Apparatus especially valuable for this method is described in a series of papers, of which this paper is the last.

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ALTERNATING CURRENT ELECTROLYSIS.

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PART I.

Manuevrier and Chappius[1] found that, when an alternating current is passed through electrodes of very fine platinum wires dipped into a sulfuric acid solution, there is an immediate and abundant evolution of gas. They also found that the higher the frequency the less the amount of decomposition.

Ayrton and Perry[2] used alternating currents having a frequency of 10,000 per minute, and made the interesting observation that a deposition of hydrogen gas on a platinum electrode hinders visible decomposition by alternating currents, while deposition of oxygen favors such decomposition. Hopkinson, Wilson and Lyddal[3] also investigated the nature of electrolysis by alternating currents, but they laid more stress on the physical side of the question. M. LeBlanc[4] passed an alternating current between copper electrodes in a cyanide solution and found that, with the rate of reversal of 1000 per minute, copper passed quantitatively into solution; while, with the rate of 38,000 reversals per minute, only 33% of the theoretical quantity dissolved. LeBlanc holds that the copper passes into solution if the copper dissolved at the anode has time to be converted into the complex cuprocyanide ion before the reversal of the current.

Brochet and Petit[5] do not share the view that the possibility of alternate current electrolysis depends on the formation of a complex ion. They conceive the general condition for the formation of a new compound to be, that the ion, on reaching the electrode, has had time to part with its charge before reversal produces the ion of the opposite charge, at the same electrode. Ostwald also holds the above view. It frequently happens that the immediate product of the chemical processes at the electrodes undergoes further changes which are difficult to reverse. He considers that reversibility is often merely a question of time and for short intervals of time is always present. This is shown by the fact that

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[1] *Compt. rend.*, 106, 1719–22; 107, 37–40.

[2] *Electrician*, 21, 299–300.

[3] *Proc. Roy. Soc.*, 54, 407–417.

[4] *Z. Electrochem.*, 11, 705 (1905).

[5] *Ibid.*, 10, 909 (1904); 11, 441 (1905).

in using alternating currents to measure electric conductivity no deviation from Ohm's law has been observed. This proves that the energy of one current which has disappeared in polarizing the electrodes reappears in the next current of opposite direction, *i. e.*, the chemical decomposition effected by the passage of the alternating current in one direction is completely reversed by the succeeding identical current in the opposite direction, and the resultant chemical action thus becomes nil. The direct experimental verification of this view is, however, a very difficult one, since, even if any chemical action takes place on the passage of a high frequency alternating current through an electrolyte, it will be so minute that our ordinary methods of chemical analysis would fail in detecting it. It occurred to the author that by measuring the potential differences between an electrode and an electrolyte, before the passage of an alternating current, and then during or just after the passage of the same, a clue might be obtained as to whether any chemical action has taken place on the electrode surface. It was also thought possible that, since the electrode potential is due to the electrical double layer at the surface of separation between the electrode and the electrolyte, the amount and direction of variation of electrode potential may throw light on the nature of the chemical changes at the electrode surface.

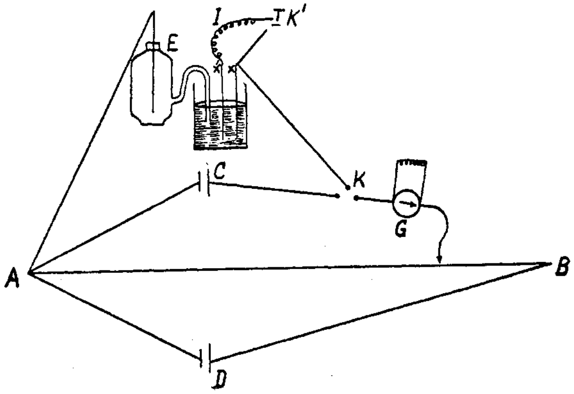

Fig I.

The following method of experimental procedure was adopted: A B is a potentiometer wire (see Fig. I) through which a constant current from a four-volt battery D is passing. C is a Weston cadmium element and E is a decinormal calomel electrode of comparatively high resistance. X and X′ are the electrodes dipped into the electrolyte whose electrolysis on the passage of an alternating current is to be studied. They are joined through a key, K′, to the two terminals of the secondary I of an induction coil. The key K′ consists of a mercury cup in which the two connecting wires are dipped, and should be placed nearby on the potentiometer table. Since it is necessary to measure the electrode potential of either X or X′ just after the passage of an alternating current, the time between breaking contact at K′ and making the galvanometer contact with the potentiometer wire should not be at all appreciable. The induction coil used is a very small one, such as is generally used in the conductivity measurements according to the method of Kohlrausch. The frequency of alternation was 30,000 per min. approximately. The current passing through the primary was measured by an ammeter placed in the circuit. K is a three-way key and G a galvanometer. The galvanometer was shunted off by means of a sliding resistance (which should be near at hand). The E. M. F. of the combination E and X is measured by comparison against C.

The first experiments were carried out to determine whether there is any variation in the electrode potential on the passage of an alternating current through two pieces of the same metal dipped in its own salt solution. Two clean zinc rods were taken and immersed in a normal solution of zinc sulfate. The internal resistance of the cell thus obtained was about one ohm. The current strength through the primary of the induction coil was $^3/_{15}$th of an ampere.

E. M. F. of the combination of E and X before the passage of the alt. current = 1.105 volt.

E. M. F. of the combination of E and X during to passage of the alt. current = 1.105 volt.

E. M. F. of the combination of E and X just after the passage = 1.105 volt.

The same constancy of behavior was obtained in the case of cadmium in cadmium sulfate solution and copper in copper sulfate solution. In the case of metals dipped in their own salt solutions such constancy of behavior is to be expected, for here the question of an irreversible change being conducted reversibly does not come in. These results also justify the assumption that only when there is some such change as would alter definitely the chemical nature of the electrical double layer, is its effect noticeable by the measurements of the electrode potentials.

The next investigation carried out consisted in determining the changes in the electrode potentials in cells consisting of two platinum electrodes dipped in any electrolyte. The great disadvantage of these determinations lies in the fact that we seldom get a constant value of the electrode potentials in these cases, and therefore these measurements cannot be exactly repeated. But, since the variation of electrode potential is the only point of importance, the uncertainty in the absolute values of these potentials does not affect the worth of these measurements. Two pieces of polished platinum of equal area—3.5 cm. in length and 1 cm. in breadth, were cut out from the same foil, cleaned, ignited red hot and then kept dipped in the given electrolyte for about 24 hours. It was found, in accordance with the observation of Smale[1] and others, that, in order to obtain a maximum constant potential difference between the electrodes and the electrolyte, it is necessary to keep the electrodes immersed in the

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[1] *Z. phys. Chem.*, 14, 577 (1894).

given solution for quite a long time. The electrodes were washed and ignited red hot each time they were used for potential measurements

TABLE I.

Acid.	Concentration.	E. M. F. before passage.	E. M. F. during passage.	E. M. F. after passage.
HCl	1.0 *N*	+0.52	+0.31	+0.35
HNO_3	1.0 *N*	+0.68	+0.48	+0.52
CH_3COOH	0.2 *N*	+0.25	−0.02	−0.01
HCOOH	0.2 *N*	+0.07	−0.37	−0.30
COOH │ COOH	0.2 *N*	+0.31	−0.02	+0.01
H_2SO_4	0.2 *N*	+0.51	+0.61	+0.60
H_2CrO_4	1.0 *N*	+0.80	+0.96	+0.92
Monochloroacetic	0.2 *N*	+0.31	+0.60	+0.57
Trichloroacetic	0.2 *N*	+0.35	+0.52	+0.49
Lactic acid	0.2 *N*	+0.34	+0.51	+0.50
Tartaric acid	0.2 *N*	+0.34	+0.54	+0.52
Malonic acid	0.2 *N*	+0.35	+0.61	+0.60
Malic acid	0.2 *N*	+0.31	+0.42	+0.39
Citric acid	0.2 *N*	+0.36	+0.58	+0.54
Benzene sulfonic acid	0.2 *N*	+0.34	+0.54	+0.51

TABLE II.

Potassium hydroxide	1.0 *N*	+0.05	−0.02	+0.01
Sodium hydroxide	1.0 *N*	+0.06	−0.02	+0.01
Sodium carbonate	0.1 *N*	+0.09	+0.02	+0.03

TABLE III.

Potassium permanganate	0.1 *N*	+0.45	+0.54	+0.49
Potassium dichromate	0.1 *N*	+0.35	+0.45	+0.41
Potassium nitrate	1.0 *N*	+0.2	+0.30	..
Potassium chlorate	1.0 *N*	+0.22	+0.31	..
Potassium bromate	1.0 *N*	+0.35	+0.43	..

TABLE IV.

Hydroxylamine hydrochloride	1.0 *N*	+0.02	−0.05	−0.01
Hydrazine sulfate	1.0 *N*	−0.13	−0.18	−0.16
Sodium sulfite	1.0 *N*	−0.16	−0.21	−0.17
Potassium iodide	1.0 *N*	+0.10	−0.08	+0.05

TABLE V.

Salt.	Concentration.	E. M. F. before passage.	E. M. F. during passage.	E. M. F. after passage.
Potassium chloride	1.0 *N*	+0.15	+0.30	+0.25
Potassium bromide	1.0 *N*	+0.12	+0.26	+0.22
Potassium sulfate	1.0 *N*	+0.15	+0.21	+0.20
Zinc sulfate	1.0 *N*	+0.14	+0.28	+0.21
Copper sulfate	1.0 *N*	+0.30	+0.38	+0.36
Zinc chloride	1.0 *N*	+0.21	+0.40	+0.38
Sodium tartrate	1.0 *N*	+0.05	+0.024	+0.03
Sodium citrate	1.0 *N*	+0.11	+0.21	+0.20
Chromium sulfate	1.0 *N*	+0.41	+0.50	+0.48

against a fresh solution. The electrodes were kept 1 cm. apart and an alternating current passed for 15 min. The current strength through the primary was $^2/_{15}$th of an ampere. The E. M. F. was measured just before the passage of the alternating currents during the passage, and then just after the stoppage of the alternating current. The secondary circuit was always kept closed.

It was found that, although the absolute values of the E. M. F. depend much on the concentration of the electrolyte, the amount of variation of E. M. F. is much the same for all concentrations between 1.0 *N* and 0.1 *N*. The variation depends much on the time of the passage of the current, rising to a maximum after a definite interval which did not exceed 15 minutes in any of the cases studied. In the tables, therefore, the maximum variation has been noted down. The negative values of E. M. F. in the tables mean that in these cases the calomel electrode is positive. It will be noticed that, in all the cases recorded above, the E. M. F. just on stopping is nearer the initial E. M. F. than the E. M. F. during the passage of the alternating current. Indeed, in all the cases investigated, a complete recovery curve was obtained. They are all similar in nature and only some of the typical ones are given in Figs. II, III and IV. It will be noticed that, in the beginning, the recovery is quite rapid but afterwards it becomes quite slow. The fact that in each case the E. M. F. gets back to the original value goes to show that they are tending towards stable conditions. The new chemical substances produced by the action of the alternating current alters the nature of the electrical double layer, but they soon disappear by diffusion and we get the old values of the E. M. F. again.

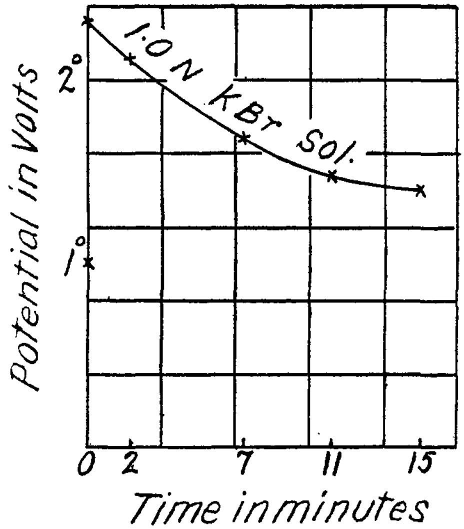

Fig. II

On examination of Table I, it will be noticed that the acids may be divided into two groups. For the acids 1–5 the E. M. F. diminishes on the passage of the alternating current, while for the rest the opposite is the case. The latter class of acids are all characterized by either containing Cl or (OH) groups. Thus the behavior of lactic, tartaric, or monochloroacetic acids is quite different from that of formic, acetic or oxalic acids. It will also be observed that the E. M. F. of acids undergoes greater variation that the E. M. F. of other electrolytes—the amount of variation being from 0.2 to 0.4.

In Table II it will be observed that the variations are in the same direction—the E. M. F. diminishing during the passage of the alternating current. The variations here are also relatively small.

In Table III all the substances are oxidizing agents and we find that the E. M. F. increases during the passage of the alternating current. With the reducing agents the contrary is the case—the E. M. F. diminishing during the passage of the current.

In the case of the salts *e. g.*, potassium chloride, sodium chloride, the E. M. F. generally increases with the passage of the alternating current. Now the electrode potential observed on the platinum surface is always referred to as being the potential difference between the air and the solution, or more particularly between the oxygen gas of the atmosphere and the O″ or OH″ ions of the solution. A diminution in the value of the electrode potential must therefore be attributed to a diminution in the concentration of the oxygen gas. We may expect a diminution of the value of the electrode potential on the passage of an alternating current in the case of platinum foils dipped in solutions of reducing agents, if we believe that the anion of the electrolyte breaks up at the electrode surface and combines with the oxygen there to form more stable bodies. The diminution of electrode potential in the case of certain acids is also intelligible on the assumption that the discharged hydrion goes to combine with the oxygen of the double layer. Similarly, by assuming the decomposition of the anion of an oxidizing electrolyte and the consequent setting

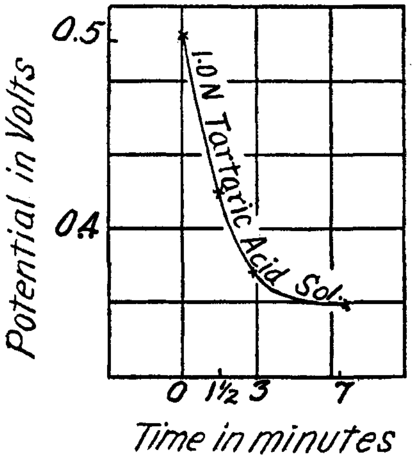

Fig. III.

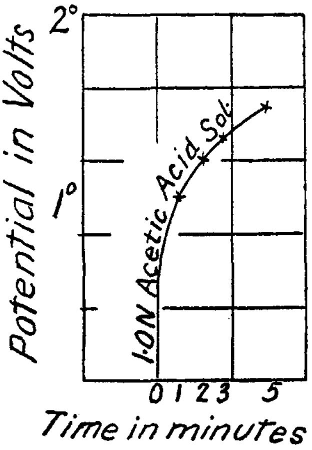

Fig. IV.

free of oxygen gas, we may explain the increase in the electrode potential observed in those electrolytes. The above variations in electrode potential therefore give us a direct experimental evidence of the fact that on a polished platinum surface, even for such short intervals of time as 1/2 × 30000 minute, the chemical process at the electrode is not a reversible one, *i. e.*, the ion has had time to part with its charge and form other more stable bodies.

When the platinum electrodes in the previous cases were substituted by mercury electrodes, a good deal of the variation in the electrode potential on the passage of the alternating current was also noticed. Here, however, it is very difficult to obtain fairly concordant results, even after taking all the precautions used in the case of platinum electrodes. Here the electrolytic cell of the previous cases was replaced by a H shaped cell, at the bottom of the two limbs of which there is a sufficient quantity of pure mercury to act as electrode. The cross-section of the surface of mercury was 0.75 cm. sq. and the distance between the surfaces of the electrodes 1.2 cm.

TABLE VI.

Electrolyte.	Concentration.	E. M. F. before passage.	E. M. F. during passage.	E. M. F. after passage.
H_2SO_4	1.0 *N*	+0.20	+0.23	+0.22
HCl	1.0 *N*	+0.11	+0.15	+0.12
$K_2Cr_2O_7$	0.1 *N*	+0.272	+0.32	+0.31
$Na_2S_2O_3$	0.1 *N*	−0.40	−0.51	−0.42
KI	0.1 *N*	−0.46	−0.49	−0.48
Na_2SO_3	1.0 *N*	−0.05	−0.06	−0.05

The amount of variation to be observed in these cases is not so great as in that of platinum. The nature of variation is also, in many cases, quite unlike that of platinum. The peculiarity was observed that after the passage of the alternating current the mercury surface in most cases lost its brilliancy, and it was therefore suspected that some chemical compounds might have been formed. Indeed Manuevrier and Chappius[1] noticed that when an alternating current was passed through mercury electrodes in sulfuric acid solution there was formation of mercurous sulfate on the electrode surface.

When, however, electrodes of platinum black are used the above variation in electrode potection on the passage of alternating currents almost disappears. In no case were the fluctuations more than 0.015 volt. This proves that there is no appreciable consumption of energy at the electrode surface and the condition which Ostwald lays down for the trustworthiness of conductivity measurements by means of alternating current is almost fulfilled.

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[1] *Loc. cit.*

The variations, under the influence of alternating currents, of the single electrode potentials of combinations which have an E. M. F. of their own was next studied. Here it is impossible to observe the fluctuations in electrode potentials during the passage of the alternating current, for there the two dissimilar electrodes are in metallic contact through the secondary of the induction coil. The readings are therefore taken for each electrode, before and just after the passage of the alternating current—the arrangements, as has been previously mentioned, being such that no appreciable time passes between the breaking of the secondary circuit and the determination of the null point. A completely reversible element shows no peculiarity, inasmuch as the electrode potential remains absolutely the same before and after the passage of the alternating current.

The study of cells containing an electrode consisting of a metal surrounded by its insoluble salts gave quite interesting results. In this type of cells, which have an E. M. F. of their own, the electrode gets polarized when the cell is allowed to work for itself. Here, in order to determine the effect of the alternating current, it is necessary to study first the behavior of the cell as regards its E. M. F. after it has been allowed to work for itself for a certain amount of time; the cell is then left to itself to recover its normal condition, and when the recovery is complete it is again allowed to work for the same interval of time under the influence of an alternating current, and its behavior as regards E. M. F. again studied. The Helmholtz calomel element, zinc-zinc chloride-mercurous chloride-mercury, was taken up for study. The cell, after preparation, should be left to itself for a few days, so that mercurous chloride may settle completely and in a compact condition on the surface of mercury. This is necessary in order to secure standard conditions as regards the depolarizing capacity of the cell. The electrodes of the cell were corrected through a resistance box and the mercury cup K′ to the two terminals of the secondary coil. Here there is no necessity of the calomel electrode, A and B being directly connected to the electrodes of the calomel element.

Initial E. M. F. of the cell = 1.02 volt. The circuit is closed through a resistance of 460 ohms. E. M. F. of the cell just on breaking circuit after 10 min. 0.61 volt. The cell is allowed to recover, and then after 2 hours, external circuit is closed with an alternating current passing through the secondary coil—the current strength through the primary being $^2/_{15}$th of an ampere. E. M. F. of the cell just on breaking circuit after 10 min. = 0.15 volt. By varying the external resistance, different reading for the two sets of values of E. M. F. could be obtained. The circuit is kept closed in each case for 5 minutes.

TABLE VII.

Resistance. Ohms.	Initial E. M. F. Volt.	E. M. F. after closing circuit simply.	E. M. F. after closing circuit with an alt. current.
400	1.02	0.51	0.12
700	1.02	0.76	0.16
900	1.02	0.84	0.20
500	1.07	0.45	0.11
700	1.07	0.64	0.16
900	1.07	0.81	0.20

TABLE VIII.

Resistance. Ohms.	Initial E. M. F. Volt.	E. M. F. after closing circuit simply.	E. M. F. after closing circuit with an alt. current.
200	0.8	0.49	0.26
300	0.8	0.18	0.16
500	0.8	0.19	0.16

. In the cell whose E. M. F. was 1.07 volt the zinc chloride solution was more dilute. The recovery curve could also be easily traced in the case where the external circuit was kept closed through a small resistance for about 15 minutes. Fig. V shows a typical one. The rate of recovery is slow at the beginning, very rapid after some time, and then again slows down as the normal E. M. F. is approached. The curve in the case where no alternating current passed is always above the curve of the case where the alternating current did pass.

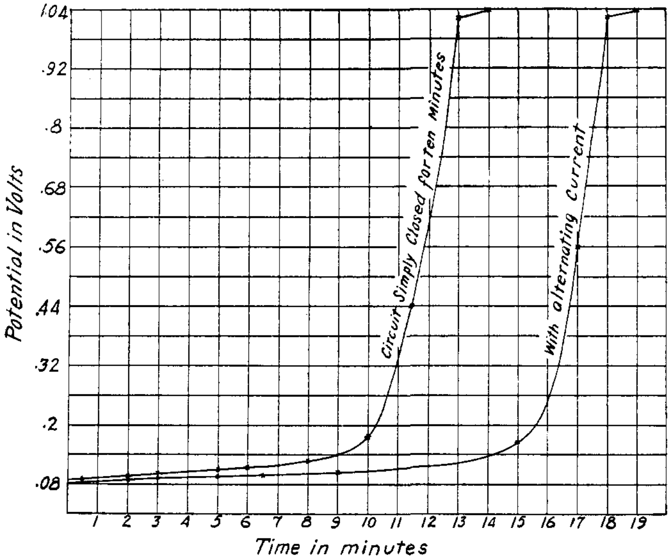

Fig. V.

The cell Cd–$CdCl_2$–Hg_2Cl_2–Hg also lends itself to study in the same manner.

The recovery curve is given in Fig. VI. It will be noticed that in the case of these cells, even when there is sufficient resistance in the external circuit, the rate of recovery is slow enough to be accurately traced.

The cell zinc-zinc sulfate-mercurous sulfate-mercury was also studied.

The external resistance in the circuit should be as small as possible, mercurous sulfate being soluble enough to give unpolarizable electrodes for small current densities. In this case, the recovery curves are similar to those of the calomel cell. Now, since in all the cells studied, there remained always a sufficient amount of mercury salt on the surface of the mercury electrode, we may reasonably hold that the depolarizing capacity of each cell retained a constant value. Now the curves of recovery to the normal E. M. F. with time, as also the values of E. M. F. just on the breaking of circuit, show unmistakably that the cell retains its polarization longer in the case when an alternating current plays in the external circuit than in that in which the external circuit is simply kept closed. If therefore we attribute a constant value to the depolarizing capacity of each cell we may conclude that a greater amount of polarization takes place in the former case than in the latter.

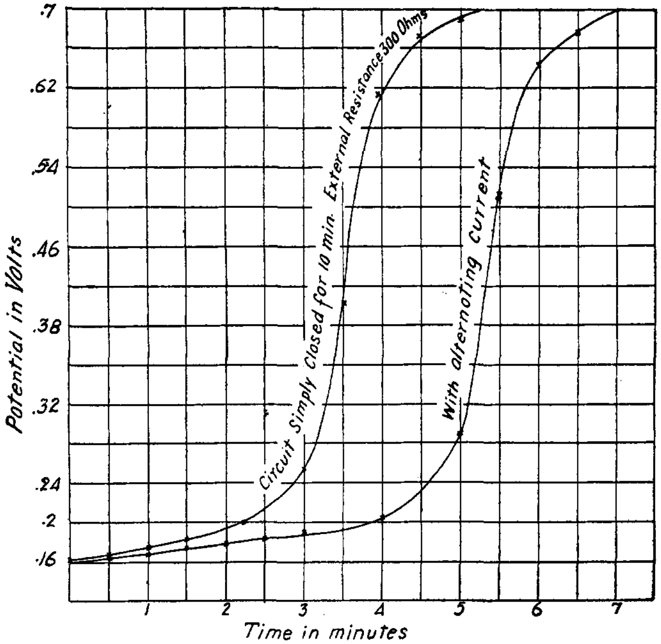

Fig. VI.

The effect of impressing an alternating current to the above type of cells is therefore to increase the amount of polarization at the mercury electrode, and necessarily to increase the amount of the polarizing current which the cell furnishes of itself.

The behavior of cells containing an electrode which is very easily polarizable was next studied. The internal resistance of the cell was always very small—never greater than one ohm.

TABLE IX.

Cell.	E. M. F. before passage.	E. M. F. after simply closing circuit.	E. M. F. after closing circuit with alt. current.
Zn-ZnSO$_4$-Pt	1.41	0.05	0.05
Cu-CuSO$_4$-Pt	0.31	0.04	0.04
Cd-CdSO$_4$-Pt	1.20	0.05	0.05

TABLE X.

	E. M. F. of the mercury electrode	
Cell.	Before passage.	After passage of alt. current.
Cd-ZnSO$_4$-Hg	−0.05	+0.98
Al-ZnSO$_4$-Hg	−0.07	+1.01
Fe-ZnSO$_4$-Hg	−0.06	+1.02
Ni-ZnSO$_4$-Hg	−0.1	+1.00
Ca-ZnSO$_4$-Hg	−0.08	+0.10

Quite a number of such cells were studied, but in no case was a great difference found between the values in the 3rd and the 4th column. The rate of disappearance of polarization with time did not yield reliable results. However, in the case of those cells where mercury is the polarizable electrode, *e. g.*, zinc-zinc sulfate-mercury, magnesium-magnesium sulfate-mercury, it is observed that ripples begin to play more violently on the mercury surface when an alternating current plays in the external circuit.

The next type of cells consisted of electrodes both of which were easily polarizable. The electrode potential of each electrode of the cell was measured against a decinormal calomel electrode, before and then just after the passage of the alternating current. The salt solutions used were quite concentrated and the internal resistance of the cell was, as in the previous ones, very small. The alternating current was allowed to pass for 15 minutes.

Except in the case of nickel, the electrode potential of the more electro positive metals of the above cells did not change appreciably. In the case of the cell Ni-ZnSO$_4$-Hg the electrode potential of nickel rises from +0.24 to +0.42, but this high value is not retained long enough. In all the above cells, except in the case of the cell Cu-ZnSO$_4$-Hg, it will be observed that the mercury electrode assumes a potential value which is almost equal to that of metallic zinc against a zinc sulfate solution. Evidently zinc has formed an amalgam with mercury. The mercury electrode loses its high E. M. F. only very slowly.

TABLE XI.

	E. M. F. of the platinum electrode	
Cell.	Before passage.	After passage of the alt. current.
Cd-ZnSO$_4$-Pt..	−0.25	+0.95
Fe-ZnSO$_4$-Pt..	−0.22	+0.56
Ni-ZnSO$_4$-Pt..	−0.23	+0.62

TABLE XII.

	E. M. F. of mercury electrode	
Cell.	Before passage.	After passage of alt. current.
Ni-CdSO$_4$-Hg..	−0.12	+0.62
Fe-CdSO$_4$-Hg..	−0.15	+0.63
Ca-CdSO$_4$-Hg..	−0.16	+0.60

It is to be noticed that the platinum electrode attains the E. M. F. of zinc only in the case of the cell Cd-ZnSO$_4$-Pt. Unlike the behavior of the mercury electrodes, platinum does not retain this high potential for a long time. Fig. VII is a typical recovery curve of the platinum electrode in the case of the cell Cd-$ZnSO_4$-Pt. The two breaks at 0.83–0.86 volt and again at 0.2–0.25 volt are very peculiar. The first break perhaps indicates the lower limit of existence of zinc and the other at 0.23, the limit of existence of hydrogen gas which is perhaps evolved by the solution in water of zinc deposited or the platinum surface. In this connection the work of Oberbeck[1] and Königsberger and Muller[2] on the concentration of the massive metal, may be referred to. Cells were then studied in which the electrolyte was a salt of cadmium.

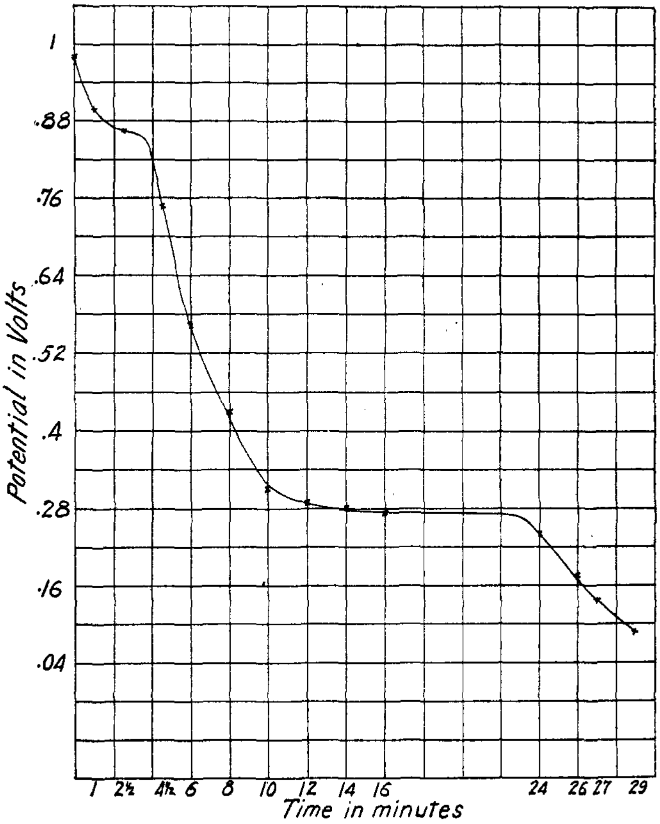

Fig. VII

In all the above cases the electrode potential of mercury, after the passage of the alternating current, approaches the potential value of cadmium against cadmium sulfate solution. Here also mercury loses its high E. M. F. only very slowly. In the cell Cu-$CdCl_2$-Hg, mercury did not

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[1] *Wied. Ann.*, **31**, 336 (1887).

[2] *Phys. Z.*, **6**, 847, 849 (1905).

exhibit the E. M. F. of cadmium, and the contrast between the behavior of the two salts is quite marked.

TABLE XIII.

Cell.	E. M. F. of the platinum electrode Before the passage.	 After the passage of the alt. current.
$Ni-CdSO_4-Pt$	—0.26	+0.61
$Cu-CdSO_4-Pt$	—0.25	+0.02

Platinum in the case of the first cell approaches the potential value of cadmium, but not in the case of the second cell. However, the cell $Ni-CdSO_4-Pt$ shows quite an anomalous behavior. The behavior of the platinum electrode of the cell depends essentially on the condition of the nickel electrode. If the alternating current be passed through the cell just after the nickel wire, thoroughly cleansed and polished with emery paper, is dipped into the electrolyte, platinum could be made to attain the potential value of cadmium. If, however, the alternating current is passed, several hours after the cell has been prepared, the E. M. F. of platinum rises from —0.27 to +0.01 volt. The behavior of nickel electrode itself also indicates this change in the condition of its surface on being kept dipped into the electrolyte. The E. M. F. of nickel against a decinormal calomel electrode just on dipping it into the solution was +0.2 volt, and after the passage of the alternating current for 10 minutes was 0.5 volt. However, if the electrode be kept immersed in the solution for several hours the initial value is only +0.08 volt, and that after the passage of the alternating current only +0.10 volt. No change in the surface of the nickel electrode could be observed with the eye.

Some cells formed by the combination of two electrolytes were next studied. It has been stated before that when an alternating current passes through the cells $Cd-ZnSO_4$ sol.-Hg, $Cd-ZnSO_4$ sol.-Pt, the mercury or platinum exhibits the electromotive force of zinc. But the behavior of the cells $Cd-CdSO_4-ZnSO_4-Hg$, $Cd-CdSO_4-ZnSO_4-Pt$ is quite otherwise. In no case could the value of the electrode potential of mercury or platinum be made to exceed the electrode potential of cadmium against cadmium sulfate solution. In cells of the type $M-MX-M_1X-M_1$, where M is the more electropositive metal, it was found that M_1, even under the influence of a fairly strong alternating current, could not be made to attain an electrode potential greater than that of M.

The cells $Ni-ZnSO_4-CdSO_4-Hg$, $Ni-ZnSO_4-CdSO_4-Pt$ were next studied. It was observed that after the passage of the alternating current both mercury and platinum electrodes assumed the electrode potential of cadmium.

Further work on the nature of electrolysis under the simultaneous influence of a direct and an alternating current is in progress.

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EQUILIBRIUM IN THE SYSTEM: LEAD ACETATE, LEAD OXIDE, WATER, AT 25°.

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The basic acetates of lead owe a considerable importance in applied chemistry to the fact that, for a large class of crude substances, they are the most effective and most convenient clarifying agents known. In the analysis of crude saccharine products the question of clarification is assuming an ever-increasing importance, as the sugar analysis approaches a continually higher precision. In order that further advances may rest upon a firm basis, it seems highly advisable that in place of acquiring more empirical data on the crude products themselves, we turn our attention to some of the more fundamental problems involved. The present work was undertaken in order to contribute to our very meager knowledge of the basic acetates themselves and their behavior in aqueous solution. Its application to the complicated problem of sugar clarification will form the subject of a special investigation.

A glance into the history of the study of this problem reveals the fact that while a number of compounds have been reported, no work has been done in the light of modern knowledge. Much of the work which has hitherto been accepted was done under assumptions which we now know to be radically erroneous. As an instance of this the work of Löwe[1] may be cited. This investigator boiled lead oxide and lead acetate for an arbitrary length of time and, upon obtaining a solution and a residue, he assumed that each represented a compound. In order to identify these compounds he used them to precipitate the insoluble basic nitrate of lead, which was then recrystallized before analysis. Its analysis was assumed to indicate the proportion of basic to neutral lead in the original compound. The conclusions based upon this procedure must be considered invalid.

In other instances investigators have attempted to isolate and purify the basic compounds and have reported the formulas on the basis of the direct analysis of these substances. In most cases the substance obtained must have been heterogeneous. Indeed, as will appear from the present work, it is almost, if not quite, impossible to isolate at least one of the basic compounds, while the danger of obtaining a mixture is so great that it makes this method of investigation unreliable.

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[1] *J. prakt. Chem.*, 98, 385 (1886).