A STUDY OF SOME CHANGES IN THE AIR-LIQUID CONTACT POTENTIAL DIFFERENCE.

BY G. W. MOFFITT.

IN spite of the fact that much work has been done on the investigation of contact potential differences very little can yet be said with certainty, except in the case of metals, concerning either the nature or the magnitudes of the potential differences between different substances in contact. The early investigators were handicapped by apparatus of low sensitiveness and in some cases by a preconceived and decided notion of the phenomenon under investigation. In fact, the history of the subject presents to us a long series of lengthy wordy arguments between the exponents of the electrochemical theory and those of the contact theory. Often there is little experimental foundation for the conclusions reached, direct experimental results being discordant seemingly from the very nature of the phenomenon. And yet we find instances where results are given to the fourth decimal place when the apparatus was inaccurate in the third place and the observed quantity varied in the second place.

The greater part of the time and thought of investigators in contact electricity has been directed toward the solution of the problem for metals. Nevertheless we find at an early date a few investigators who did very good work in pioneering the difficult problem of metal-liquid and liquid-liquid contact potential differences. We find that Volta, Davy, Buff, Becquerel, Pfaff, Péclet, Kohlrausch, Hankel, Gerland, Clifton, Ayrton and Perry, and others have made experiments using various inductive methods.

As early as 1807 Davy,[1] in a paper entitled "Some Chemical Effects of Electricity," describes some condenser experiments which he had made using various liquids.

In 1824 Becquerel[2] attempted the investigation of metal-liquid contact potential differences. He placed the liquid in a metal vessel which stood on the upper plate of a condenser connected to an electroscope, and connected the liquid to the condenser with his fingers. He tried merely to find the sign of the electrification.

[1] Ann. de Chim. [I.], LXIII., p. 230, 1807.

[2] Ann. de Chim. et de Phys., XXV., p. 405, 1824.

Buff[1] made the lower plate of his condenser of the metal to be examined. Above it he placed a sheet of glass and on the glass a piece of filter paper soaked in the liquid. He connected the moist filter paper to the metal plate by means of a wire of the same metal.

Kohlrausch[2] made some experiments on the difference of potential of liquids in contact. He too used filter paper wet with the liquids as his condenser plates. For this reason, as we shall see later, we cannot give much weight to his results.

Hankel[3] used a modified Kohlrausch method and investigated metal-liquid potential differences without introducting blotting paper, fingers, or glass, as the earlier experimenters had done. He employed a wide funnel connected by a tube to a small cup. The vessel was filled level full of the liquid and the metal electrode was placed in the cup. Immediately above the liquid in the funnel was a copper plate. This plate was put in metallic contact with the electrode, then insulated, lifted, and connected to a Hankel electrometer. A zinc plate was then substituted for the liquid and the experiment was repeated. The metal-liquid potential difference was then deduced in terms of the contact potential difference between zinc and copper. Air-liquid contacts were neglected throughout the work. The observed values were found to vary considerably; for instance, freshly polished copper and water gave values from 0.09 to − 0.11 Zn/Cu.

Clifton[4] used a quadrant electrometer, one pair of quadrants connected to the upper condenser plate, the other pair to the lower plate. The upper plate was of the metal under observation. On the lower plate was placed a dish of the liquid to be used and an electrode of the same metal as the upper plate dipped into the liquid and made metallic contact with the lower plate. A means of charging the quadrants and the connected condenser to any desired potential difference was supplied through a key which could also serve to bring the quadrants to the same potential.

He assumed that the surface condition of his condenser plate was a constant and made no mention of the possible existence of a potential difference at the air-liquid contact. His results are referred to Zn/Cu, which he seemed to think was more constant than a Daniell or a Clark cell. He gave it as 0.8516 volt, but it is to be noticed that separate determinations disagreed in the second decimal place. He also gives potential diagrams of various voltaic circuits. These diagrams are apt to prove misleading, however, because the magnitudes of the different

[1] Ann. d. Chem. u. Pharm., XLII., p. 5, 1842; XLV., p. 137, 1844.
[2] Pogg. Ann., LXXVI., p. 200, 1850.
[3] Pogg. Ann., CXXVI., p. 286.
[4] Proc. Roy. Soc., XXVI., p. 299, 1877.

potential differences in the circuit, to say nothing of their signs, are as yet wholly undetermined.

A most thorough and comprehensive investigation of contact potential differences with liquids was begun in 1876 by Ayrton[1] and Perry in Japan. They devised an ingenious method but the apparatus required was ponderous and cumbersome. With it they made a great many determinations of metal-metal, metal-liquid, and liquid-liquid potential differences. The principle of their method was as follows:

"Let 3 and 4 be two insulated gilt brass plates connected with the electrodes of a delicate quadrant electrometer. Let 1 under 3 and 2 under 4 be the surfaces whose contact potential is to be measured. 3 and 4 are first connected together and then insulated, but remain connected to their respective electrometer quadrants. Now 1 and 2 are made to change places with one another, 1 being now under 4 and 2 under 3, then the deflection of the electrometer will give a measure of the difference of potential between 1 and 2."

The experimental difficulties encountered in interchanging 1 and 2 and still preserving the necessary constant capacity relations, especially when one or both surfaces were liquids, will be at once realized.

In their measurements no account is taken of air-metal contacts, and air-liquid contacts were considered negligible, if they had any influence at all. Before they finished their work, however, their views underwent a change and in their last paper they clearly state that their experiments leave the question of air-liquid contacts undecided. If 1 and 2 were two liquids, L_1 and L_2, what they really measured was

$$L_1L_2 + L_2 \text{ air} - L_1 \text{ air},$$

that is, the liquid-liquid contact potential difference plus the difference of the two air-liquid contact potential differences. They placed great confidence in the constancy of the contact potential difference between zinc and copper which they used as a standard at 0.75 volt (Clifton gave it as 0.8516 volt). And they agreed with Clifton that it was more constant than a Daniell or a Clark cell, although Pellat found it to vary as much as three tenths of a volt. They have tabulated the results of numerous observations which on examination reveal discrepancies many times larger than the limit of sensibility of their apparatus.

Turning to electrochemistry we have the solution pressure theory of electrode potentials and of diffusion potential differences developed by Nernst, Ostwald and others. For dilute solutions of electrode salts theory agrees fairly well with experimental results on concentration cells.

[1] Phil. Trans., Part I., 1880.

For measurements of single potential differences the electrochemists depend on the Lippmann electrometer and the dropping mercury electrode, which are based on the Helmholtz theory of the electric double layer. These are familiar to most physicists and it is not the writer's intention to review the numerous researches in this field of electrochemistry. There are, however, a few papers that may well be noticed here. Billitzer[1] has shown that the maximum surface tension for mercury in contact with a liquid does not necessarily occur when there is no difference of potential between the metal and the liquid. He showed by several methods that it may vary as much as several tenths of a volt, and he came to the conclusion that methods of measuring metal-liquid contact potential differences depending on the Helmholtz theory of the electric double layer are inaccurate. Krouchkoll[2] found similar results with wires under tension as electrodes. These results were also confirmed by Exner and Tuma, and also by Brown.[3]

Summing it all up, we may say that no experimental determination that is entirely free from objection has as yet been made of any electrode potential, or of any liquid-liquid potential difference, and that the question of the air-liquid contact potential difference has merely been raised.

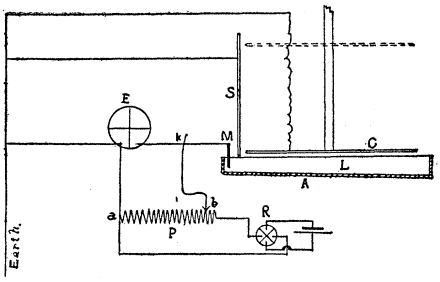

Fig. 1.

The purpose of this investigation was to devise a simple and satisfactory method for the study of contact differences of potential in those cases where liquids enter into consideration, and to seek out and eliminate if possible the unknown sources of erratic error which have caused such discrepancy in the experimental results of previous investigators. As is usually the case, the whole aim of the work has not been realized, but enough has been done to show that the problem of contact potential differences with liquids is more complex than has been thought. Factors heretofore neglected will be shown to play an important part, at least at the air-liquid contact.

A form of the compensation method was used. Fig. 1 is a diagram of the electrical connections. *A* is an insulated glass vessel 24 centimeters in diameter and less than a centimeter in depth, in which is placed the

[1] Zeitschr. Electrochem., 14, p. 624, 1908.
[2] Ann. chem. phys. [VI.], 17, p. 129, 1889.
[3] Phil. Mag. [V.], 17, p. 384, 1889.

liquid (L) under observation. C is a lacquered brass plate 20 centimeters in diameter, which, in its lowest position, stands a few millimeters above the surface of the liquid. It is arranged so that it may be easily raised to a height of 6 or 8 centimeters above the liquid while the observer is watching the electrometer scale. This plate is connected permanently to earth. M is a small electrode of the metal under observation. It is supported on an insulating stand entirely separate from the glass vessel and it is connected permanently, during an experiment, to he insulated quadrants of a Dolazalek electrometer, by means of a mercury cup and a brass wire. The other pair of quadrants is permanently connected to earth. S is an earthed electrode screen that prevents any inductive effect on the electrode by the motion of the plate C. P is a Wolff potentiometer by means of which the insulated quadrants and the electrode are brought to any desired potential through the key k, which also serves as the earthing key. R is a reversing key in the main circuit of the potentiometer which permits either positive or negative potential to be applied to the electrode. The entire apparatus, except the main potentiometer circuit and the galvanometer, is protected by earthed screens.

In some of the later experiments metal cell vessels were used instead of the glass vessel. One of these was plated with tin, the other with copper, so that various solutions might be used without chemical action on the containing vessel. When the metal vessels were used they were not filled level full, as was the glass vessel, and to prevent error due to induction between the condenser plate and the vessel rim a cylindrical guard ring of lacquered brass was used as shown in Fig. 2. This guard ring was also used in place of the electrode screen in the later experiments using the glass vessel.

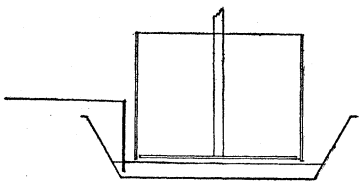

Fig. 2.

In making a reading the vessel was carefully cleaned, placed in position, and filled with the liquid to be investigated. The electrode was then rubbed bright with sandpaper, cleaned with dry filter paper, and placed in position. The condenser plate was placed at the bottom of its range of motion, and a little time allowed for the electrode potential to become steady. The potentiometer circuit was closed and the dials adjusted to any desired potential drop along ab. Then the key k was opened. On raising the plate C there was, in general, a rush of electricity to or from the electrometer. But if the *surface* of the plate and the *surface* of the

liquid were at the same potential no redistribution of charge would take place and no *change* of the electrometer reading would be observed. The potentiometer reading would be the value sought. The electrode was then removed, wiped with clean filter paper, replaced, and after a short time, the reading was checked.

It will be seen that all the advantages of a null method are retained, the electrometer acting merely as an indicator. The sensitiveness of the apparatus depends not only upon the electrometer, but also upon the ratio of the electrometer capacity to the cell capacity, and with the apparatus used it was possible to determine the balanced point within 0.002 volt. This was sufficiently sensitive for the work.

Before readings of any value could be made it was necessary to obtain a plate C whose surface potential would remain nearly constant. Pfaff and others have found that for dry or moist air and other gases, the surface potential of lacquered plates is not affected as long as there is no visible chemical action. Although used a few millimeters above the surface of liquids the plate gave no trouble. During eleven days the observed values for a copper electrode in glycerine did not vary by 0.01 volt. Copper-glycerine was occasionally used as a check on the constancy of the plate surface.

From Fig. 1 it is easily seen that what is experimentally determined is

$$K + aL + LM = E, \tag{1}$$

where K is the constant potential difference between the plate and the air, aL the potential difference between the air and the liquid, and LM that between the liquid and the electrode. If two liquids be used in succession with the same electrode we have

$$K + aL_1 + L_1M = E_1, \tag{2}$$

$$K + aL_2 + L_2M = E_2. \tag{3}$$

If a diffusion cell be set up using the two liquids we measure

$$ML_1 + L_1L_2 + L_2M = V. \tag{4}$$

Combining these three equations we have

$$L_1L_2 + L_2a - L_1a = V + E_1 - E_2. \tag{5}$$

This is in fact, what Ayrton and Perry measured, considering L_2a and L_1a negligible. With their apparatus air-liquid contacts could not be studied separately.

Consider again the observation equation

$$K + aL + LM = E.$$

The value of K may by reason of occasionally repeated check determinations, be assumed constant, although we have no means of knowing its actual magnitude. For a given liquid it is hardly possible that LM varies from time to time, and at any rate it is subject to experimental determination. We are in a position to find out whether La is a variable depending on surface condition of the liquid, gas content, and so on, and thus show its existence. And since the influence of the negative radical on the electrode potential is known to be small by reason of electrochemical data, LM will not vary much for different electrode salts. The influence of the negative radical on the air-liquid contact may then be studied.

A number of solutions of copper sulphate of different concentrations were made up. A copper electrode was used and E determined for the different concentrations. The results are plotted in Fig. 3, Curve I. This curve shows the variation of $aL + LM$ with concentration of the solution, but it does not give actual values since all readings are affected by the constant K. The same solutions were used two weeks later and Curve II. shows the results. Later on fresh solutions were made up and used with the results shown by Curve III. With zinc and zinc sulphate solutions the results were even more erratic as is shown by Curves IV. and V., which are for two sets of solutions.

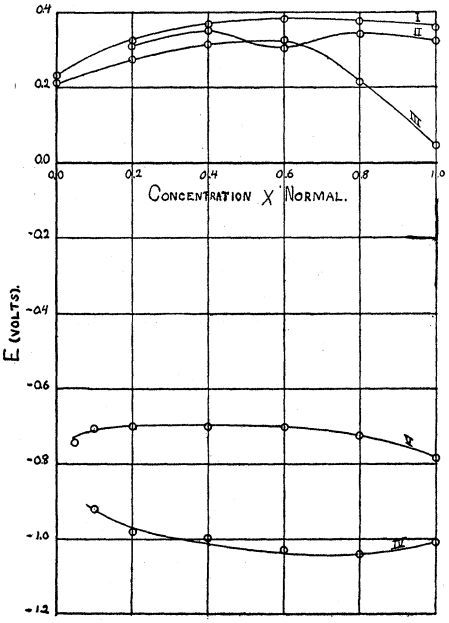

Fig. 3.

As long as results vary in this erratic way it is useless to measure the E.M.F. of the various concentration cells needed to compute $L_1L_2 + L_2a - L_1a$ for different concentrations of the same solution, and to tabulate results.

If these erratic values were due to a change in the value of K from day to day the result would be to add a constant to all the observed values, and the form of the curve would not be changed. Irregular variations of K large enough and rapid enough to account for the discrepancies seem very improbable. It is also improbable that LM can differ much for two solutions of the same salt at the same concentration. Neither is it

conceivable how *LM* for the same solution could change so much in a few days when the solution was kept in a clean glass-stoppered flask. The most probable place for differences to occur seemed to be at the air-liquid contact, and experiments were then performed to determine this point.

It was thought that the gas content of the solution might affect the air-liquid contact potential difference and with this in mind the following experiments were performed. The time of observation is recorded merely to show that the readings were made rapidly enough to eliminate the possibility of any disturbing variation of *K*. The experiments given are only a few of those performed with the same general results.

Copper Electrode. Normal Sodium Chloride Solution. Tinned Cell Vessel without Guard-Ring.

Liquid Surface Condition.	*E* (Volts).	Time.
Solution placed in cell	−0.01	3:45
Air bubbled into the solution	−0.11	4:00
Solution poured into beaker and at once poured into cell	−0.02+	4:18
	−0.03	4:30
Air bubbled in place	−0.13	4:35
	−0.13	4:50
Air bubbled again	−0.14	5:00
Poured into beaker and at once returned to cell	−0.04	5:10
Air bubbled in place	−0.12	5:15

Copper Electrode. Normal Sodium Chloride Solution. Tinned Cell Vessel with Guard-Ring.

Liquid Surface Condition.	*E* (Volts).	Time.
Solution placed in cell	−0.11	9:00
Air bubbled in place	−0.16+	9:10
Air bubbled again	−0.17	9:20
Poured into beaker. At once returned to cell	−0.05+	9:30
Air bubbled in place	−0.16	9:45
Swept with clean filter	−0.23	9:50
Poured into beaker and at once returned to cell	−0.09	10:00
Swept with clean filter	−0.24	10:10

From the first experiment it is evident that the variation in the air-liquid contact potential difference is not wholly due to dissolved gases since pouring the solution out of the cell and at once returning it returns the reading to its first value. The change due to air bubbling is practically the same in each case, and causes a shift toward negative values. In the second experiment the guard-ring was used and actual values are different, but the same general effect due to pouring and to air bubbling is noticed. Sweeping with filter paper produces an effect

much greater than that produced by air bubbling and in the same direction.

In the following trial with a 0.4 normal copper sulphate solution in the copper-plated vessel using a copper electrode, the liquid surface was repeatedly swept until a steady value was obtained.

Liquid Surface Condition.	E (Volts).	Time.
Solution placed in cell	+0.31−	1:55
Swept with clean filter	+0.21	2:00
Poured into beaker and at once returned to cell	+0.27	2:07
Swept with filter paper	+0.17−	2:13
Air bubbled in place	+0.13	2:25
Swept with clean filter	+0.06	2:30
Air bubbled in place	+0.06	2:40
Swept with clean filter	+0.03	2:43
Again swept with filter	+0.01	2:46
Again swept with filter	−0.00+	2:50
Again swept with filter	−0.02	2:55
Again swept with filter	−0.03−	3:00
Poured into beaker and at once returned to cell	+0.11	3:06
Again poured into beaker and returned to cell	+0.20	3:15
Again poured into beaker and returned to cell	+0.22	3:25
Again poured into beaker and returned to cell	+0.24	3:30
Drop of kerosene on surface	0.00	3:37
Another drop added	−0.02−	3:41
Poured into beaker, vessel cleaned, solution returned	+0.02	4:25
A drop of kerosene added	−0.02	4:30
About 1 c.c. kerosene added	−0.01	4:35

It is seen that a limiting low value was approached as the surface was repeatedly swept with filter paper. It is also of interest to note that a few drops of kerosene instantly produced the same effect as did continued sweeping with filter paper, and the addition of considerable kerosene produced the same change as did a very thin film of it.

The effect of drawing a clean glass rod reaching clear across the vessel, over the surface thus securing a clean surface, was then tried. In order to do this the glass vessel was used level full of the liquid. The copper electrode and the 0.4 normal copper sulphate solution was used with the following results.

Liquid Surface Condition.	*E* (Volts).	Time.
Poured into vessel	+0.17−	10:00
Swept with clean filter	+0.12	10:08
Again swept with filter	+0.10	10:11
Swept with clean glass rod	+0.29	10:20
Swept with filter paper	+0.21−	10:30
Swept with clean glass rod	+0.36	10:36
Again swept with rod	+0.39	10:44
Again swept with rod	+0.42	10:49
Again swept with rod	+0.43	10:52
Again swept with rod	+0.43+	10:55
Swept with clean filter	+0.29	11:00
Again swept with filter	+0.19	11:02
Again swept with filter	+0.14	11:06
Small drop kerosene added	+0.10	11:08
Another drop kerosene added	+0.09	11:12
Swept with clean glass rod	+0.14	11:16

In every case sweeping with the glass rod raised the value toward a maximum limit, and continued sweeping with filter paper reduced the value toward a lower limit.

A normal sodium chloride solution was next tried with the copper electrode, and the effects of alcohol and ether vapor and kerosene are shown below.

Liquid Surface Condition.	*E* (Volts).	Time.
Swept several times with glass rod	+0.05	9:15
Again swept with glass rod	+0.06	9:22
Undisturbed	+0.06−	9:36
Three drops alcohol put on. Negative at first but before a reading could be made was	+0.03	9:44
Three more drops alcohol, first reading	0.00	9:49
	0.00	10:12
Ether vapor poured on	−0.10	10:15
Undisturbed	−0.03	10:28
Undisturbed	−0.05	10:39
Drop kerosene put on	−0.18	10:46
Another drop kerosene put on	−0.21+	10:50
Another drop kerosene put on	−0.22	10:52
Another drop kerosene put on	−0.22−	10:55

Besides showing the effects produced by various substances this experiment shows three separate determinations with distilled water agreeing well among themselves. In all the cases tried the difference between the high clean surface value and the low filter swept or kerosene surface was found to be about 0.3 volt.

Copper Electrode with Distilled Water using Glass Vessel with Electrode Screen.

Liquid Surface Condition.	E (Volts).	Time.
Swept several times with glass rod	+0.29	9:30
Again swept with rod	+0.29	9:34
Again swept with rod	+0.29−	9:36
Screen replaced by guard ring	+0.29	9:48
Vessel emptied. Refilled. Swept with glass rod	+0.28	9:55
Swept some more with rod	+0.27+	
Some cork dust sprinkled on	+0.26	10:00
Drop of kerosene. Cork dust swept to edge of vessel	+0.01	10:06
Another drop of kerosene	−0.03−	10:10
Another drop of kerosene	−0.03−	
Cell emptied, cleaned and refilled. Swept with rod	+0.28+	10:24
Drop toluene added. A decrease but before a reading could be made it was	+0.27	10:39
More toluene added	+0.25	10:42
Drop cotton-seed oil added	+0.04	10:55
Several drops more	+0.04	10:57
Drop of kerosene added	+0.04+	10:59
Several drops more	+0.03−	11:02
Cell emptied. Refilled without cleaning. Some oil still on the surface	+0.03	11:20
Swept[1] several times with rod	0.00	11:30
Swept[1] several times with rod	−0.04	11:35
Swept[1] several times with rod	−0.05	11:41

Since the air-liquid contact potential difference has thus been varied as much as three tenths of a volt its general existence cannot be denied. In what special cases it may be zero or negligibly small we do not know Neither do we know its magnitude nor its sign in any case, but we see from the above experiments that the clean liquid surfaces used are more positive to air than are the contaminated surfaces.

Experiments were next made to find the variation of E with the concentration of the solution, taking in each determination the final value for a clean liquid surface. The copper electrode was used in all these experiments.

NaCl (Normal Solution).

Swept with glass rod	−0.05
Swept some more	−0.02
Swept some more	0.00
Swept some more	+0.01−
Swept some more	+0.01−

NaCl (0.4 Normal).

Swept as before	−0.03
Swept some more	+0.05
Swept some more	+0.04
Swept some more	+0.05

[1] The sweeping removed the small globules of cottonseed oil leaving a film of kerosene.

NaCl (0.2 *Normal*).

Swept as before	+0.08
Swept some more	+0.11 −
Swept some more	+0.10 −
Swept some more	+0.10
Swept some more	+0.10

Water (*Distilled*).

Swept as before	+0.28
Swept some more	+0.28

This gives clean liquid values for E as follows:

Water	+0.28
NaCl (0.2 normal)	+0.10
NaCl (0.4 normal)	+0.05
NaCl (normal)	+0.01 −

Solutions of copper sulphate, copper chloride, sodium chloride, bromide, and sulphate were used in the same way. The results in volts are tabulated below and curves are plotted in Fig. 4.

Curve.	Conc. →	00	0.15	0.20	0.25	0.30
A	NaCl	+0.28		+0.10		
B	$CuSO_4$	+0.28+		+0.30		
C	$CuCl_2$	+0.28+			+0.33−	
D	$CuCl_2$	+0.28			+0.32	
E	NaCl	+0.29	+0.10			+0.07
F	Na_2SO_4	+0.29	+0.22−			+0.20−
G	NaBr	+0.28	+0.06			+0.03
H	$CuSO_4$	+0.28+	+0.35			+0.37−

Curve.	Conc. →	0.40	0.50	0.60	1.00
A	NaCl	+0.05			+0.01−
B	$CuSO_4$	+0.31−			+0.31−
C	$CuCl_2$		+0.33		+0.30
D	$CuCl_2$		+0.33+		+0.30
E	NaCl			+0.05+	+0.04−
F	Na_2SO_4			+0.19−	+0.19
G	NaBr			+0.00+	−0.02+
H	$CuSO_4$			+0.36	+0.36−

A and *E* were made with entirely different solutions, as were also *B* and *H*. *C* and *D* were made with solutions diluted from the same stock solution, but otherwise they are entirely separate. The two curves differ at no point by a hundredth of a volt. *F* and *G* were not repeated.

We see in these results much better duplication of readings than was possible before, but the discrepancies are still quite large and it does not yet seem advisable to compute and tabulate values of $L_1L_2 + L_2a$

$-L_1a$. To do so before the causes of the discrepancies are better understood would be to add to an already confusing mass of more or less conjectural data of doubtful value.

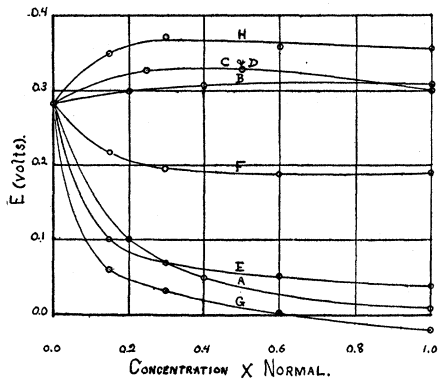

Fig. 4.

The following concentration cells were set up and the electromotive force measured with the potentiometer.

Cu-Na_2SO_4 (n)–NaCl (n)-Cu	0.164 volt.
Cu-$CuCl_2$ (n)–$CuSO_4$ (n)-Cu	0.004
Cu-$CuSO_4$ (n)–NaCl (n)-Cu	0.27
Cu-$CuSO_4$ (n)–NaBr (n)-Cu	0.35
Cu-Na_2SO_4 (n)–NaBr (n)-Cu	0.208

Combining these with the values of E taken from the curves we have the following table.

The Following Has	To the Following	A Contact P.D. in Volts.
$Na_2SO_4(n)$	NaCl(n)	$\begin{cases} +0.01 \\ -0.02 \end{cases}$
$CuSO_4(n)$	$CuCl_2(n)$	−0.01
$CuSO_4(n)$	NaCl(n)	$\begin{cases} -0.03 \\ 0.00 \end{cases}$
$CuSO_4(n)$	NaBr(n)	+0.02
$Na_2SO_4(n)$	NaBr(n)	0.00

These results are the differences of the two air-liquid contact potential differences plus the diffusion potential between the two solutions. This last, according to the electrochemists, is small for the solutions used. Then it would seem that the air-liquid contact potential differences for normal solutions with clean surfaces has approximately the same value for the solutions examined.

It was pointed out by Ayrton and Perry that if their experiments were performed in gases other than air the question of air-liquid contact potential differences could be solved. Their apparatus would have given differential results, however, and would have left the question of gas-liquid contact potential differences unanswered. With the writer's apparatus this problem may be more easily attacked, and if the surface potential of the condenser plate does not change when immersed in different gases, the difference of the gas-liquid potential difference for different gases may be directly observed.

At best experimental work in this field is tedious. Slight impurities in the water used in making the solutions seem to have considerable effect especially with solutions of low concentration. Distilled water of the best quality and in quantity sufficient for work of this kind could not be had, and it is possible that the discrepancies still in evidence may be traceable to this cause. It is the writer's intention to so modify the apparatus that a much smaller quantity of solution will suffice, and to investigate further the questions that have arisen.

The writer's thanks are due to Professors Sanford and Rogers for their kindly suggestions and criticism during the progress of the work.

SUMMARY.

1. Contact potential differences with liquids have been studied by means of the inductive method.

2. The general existence of a potential difference at the air-liquid contact has been definitely shown.

3. The air-liquid contact potential difference may vary as much as three tenths of a volt, depending on the condition of the liquid surface.

4. Water and the aqueous solutions used are more positive to the air when the surface is clean than when it is contaminated.

5. The value of the air-liquid contact potential difference (for the solutions studied) is approximately the same for aqueous solutions of different salts at normal concentration.

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