phenomena and electrostatic differences of potential.

The dropping electrode and the capillary electrometer were developed shortly after Helmholtz¹ enunciated his theory of the so called "electrical double layer". In this theory, it was assumed that when an electrode was placed in an electrolyte of the proper concentration, there is immediately set up a charge of one sign on the electrode and a charge of the opposite sign on the electrolyte. It was thermodynamically shown that when the magnitude of these charges was at a minimum, the surface tension was at a maximum.

Acting on this theory, Lippman², in 1875, measured

¹Wied. Ann., 7, 340

²Compt. Rend. 83, 192 and 95, 686.
Ann. Chem. Phys. 5, 532.

the surface tension of mercury in contact with sulfuric acid solutions of different concentrations, and at that concentration at which the surface tension was at a maximum he assumed that the difference of potential was zero, that is, that the electrical double layer did not exist. Conversely, if we impose a potential upon mercury in contact with a sulfuric acid solution, of such magnitude and opposite in sign to that resident upon the mercury, to cause the surface tension to increase to a maximum, this is the magnitude of the potential resident upon the mercury because of the electrical double layer.

By a somewhat similar line of reasoning, it was thot that a mass of mercury placed in contact with a calomel solution and a second connection made by means of an electrode, the surface of which was changing so rapidly that the electrical double layer could not form, should give the potential of massive mercury against its salt solution.

The two methods described above gave for the absolute potential of the normal calomel electrode, +0.593 volts. The positive sign indicating that the mercury was more positive than its salt solution.

The next work done on the subject of absolute potential measurements was by Billitzer³ in 1903. He observed the behavior of minute metallic particles and of fine platinum wires suspended in solutions of different concentra-

³Zeit. fur Elekt. Chem. 12, 192
and 8, 638.

tions when acted upon by an electrical field. He reasoned that when the concentration of the solution was such that the fine particles in the one case and the platinum wires in the other did not move under the influence of an electrical field, the particle or wire was at zero potential with respect to the solution, or, in other words, this was the iso-electric point. From this work, he showed the absolute potential of the normal calomel electrode to be -0.125 volts. This shows the electrode to be about 0.7 volts more negative than the generally accepted value, obtained by the dropping electrode and the capillary electrometer. Billitzer says this is due to the dependence of the surface tension upon the applied E.M.F., the maximum surface tension appearing when the electrode is about 0.7 volts negative to the solution.

Ewell⁴, working by electrostatic methods, found the absolute potential of a metal electrode to be about 0.5 volts more negative with respect to its solution than is the value given by the capillary electrometer. He states that increasing the concentration of the salt solution seems to decrease the potential, that is, that the effect is opposite to Nernst's theory.

Various experimenters who have found it necessary to use reference electrodes have, after critical examination, concluded that the value for the potential of the calomel

⁴Phys. Rev. 6, 271.

electrode as given by the dropping electrode and the capillary electrometer is in error. This, together with the fact that endosmosis method and the electrostatic method give results at wide variance from the accepted value, indicates the necessity for further research along this line.

Dr. H. P. Cady and Mr. E. F. Stimpson commenced work on the present method of measurement of absolute potentials in 1903 but due to the illness of Mr. Stimpson, the work was discontinued and not taken up again till the fall of 1921 when Mr. George Lynn started working on the problem.

Mr. Lynn built an electrometer of the same general type as that used in the present work, and with this, secured results, which, as he says, "are not clear cut in their indications", but which demonstrated the practicability of the method, and indicated that instead of being positive with respect to a normal potassium chloride calomel solution, mercury was probably negative.

The work was taken up by the author and an electrometer built which differed from that of Mr. Lynn's in that his was of the co-axial needle type, while that used in the present work was of the plane needle type. By this modification, it was possible to have no solid dielectric between the needle and quadrants, and at the same time not introduce serious complications in the method of operation.

DESCRIPTION OF THE INSTRUMENT.

The quadrant electrometer consists of four hollow metal quadrants, produced by cutting a hollow cylinder along two mutually perpendicular diameters, inside of which is a needle shaped in the general form of two opposite quadrants. This needle is made of any light electrically conducting material and is suspended by means of an electrically conducting filament. The quadrant and needle system is shown diagrammatically and in section in Figures I and II respectively.

Now, if each pair of opposite quadrants are electrically connected, and are insulated from the other pair of quadrants and a charge of electricity is placed upon the needle, which is placed symmetrical with respect to a diameter, it can be seen that any difference of potential existing between the quadrants will produce an electrostatic attraction of the needle by one pair of quadrants and a repulsion by the other pair.

The magnitude of this movement can be shown to be nearly proportional to the difference of potential between the pairs of quadrants, provided the needle potential be kept constant. The needle would place itself entirely inside the pair of quadrants which was oppositely charged were it not for the restoring effect of the suspension. Thus, we have two opposing effects; the deflecting couple, produced by the electrostatic difference of potential, and the re-

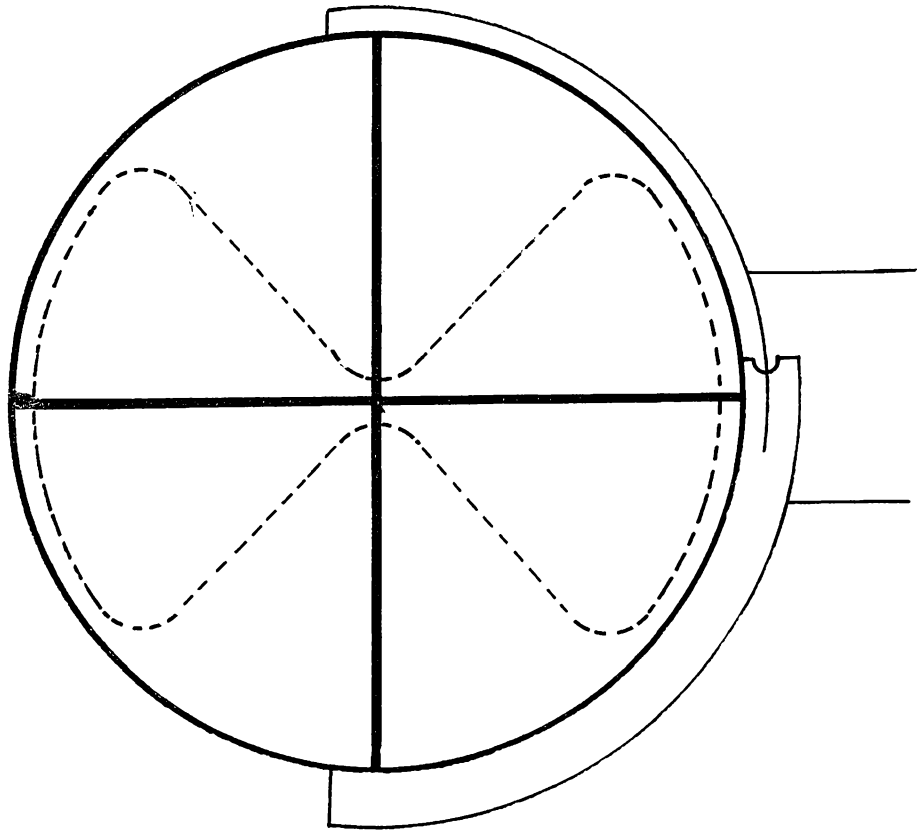


Fig 1

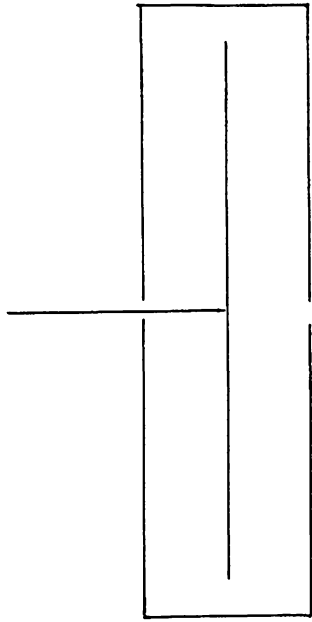


Fig 2

storing couple of the suspension.

The amount of deflection caused by a difference of one volt across the pairs of quadrants when the needle is charged to any given potential is a measure of the sensitivity of the instrument at that potential.

The instrument which was built for this work was a modification of the conventional quadrant electrometer. The metal quadrants were replaced by quadrant shaped glass cups (a, a) and (b, b) each of which was connected with a glass tube syphon system (c) which terminated in a well (e) as shown in Figure III.

The quadrants (a, a) were filled with mercury as were the syphon tubes and wells in connection and the quadrants (b, b) were filled with salt solution in contact through the syphon tubes with mercury and calomel paste in the wells. The mercury quadrants were connected through a potentiometer circuit to the mercury in contact with the solution in quadrants (b, b) thus giving us a half cell built in the electrometer itself. Provision was made for raising and lowering the needle (d) and for rotating it through small angles. Now, it can be seen that if a difference of potential existed between the mercury which filled quadrants (a, a) and the solution which filled quadrants (b, b) its magnitude could be known if the sensitivity of the electrometer were known, and the direction of the movement of the needle would clearly indicate

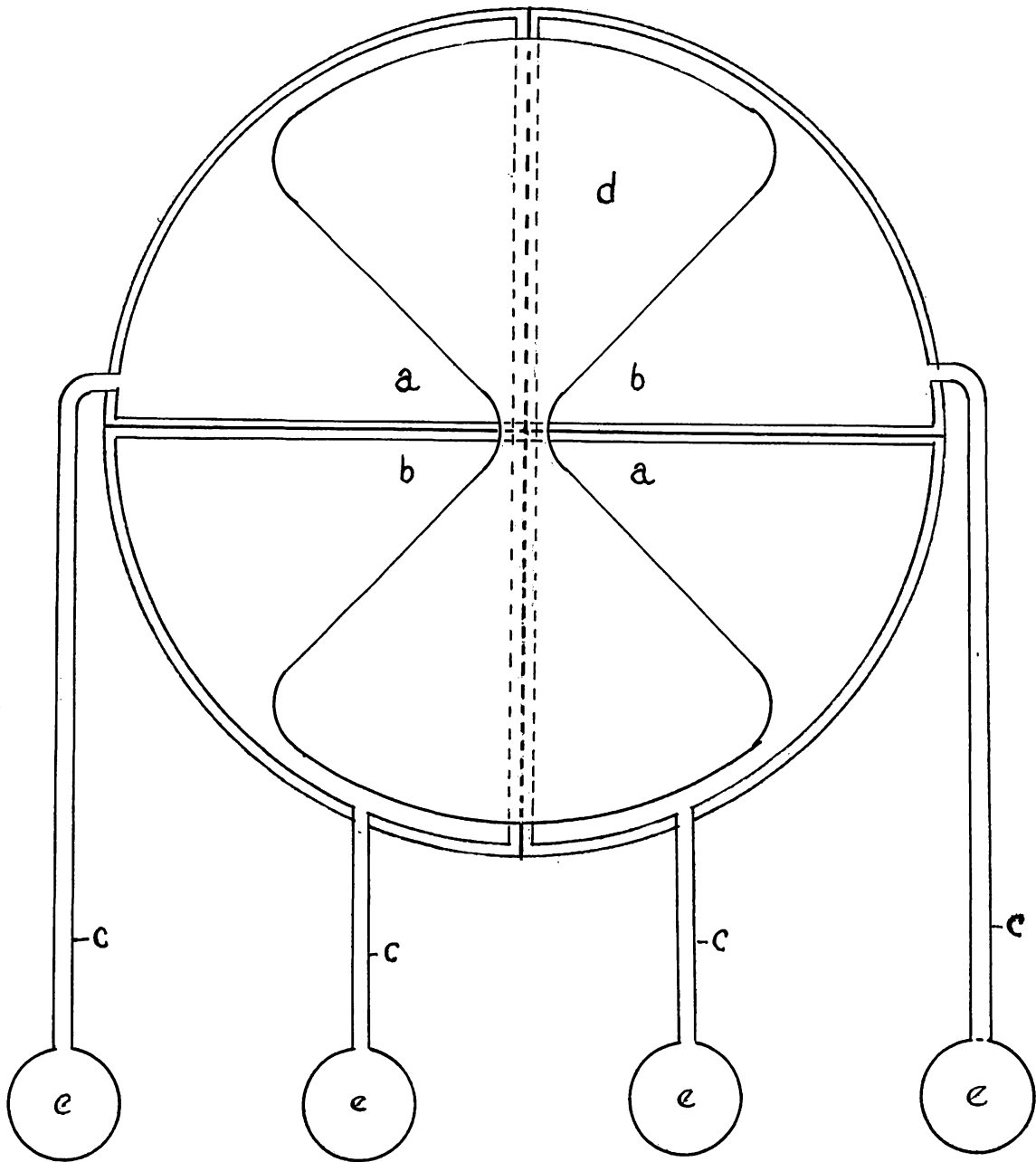


Fig 3

the sign of the charge upon the mercury or upon the solution.

The instrument was mounted upon a block of lead weighing 100 pounds, which in turn rested upon small rods set in the foundation. This foundation went to bed rock. This arrangement stabilized the instrument against horizontal displacement. The case of the electrometer was earthed, as were the quadrants which were permanently filled with mercury. Surrounding the electrometer was a metal box which was also earthed to shield out any external electrical fields. Lead in wires were passed into the metal box through sulfur insulators. The potentiometer was mounted on a separate table on a dry pine board which was insulated from the table by sulfur blocks. The needle charging battery of dry cells, of a potential of 225 volts was similarly mounted. The telescope and scale were mounted on a wall shelf at a distance of three meters from the electrometer.

Connections with the needle charging battery and the potentiometer circuit are shown in the diagram, Figure IV. The switch "S" is a reversing switch for changing the sign of the potential on the needle. "S₁" is a switch for connecting either the standard cell "W" and the galvanometer "G" or the quadrant electrometer in the potentiometer circuit. "K" is a key for closing the galvanometer circuit.

The sensitivity of the electrometer was determined by

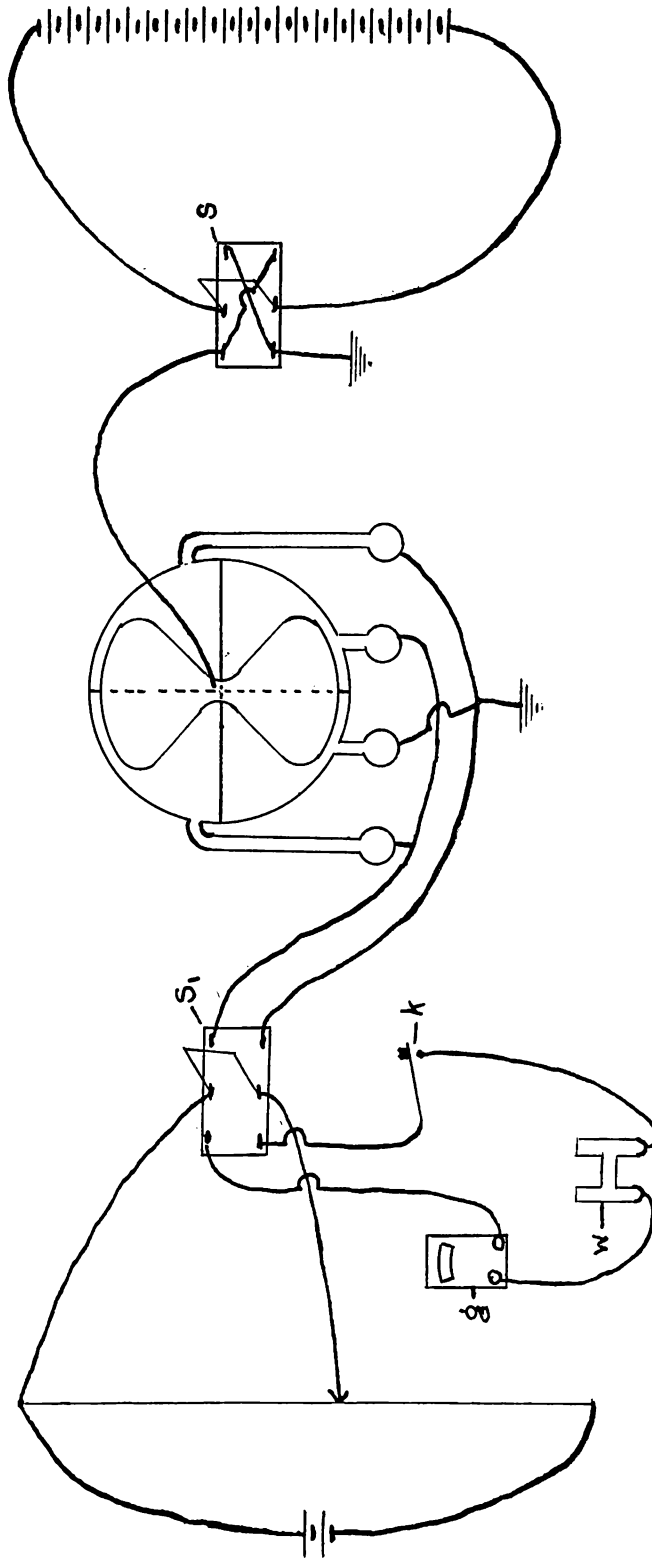


Fig 4

filling all quadrants with mercury and applying a known difference of potential across them, the needle potential being varied between 25 and 225 volts. It was found that the maximum sensitivity compatible with stability was secured with a potential of 155 volts on the needle. The sensitivity thus obtained was 132 millimeters per vole. This seemed sufficient for our purpose.

EXPERIMENTAL.

In the early experimental work of this investigation, the sensitivity of the electrometer was determined by filling both pairs of quadrants with mercury and determining the deflection caused by a known potential across the quadrants. Then, while leaving the needle potential the same, the mercury was drawn off from one pair of quadrants and solution substituted, thus giving a complete half cell. From the deflection produced by the half cell and the sensitivity of the instrument, attempts were made to compute the E.M.F. of the half cell. Difficulty was met with in getting the level of the solution exactly the same as the level of the mercury when the sensitivity was determined, so this method gave very erratic results and the method of manipulation was changed. The method next tried, was to earth the needle, and, when it had come to rest, read its zero position. Then, a potential was placed on the needle and a counter E.M.F. of sufficient magnitude placed across the quadrants in the proper sense to return the needle to

its zero position. This should be the potential of the half cell.

The undesirable feature in this method, was that the rapid movement of the needle when charged, caused convection currents in the air inside the electrometer case which were in some instances, several hours in dying out.

The last, and most successful method used was to connect the quadrants through the potentiometer circuit, but have a zero potential across the quadrants from the potentiometer circuit, that is, the only potential on the quadrants was the potential of the half cell. With the needle charged, the position was read by means of the telescope and scale and the sign of the needle potential changed but the magnitude kept constant. This, of course, caused the needle to be deflected in the opposite direction. Now, sufficient E.M.F. from the potentiometer circuit was placed across the half cell to bring the needle to the position which it had before the sign of the needle potential was changed. This was twice the potential of the single electrode.

Under these conditions there were, of course, currents of air set up in the case of the electrometer which were slow in dying out. However, this was eliminated as soon as the E.M.F. of the half cell was approximately known, as it was possible to reverse the sign of the needle potential and at the same time rotate the potentiometer to the potential reading which prevented deflection except a very

small amount which was compensated for in the final adjustment of the potentiometer.

This method proved quite satisfactory. There were, however, other difficulties which prevented the results from being reliable at first. Electrical effects due to the passing of street cars were without difficulty shielded to earth, but a stray electrical effect made the results erratic for weeks in spite of every effort to locate the source. It was finally found that the wind blowing against a window near the electrometer was causing the trouble, and when the glass was washed with a solution of calcium chloride and earthed, this difficulty was removed.

A more detailed description of the manipulations in securing a reading follows:

The mercury in one set of quadrants was drained off and the quadrants filled with tenth normal potassium chloride-calomel solution. Mercury and calomel paste were placed in the wells in contact with the solution.

The needle was charged at a positive potential and the scale read with no potential on the quadrants other than the potential of the half cell itself. The sign of the potential on the needle was reversed and sufficient E.M.F. applied to the quadrants in the proper direction to return the needle to the position which it had when it was positively charged. Half of this quadrant potential would prevent the deflection of the needle when the sign

of the needle potential was reversed, so is the absolute potential of the half cell. In order to use this method, it was necessary to have the needle exactly symmetrical with respect to the quadrants⁶, and the quadrant surfaces at the same height. If the first point was neglected, half the potential, as indicated above, would not keep the needle at zero position when the sign of the needle potential was reversed. The accurate leveling of the conducting quadrant surfaces was necessary only to secure maximum sensitivity.

When the solution quadrants were filled with N/10 KCl - Hg₂Cl₂ solution, it was found that the positively charged needle was deflected from its zero position toward the mercury filled quadrants and on reversing the sign of the needle potential, was deflected toward the solution filled quadrants, which would clearly indicate the negative character of the mercury with respect to its salt solution. The potential necessary to be placed across the quadrants to restore the needle to the position which it had before the sign of the needle potential was reversed was -0.634 volts. The negative sign indicates that the mercury was negative with respect to the solution. After each days work, the instrument was torn down and the quadrants, syphons and wells thoroughly cleaned. The instrument was then rebuilt and the quadrants refilled for the next days readings. It was possible to secure about fifteen readings per day.

⁶Phys. Rev. 13, 228.

The results given below are the counter E.M.F.'s necessary to restore the needle to the position which it had before the reversal of the sign of the needle potential. The readings for any one day are more concordant than are the means for the different days. No reason can be given for this as the experimental conditions were duplicated as exactly as possible.

Each column of data given below is the readings taken during one day when the tenth normal calomel electrode was used.

-0.682	-0.685	-0.683
-0.677	-0.685	-0.683
-0.680	-0.685	-0.690
-0.679	-0.685	-0.685
-0.680	-0.685	-0.686
-0.680	-0.685	-0.685
-0.680	-0.685	-0.685
-0.680	-0.685	-0.685
-0.679		-0.684
-0.681		-0.685
-0.679		-0.683
		-0.684

-0.565	-0.650	-0.535
-0.565	-0.650	-0.544
-0.565	-0.650	-0.594
-0.564	-0.650	-0.595
-0.531	-0.650	-0.593
-0.565	-0.650	-0.594
-0.532	-0.650	-0.594
-0.576	-0.651	-0.542
-0.598	-0.650	-0.551
-0.608	-0.650	-0.542
-0.608	-0.651	-0.546
	-0.650	
	-0.651	
	-0.650	

-0.654	-0.660	-0.660
-0.660	-0.660	-0.659
-0.664	-0.658	-0.660
-0.660	-0.656	-0.662
-0.661	-0.602	-0.656
-0.662	-0.661	-0.657
-0.664	-0.658	-0.661
-0.661	-0.662	-0.660
-0.660	-0.660	-0.659
-0.658	-0.661	
	-0.658	
	-0.660	
	-0.660	

-0.661	-0.630
-0.660	-0.631
-0.660	-0.631
-0.660	-0.652
-0.661	-0.660
-0.658	-0.620
-0.660	-0.621
-0.660	-0.621
-0.660	-0.621
-0.660	-0.621
-0.661	-0.621
-0.660	-0.621

The mean double E.M.F. for the N/10 electrode was -0.634 volts, which would give as the potential of the single electrode -0.317 volts.

Similar data for the N/1 calomel electrode follows:

-0.686	-0.735	-0.701
-0.688	-0.740	-0.700
-0.690	-0.729	-0.698
-0.688	-0.730	-0.700
-0.710	-0.730	-0.699
-0.708	-0.730	-0.697
-0.710	-0.726	-0.700
-0.700	-0.729	-0.693
-0.700	-0.730	
-0.700	-0.730	
-0.700		
-0.700		
-0.702		
-0.699		
-0.700		

-0.686	-0.700	-0.700
-0.684	-0.700	-0.700
-0.686	-0.700	-0.700
-0.686	-0.702	-0.700
-0.688	-0.700	-0.698
-0.692	-0.721	
-0.691	-0.720	
-0.691	-0.718	
-0.691	-0.720	
-0.690	-0.722	
-0.690	-0.720	
-0.690	-0.720	
-0.692	-0.720	
-0.691	-0.720	
-0.692		
-0.692		

92 trials

.684 - 1/3 #2
802 1/4 01

-0.724	-0.730	-0.800
-0.730	-0.746	-0.800
-0.724	-0.729	-0.800
-0.726	-0.765	-0.802
-0.772		-0.800
-0.769		-0.801
-0.770		-0.800
-0.770		
-0.770		
-0.769		
-0.771		

The average double value here is -0.730 so the potential

of the half cell is -0.365 volts.

It will be observed that the difference of potential between the normal and the tenth normal electrodes is 0.048 volts which is very close to the value to be computed from the ion concentration by the Nernst formula.

After these data were taken, the calomel cell was replaced by the electrode $\text{Hg} \parallel \text{HgO} - \text{NaOH}$. After allowing the half cell to stand for three days to come to constant potential, the potential was determined in the same manner as that for the calomel electrodes.

For the tenth normal basic half cell, the following data were taken:

-0.761	-0.759	-0.765	-0.763
-0.760	-0.759	-0.766	-0.762
-0.764	-0.760	-0.766	-0.763
-0.760	-0.761	-0.769	
-0.760			

The average double value here is -0.762 volts or the E.M.F. of the single electrode is -0.381 volts. Here again, the mercury is negative with respect to the solution.

Using the normal basic half cell, the following data were obtained:

-0.895	-0.879	-0.900
-0.897	-0.876	-0.888
-0.885	-0.890	-0.881
	-0.881	
	-0.882	

-0.880	-0.886
-0.890	-0.886
-0.891	-0.885
	-0.884

The average for these gave as the potential of the half cell, -0.444 volts.

The difference of potential of 0.079 volts for the cell



does not agree well with the value 0.1541 volts⁷ which is obtained by the potentiometer method. Applying the correction for the difference of potential between the two solutions does not entirely correct this discrepancy. The difference of potential between the normal and the tenth normal basic half cell is closely in keeping with that to be expected from cells of this type.

CONCLUSIONS.

From this work, it appears that mercury, instead of being positive with respect to its normal and tenth normal KCl - Hg₂Cl₂ and NaOH - HgO solutions, is in fact negative. Our reference electrodes give, by electrostatic measurements a potential about .92 volts more negative than the values which are at present accepted.

We must conclude, therefore, that the value of +0.61 volts for the decinormal and +0.56 volts for the normal calomel electrodes which are given by the dropping electrode are not the electrostatic differences of potential

⁷ Tables Annuelles de Constants et Bonnees Numeriques, (1911).

existing between the metal and the solution, and that at the condition of maximum surface tension of mercury, the mercury and solution are not iso-electric.

ACKNOWLEDGEMENT.

The writer wishes to state again that the fundamental idea underlying this investigation was Dr. Cady's, and to thank Dr. Cady for his helpful supervision and timely suggestions throughout the work.

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[#]A very extensive bibliography on the subject of absolute potential measurement is attached to this article.