ABSOLUTE-POTENTIAL MEASUREMENTS

by means of

THE QUADRANT ELECTROMETER

---

by

George Lynn.

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Science.

Approved by:

H. P. Cady

Dept. of Chemistry.

May 20, 1922.

CONTENTS

INTRODUCTION.

Electrical potential differences are found to exist at the junction of two dissimilar metals and especially at the junction of a metal with a solution of one of its salts. The latter are called electro-chemical potentials and on the solution side of the surface of contact, the phenomena are tied up with the concentration of the metallic ions in solution according to the well known logarithmic law.

Attempts have been made to measure these potentials at a single surface, or single-potentials as they are called. Lippmann (1) was the first to attempt such measurement by means of a capillary electrometer, which was discussed theoretically by Helmholtz (2). This instrument is based on the principle that the surface tension of mercury is a maximum when the potential difference between it and a solution in contact with it is zero.

---

(1) Ann. Chem. Phys. V.5, p 532; 1875.
Compt rend. v. 83, p 192; 1876.

(2) Wied Ann. 7, 340; 1879.

A. Konig (3) used a modification of this method by measuring the curvature of mercury drops in sulphuric acid. His method also gave the surface tension but was difficult to carry out to any degree of accuracy.

Helmholtz (4) applied the dropping electrode idea first proposed by Kelvin for measurments of the potential of the atmosphere, to the problem. Ostwald repeated these experiments and Paschen (5) successfully worked on the problem. Nernst(6) explained the action of the dropping electrode in terms of the double layer theory of Helmholtz, and proposed a modification of the method which was carried out by Palmaer (7).

---

(3) Wied. Ann. 16, 1; 1882.

(4) Gesammelte Abhandl. I, 934.
Monatsber. Berl Akad. Nov. 1881

(5) Wied Ann. 41, 42; 1890.

(6) Zeit Phys Chem 25, 265-8; 1898.

(7) Zeit Phys Chem 28, 257; 1899.
59, 129; 1907.

Billitzer (8) attacked the problem from a different angle. He found that a small sphere made by fusing the end of a very fine wire of platinum or silver, when suspended pendulum-like in a solution of, say, formaldehyde and subjected to an electric field between two electrodes placed on either side ofthe small sphere, could be made to move with the field or against it, depending on the strength of the solution. It thus acted as though it were positively charged part of the time and negative part of the time. He assumed that it was not charged when the solution was of such strength that it was not moved by the field, i.e. that it was at the same potential as the solution. The potential between the sphere and a calomel electrode was then taken as the absolute potential of the calomel electrode.

Dr. H.P.Cady and Mr. E.F. Stimpson of the University of Kansas in 1903 started to work on the present method of measurement but due to the ill-

---

(8) Zeitschrift Electrochem. 8,638; 1902

ness of Mr. Stimpson the work was dropped. About a year ago the problem was again taken up by Drs. H.P. Cady and H.M. Elsey. At this time the design of instrument which was used in the following experiments was worked out by them and an instrument constructed which gave indications that the method would work. The problem was than turned over to me.

This method is based on the principle of the quadrant electrometer, of which a special one was made with hollow quadrants, in stead of the usual metallic ones. These quadrants can be filled with mercury or a salt of mercury in the form of a solution of definite composition. In this way any potential difference between the metal and the solution would affect the needle the same as an equal potential applied to the quadrants when they are all filled with mercury.

General Theory of the Quadrant Electrometer.

The quadrant electrometer, so called from its structure, was invented by Lord Kelvin in the year 1855 (?)#. By its use one is enabled to measure voltages or potentials astatically, that is by means of the attraction which exists between electric charges of unlike sign, without drawing any current.

It differs from other potential measuring instruments in this respect since the latter depend on the electro-magnetic effect of a current of electricity. Electric currents cause polarization in electro-chemical cells, and therefore the quadrant electrometer should be especially adapted to measurements of electro-chemical potential.

Before going into experimental details, let us look into the theory of the quadrant electrometer:

#. See: "Electrometers and Electrostatic Measurements" by Sir W. Thomson; in 'Reprint of Papers on Electrostatics and Magnetism', 2nd. Ed. P. 263-314. 1884, McMillan and Co.

Suppose a vertical metallic cylinder to be cut into four equal portions, called quadrants, by two mutually perpendicular planes which intersect on the axis of the cylinder. Further suppose a similarly cut smaller cylinder, called the needle, with two opposite quarters removed, to be suspended coaxially within this quartered cylinder in such a way that it is symmetrical with respect to one of the above cutting planes.

Now let the needle be charged, say, positive with respect to the quadrants which are grounded. The quadrants are to be so connected that one of them and its mate diametrically opposite can be disconnected from the ground and together be charged to a potential, say, of slightly above that of the earth, which is taken as zero. When this is done the needle will turn through an angle, say θ, being repelled by the positive quadrants and attracted by the negative ones.

The needle will come to rest when the resultant of all couples acting on it is equal to zero.

In the following, k's are constants of the instrument, θ the angle of deflection, and V the needle potential, large with respect to the potentials of the two quadrant systems, v_1 and v_2.

According to the elementary theory of the quadrant electrometer# the deflecting couple is:

$$k_3 V (v_1 - v_2),$$

and the mechanical restoring couple due to the torsion in the suspending fibre is:

$$k_1 \theta .$$

All the phenomena of the electrometer cannot be explained on the assumption that these are the only couples acting on the needle.

Apparently there is a further electrostatic restoring couple depending for its action on the distortion of the electric field between the needle and the quadrants, and equal to:

See under 'Quadrant Electrometer' in "Elements of Electricity and Magnetism" P.98-104. by J.J. Thomson. Cambridge Press 1904.

$$k_2 V^2\theta.$$

This latter couple may be in a positive sense, if it helps to restore the needle to its original position, or in a negative sense, if it tends to deflect the needle.

Equilibrium results when the deflecting couple is equal to the algebraic sum of the two restoring couples or when:

$$k_3 V(v_1-v_2) = k_1 \theta \pm k_2 V^2 \theta.$$

Solving this equation for the sensitivity, $\frac{\theta}{(v_1-v_2)}$ we get:

$$\frac{\theta}{(v_1-v_2)} = \frac{k_3 V}{k_1 \pm k_2 V^2} .$$

For all ordinary electrometers the sign of the electrostatic restoring couple is always plus; therefore using this as positive and differentiating the above expression with respect to V and equating to zero, we find:

See 'The Electrician' Vol. 65, P 729-733. Aug. 12, 1910. By R. Beattie D. Sc.

$$\frac{k_1k_3 + k_2k_3V^2 - 2k_2k_3V^2}{(k - k V)} = 0$$

or

$$\frac{k_3(k_1 - k_2V^2)}{(k_1 - k_2V^2)^2} = 0$$

This is true only when $k_1 = k_2V^2$; therefore the sensitovity is at a maximum for such a value of the needle potential V that theis relation holds. For values less or greater than this potential, the sensitivity of the instrument is less than the maximum.

Figures 1 and 2 will give a better idea of the electrostatic restoring couple. Figure 1 represents the lines of force between the needle and the quadrants when the former is in the zero position. Figure 2 shows them when the displacement θ has occured. It is readily seen that the lines of force have a tendency to restore the needle to its original position.

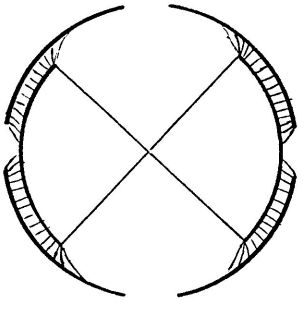


Fig. 1.

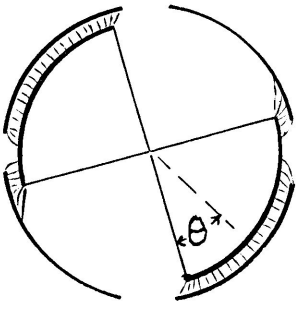


Fig. 2.

Since both the mechanical and the electrostatic restoring couples are proportional to the angular displacement, the needle will execute simple harmonic motion if displaced and released. The period of this simple harmonic motion is inversely proportional to the sensitivity and this fact gives a convenient method of finding the maximum of sensitivity. All that is necessary is to determine the period at several different needle potentials and plot this as a function of the potential. Where this curve reaches a minimum corresponds to the maximum sensitivity of the instrument.

THE METHOD.

The Instrument

If the quadrants of an ordinary electrometer be made, not of metal, but are carved out of some non-conductor in such a way that the space can be filled with a liquid which constitutes the quadrants, then this liquid can be changed without disturbing the adjustment of the instrument and the latter can be used for the determination of single potential measurements between a metal and a solution of one of its salts.

The instrument which was finally constructed is pictured on the following page. The essential part is the block of Redmanol machined out to constitute the quadrants. This was accomplished on the milling machine with a usual 5/8 inch end mill. The only precaution is that the cut be not too heavy. Redmanol caps with small vertical glass tubes in them were attached to the quadrants in order to avoid the different edge effect due to the different capillary action of the mercury and solution. If the quadrants were filled up to a pointer as was done at first, and not completely full, the edge of the mercury next to the

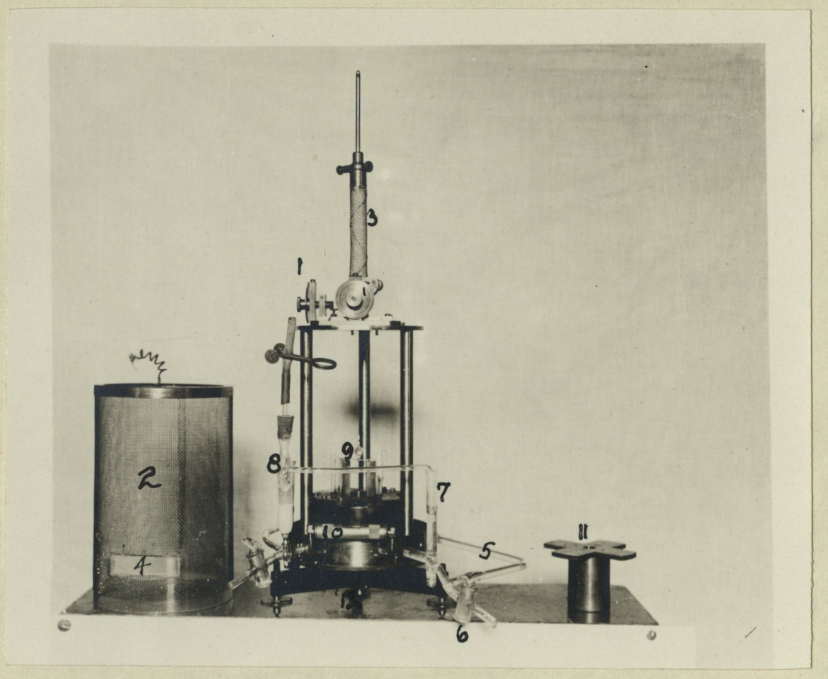


Fig. 3.

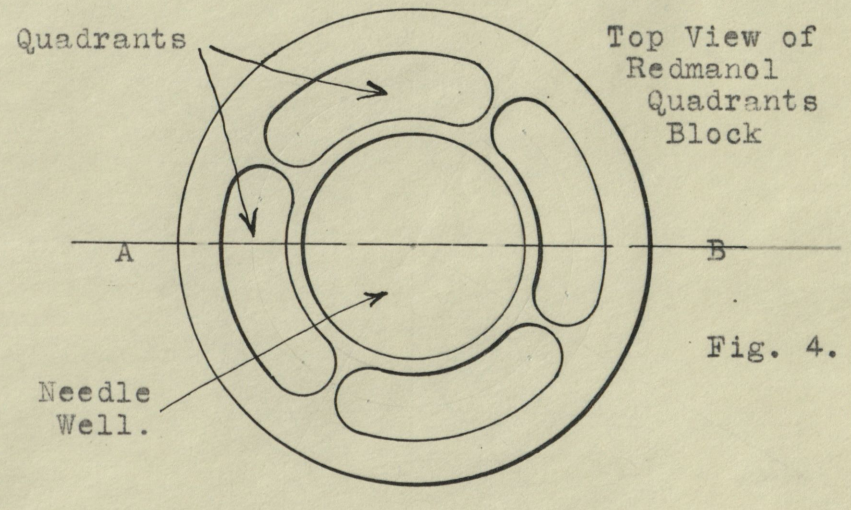


Fig. 4.

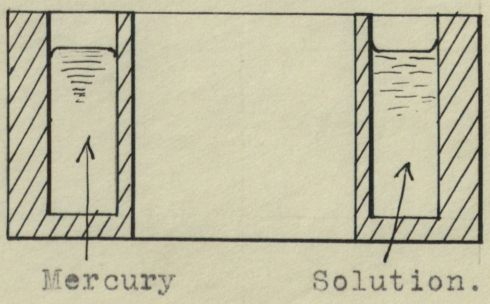


Fig. 5.

Vertical Section through A-B.

needle would have been depressed while it would have been correspondingly raised in the case of the solution, thus introducing an experimental error. (See fig. 5.)

For mechanical reasons the cylindrical-needle type of instrument was decided on instead of the plane-needle type, although the former is much more difficult to use. This is occasioned by the very carefull centering of the needle which must be done. To accomplish the latter, two cross feeds[1] at right angles and moving in ground brass slideways were constructed and equipped with screws with divided heads. In this manner the needle could be exactly centered.

A worm gear was attached to the suspended system in order to move it through very small angles. (These angles were in the order of 2-5 mm. at a distance of about three meters, or rather, one half of this since a mirror and telescope and scale were used for measuring deflections.)

The whole instrument (with the exception of the tripod base) was covered with a glass cylinder

sheathed in copper wire screen,(2) which was grounded, together with all the other metal parts except the needle and quadrants. The needle was insulated by means of a pyrex glass tube (3) also sheathed with copper screen to keep out stray electric fields.

It was necessary to cut out a section of the glass cylinder immediately in front of the mirror and set in a piece of plane glass, in order to be able to read the scale. This was accomplished by means of a revolving copper disk with carborundum and water which quickly cut through the glass; a narrow strip of plate glass was then cemented in the hole with litharge-glycerine cement. (4)

The two sets of quadrants were connected by means of the system of glass tubes (5) one of which was so arranged that its two quadrants could be completely drained by means of the stop-cock (6). Connections were made to the liquid quadrants through the two wells (7). This was accomplished by platinum electrodes which dipped into the mercury in the bottom of the wells or by means of a connecting glass tube device (8) similar to a dipping electrode. In this manner any contact potentials other than that between the metal and solution were eliminated.

The needle was built up by Dr. Elsey from sheet aluminum with a brass shaft and weight.[9] The latter was added in order to increase the stability of the adjustment, since an increased mass increased the horizontal force necessary to displace the needle from its neutral position against the force of gravity. The needle was supported by phosphor-bronze strip about 25 to 30 cm long which was soldered at both ends.

The Setup.

The instrument was mounted on a tripod base with leveling screws and could be adjusted to a level position by means of the attached level (10) and rotation of the instrument on its cone bearing at the center of the tripod. However, in the latter part of the experiments, it was leveled by means of a brass jig (11) consisting of a cylinder which fit snugly into the needle well and a brass plate carefully turned out perpendicular to the cylinder. The cylinder was inserted into the needle well and a small machinest's level was used on the top of this plate. The instrument could be locked into position by means of the lock-nut (12).

A 100pound lead cylinder rested on three iron supports which reste d in turn on a foundation going down to bed rock. Molten sulphur was poured on top of this lead cylinder and the cups in which the leveling screws of the instrument fitted rested on this sulphur. Vibrations were cut down to a minimum in this manner and a good,level,insulated, table was secured.

In order to prevent "creeping" of the needle due to air currents and heat, it was found necessary to enclose the whole instrument in a nearly air-tight box of 'beaverboard' with only a small hole for observing the mirror. The front of the box was hinged in order to have ready access to the instrument for adjustment. The connecting leads were insulated by sulphur at the points where they passed through the walls of this box.

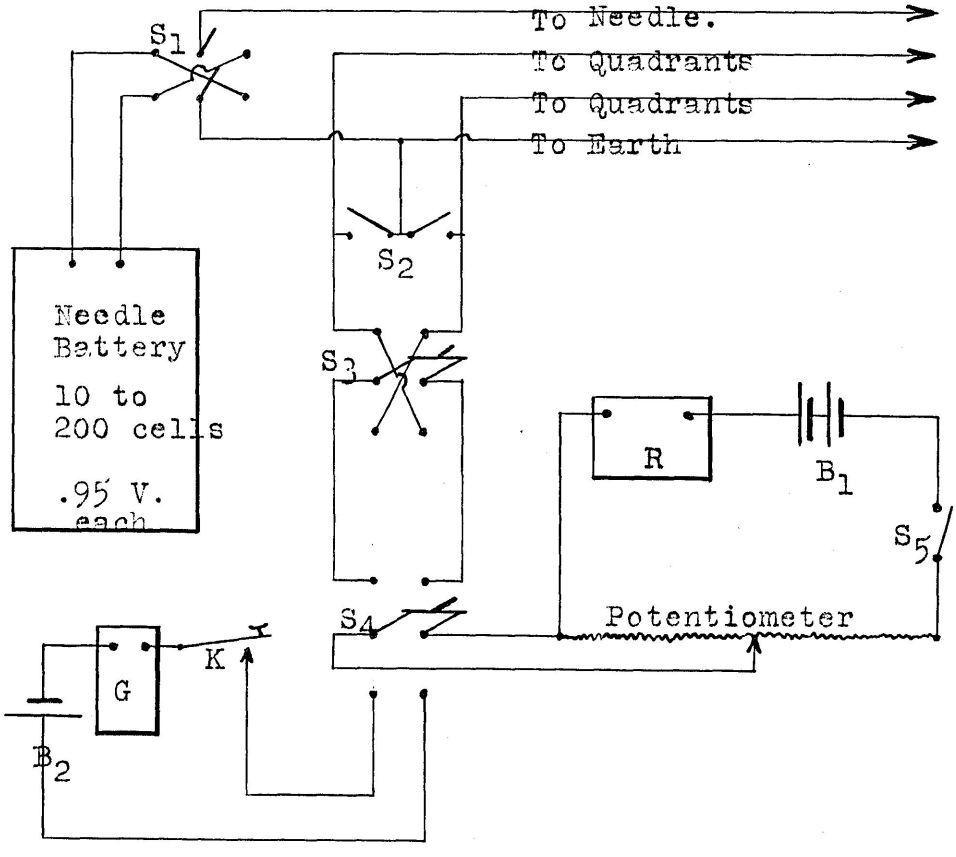
A separate ground connection was made in order to avoid stray currents which might be present on the water pipes. All connections were soldered and sulphur insulators were used wherever possible. The instruments other than the electrometer were

mounted on dry pine boards which were supported above the table top on sulphur blocks.

For charging the needle, a battery of 200 water cells consisting of copper and zinc strips immersed in specimen tubes full of water was used. This was so connected that 10, 30, 70, 100, 110, 130, 170, or 200 cells could be cut into the circuit. A Kelvin type static-voltmeter was connected permanently in the needle circuit in order to check the needle potential at all times. By this means it was found that the fibre bar connecting the two blades of a double pole switch was conducting some of the current, so all such bars were sawed in two with a hack saw.

A Leeds and Northrup Student type Potentiometer was used in the potential measurements in connection with a working standard-cell which was checked against the laboratory standard, a Weston cell made by the Weston people and checked by the Bureau of Standards. The complete wiring diagram is given on the following page.

WIRING DIAGRAM.



Key: S_1 is needle potential switch
S_2 is quadrant earthing switch
S_3 is quadrant potential switch
S_4 is standard cell switch
S_5 is potentiometer circuit switch
B_1 is the working potentiometer battery
B_2 is the standard cell
R is a resistance box
G is a galvanometer
K is a key

The mercury used was purified by agitation occasionally for several days with dilute sulphuric acid and potassium dichromate and then distilling under reduced pressure in a stream of air. The calomel solutions were made by extracting (with water) $HgCl$ about ten times in a Soxhlet and then drying over P_2O_5 in a vacuum dessicator. The KCl used was some Kahlbaum salt recrystallized by Dr. Elsey from HCl solution and dried for several weeks over KOH. It was then heated in a platinum dish until decreppitation ceased, weighed out and made up to volume with conductivity water at 15° C. These solutions were then saturated with calomel by adding an excess of the dried calomel and some mercury and agitating the flask.

One liter of each of normal calomel, tenth normal calomel, and saturated calomel were made in the above manner. The containing vessels and flasks were steamed out before use as is customary in making conductivity measurements.

The mercurous sulphate was prepared by the crystallizing dish method as described by Hulett #

Physical Review, V. 32: p 257. March, 1911.

and washed several times in a Buckner funnel with the acid before being added in excess to a liter of normal and the same volume of tenth normal sulphuric acid. The latter was standardized against sodium carbonate made by heating C.P. sodium bicarbonate for one-half hour at 270°- 300° C, and was made up from Baker's Analized Acid of specific gravity 1.84. The normal acid so made was then diluted to tenth normal in calibrated flasks.

Procedure.

Both sets of quadrants were filled with mercury and the instrument was leveled. It was then turned on its axis until the quadrants were symmetrical with respect to the line of sight of the telescope as shown by a wire stretched from the latter to the electrometer. It was then clamped in this position.

The needle was then suspended in the well at the right height and rotated by means of the worm gear until the mid-point of the scale as seen in the mirror coincided or nearly coincided with the vertical cross hair.

The cover glass was then lowered into position, the cover box put on, and the connection s were made from the needle, quadrants and case to the corresponding terminals as shown on the diagram.

Now the zero-point was noted in the telescope and the potential given by ten of the water cells was applied to the needle. The latter was in general deflected from the zero point. It was then brought nearly back to the zero point by turning the centering screws. The needle potential was then increased in a series of steps as described above and similar adjustments made until a satisfactory adjustment had been made for the potential desired. This adjustment in general took several hours, and in one instance was not accomplished even after twenty hours of intermittent work.

The needle was allowed to rest for about a half hour at the working potential to be sure that it was in equilibrium, and then the mercury was drawn out of one of the sets of quadrants with the exception of that in the bottom of the well which

was made deep for this purpose. The solution to be tested was run into the quadrants, care being taken to cover the top of the mercury in the contact well with a layer of the solid salt with which the solution was saturated.

Connection between the two quadrants was made in either of two ways, (1) by direct connection from the solution in one set of quadrants to the mercury in the other through the hollow glass electrode, or (2) by means of two platinum electrodes which dipped into the mercury through the two contact wells. The platinum was insulated from the solution, of course, by means of a small glass tube sealed over the metal.

In the latter case two methods of measurement were open, (1) to apply a counter E.M.F. and bring the instrument back to zero (called the zero method) and (2) reading the deflection produced and taking the E.M.F. from a previously run calibration curve of the instrument. Only the latter method could, of course be used in the first method of connection cited above.

It was found that the best method of determining the E.M.F. was a combination of the two methods, namely: To plot a curve of applied E.M.F.'s as abscissae and corresponding deflections as ordinates, first with mercury in all the quadrants, and then with solution in one set of quadrants. This gave two parallel straight lines and the harizontal distance between them in terms of the scale of abscissae gave the required E.M.F, This had the further advantage of graphically averaging several readings both with mercury and with solutions.

RESULTS.

Preliminary.

In order to give some idea of the difficulty which was at first encountered due to 'creeping' of the needle, the following data was taken. This difficulty was remedied, as stated in the previous section on the method, by enclosing the instrument in a nearly airtight box.

Aberrations of the Needle
(Quadrants and needle earthed)

Date			Scale Reading
Feb.	20 1922	10;00 P.M.	20.00
"	21 "	9:30 A.M.	20.20
"	" "	11:30 "	18.75
"	" "	1:20 P.M.	17.45
"	" "	3:30 "	15.70
"	" "	4:40 "	14:90
"	" "	5:00 "	16:30
"	" "	5:06 "	15:55
"	" "	5:10 "	15:90
"	22 "	8:20 A.M.	16:00
"	" "	10:40 "	14:95
"	" "	12:10 P.M.	15:70
"	23 "	8:20 A.M.	14:85
"	" "	10:30 "	15:40
"	" "	12:30 P.M.	13.35
"	" "	1:25 "	13.40
	(Box was put on)		
March	6, 1922	9:30 A.M.	25.03
"	" "	10:00 "	25.02
"	" "	11:20 "	24.85
"	" "	12:25 P.M.	24.62
"	" "	1:30 "	24.50
"	" "	2:00 "	24.45

In order to get a rough idea of the sensitivity of the instrument, the period of the free-swinging needle with different potentials applied to it was determined. The potential of each of the little water cells was found to be 0.95 volts as shown by a Kelvin Electrostatic voltmeter. For convenience the needle potentials will be expressed in terms of the number of cells in the needle circuit; the voltage can be found by multiplying this number by 0.95.

No. of cells in needle circuit	Period (in sec.)	Average
0	35.3 - 34.8	35.0 sec.
30	25.7 - 25.8	25.8 "
70	14.2 - 13.8	14.0 "
100	9.8 - 10 - 10.2	10.0 "

It was found that the sensitivity corresponding to 30 cells was sufficient, so this was used in most cases.

The standard cell used was checked against the laboratory standard, a Weston Standard Cell No. 370 made by the Weston Instrument Co. of Newark, New Jersey, with the following results:

Weston Standard No. 370..... 1.0183
Standard Cell used..... 1.0182

Measurements- Calomel solutions.

(1) No. cells in needle circuit 100
Temperature 22° C
Zero point (Hg in all quads) 19.9
Hg replaced with N calomel
Counter EMF applied + 0.283

Potential of Hg rel. to sol..... - 0.283

Same as above except N/10 calomel
Counter EMF applied + 0.157

Potential of Hg rel to sol..... - 0.157

(2) No. cells in needle circuit 30
Temperature 22° C.
Hg in all quadrants

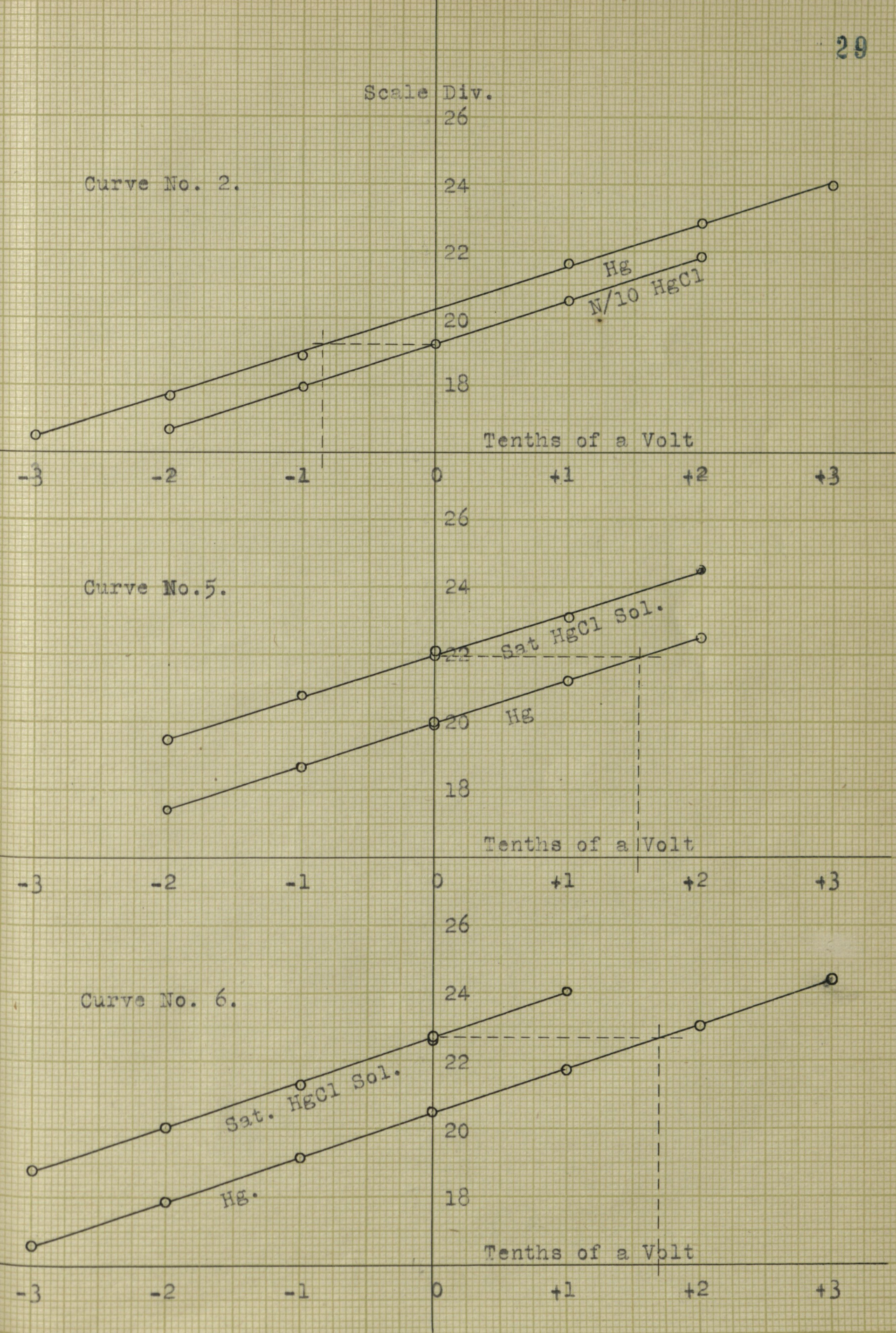
Applied EMF #	Scale reading
+ 0.1	21.62
.2	22.84
.3	24.00
.4	25.20
.5	26.44
.6	27.68
.7	28.90
- 0.1	18.89
.2	17.66
.3	16.47
.4	15.27
.5	14.10
.6	12.95
.7	11.80

Added N/10 calomel solution:

0.0	19.22
- .1	17.95
.2	16.70
+ .1	20.53
.2	21.84

Pot. of Hg rel to sol (Seecurve 2)... -0.080

The sign refers to the sign of the EMF applied to the permanent Hg quadrants.


Scale Div.
26
24
22
20
18
Curve No. 2.
Hg
N/10 HgCl
Tenths of a Volt
-3
-2
-1
0
+1
+2
+3
Curve No.5.
Sat HgCl Sol.
Hg
Curve No. 6.
Sat. HgCl Sol.
Hg.

(3) No. cells in needle circuit 70
Temperature 22° C.
Zero Point (Hg in all quads) 20.72
Added N-claomel
Counter E.M.F. applied + .170

Potential of Hg rel to sol - .170

(4) No. cells in needle circuit 70
Temperature 22° C.
Hg in all quadrants

Applied EMF	Scale Reading
0.0	18.70
- .2	14.03
- .4	9.28

Added N/10 calomel; connected quadrants with siphon electrode:
Zero Reading 13.65

Calculations:
18.70 - 9.28 = 9.42 div. per 0.4 V.
(9.42 ÷ 0.4 = 23.55 " " volt)

18.70 - 13.65 = 5.05 div.
5.05 ÷ 23.55 = 0.212 V. (Neg)

Potential of Hg rel to sol -. 212

(5) No. of cells on needle 30
Temperature 22.5° C.
Hg in all quadrants

Applied EMF	Scale reading
0.0	19.90
-.1	18.70
.2	17.44
+.1	21.21
.2	22.58
.0	20.00

Added saturated HgCl solution

Applied EMF	Scale reading
0.0	22.1
- .1	20.8
.2	19.5
+ .1	23.1
.2	24.4
0.0	21.96

Potential of Hg rel. to Sol. + .150 V.
(see curve (5))

(6) No. of cells in needle circuit 30
Temperature 23° C.

Applied EMF	Scale Reading
0.0	20.49
+ .1	21.76
.2	23.04
.3	24.38
- .1	19.17
.2	17.88
.3	16.59
0.0	20.43

Added Saturated HgCl solution

0.0	22.60
- .1	21.30
.2	20.05
.3	18.78
.4	17.57
0.0	22.70
+ .1	24.02
0.0	22.60

Potential of Hg rel to sol. +.175
(see curve 6)

(7) No. cells in needle circuit 30
Temperature 23° C.
Hg in all quadrants

Applied EMF	Scale reading
0.0	19.56
+ .2	22.11
.4	24.71
0.0	19.52
- .2	16.97
.4	14.44

Added Sat. HgCl; let stand till next morning

0.0	22.32
- .2	19.79
.4	17.23
0.0	22.40

Potential of Hg rel to sol. + .215
(See curve 7)

Replaced Sat. HgCl by N/10 claomel

0.0	20.00
-.2	17.42
+.2	22.62
0.0	20.01

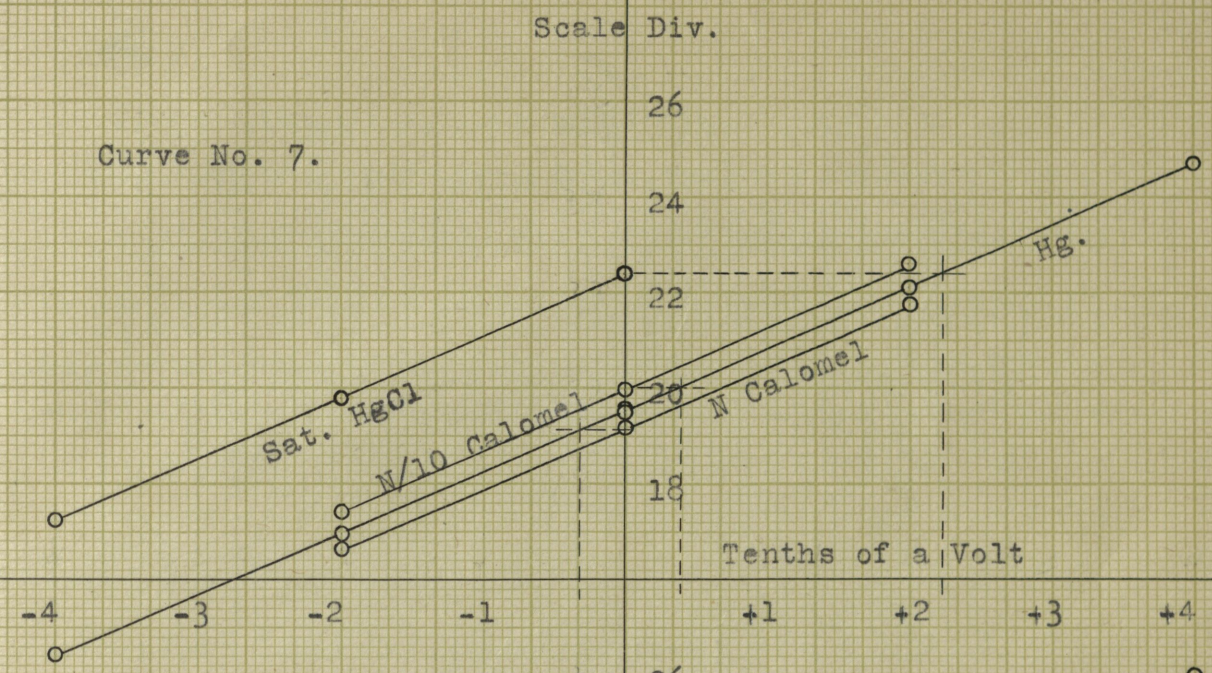
Potential of Hg rel. to Sol + .040
(see curve 7)

Replaced N/10 by N calomel

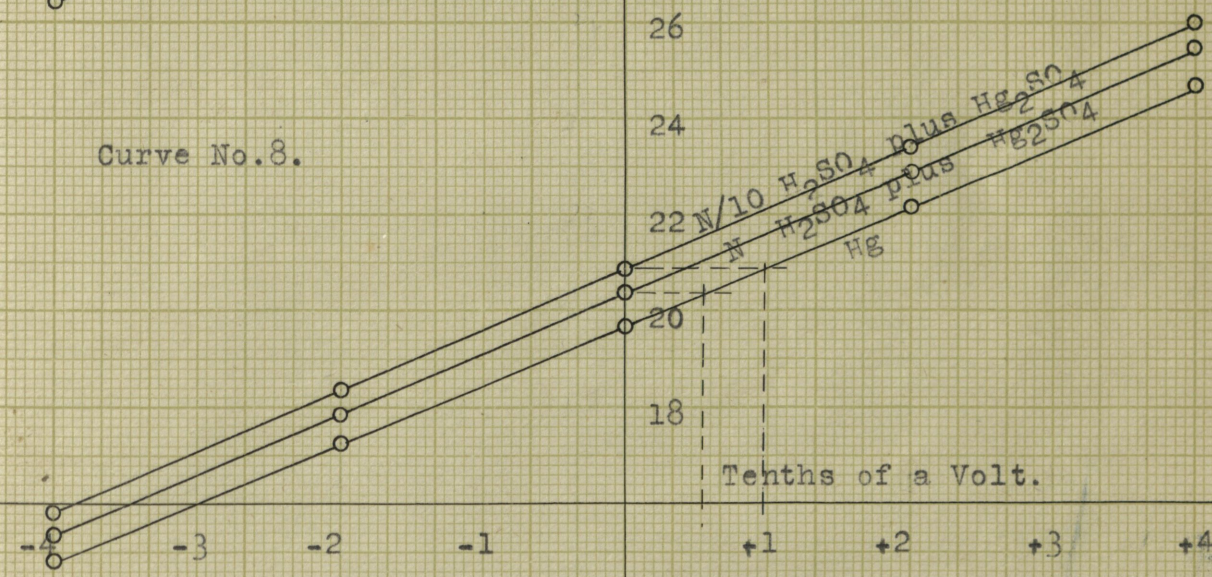
0.0	19.19
- .2	16.61
+ .2	21.77
0.0	19.19

Potential of Hg Rel. to Sol. - .025
(See curve 7)

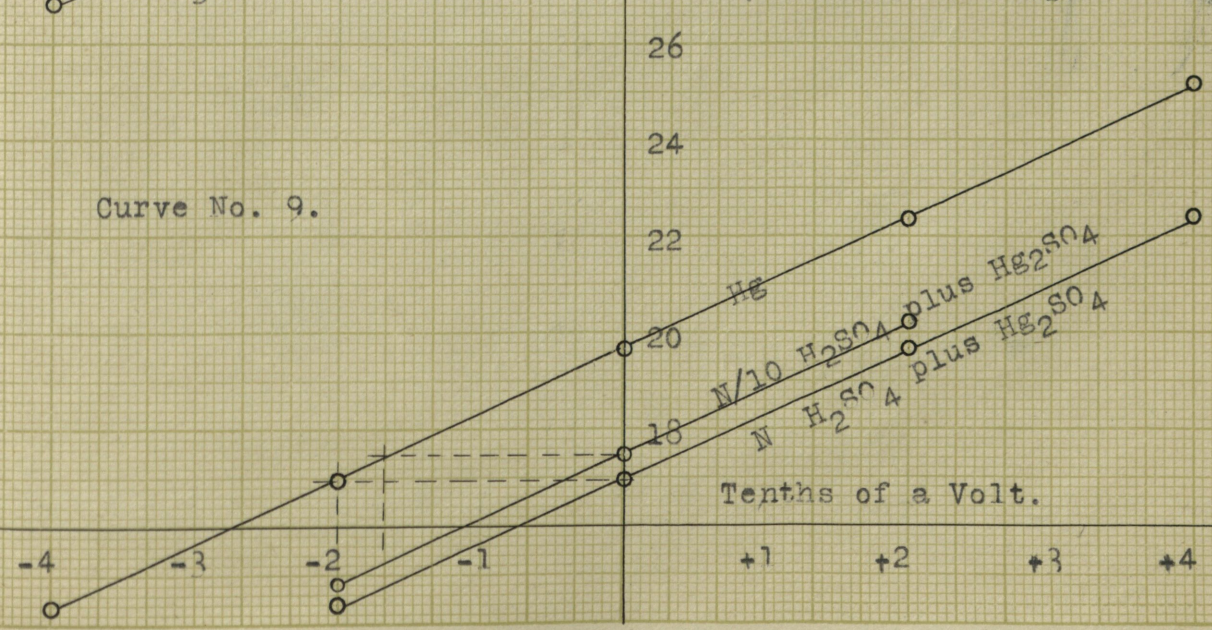
Curve No. 7.



Curve No.8.



Curve No. 9.



(8) No. cells in needle circuit 30
Temperature 24.5° C.
Hg in all quadrants.

Applied EMF	Scale reading
0.0	19.69
+.2	22.18
.4	24.69
.6	27.26
-.2	17.26
.4	14.80
.6	12.44
0.0	19.71

Added N mercurous sulphate solution

0.0	20.36
+.2	22.89
.4	25.47
-.2	17.86
.4	15.38
0.0	20.38

Potential of Hg relative to sol. +.050
(See curve 8)

Replaced solution with N/10 solution

0.0	20.88
+.2	23.42
.4	26.01
-.2	18.36
.4	15.86

Potential of Hg rel to sol. +.097

(9) No. cells in needle circuit 30
Temperature 25°C.
Hg in all quadrants

Applied EMF	Scale reading
0.0	19.65
+.2	22.38
.4	25.19
0.0	19.69
-.2	16.99
.4	14.33
0.0	19.70

Added N mercurous sulphate solution

Applied EMF	Scale Reading
0.0	16.95
+.2	19.67
.4	22.40
0.0	17.00
-.2	14.38
.4	11.80
0.0	17.02

Potential of Hg rel. to solution -.200
(See curve 9)

Replaced N with N/10 solution

0.0	17.46
+.2	20.12
0.0	17.43
-.2	14.79
0.0	17.40

Potential of Hg rel. to Sol. -.160
(Seecurve 9)

(10) No. cells in needle circuit 30.
Temperature 20° C.
Mercury in all quadrants

Applied EMF	Scale Reading
0.0	19.28
+.2	21.90
-.2	16.76
0.0	19.24

Added N mercurous sulphate solution

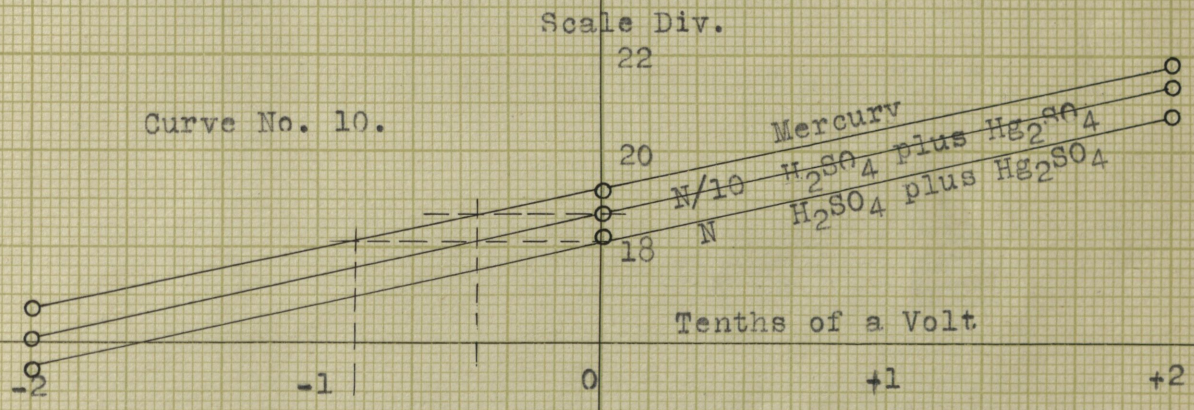
0.0	18.12
+.2	20.80
-.2	15.46
0.0	18.10

Potential of Hg rel. to Solution. -.085
(See curve 10)

Replaced N by N/10 solution

0.0	18.73
+.2	21.42
-.2	16.09
0.0	18.74

Potential of Hg rel to sol. -.047
(See curve 10)


Scale Div.
22
20
18
Curve No. 10.
Mercury
N/10 H_2SO_4 plus Hg_2SO_4
N H_2SO_4 plus Hg_2SO_4
Tenths of a Volt
-2
-1
0
+1
+2

SUMMARY OF RESULTS

Trial No.	Needle EMF	Tem.	Method	Potential of Hg				
				Calomel			Hg_2SO_4	
				Sat.	N/10	N	N	N/10
1	100	22°	Zero		-.157	-.283		
2	30	22°	Deflec.		-.080			
3.	70	22°	Zero			-.170		
4.	70	22°	Deflec. (Siphon)			-.212		
5.	30	22.5	Deflec.	+.150				
6.	30	23	"	+.175				
7	30	23	"	+.215	+.040	-.025		
8	30	24.5	"				+.050	+.097
9	30	25	"				-.200	-.160
10	30	20	"				-.085	-.047

Discussion:

While the above results are not clear cut in their indications, yet the following can be seen: None of the results even remotely approach the value of +.56 Volts for the N and +.61 Volts for the N/10 calomel electrode, which values were indicated by the capillary electrometer and the dropping electrode methods. Rather, the results indicate (with one exception No. 7) that the mercury is really negative to the solution for both the N and N/10 calomel electrodes. If this is the case, then the surface tension phenomena, on which both the capillary electrometer and the method of A. Konig (See introduction) are based, must be some function of the potential other than that of electrostatic attraction phenom-

ena on which these experiments are based.

The results indicate that mercury is from 0.15 to 0.20 volts positive to a saturated solution of mercurous chloride. The difference in potential between normal calomel and tenth-normal calomel (No.7) is seen to be 0.065 volt which checks fairly well with the theoretical value or 0.057 volt calculated by the Nernst logarithmic formula.# The corresponding difference in the case of individual trials for the mercurous sulphate is 0.47 V., 0.040V, and 0.038 V. (Trials 8,9, and10).

Considering the electrode in the case of the mercurous sulphate reversible with respect to the sulphate ion, the potential difference to be expected between N and N/10 solution is:

$$EMF = \frac{0.058}{2} \log_{10} \frac{C_1}{C_2}$$

where the C's represent the concentration of the sulphate ion in the two solutions. Taking into account the different degree of dissociation, this comes out to be 0.026 volts. The experimental results do not check so well with this value as they did in the case of the shloride.

See "Electro Chem." by Le Blanc. Translated by Whitney and Brown, 1907 Chap. IV, p. 201. McMillan.

Luther and Michie[#] set up the two cells

H_2 / 0.1 N H_2SO_4 + Hg_2SO_4 / Hg and

H_2 / N H_2SO_4 + Hg_2SO_4 / Hg ,

calculated the potential difference at the hydrogen electrode due to the different concentration, and subtracted this from the difference of the two measured potentials of the cells. This value should, then, be the potential, experimentally determined, of normal mercurous sulphate against tenth normal. They found the value to be + 0.003 Volts. It is seen that the values found in the present set of experiments is closer to the calculated value, but on the other side .

The results by the capillary electrometer and by the dropping electrode methods, similarly, have unexplained discrepancies. Since the dropping electrode only approaches the potential of the solution as a limit, one would expect it to give slightly lower values than the capillary electrometer; its value is slightly higher. The Nernst modification of the dropping electrode, similarly, should give a higher value than the simple dropping electrode; it gives a lower value (0.616 - 0.5745 Volts)

Further perfections must be made on the quadrant-electrometer before before more reliable results can be obtained by this method.

Z.f. Electrochem., 14, 828

BIBLIOGRAPHY.

1875 Lipmann, Relations entre les phenomenes electriques et capillaires, Ann de chim et de phys. (5) 5, 494-549
1877 -- Relation entre les proprietes electriques et capillaires etc, Ann de chim et de phys (5) 12, 265-276.
1878 Gibbs, Trans of the Conn Acad. 3, 380.
1880 Gore, On the Capillary electroscope Proc Roy Soc 30, 32,38.
1881 Lippmann, Bemerkungen uber einige neuere elektrokapillare Versuche, Wied Ann 11, 316-324.
1882 H. Helmholtz, Uber galvanische Polarisation des Quecksilbers usw. Monats bericht der Berliner Akad. Nov. (Wissenschaftl. Abhandl. I,925-938.
Konig, Uber die Beziehungen zwischen der galvanischen Polarisation und der Oberflachenspannung des Quecksilbers, Wied Ann. 16, 1-38.
Lippmann, Sur la theorie des couches doubles etc, Compt rend. Paris 95, 686-688.
1887 Ostwald, Studien zur Kontaktelektrizitat, Zeit. fur Phys Chem. 1, 583-610.
Pellat, Mesure de la difference de potentiel vraie etc., Compt rend Paris 104, 1099-1102.
1888 Bichat u. Blondlot, Uber die Bestimmung der Potentialdifferenzen zwichen Quecksilber und Elektrolyt, Zeit Phys Chem, 2,98-99.
Pratt, Experiments with the capillary electrometer, Amer. Jour of Science, 35, 143-151.
1889 Brown, On Helmholtz's theory of mercury dropping electrodes etc, Phil Mag 27, 384-392.
Ostwald, Uber Tropfelektroden, Zeit Phys Chem. 3, 354-358.
1890 Paschen, Zur Oberflachenspannung vom polarisierten Quecksilber, Wied Ann, 41, 42-70. 40, 36-52.
-- Eine Losung des Problems der Tropfelektrode, wied Ann, 41, 42-70
Eine Metellkontaktpotentialdifferenz, Wied Ann., 41, 186-209.
-- Nachtrag, Wied Ann. 41, 899-900.
1891 Paschen, Elektromotorische Krafte, Wied Ann, 43, 568- 609.
Planck, Uber das Prinzip der Vermerhung der Entropie, Wied Ann, 44, 385- 428.
1892 G. Meyer, Zur Theorie des Kapillarelektrometers, Wied Ann, 45, 508-522.
1894 Rothmund, Die Potentialdifferenzen zwischen Metallen und Elektrolyten, Zeit Phys Chem, 15,1-32.

1895 Lietzau, Zur Kenntnis der Polarisationsapazitat des Quecksilbers, Wied Ann 55, 338-360.
Wiedenburg, Die Gesetze der Oberflaschenspannung von polarisiertem Quecksilber, Wied Amn. 54, 64-83
1896 S. Meyer, Uber den Sitz der Potentaldifferenzen in Tropfelektroden usw., Sitzungsber. der Wiedner Akad. 105, 139-160.
Nernst, Über Beruhrungselektrizitat, Beilage zu Wied Ann., 58, 16 S.
1897 Behm, Uber die Vorgange im Kapillarelektromteter, wied Ann 61, 748- 759.
1898 Carveth, Single differences of Potential, Jour. Phys Chem 2, 288-321.
Palmaer , Uber die Wirkungsart der Tropfelektroden Zeit Phys Chem 25, 265-283.
1899 Palmaer, Chemischer Nachweis Der Konzentrationsanderungen bei Tropfelektroden, Zeit Phys Chem. 28, 257-279.
1900 Nernst, Uber Elektroden potentiale, Z f Electroch. 7, 253-257.
Rothè, Sur les differences de potentiel au contact entre le mercure et les chlorures de potassium et de sodium, Jour. de Phys 9, 543-45.
1901 Bernstein, Ein Versuch zur Theorie der Tropfelektrode, Z.f. Phys Chem. 38, 2009204
1902 Amelung, Methode zur Bestimmung der potentialdifferenz: Metall/Elektrolty, dissert, Gottingen, P 14- 45.
Billitzer, Elektrische Doppelschicht und Absolutes Potential, Z.f. Elektrochemie 8, 638-642
Van Laar, Uber die Asymmetrie der Elektrokapillarkurve Z.f. Phys. Chem. 41, 386-398.
1903 Billitzer, Elektrische Doppelschicht und absolutes Potential, Drud. Ann. 11, 902-936.
--- Uber die Elektrizitats-erregung durch die bewegung fester Korper in Flussigkeiten, Drud. Ann. 11, 937-956
Palmaer, Uber das absolute Potential der Kalomelektrode Z.f. Electro. 9, 754-757
1904 Billitzer, Zur Theorie der kapillarelektrischen Erscheinungen I,II, Z.f. Phys Chem 48, 513-548.
--- Nachtrag, Z.f. Phys Chem. 49, 709-710
1905 Billitzer, Zur Theorie der kapillarelektrischen Erscheinungen III, Z.f. Phys Chem. 51, 167-192.
1906 Billitzer, Zur bestimmung absoluter Potentialdifferenzen., Z.f Elektrochemie 12, 281-282.

1907 Palmaer,# Das absolute Potential der Kalomelelektrode. Z.f. Phys Chem, 59, 129-191.

--- A. Anderson, Theory of Behavior of the Quadrant Electrometer Phil Mag 23, 380-385.
1916 The Potential of Mercury against Hg ion (ous). J.A.C.S. 38, 2356.
1896 Ostwald, 'Elektrochemie' Veit & Co., Leipzig.
1907 M. LeBlanc, A Text-Book of Electro-Chemistry Translated from the fourth enlarged German edition by W.R. Whitney and J.R. Brown. McMillan Co.
1918 R.A. Lehfeldt, Electro-Chemistry, Part I Longmans, Green and Company. New York.
1884 Sir W. Thomson, "Electrometers and Electrostatic Measurements" in 'Reprint of Papers on Electrostatica and Magnetism' 2nd, Ed. McMillan &Co.
1904 J.J Thomson, Elements of Electricity and Magnetism" Cambridge Press.
1910 R. Beattie, Theory of the Quadrant Electrometer, Electrician 65, 729-733.
1911 Hulett, Construction of Standard Cells and Constant Temperature Baths, Phys Rev. 32,257-80.

This bibliography thus far is abridged from that attached to this article of Palmaer's.

INDEX