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ON BILLITZER'S METHOD FOR DETERMINING AB-SOLUTE POTENTIAL DIFFERENCES.

By H. M. Goodwin and Robert B. Sosman.

IN an interesting article on Absolute Potential Measurements which appeared in Drude's Annalen,[1] in 1903, Mr. J. Billitzer describes three new experimental methods of determining the absolute potential between a metal and a liquid, and presents results obtained by these methods which, although sufficiently concordant among themselves, are completely at variance with those generally accepted, based upon the well-known surface tension phenomena. The magnitude of the discrepancy may be judged of by the fact that the value of the potential of a normal calomel electrode determined by the proposed methods is 0.74 volt above the value generally assumed. To explain this discrepancy the author suggests a modification of Helmholtz's double layer theory, namely that the opposed charges of a double layer are not, as heretofore assumed, equal, but that a positive or negative charge preponderates according to circumstances.

The theoretical importance of the questions thus raised by the results of this investigation seemed to us to make a further verification of the experiments on which the conclusions of the articles are based desirable. With this in view we undertook to repeat with as great care as possible the experiments described. As the exact conditions under which the experiments were carried out, particularly as regards the concentration of the solutions used, are stated

[1] Ann. der Phys , 11, 902, 937, 1903.

very vaguely by the author, it was difficult or impossible to know just what the exact conditions were. We have attempted however to reproduce them as nearly as possible. It may be stated in advance that our experiments do not furnish a satisfactory confirmation of the results in question.

THE PROPOSED METHODS.

The line of reasoning on which the proposed methods are based may be briefly stated as follows. If a minute metallic ball or particle be suspended in a liquid between which and the particle a difference of potential exists, there is formed at the surface of contact of the two a double layer (Helmholtz). The metal may possess a positive or negative charge with respect to the liquid depending upon the electrolytic solution pressure of the metal (Nernst), and on the concentration of the ions of the metal in the solution. If such a suspended ball or particle, supposed positively charged, be placed in the path of a strong potential gradient maintained from an external source by immersing two electrodes in the liquid, the positive charge on the particle will be attracted to the negative electrode or cathode, and the negative charge of the double layer in the liquid will tend to move in the opposite direction to the positive pole or anode. A motion of the particle in the direction of the current, *i. e.*, toward the cathode should result. If the polarity of the double layer be reversed, the motion should be in the opposite direction. If the potential between particle and liquid is zero, *i. e.*, the double layer disappears, there should be no motion. Electrostatic effects arising from induction due to unsymmetrical disposition of the ball with respect to the electrodes are of course supposed to be eliminated by observing with reversals of the polarity of the electrodes producing the field. Absence of motion of a particle or minute metallic ball suspended in a liquid through which a potential drop is maintained is taken therefore as indicating zero potential between the metal in question and the liquid, and if an auxiliary electrode of the same metal as the suspended particle be immersed in the liquid the potential between it and the liquid is also assumed zero. Such an electrode can then be used as a standard of reference in combination with other electrodes to deter-

mine the absolute potential difference between them and the solution in which they are immersed respectively.

The three following methods all based on this principle are proposed. The essential difference between them is the mode of observing the reversal point or disappearance of the double layer.

1. The deflection of a minute ball fused at the end of fine wire and suspended in a liquid by a quartz fiber is noted.

2. The direction of migration of a colloidal metallic suspension is noted.

3. The potential difference produced at the ends of a tube of liquid when a metallic suspension is allowed to fall through the liquid is noted.

In the experiments described by Billitzer all three methods lead to practically the same result, namely that a reversal of motion in case 1 and 2 and reversal of potential in case 3 occurs when the potential between the auxiliary electrode in the solution under investigation and a 0.1-normal calomel standard electrode is + 0.125 volt, or in other words assuming the P.D. at the auxiliary electrode to be zero, the P.D. (solution to metal) of a 0.1-calomel electrode is + 0.125 volt, *i. e.*, 0.74 volt greater than the value — 0.614 volt usually assumed.[1]

In the present paper we have repeated the experiments made by the first method. The experiments described under the second method have at the same time been made the subject of an investigation by Dr. J. C. Blake in connection with an extended research on colloids.[2] The results obtained by him failed completely to confirm those obtained by Billitzer, for it was found that the direction of migration of the metallic colloid (Bredig) could be varied at will by the addition of a greater or less amount of gelatine which it was necessary to add to prevent coagulation of the colloid when an electrolyte was added to the solution. Billitzer also used

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[1] Billitzer erroneously adopts in his computation the P.D. of a normal calomel electrode instead of that of 0.1-normal electrode which he used in his experiments, *i. e.*, he bases his potentials on the value — .277 volt (normal hydrogen electrode = o) instead of the correct value — .337 volt. The first of these values is moreover incorrect; the value should be taken as — .283 volt. See Wilsmore, Zeit. für Phys. Chem., 36, 91, 1901.

[2] Am. Journ. Chem. Soc., 26, 1378.

gelatine for this purpose in all of his experiments, but he fails to state in his article exactly how much was added. In his paper " ein Spur " is stated as being sufficient, while in a letter to Blake he states that " recht viel " was added.[1] The reversals observed by Billitzer in these experiments would seem therefore to be due to the variable gelatine concentration rather than to the disappearance of the double layer on the suspended particles, and hence his conclusions relative to the potential of reversal, so far as they rest on experiments based on the second method, do not appear to be warranted.

In view of the above results and those described below, the third method has not been further investigated.

Apparatus and Method.

The form of apparatus employed in our investigation was essentially that described by Billitzer. The following details are given for completeness and reference.

The Suspension. — A platinum wire 1.5 cm. long and 0.025 mm. in diameter with one end fused to a minute sphere was attached to a quartz fiber 26 cm. long by means of a bit of sealing wax. The fiber was suspended by means of a small loop of wire attached to its upper end from a hook of fine wire sealed into a glass tube.
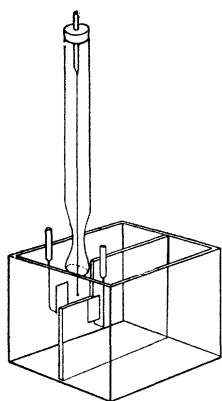

Fig. 1.

This tube could be raised or lowered through a cork which fitted the upper end of a glass guard tube to protect the fiber from air currents. The guard tube was 2.5 cm. in diameter and 35 cm. long. The lower end was drawn down and flared at the bottom as shown in Fig. 1.

The Electrodes. — The electrodes to which the 110-volt or 220-volt circuit was applied to produce a potential gradient through the liquid in which the wire was suspended were of platinum foil 4 mm. × 8 mm. to which platinum wires were welded and sealed into glass tubes, contacts being made in the tube by means of mercury.

[1] Journ. Amer. Chem. Soc., 26, 1378.

Two auxiliary platinum electrodes for measuring the potential of the liquid were used, one platinized and the other smooth. These were each 0.5 cm. × 1.0 cm.

The Vessel. — The vessel for containing the liquid was a cubical glass cell 5 × 5 × 5 cm. To concentrate the potential gradient at the suspended ball a glass partition was introduced as shown in Fig. 1. The opening in which the suspension hung was about 1 × 2 cm. The electrodes were placed one on each side of this partition. The whole vessel could be set into a beaker, the top of which was hermetically sealed by a paraffine cover through which the guard tube, electrodes, siphon and auxiliary tubes for withdrawing and admitting gases other than air were sealed. This permitted working in an atmosphere of hydrogen, carbon dioxide, etc.

Mounting. — With so delicate a suspension as that employed, the effect of mechanical jar had to be eliminated as far as possible. For this purpose the apparatus was set up on a brick and masonary pier free from the walls and floor of the building but still far from steady owing to heavy traffic in the street. On this was placed a slate block 51 × 51 × 15 cm. resting on hair felt, and on the slate block was placed a massive iron block 30 × 30 × 15 cm. The best results were obtained by supporting the iron block on three rubber stoppers placed at the vertices of an equilateral triangle. All of the apparatus was mounted on the iron block with the exception of the microscope which rested on the slate block, to permit adjustment without jarring the suspension and liquid. Even with this arrangement occasional vibrations were noticeable, but these were so small as not seriously to interfere with the observations.

Potential Measuring Apparatus. — For measuring the potential of the auxiliary electrodes against a 0.1-normal calomel electrode, the usual Poggendorff compensation method was used with a Lippmann electrometer sensitive to 0.001 volt as indicating instrument. The bridge constant was determined before each set of measurements by means of a Weston cadmium cell whose electromotive force determined against the laboratory standard Clark cell was found to be 1.020 volts.

The liquid in the cubical-shaped cell described above was connected with a 0.1-normal calomel electrode through an intermediate

vessel containing o. 1-normal potassium chloride.   Connection was made by means of a siphon containing o. 1-normal potassium chloride
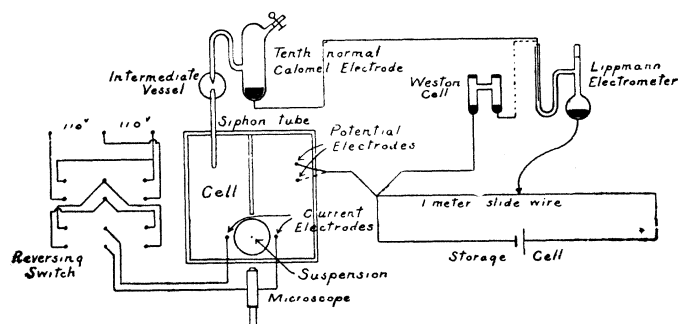

Fig. 2.

solution gelatinized by a little agar-agar.   The complete arrangement of the apparatus is shown in Fig. 2.

EXPERIMENTAL RESULTS.

We first made a number of preliminary qualitative experiments with the substances examined by Billitzer.   The results agreed in the main with his, although there were several notable exceptions as will be seen from Table I.

TABLE I.

Qualitative Experiments.

Substance.	Billitzer. Charge of Pt. vs. Solution.	Goodwin & Sosman. Charge of Pt. vs. Solution.	Remarks.
Air.	—	—	
Distilled water.	—	—	
Water + trace NaCl.	—	—	KCl added instead of NaCl.
" + " acid.	—	—	HCl added.
" + Br.	—	—	
Acetone.	—	+	
Ethyl alcohol.	+	—	No deflection observed at first.
Formaldehyde.	+	+	
Hydrogen peroxide (40 per cent.).	+	—	2 per cent. was found to evolve too much gas for observation.
Ether.	+	+	
Chloroform.	+	+	No deflection at first.

A disagreement between our results and Billitzer's, which numerous repetitions of the experiment failed to remove, was found in

the sign of the deflections in the case of acetone, ethyl alcohol and hydrogen peroxide. We were first inclined to attribute the disagreement to possible differences or impurities in the solutions, and proceeded at once to quantitative measurements in which the concentrations of our solutions were definitely known.

The first solutions thus investigated were mixtures of alcohol and water as the concentrations used by Billitzer were definitely stated for this particular case, and an exact repetition of the experiments seemed possible. The solutions used in our experiments were made up from 96 per cent. alcohol, while Billitzer states 94 per cent. as the strength used by him. Three concentrations were studied, 96, 81 and 32 per cent. respectively, thus covering the extreme range of concentrations previously investigated. Our results together with the corresponding ones obtained by Billitzer are given in Table II. In this and the following tables a negative deflection signifies that the motion was towards the anode, *i. e.*, the suspended wire was negatively charged with respect to the solution. The "deflections" are expressed in arbitrary divisions of the filar micrometer, their sign only being significant.

TABLE II.

Alcoholic-Aqueous Solutions.

Goodwin & Sosman.						Billitzer.		
Per Cent. Concentration.	E. M. F.	Deflection.	Platinized Pt. vs. 0.1 Normal Electrode.	Polished Pt. vs. 0.1 Normal Electrode.	Fine Pt. Wire vs. 0.1 Normal Electrode.	Per Cent. Concentration.	Platinized Electrodes vs. 0.1 Normal Electrode.	Deflection.
96	220	−2 to −3.	+0.050		+0.07	94	+0.155	+
96	220	−1.0	+0.003	+0.15		85	+0.15	+
81	220	−0.3 to −1.0	+0.037		+0.12	70	?	?
32	220	−3.5 to −4.0	+0.086	+0.10	+0.14	31	+0.139	—

The observations were taken after the lapse of one half hour to an hour to allow an equilibrium condition to be established between electrodes and solution. The variable values of the "deflection" are the result of a new vertical or lateral adjustment of the position of the suspended wire between the polarizing electrodes. It is to be noted that no positive deflection could be obtained even in 96

per cent. alcohol although Billitzer's results showed such deflections to occur in 78 per cent. alcohol and even 70 per cent. solutions. Moreover the potentials of the three types of auxiliary electrodes used, namely, platinized platinum, smooth platinum and wire similar to the suspended wire, showed no satisfactory agreement either with Billitzer's corresponding values or with each other. Results obtained with the platinum wire agreed on the whole best with Billitzer's. As to the best form of auxiliary electrode to use and the probable cause of the above discrepancies reference will be made later.

The power which alcohol possesses of reversing the potential of a platinum electrode as observed by Billitzer, is explained by an auto-oxidation by which hydrogen peroxide is formed. Hence it was concluded that addition of small amounts of this latter substance should also have the power of reversing the potential of platinum in acid solution. This prediction was borne out by Billitzer's results, a reversal occurring as before at approximately 0.125 volt, *i. e.*, platinized platinum *vs.* 0.1-normal calomel electrode. We repeated these experiments varying the concentration of hydrogen peroxide from 0.2 per cent. to 0.001 per cent., but obtained in every case a negative deflection. The condition of our solutions must have been essentially the same as Billitzer's, as the potential of the platinized electrode *vs.* 0.1-normal calomel electrode agreed fairly well with that found by him. It may be noted here that hydrogen peroxide was one of the substances which in our preliminary experiments was found to give results disagreeing with the published ones. Billitzer obtained a positive deflection in 40 per cent. hydrogen peroxide. We were unable, however, to obtain reliable deflections with even a 2 per cent. solution on account of the violent disturbances in the liquid arising from the decomposition of hydrogen peroxide in the presence of platinum. Our results are given in Table III. together with Billitzer's first series with hydrogen peroxide for comparison. The concentrations in his experiments were not stated.

As an example of a strong reducing agent capable of effecting a potential reversal, formaldehyde was found by Billitzer to reverse the deflection when the platinum potential *vs.* 0.1 normal calomel electrode was as before 0.125 volt. As no statement is given to in-

TABLE III.

Hydrogen-peroxide Solutions.

Concentration in Per Cent.	Goodwin & Sosman.				Billitzer.	
	E.M.F.	Deflection.	Platinized Pt. vs. 0.1-Normal Calomel Electrode.	Smooth Pt. vs. 0.1-Normal Calomel Electrode.	Deflection.	Platinized Pt. vs. 0.1 Normal Electrode.
0.2	220	−1.0 to −1.5	+0.29		+	−0.4
0.1	220	−5.0 to −6.0	+0.28	+0.28	+	+0.3
0.02	220	−6.0	+0.23		+	+0.2
0.004	110	−2.5	+0.20		+	+0.15
0.001	220	−3.5	+0.19	+0.20	?	+0.12
					—	+0.10
					—	+0.08

dicate whether weak or strong solutions of the substance were used we extended a series of measurements from a 40 per cent. to a 0.04 per cent. solution. In this case we were able to detect a reversal in the deflection in passing from a 10 per cent. to a 36 per cent. solution. The reversal potential however did not check Billitzer's, as will be seen from the results given in Table IV.

TABLE IV.

Formaldehyde Solutions.

Concentration in Per Cent.	Goodwin & Sosman.				Billitzer.	
	E. M. F.	Deflection.	Platinized Pt. vs. 0.1-Calomel Electrode.	Smooth Pt. vs. 0.1-Calomel Electrode.	Deflection.	Platinized Pt. vs. 0.1-Normal Electrode.
40	220	0 to +0.3	−0.02	+0.06	+	+0.17
36	220	+0.3	−0.03	+0.04	+	+0.15
36	220	+0.2	+0.02	+0.07	+	+0.14
10	110	−1.5 to −2.0	−0.04		+(?)	+0.13
10	220	−2.5	−0.04		—	+0.12
2	220	−2	−0.06	+0.06	—	+0.11
0.4	110	−1.5 to −2	−0.10	+0.01	—	+0.10
0.2	110	−1.0 to −1.5	−0.07	+0.03	—	−0.09
0.08	110	−2.0	+0.02	+0.04		
0.04	110	−4. to −5.	+0.01	+0.07		

Finally we repeated the series of experiments in which the variation of the reduction potential of a solution was varied between wide limits by changing the relative concentration of ferrous and

ferric ions in the solution. Billitzer found that by varying the relative concentration of these ions a reversal of the deflection of his test electrode occurred again at the characteristic potential between 0.10 and 0.13 volt. We did our best to check these results but without success. Our only guide for duplicating the concentration used was the statement that " die Koncentration der ursprünglichen Lösung wurde in verschiedenen Fällen verschieden, immer jedoch sehr klein gewählt." Billitzer used ferrous and ferric sulphates in his experiments ; we used ferric chloride and ferrous sulphate.

TABLE V.

Ferrous and Ferric Salt Solutions. $(Fe_3Cl + FeSO_4)$ *in Various Proportions.*

Goodwin & Sosman.						Billitzer.	
Concentration in Per Cent.		E.M.F.	Deflection.	Platinized Pt. vs. 0.1-Calomel Electrode.	Smooth Pt. vs. 0.1-Calomel Electrode.	Deflection.	Platinized Pt. vs. 0.1-Normal Calomel Electrode.
FeCl₃.	FeSO₄.						
0.001	0	220	0	+0.36	+0.41	+	+0.16
		110	−1.5			+	+0.15
		220	−3.0			+	+0.14
0.001	0.02	220	−2.5	+0.32		+	+0.13
0.001	0.03	220	−1.0	+0.315		(very weak.)	+0.125
0.001	0.05	220	uncertain because of electrolysis.	+0.23		—	+0.10
						—	+0.09
0.05	0	220	uncertain because of electrolysis.	+0.50	+0.46		
0.035	0	220	uncertain because of electrolysis.	+0.49			
0.035	0	220	uncertain because of electrolysis.	+0.43			
0.001	0	220	negative	+0.38	+0.29		
0	0.1	220	electrolysis.	+0.27	+0.25		

In these experiments reliable deflections could be obtained only in the very dilute solutions on account of electrolysis. Whether the solution contained ferrous or ferric ions the platinum suspension showed deflections indicating the metal to be negatively charged in all cases. The auxiliary platinum electrode was under the same conditions always positively charged referred to Ostwald's zero.

MERCURY AND SILVER ELECTRODES.

In the above experiments platinum is to be regarded as an oxidation or reduction electrode. Among other metals whose electrolytic solution pressure is such that a reversal of their potential with respect to a solution can be effected by varying the ionic concentration of the solution, may be mentioned mercury and silver. These metals were both tried by Billitzer, the former as amalgamated fine platinum wire, and the latter in the form of very fine silver wire. Auxiliary electrodes of the pure metals were used for measuring the potential of the solutions against a 0.1-normal calomel electrode as before.

We tried both of these metals but obtained a reversal only with mercury. A reversal was observed by Billitzer with mercury in mercuric nitrate, in one experiment only.

In these experiments the suspended platinum wire ball was amalgamated by being placed as cathode in a solution of mercuric nitrate acidulated with nitric acid. The auxiliary potential electrode of platinum was similarly amalgamated. After amalgamation the wire showed numerous swellings along its length about 0.04 mm. in diameter, the wire being 0.025 mm. in diameter. The strongest mercuric nitrate solution used in the following measurements was 2.5 per cent. acidulated with six drops of nitric acid in 200 c.c. A solution of 0.1-normal potassium nitrate was used in the siphon to connect with the calomel electrode. The results are given in Table VI.

TABLE VI.

Mercury in mercuric nitrate solutions.

Concentration in Per Cent.	E.M.F.	Deflection.	Amalgamated Pt. vs. 0.1-Normal Calomel Electrode	Remarks.
2.5	110	+1.5 to +4	+0.405	No deflection at first.
1.25	110	+2.5	+0.403	" " "
0.13	110	+0.3 to +0.4	+0.385	
0.025	110	−0.4	+0.364	
	220	−0.4		
0.013	220	−1.5	+0.350	

It is to be noted that the reversal potential (between + 0.36 and + 0.39 volt) does not agree with Billitzer's + 0.125 value.

In the case of silver Billitzer could get no reversal by diluting a silver nitrate solution. The reversals all indicated the silver was positively charged *vs.* the solution. By the addition of potassium cyanide the concentration of silver ions can be almost indefinitely diminished and it is well known that the metal becomes negatively charged with respect to such a solution. Billitzer observed by his second method (direction of migration of colloids) that addition of potassium cyanide produced a reversal when the auxiliary electrode indicated a potential of between + 0.11 and + 0.16 volts *vs.* 0.1-normal electrode. We tried the experiment of noting the deflection of a very fine silver wire 0.043 mm. diameter suspended as before by a quartz fiber in an excessively dilute silver nitrate solution to which potassium cyanide was added. No trustworthy observations could be obtained at concentrations greater than about 0.0005 normal on account of electrolysis. As will be seen in Table VII., deflections were always negative even when the auxiliary silver electrode changed in potential from + 0.27 volt to — 0.30 volt *vs.* the 0.1-normal calomel standard. In silver nitrate alone we have certainly every reason to regard silver as positive *vs.* the solution, yet the sign of the deflections observed, if they are determined by the charge alone, would indicate the contrary.

TABLE VII.

Silver in silver nitrate + potassium cyanide.

Concentration in Mols. $AgNO_3$.	E.M.F.	Deflection.	Ag. Electrode vs. 0.1-Normal Calomel.	Remarks.
0.01'	110	uncertain	+0.35	Electrolysis.
0.005	110	"	+0.33	"
0.0005	110	−1	+0.27	
	220	−1.5+	+0.27	
0.0001	220	−0.5	−0.30	.01-Normal $AgNO_3$ ppt. and redissolved in KCN and diluted ten times.

DISCUSSION.

A consideration of the preceding results show that :

First: The phenomenon in question, *i. e.*, of the reversal in deflection of the suspended wire does not appear to be general, but

occurs only in exceptional cases.   The general phenomenon would seem to be a motion of the suspended metal towards the *anode*.

Second: The reversal phenomenon does not appear to stand in any definite relation to the potential between the auxiliary electrode and the solution, the characteristic reversal potential of + 0.125 volt (platinum *vs.* 0.1-normal calomel electrode) found by Billitzer being in no case observed.

These two experimental facts seem to us to be reasonably well established by our experiments.   We do not attempt to offer an explanation for the remarkably concordant results of Billitzer leading to entirely contrary conclusions.   It is possible that some essential condition was observed in his work not sufficiently stated in his article to enable us to duplicate it in our experiment.   If so we trust that it will be more clearly pointed out.   Attention may be called, however, to several factors which impressed themselves upon us in the course of our work, which have a direct bearing on the phenomenon under discussion and which may lie at the foundation of the results observed.

Effect of Electrode Surface.

Does the auxiliary electrode indicate the same potential as that existing between the fine suspended wire and the same liquid ? This is evidently a fundamental question as the interpretation of all results obtained by Billitzer rests on the assumption that the two are identical.

We carried out several experiments to test this point by comparing against a 0.1-normal calomel electrode the potential drop between a platinized electrode, a polished electrode and an electrode consisting of a fine wire used for the suspension.   It might be expected that since the last is smooth wire with a ball fused at the end, it would comport itself electrometrically more nearly like the polished platinum electrode than the platinized electrode.   It was found that potential measurements with such extremely fine wire electrodes and even with electrodes consisting of a bunch of such wires were difficult to make and rather uncertain in their results.   The following figures show that the potential of a fine wire electrode and a platinized electrode in the same liquid may differ by several hundredths of a volt, the former being always higher.

Solution.	Wire.	Platinized.	Polished.
Formaldehyde.	+0.02	−0.064	+0.059
"	+0.10	+0.019	+0.041
Alcohol-water.	+0.07	+0.050	
"	+0.12	+0.037	
"	+0.14	+0.086	+0.100

Polished electrodes were found to be far less certain in their behavior than platinized electrodes, as was to be expected, and it might be fairly assumed that the wire electrodes would show similar irregularities. Platinized electrodes, on the other hand, when properly prepared by treating as cathode in dilute sulphuric acid to reduce and remove residues of the platinizing liquid (Ostwald), then washed in boiling water, gently heated and finally allowed to stand in distilled water, always gave concordant results among themselves.

Effect of Time on Potential Equilibrium. — A very marked effect of time on the potential of the auxiliary electrode was noted in some cases which was different for platinized and unplatinized electrodes. This was most marked in the case of formaldehyde solutions, and was noticeable in all other solutions except those of hydrogen peroxide and mercuric nitrate.

A gradual change in the solution may account in part for the progressive rise in potential observed : the point we wish to make however is, that the time required to reach equilibrium was much greater in the case of the platinized than in the case of the unplatinized electrode, and if the unplatinized suspended wire comports itself like the polished potential electrode the same kind of uncertainty in its indications as to deflections would result.

The cause of the gradual rise of potential of the auxiliary electrode potential, observed in distilled water was also investigated. The potential was lower in freshly boiled water than in water which had stood some time in air : the effect was therefore ascribed at first to dissolved oxygen, but when pure air was passed through carefully boiled water to resaturate it, the potential fell instead of rising. This suggested at once that carbon dioxide caused the change. Carbon dioxide from the lungs was passed through the water, and the potential rose; this carbon dioxide was then washed out by a current of pure air, and the potential fell to the value first obtained in

air-washed water.   Saturation of the water with pure carbon dioxide brought the potential up somewhat above that obtained in water which had stood in contact with air.   Tory and Barnes[1] have observed such an effect with platinum, and ascribed it to air; it may be possible to explain their results by the presence of carbon dioxide.

Effect of Liquid Junction. — Of minor importance in the present investigation is the value of the potential difference arising at the junction of the o.1-normal electrode and liquid under investigation. This is at best uncertain in experiments like the above, and although in many cases it is probably small owing to the nearly equal migration velocities of potassium and chlorine ions, yet with the somewhat complicated nature of the solutions and solvents used and their extreme dilution it is possible that it may attain a very appreciable value.

EFFECT OF DISSOLVED GASES ON THE SIGN OF THE DEFLECTION.

We would like to point out one other factor which seems to us of much greater importance on the phenomenon in question than any of the preceding, and one which apparently has not been considered by Billitzer.   We refer to the phenomenon described and investigated in 1861 by Quincke,[2] who found that minute bubbles of hydrogen, oxygen and air act exactly like solid particles when suspended in a liquid and *migrated towards the anode* when a current was passed through an aqueous solution containing them.   In turpentine, however, he found that all substances which he investigated (except sulphur) migrated *positively*, *i. e.*, towards the cathode. Now it was frequently observed in our experiments that no deflection was produced at the first instant the voltage was applied.   After visible electrolysis had taken place and minute bubbles appeared in the liquid, a deflection of the wire became evident and the deflection was always towards the anode.   This seems to us significant, for although it is true that deflections were repeatedly observed at the instant the current was established and when no bubbles were visible on the end of the suspended wire, yet is quite conceivable, and indeed probable, that in the process of immersing the wire in the

[1] Trans. Amer. Electrochem. Soc., 3, 95, 1905.
[2] Pogg. Ann., 113, 565, 1861.

liquid from the air, very minute particles of air might remain attached to it, or might separate out on it from the liquid.   The following experiment in the light of Quincke's results seem to bear out the above hypothesis.   The platinum wire was suspended in turpentine and deflections observed with 220 volts applied.   They were unmistakably positive.   The resistance of the cell was so high that the current was less than 0.00001 ampere.   In distilled water saturated with pure hydrogen, the deflection was distinctly negative. The presence of minute, even invisible, bubbles of gas on the suspended electrode which may arise from gases in the solution, from the air or from electrolysis, seems therefore to offer a very plausible explanation of the results observed.

Another factor which may also have at least a secondary influence on the deflections, is the possible motion of the liquid surface under the action of the applied voltage.[1]   Such a motion of the surface was frequently noticed on closing the circuit, when the microscope happened to be focused so that the surface was in the field of view.   Since a difference of potential exists between a liquid surface and the gas above it, such a motion does not seem *a priori* unlikely.   This phenomenon is worthy of further investigation.

CONCLUSION.

The present investigation was undertaken in order to obtain a confirmation of Billitzer's results on absolute potentials by the method of deflections of a minute metallic electrode suspended in various solutions, under the influence of an electric current.   The results obtained have failed completely to confirm the measurements obtained by him, and we are forced to the conclusion that the method proposed is not to be relied upon for the purpose for which it was developed.   This conclusion is further strengthened by the results obtained by Blake on the migration of colloids, who has also failed to confirm Billitzer's measurements using the colloid method.

So far as our experiments go, it would seem that most of the phenomena observed may be explained on the assumption of the negative migration of gaseous particles in the liquid, as first demonstrated by Quincke in 1861.

[1] F. B. Kendrick, Zeitschr. f. Physikal. Chem., **19**, 625, 1896.

We believe therefore that the results obtained by Billitzer by the above described method afford as yet no sufficient grounds for rejecting the generally adopted values for the potential of the normal (or tenth normal) calomel electrode.

Since the above work was completed two other articles[1] have appeared by the same author in which he has determined absolute potentials by investigating the phenomena of concentration changes produced by the dropping electrodes first studied by Palmaer, and by a modification of Pellat's surface tension method. As the results obtained by both of these methods confirm approximately the author's previous results, a description of the precise conditions under which the former experiments were carried out seems all the more desirable.

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THE ROGERS LABORATORY OF PHYSICS (LABORATORY OF ELECTRO-
CHEMISTRY), MASSACHUSETTS INSTITUTE OF TECHNOLOGY.