

TABLE IV.

Case.	Concentration.	Temperature.	$\eta$ .	$K$ .
Hydrodiffusion of nonelectrolytic organic compounds.....	0.25	20°	1.505	7.00
Hydrodiffusion of nonelectrolytic organic compounds.....	zero	20°	1.489	6.66
Hydrodiffusion of nonelectrolytic organic compounds <sup>1</sup> .....	0.25	10±1°	1.489	4.77
Hydrodiffusion of gases.....	very low	18±2°	1.533	10.0
Diffusion of metals and metallic compounds in mercury.....	very low	10±2°	1.458	13.9
Hydrodiffusion of highly ionized (hydrated) electrolytes.....	0.01	18°	1.867	270
Independent diffusion of hydrated univalent ions ( $LM^{n-1} = K$ ).....	zero	18°	1.909	8378

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## THE INFLUENCE OF AN ALTERNATING CURRENT ON ELECTROLYSIS BY A DIRECT CURRENT.

[PART II.]

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In a previous communication<sup>2</sup> the action of an alternating current of high frequency on simple voltaic cells was studied. In this communication the influence of an alternating current on electrolytic cells will be described.

Löb<sup>3</sup> investigated the solution of metals in potassium cyanide solution under the influence of unsymmetrical alternating currents. Von Wartenburg and Archibald<sup>4</sup> investigated the formation of ozone at the anode in sulfuric acid solution by means of an alternating current impressed on a direct current. The object of this investigation, however, is to determine how an alternating current affects the phenomenon of electrolysis in general.

The poles of a four-volt lead accumulator were connected through the secondary circuit of an induction coil, and a suitable resistance, to the two electrodes of a voltameter. The induction coil used was a small one,

<sup>1</sup> In the former paper, the values given for this case are erroneous. Only a portion of Öholm's data was available at that time, and upon taking into consideration also his later work at 10°, the values given in this table are found to be correct (cf. L. W. Öholm, *Z. physik. Chem.*, 70, 393ff. (1910); Medd. k. Vetenskapskad. Nobelinst., Vol. 2, No. 23 (1913)).

<sup>2</sup> THIS JOURNAL, 36, 2333 (1914).

<sup>3</sup> *Z. Elektrochem.*, 12, 79 (1906).

<sup>4</sup> *Ibid.*, 17, 812 (1911).

as is generally used in the measurement of conductivity by the Kohlrausch method, and had a frequency of about thirty thousand per min. The amount of electrolytic decomposition in a given amount of time was estimated—firstly when there was an alternating current in the circuit and secondly, when there was no such current.

**Electrolysis in Reversible Cells.**—The silver voltameter was the first cell to be studied. Care was always taken that the voltameter in the two cases should be identical; otherwise, there is the possibility of the resistance of the circuit being different in the two cases, thus vitiating the accuracy of the results. This was secured by using the same platinum crucible, by filling it up with the silver nitrate solution to the same height, and by using identical silver anodes.

No. 1. (a) Weight of silver when there were both the direct and the alternating current in the circuit, 0.2451 g. in two hours.

(b) Weight of silver when the direct current was flowing through the above circuit for two hours, 0.2415 g.

No. 2. (a) Weight of silver, 0.2873 g.

(b) Weight of silver, 0.2904 g.

It will be seen that there is practically no difference in the amount of electrolytic decomposition in the two cases. We have already seen that, when an alternating current is passed through a reversible voltaic cell, there is no change in the electrode potentials of the cell. A reversible electrolytic cell remains likewise unaffected by an alternating current.

**Electrolysis in Irreversible Cells.**—In this type of cells it is rather difficult to get correct results. The back electromotive force of polarization becomes constant when the current has passed through the circuit for a considerable time; furthermore, the gases evolved are somewhat soluble in water. These sources of error could be partially eliminated by making the measurements after the current has already passed through the circuit quite a long while. In all the experiments the source of the current was a four-volt battery of two lead accumulators and the current passing through the primary of the induction coil was 0.33 ampere. The external metallic resistance was always kept constant. The results obtained are given in the following tables.

It will be seen that in most of the cases studied, a greater amount of current flows through the circuit during the passage of an alternating current. The exceptions are No. 4 in Table I, No. 5 in Table II, and No. 5 in Table IV. In these exceptional cases the cathodes used were of Pt black, copper or iron. It will also be observed that the smaller the area of the electrodes, the greater is the actual difference between the amount of current in the two cases. In the electrolysis of acids the alternating current is specially efficacious in the case of the cell where mercury is the cathode.

TABLE I.—ELECTROLYTE 0.5 M H<sub>2</sub>SO<sub>4</sub>.

	Cathode.		Anode.		Cc. H <sub>2</sub> in 30 min.	
	Metal.	Sq. cm.	Metal.	Sq. cm.	DC.	DC + AC.
1.....	Pt	8.5	Pt	8.5	7.00	7.95
2.....	Pt	1.5	Pt	1.5	6.70	8.60
3.....	Pt	8.5	Pt bl.	large	8.50	8.90
4.....	Pt bl.	large	Pt	8.5	9.50	9.60
5.....	Hg	3	Pt	8.5	4.20	6.30
6.....	Hg	3	Pt bl.	large	6.50	8.00

 TABLE II.—ELECTROLYTE 0.1 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

1.....	Pt	8.5	Pt	8.5	5.60	6.70
2.....	Pt	1.5	Pt	1.5	3.40	4.65
3.....	Hg	3.0	Pt	8.5	3.40	4.90
4.....	Hg	7.5	Pt	3.0	2.84	5.40
5.....	Pt bl.	large	Pt	2.0	7.40	7.50

TABLE III.—ELECTROLYTE 0.1 M NaOH.

1.....	Pt bl.	8	Pt	1.5	3.90	4.30
2.....	Pt	1.5	Pt	1.5	3.10	4.05
3.....	Cu	3	Pt	1.5	2.95	4.10
4.....	Sn	3	Pt	1.5	2.10	3.30
5.....	Fe	...	Pt	1.5	4.80	5.80

 TABLE IV.—ELECTROLYTE 0.5 M Na<sub>2</sub>SO<sub>4</sub>.

1.....	Pt	8.5	Pt	8.5	3.50	4.10
2.....	Pt	1.5	Pt	1.5	2.55	4.20
3.....	Pt	3.5	Pt bl.	large	4.10	4.50
4.....	Cu	3.0	Pt	3.0	3.30	3.40
5.....	Fe	...	Pt	3.0	2.20	2.10

### Alternating Current of Itself Ineffective to Bring about Visible Decomposition.

It might be supposed that the alternating current of itself forms the electrolytic gas, as had been observed by Van Name and Grafenberg<sup>1</sup> who used an alternating current having a frequency of 6600 per minute. Experiments were therefore performed to determine whether an alternating current from a small induction coil having a frequency of 30000 per minute could produce any perceptible amount of gas. The results obtained were always in the negative. This result is quite in accord with the observation of LeBlanc<sup>2</sup> that the action of alternating current diminishes regularly as the number of alternations per minute increases. Besides the strength of the alternating current is too small. The increase in the amount of electrolysis, when there is an alternating current in the circuit, is therefore not due to the electrolysis caused by the alternating current of itself.

<sup>1</sup> *Z. Elektrochem.*, 10, 303 (1904).

<sup>2</sup> *Ibid.*, 11, 705 (1905).

The only assumption that could reasonably be made as to the cause of this great increase in the amount of current, when an alternating current plays in the circuit, was that the alternating current in some way decreased the back electromotive force set up in the cell. We may refer in this connection to the work of K. Bennewitz<sup>1</sup> who noticed that when electromagnetic waves were allowed to pass through an electrolytic cell, the decomposition potential sank to 1.24, the theoretical value for the oxygen-hydrogen cell.

**Experimental Method.**—The experiment to determine how the discharge potentials of ions are affected by an alternating current, was arranged in the following way:

A is a battery from which a current of variable voltage passed through the electrolytic cell C. Between the battery and the cell are interposed a milliammeter and the secondary of the induction coil. An alternating current is developed in the secondary by passing a current of 0.33 ampere through the primary and the milliammeter is read when the current

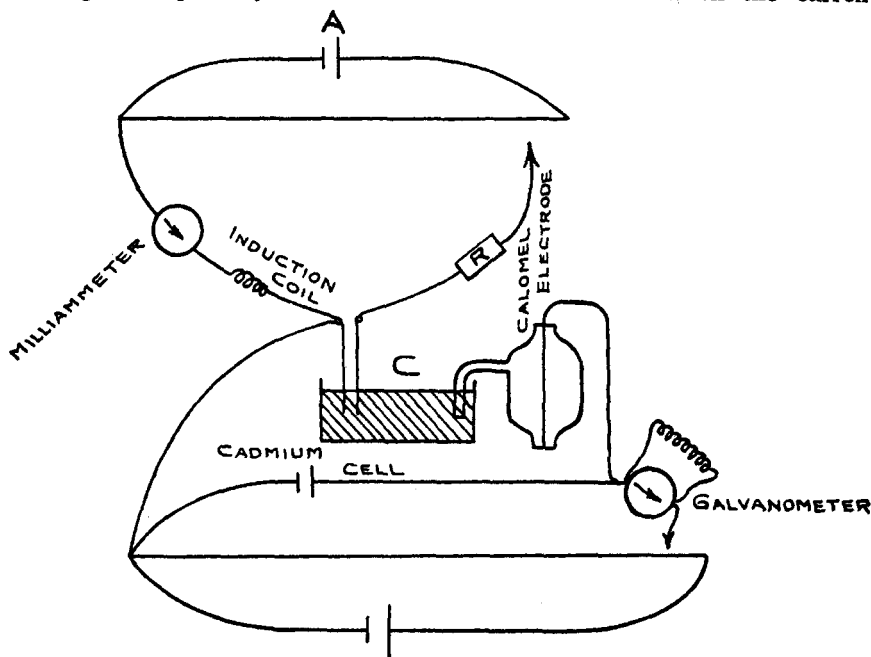


FIG. 1.

passing through the circuit has become constant. In this connection, it may be remarked that the milliammeter remains absolutely steady during the passage of the alternating current. That the milliammeter also records the exact current strength during the passage of the alternating

<sup>1</sup> *Z. physik. Chem.*, 72, 223 (1910)

current was tested by interposing a silver voltameter in the circuit and comparing the readings of the ammeter with the weight of silver obtained. The E. M. F. at each electrode of the electrolytic cell against a decinormal calomel electrode is then measured by means of the potentiometer. The alternating current is now stopped, the milliammeter again read, and the new electrode potentials of the electrolytic cell measured.

The diminution in discharge potential completely accounts for the increase in current strength on the passage of the alternating current. The results obtained with some of the typical electrolytes are given in the following tables. The remarkable drop in the value of the discharge potential will be at once evident. Now, the strength of the current  $C = (E - E')/R$ , where  $E$  is the voltage of the electrolytic current,  $E'$  the back electro-motive force of polarization. It was always found, that the diminution in the value of  $E'$  on the passage of the alternating current completely accounted for the increase in current strength.

TABLE V.

 Electrodes of Pt 8.5 sq. cm., each dipped in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

	Strength of current. Amp.		E. P. at cathode. Volt.		E. P. at anode. Volts.	
	DC.	DC + AC.	DC.	DC + AC.	DC.	DC + AC.
1.....	0.0336	0.0375	-0.820	-0.660	+1.650	+1.630
2.....	0.0242	0.0275	-0.790	-0.610	+1.600	+1.600
3.....	0.0170	0.0210	-0.745	-0.570	+1.580	+1.580
4.....	0.0095	0.0110	-0.580	-0.530	+1.530	+1.530
5.....	0.0040	0.0052	-0.530	-0.490	+1.510	+1.510
6.....	0.0012	0.0020	-0.290	-0.280	+1.440	+1.445

TABLE VI.

 Cell consists of Pt 1.5 sq. cm., each dipped in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

1.....	0.0330	0.0400	-0.910	-0.630	+1.680	+1.650
2.....	0.0228	0.0300	-0.850	-0.590	+1.630	+1.590
3.....	0.0160	0.0230	-0.810	-0.550	+1.620	+1.590
4.....	0.0060	0.0121	-0.770	-0.520	+1.550	+1.550
5.....	0.0028	0.0040	-0.505	-0.500	+1.490	+1.480

The E. P. of the calomel electrode is taken as zero.

The current strength is altered by varying the voltage of the electrolytic current. The current potential curve is given in Fig. 2.

The electrode potentials at the cathode appear very great but they are in fair accord with those obtained by Newbury<sup>1</sup> with his commutator short-circuited. The diminution in the cathode discharge potential when the alternating current passes through the circuit simultaneously with the direct current, is far greater than the diminution in the anode discharge potential. The effect of decreasing the size of the electrodes could be easily seen by comparing the values recorded in Tables V and VI.

<sup>1</sup> J. Chem. Soc., 14, 19 (1914).

In Expt. 1, Table VI, the cathode discharge potential falls from 0.91 to 0.63 whereas in Expt. 1, Table V, the cathode discharge potential diminishes from 0.82 to 0.66 volt. The anode potential is also much more affected when the area of the electrodes is made smaller. In the current potential curves it will be noticed that in the case where simply a direct current

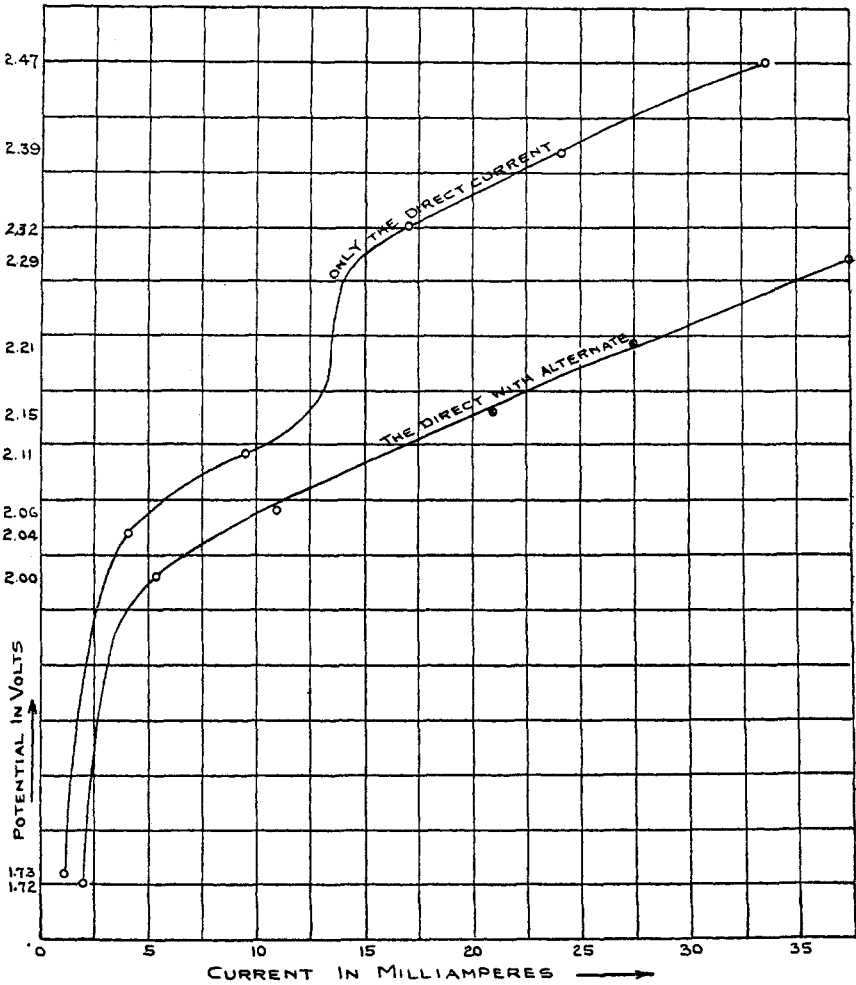


FIG. 2.

passes there is a sharp break at about 2.30 volt. This break is entirely absent when the alternating current passes simultaneously with the direct current. There is also another break in the current potential curve at about 1.95 volt. This latter break, however, occurs at a slightly lower potential when there is a simultaneous alternate current in the circuit.

Now these breaks are attributed by Nernst,<sup>1</sup> Glaser,<sup>2</sup> Bose,<sup>3</sup> to be due to a new variety of ions getting discharged at these points. It therefore follows that whenever such a break disappears on the passage of an alternating current, the liberation of these new ions has been somehow prevented.

The next cells to be studied had mercury as the cathode.

TABLE VII.

Hg as cathode (3 sq. cm.) and Pt as anode (8.5 sq. cm.), electrolyte 0.5 M H<sub>2</sub>SO<sub>4</sub>.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC + AC.	DC.	DC + AC.	DC.	DC + AC.
1.....	0.0210	0.0300	-1.535	-1.140	+1.600	+1.640
2.....	0.0095	0.0180	-1.490	-1.040	+1.540	+1.63
3.....	0.0040	0.0120	-1.360	-0.980	+1.400	+1.530
4.....	0.0010	0.0050	-1.110	-0.820	+1.370	+1.500
5.....	0.0005	0.0025	-0.820	-0.660	+1.360	+1.480

The effect of the alternating current in this cell is very great. The alternating current affects chiefly the cathode when there is a large drop in potential. It will be noticed that the anode potential increases during the passage of the alternating current. This is due to the greater amount of current passing through the circuit in consequence of the large drop in potential at the cathode, and the inability of the alternating current to exert its depolarizing action on the anode. It will also be noticed that the increase in the anode discharge potential becomes very prominent at the back E. M. F. values lower than 2.65 volt. where there is a break in the current potential curve. This value is in agreement with the data given by Caspari<sup>4</sup> for the E. M. F. required to produce visible decomposition. It is, however, very peculiar that this break disappears when an alternating current passes simultaneously with the direct current through the circuit. In this case, the break appears at a much lower voltage, about 2.2 volt. The current potential curve is given in Fig. 3.

TABLE VIII.

Hg cathode (3 sq. cm.) and large Pt black anode.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC + AC.	DC.	DC + AC.	DC.	DC + AC.
1.....	0.0310	0.0385	-1.550	-1.230	+1.325	+1.350
2.....	0.0154	0.0231	-1.490	-1.130	+1.220	+1.250
3.....	0.0080	0.0160	-1.410	-1.060	+1.220	+1.250
4.....	0.0030	0.0130	-1.375	-1.000	+1.200	+1.230
5.....	0.0010	0.0050	-1.200	-0.880	+1.060	+1.200

<sup>1</sup> *Ber.*, 30, 1547 (1897).

<sup>2</sup> *Z. Elektrochem.*, 4, 355-73-97. etc. (1898).

<sup>3</sup> *Ibid.*, 5, 153 (1868).

<sup>4</sup> *Z. physik. Chem.*, 30, 89-97 (1899).

It was thought interesting to determine whether by substituting a large foil of Pt black for the platinum anode of the previous cell, the increase in the anode discharge potential observed, during the passage of the alter-

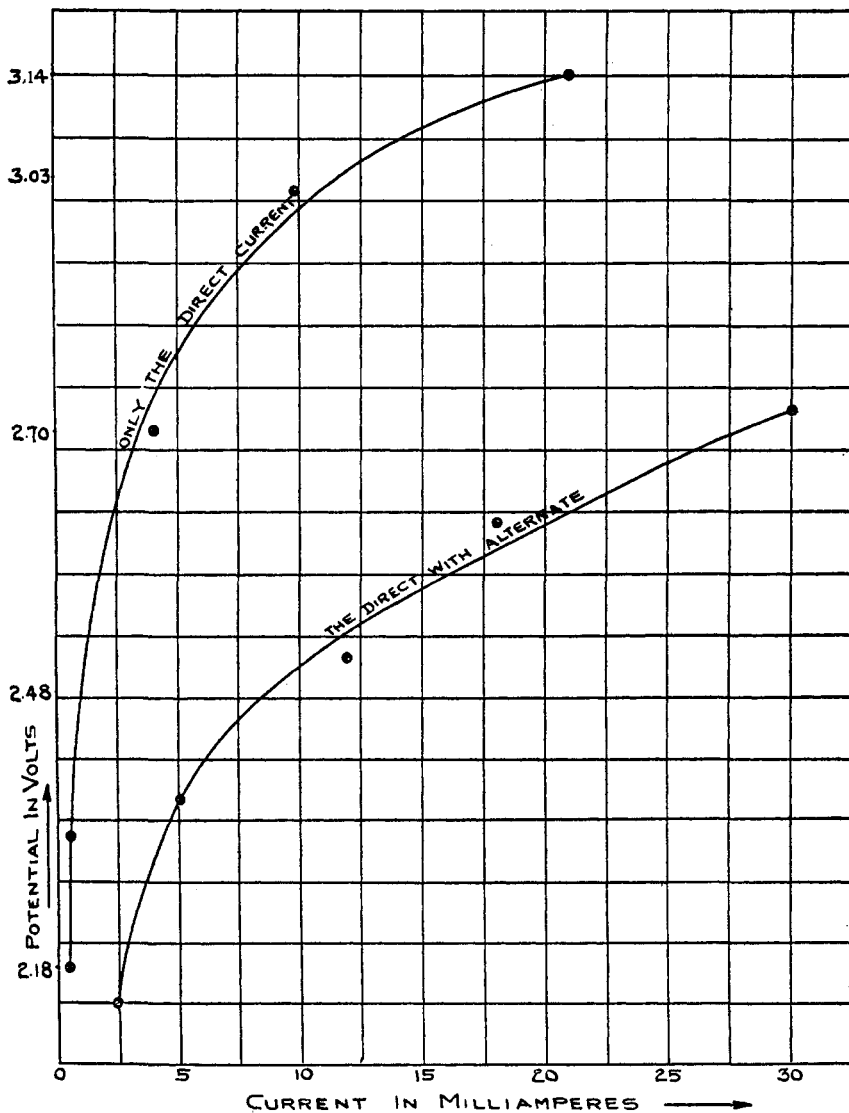


FIG. 3.

nating current, could be eliminated. The results as recorded in Table VIII show, that the increase in potential, even in this case is quite large.

Here too it will be noticed that a break in the current potential curve



occurs at about 2.4 volt. This break disappears on the passage of the alternating current and a break at a much lower voltage occurs instead.

If the sulfuric acid solution in the above cell be substituted by any other acid solution, fairly analogous results are generally obtained. In Tables IX and X are given results obtained with oxalic acid.

TABLE IX.

 Pt electrodes (area 8.5 sq. cm.) dipped in 0.1 *N* oxalic acid.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0275	0.0320	-1.157	-1.000	+1.700	+1.670
2.....	0.0195	0.0222	-1.010	-0.910	+1.590	+1.590
3.....	0.0145	0.0170	-0.965	-0.850	+1.550	+1.550
4.....	0.0121	0.0150	-0.930	-0.820	+1.520	+1.520
5.....	0.0090	0.0110	-0.890	-0.770	+1.350	+1.405
6.....	0.0065	0.0080	-0.830	-0.720	+1.210	+1.275
7.....	0.0055	0.0070	-0.818	-0.700	+0.940	+0.995
8.....	0.0030	0.0045	-0.760	-0.650	+ .770	+0.815
9.....	0.0020	0.0030	-0.690	-0.600	+0.675	+0.720

Breaks in the direct current potential curves occur at about 2.65 and at about 2.2. The first break disappears on the passage of the alternating current. The break at 2.2 was noticed by Bose<sup>1</sup> and was supposed to be due to the discharge of COOH' ions. Below the voltage indicated by the second break, the anode potential increases markedly during the passage of the alternating current.

TABLE X.

 Hg cathode (3 sq. cm.) and Pt anode (5 sq. cm.) electrolyte 0.1 *N* oxalic acid.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0168	0.0028	-1.615	-1.274	+1.750	+1.830
2.....	0.0092	0.0160	-1.520	-1.106	+1.510	+1.680
3.....	0.0068	0.0130	-1.470	-1.040	+1.480	+1.640
4.....	0.0045	0.0100	-1.430	-0.940	+1.400	+1.590
5.....	0.0032	0.0078	-1.385	-0.850	+1.210	+1.480
6.....	0.0018	0.0060	-1.330	-0.780	+1.000	+1.310

The results are quite analogous to those recorded in Table VII.

The behavior of the normal salts are quite different from that of the acids. The diminution in the cathode discharge potential, on the passage of an alternating current, which is so marked in the case of acids, is not so very prominent here, unless the size of the electrodes be made very small. The results are recorded in Tables XI, XII, XIII, XIV and XV.

<sup>1</sup> *Loc. cit.*

TABLE XI.  
Pt electrodes (8.5 sq. cm.) dipped into 0.5 M Na<sub>2</sub>SO<sub>4</sub>.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0170	0.0195	-1.770	-1.691	+1.612	+1.600
2.....	0.0085	0.0085	-1.681	-1.610	+1.520	+1.493
3.....	0.0030	0.0040	-1.532	-1.490	+1.420	+1.410

TABLE XII.  
Same as the preceding but area of electrodes 1 sq. cm.

1.....	0.0120	0.0200	-1.970	-1.670	+1.615	+1.610
2.....	0.0065	0.0128	-1.875	-1.590	+1.540	+1.520
3.....	0.0040	0.0098	-1.680	-1.530	+1.520	+1.510
4.....	0.0023	0.0055	-1.631	-1.510	+1.490	+1.465
5.....	0.0020	0.0036	-1.403	-1.350	+1.480	+1.450
6.....	0.0018	0.0020	-1.070	-1.130	+1.440	+1.355
7.....	0.0016	0.0016	-0.900	-1.020	+1.435	+1.330

The alternating current decreases the discharge potential both at the cathode and at the anode, the effect on the cathode is more prominent. Experiments No. 6 and 7 in Table XII are peculiar in so far as the cathode discharge potential increases by the action of the alternating current. There is a break in the current potential curve at about 3.2 which disappears on the passage of the alternating current.

By substituting Pt black for the Pt anode, the effect of the alternating current becomes perceptibly less, as is shown in Table XIII, while if Pt black is used as cathode the influence of the alternating current becomes almost negligible.

TABLE XIII.  
Pt cathode (3.5 sq. cm.) and large Pt black anode electrolyte 0.5 M Na<sub>2</sub>SO<sub>4</sub>.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0195	0.0210	-1.911	-1.842	+1.285	+1.292
2.....	0.0120	0.0135	-1.890	-1.823	+1.250	+1.265
3.....	0.0084	0.0097	-1.851	-1.770	+1.230	+1.240
4.....	0.0056	0.0071	-1.770	-1.690	+1.211	+1.225
5.....	0.0040	0.0050	-1.670	-1.620	+1.951	+1.200
6.....	0.0028	0.003	-1.490	-1.470	+1.150	+1.155

TABLE XIV.  
Cell consists of Pt electrodes 2.5 sq. cm. each in 0.5 M (COOK)<sub>2</sub> solution.

1.....	0.0290	0.0342	-1.761	-1.580	+1.004	+0.964
2.....	0.0205	0.0270	-1.690	-1.530	+0.937	+0.877
3.....	0.0160	0.0214	-1.643	-1.490	+0.917	+0.857
4.....	0.0115	0.0161	-1.602	-1.447	+0.905	+0.855
5.....	0.0075	0.0115	-1.530	-1.390	+0.887	+0.830
6.....	0.0045	0.0075	-1.421	-1.318	+0.835	+0.800
7.....	0.003	0.0045	-1.290	-1.252	+0.810	+0.795
8.....	0.0028	0.003	-1.121	-1.150	+0.570	+0.610

The behavior of potassium oxalate solution is quite analogous to that of sodium sulfate solution. The results are recorded in Tables XIV and XV.

TABLE XV.  
Pt cathode (1.5 sq. cm.) large Pt black anode.

	Strength of current. Amp.		E. P. at cathode Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0320	0.0349	-1.804	-1.700	+0.872	+0.880
2.....	0.245	0.0265	-1.750	-1.641	+0.840	+0.848
3.....	0.205	0.0224	-1.710	-1.610	+0.830	+0.840
4.....	0.0165	0.0185	-1.682	-1.581	+0.825	+0.832
5.....	0.0135	0.0155	-1.640	-1.551	+0.810	+0.818
6.....	0.0082	0.0102	-1.580	-1.495	+0.780	+0.790
7.....	0.0062	0.0080	-1.535	-1.440	+0.780	+0.785
8.....	0.0040	0.0060	-1.465	-1.380	+0.750	+0.750
9.....	0.0025	0.0033	-1.375	-1.340	+0.700	+0.710

By substituting Pt black for the Pt anode, there is not much change of the alternating current. Also the influence of the alternating current on electrolysis becomes perceptibly smaller. If, however, Pt black be used as cathode, the change in the discharge potential values on the passage of the alternating current becomes almost negligible.

The behavior of an oxidizing salt like potassium nitrate affords many points of interest. The results are recorded in Tables XVI, XVII, XVIII, XIX.

TABLE XVI.  
Pt electrodes (8.5 sq. cm.) dipped in 0.5 M KNO<sub>3</sub> sol.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0190	0.0230	-1.610	-1.460	+1.710	+1.680
2.....	0.0135	0.0166	-1.550	-1.400	+1.655	+1.640
3.....	0.0100	0.0138	-1.535	-1.385	+1.630	+1.615
4.....	0.0065	0.0097	-1.480	-1.365	+1.595	+1.575
5.....	0.0046	0.0065	-1.335	-1.270	+1.570	+1.555
6.....	0.0038	0.0040	-1.080	-1.090	+1.550	+1.530
7.....	0.0030	0.0030	-0.850	-0.880	+1.540	+1.510

TABLE XVII.  
Area of the electrodes 1.85 sq. cm. otherwise as preceding.

1.....	0.0140	0.0240	-1.765	-1.400	+1.780	+1.720
2.....	0.0075	0.0165	-1.660	-1.316	+1.750	+1.660
3.....	0.0057	0.0150	-1.640	-1.270	+1.718	+1.650
4.....	0.0036	0.0115	-1.520	-1.180	+1.650	+1.600
5.....	0.0032	0.1000	-1.376	-1.188	+1.680	+1.600
6.....	0.0030	0.0070	-1.092	-0.960	+1.640	+1.580
7.....	0.0023	0.0055	-0.940	-0.868	+1.620	+1.545
8.....	0.0020	0.0040	-0.832	-0.792	+1.584	+1.508
9.....	0.0016	0.0030	-0.680	-0.730	+1.568	+1.480
10.....	0.0015	0.0020	-0.560	-0.660	+1.530	+1.410

The peculiarity with potassium nitrate solution is that the anode discharge potential always diminishes on the passage of the alternating current, while the cathode discharge potential increases under conditions of very low current density. The results of Table XVI appear magnified, as it were, in Table XVII, where the area of the electrodes is much smaller. But the break in the direct current potential curves occurs in both cases at about 3 volts. This break, however, is not noticeable when the alternating current passes through the circuit simultaneously with the direct current. We have seen before that the break at 3.0 volts in the current potential curve when the electrolyte is sodium sulfate disappears on the passage of the alternating current. These breaks at such high potentials probably indicate the discharge of the ions of the alkali metals. This discharge perhaps does not take place when the alternating current passes.

TABLE XVIII.

Large Pt black cathode, an anode of Pt (2.5 sq. cm.) dipped into 0.5 M KNO<sub>3</sub>.

	Strength of current.		E. P. at cathode.		E. P. at anode.	
	Amp.		Volts.		Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0295	0.0325	-1.096	-1.100	+1.880	+1.750
2.....	0.0190	0.0220	-1.088	-1.090	+1.788	+1.630
3.....	0.0157	0.0190	-1.086	-1.086	+1.770	+1.620
4.....	0.0120	0.0150	-1.070	-1.070	+1.756	+1.610
5.....	0.0082	0.0115	-0.810	-0.850	+1.710	+1.560
6.....	0.0065	0.0090	-0.664	-0.744	+1.690	+1.540
7.....	0.0055	0.0080	-0.590	-0.672	+1.675	+1.530
8.....	0.0036	0.0055	-0.520	-0.588	+1.640	+1.500

TABLE XIX.

The same as preceding, electrodes reversed.

1.....	0.0223	0.0300	-1.848	-1.480	+1.310	+1.320
2.....	0.0155	0.0230	-1.768	-1.390	+1.265	+1.300
3.....	0.0128	0.0206	-1.740	-1.340	+1.265	+1.290
4.....	0.0096	0.0172	-1.700	-1.290	+1.240	+1.280
5.....	0.0062	0.0140	-1.640	-1.220	+1.200	+1.268
6.....	0.0040	0.0100	-1.565	-1.140	+1.100	+1.230
7.....	0.0035	0.0070	-1.510	-1.100	+0.880	+1.170
8.....	0.0030	0.0050	-1.510	-1.020	+0.740	+1.120

We have seen that by using a Pt black cathode, in the case of the electrolytes studied previously, the effect of the alternating current on electrolysis becomes negligible. But with potassium nitrate solution, such is not the case as is shown by the data in Table XVIII. The influence of alternating current is much greater when Pt black is the anode than when it is the cathode. In the former case, the anodic discharge potential increases on the passage of the alternating current, while the cathodic discharge potential decreases. There is a break in the current

potential curve at about 2.8 and it is at voltages below this break that the increase in the anode discharge potential on the passage of the alternating current becomes prominent. When Pt black is the cathode, the anode discharge potential diminishes, and the cathode discharge potential increases on the passage of the alternating current. Here too the increase in the cathode potential becomes much pronounced at voltages below the break which is noticed at about 2.55 volt.

TABLE XX.

The electrolytic cell consists of electrodes of Pt 2 sq. cm. each in a normal solution of NaOH.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0270	0.0345	-1.940	-1.620	+1.030	+0.980
2.....	0.0125	0.0195	-1.840	-1.570	+0.990	+0.930
3.....	0.0075	0.0135	-1.790	-1.570	+0.970	+0.910
4.....	0.0030	0.0060	-1.500	-1.760	+0.930	+0.860
5.....	0.0020	0.0020	-1.200	-1.300	+0.900	+0.800

At first the discharge potential at both the electrodes diminishes on the passage of the alternating current. But under conditions of very low current density the cathode discharge potential increases on the passage of an alternating current. The peculiar point was always noticed, that when the strength of the direct current passing through the circuit, was very small, the alternating current produced no change in the magnitude of the direct current. The diminution in the value of the discharge potential at one of the electrodes, was counterbalanced by its increase at the other electrode. This phenomenon occurs at only voltages below that corresponding to a break in the current potential curve. The effect of an alternating current on the electrolysis of solutions of a large number of electrolytes was studied in the elaborate manner indicated before, and the results obtained with some of the typical ones only have been given. Table XXI, however, which gives an account of the results obtained, when the source of the electrolytic current has a definite potential, *viz.*, 4 volt, show to what extent the various electrolytes agree in their behavior.

In the case of the oxidizing and the reducing salts the diminution in the anode potential on the passage of the alternating is always very prominent. In the case of the other salts such as sulfates and carbonates the effect of the alternating current is not so marked on the anodic discharge potential. Of course this relation holds good only when electrodes of platinum are used; if, however, a large foil of Pt black is used as one of the electrodes an alternating current does not much affect the discharge potential on its surface.

TABLE XXI.

Cell.	Sq. cm. electrode.	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
		DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
Pt, NaNO <sub>2</sub> 0.5 N, Pt.....	8	0.0430	0.0450	-1.440	-1.420	+0.620	+0.590
Pt, NaNO <sub>2</sub> 0.2 N, Pt.....	1.5	0.0320	0.0380	-1.900	-1.750	+0.950	+0.870
Pt, KClO <sub>3</sub> 0.2 N, Pt.....	8	0.0215	0.0235	-1.640	-1.590	+1.670	+1.636
Pt, KClO <sub>3</sub> 0.2 N, Pt.....	1.5	0.0130	0.0200	-1.900	-1.700	+1.800	+1.700
Pt, KBrO <sub>3</sub> 0.2 N, Pt.....	8	0.0290	0.0340	-1.100	-0.940	+1.900	+1.830
Pt, KBrO <sub>3</sub> 0.2 N, Pt.....	1.5	0.0150	0.0280	-1.700	-1.590	+1.900	+1.840
Pt, Ba(NO <sub>3</sub> ) <sub>2</sub> 0.2 N, Pt....	8	0.0205	0.0250	-1.600	-1.470	+1.700	+1.650
Pt, NaCOOH 0.2 N, Pt....	8	0.0250	0.0270	-1.580	-1.540	+1.350	+1.310
Pt, NaCOOH 0.2 N, Pt....	1.5	0.0200	0.0250	-1.660	-1.530	+1.470	+1.370
Pt, NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> 0.2 N Pt..	8	0.0175	0.0210	-1.650	-1.590	+1.62	+1.540
Pt, NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> 0.2 N, Pt..	1.5	0.0130	0.0212	-1.780	-1.620	+1.750	+1.530
Pt, Na <sub>2</sub> SO <sub>3</sub> 0.5 N, Pt.....	8	0.0220	0.0238	-1.360	-1.360	+1.730	+1.660
Pt, Na <sub>2</sub> SO <sub>3</sub> 0.5 N, Pt.....	1.5	0.0160	0.0220	-1.500	-1.410	+1.800	+1.650
Pt, Na <sub>2</sub> HPO <sub>3</sub> 0.5 N, Pt....	8	0.0230	0.0255	-1.360	-1.360	+1.620	+1.530
Pt, Na <sub>2</sub> HPO <sub>3</sub> 0.5 N, Pt....	1.5	0.01450	0.0208	-1.700	-1.550	+1.720	+1.550
Pt, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 0.5 N, Pt..	8	0.0250	0.0270	-1.390	-1.320	+1.6	+1.6
Pt, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 0.5 N, Pt..	1.5	0.0165	0.0230	-1.600	-1.370	+1.740	+1.710
Pt, MgSO <sub>4</sub> 0.5 N, Pt.....	8	0.0260	0.0273	-1.300	-1.270	+1.630	+1.620
Pt, MgSO <sub>4</sub> 0.5 N, Pt.....	1.5	0.0122	0.0180	-1.840	-1.630	+1.700	+1.660
Pt, Na <sub>2</sub> CO <sub>3</sub> 0.5 N, Pt.....	8	0.0213	0.0236	-1.830	-1.750	+1.460	+1.470
Pt, Na <sub>2</sub> CO <sub>3</sub> 0.5 N, Pt.....	1.5	0.0125	0.0170	-1.960	-1.780	+1.710	+1.720

**Influence of the Density of the Alternating Current.**—It has been observed before, how the diminution in the discharge potentials depends on the density of the alternating current; for the purpose of determining this factor, the area of the electrodes was varied, and an alternating current of almost constant value was sent through the circuit. This method has the disadvantage that the discharge potential, due to the direct current, increases when the electrodes were made smaller. To eliminate this difficulty, the surface of the electrodes was kept constant in area, but the external metallic resistance was varied. Care was taken that the current strength through the primary of the induction coil remained constant throughout. The results obtained are given in Tables XXII, XXIII, and XXIV. It will be at once evident from these tables that the greater the resistance of the circuit, the less is the effect of the alternating current on the discharge potentials at the electrodes.

**An Alternating Current Exerts Its Action on the Surface of the Electrodes Only.**—It has been observed above to be a general phenomenon that when an alternating current is impressed along with a direct current to an electrolytic cell the discharge potential at the surface of the electrodes is a good deal diminished. The question however, arises whether the sinuoidal current thus produced by the conjugation of the direct with the alternate current has the property of keeping the discharge

TABLE XXII.

Electrodes of Pt (8 sq. cm.) 0.5 M H<sub>2</sub>SO<sub>4</sub> sol. The source of the electrolytic current is a battery of 4 volts always.

Total resistance. Ohms.	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
50.....	0.0370	0.0400	-1.090	-0.950	+1.620	+1.610
67.....	0.0260	0.0280	-1.050	-0.930	+1.600	+1.590
107.....	0.0160	0.0170	-1.000	-0.920	+1.590	+1.590
257.....	0.0068	0.0073	-0.970	-0.910	+1.560	+1.560

TABLE XXIII.

Same as preceding, but electrodes 2.2 sq. cm.

50.....	0.0325	0.0380	-1.010	-0.770	+1.850	+1.820
67.....	0.0235	0.0280	-1.000	-1.770	+1.780	+1.770
107.....	0.0150	0.0175	-0.940	-0.750	+1.720	+1.715
250.....	0.0070	0.0075	-0.850	-0.720	+1.630	+1.625

TABLE XXIV.

Two electrodes of Pt (8 sq. cm.) in 0.1 N HCl.

47.....	0.0315	0.0345	-1.090	-1.040	+1.750	+1.670
66.....	0.0230	0.0245	-1.080	-1.030	+1.700	+1.660
106.....	0.0142	0.0150	-1.050	-1.020	+1.660	+1.630
247.....	0.0063	0.0063	-1.030	-1.020	+1.580	+1.570

potentials at a low value, analogous to that possessed by an intermittent current, or whether the alternating current exerts any specific action on the electrodes quite independent of the direct current. In order to settle this point it is necessary to isolate the alternating current from the direct current, to arrange the experiments in such a manner, that the alternating current should act on the surface of the electrodes only, but should on no account pass through the whole circuit. For the purpose the electrolytic cell was thus modified.

Each electrode was made of two metal foils dipped in the electrolyte very close to one another and connected through a key and a suitable resistance to the terminals of the secondary coil. The resistance of the main circuit was so adjusted that when the auxiliary electrodes were connected to the primary electrodes, no increase in the value of the direct current was observed. The resistance of the electrolyte between a primary and an auxiliary electrode was so small, that almost the entire alternating current passed through them. The advantage of this ar-

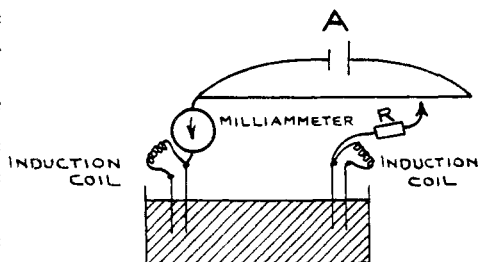


FIG. 4.

rangement lies in the fact, that the alternating current acts independently of the direct current, and that the effect of the alternating current on each of the electrodes could be studied separately.

TABLE XXV.

Two anodes of Pt (1 sq. cm.), two cathodes of Pt (3 sq. cm.), the electrolyte 0.5 *N* H<sub>2</sub>SO<sub>4</sub>. Alternating current only passed through the anodes.

	Strength of current. Amp.		E. P. at cathode. Volt.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0270	0.0295	-0.910	-0.940	+1.730	+1.580
2.....	0.0215	0.0232	-0.840	-0.870	+1.680	+1.580
3.....	0.0170	0.0190	-0.840	-0.855	+1.670	+1.570
4.....	0.0127	0.0147	-0.830	-0.850	+1.660	+1.550
5.....	0.0064	0.0077	-0.830	-0.880	+1.620	+1.500
6.....	0.0040	0.0052	-0.800	-0.840	+1.600	+1.490
7.....	0.0014	0.0018	-0.750	-0.820	+1.550	+1.440

The effect of passing the alternate current through the anodes is to diminish markedly the discharge potential at that electrode. There is a simultaneous increase in the cathode discharge potential. This increase is to be attributed to the greater amount of current passing through the circuit. During conditions of very low current density the decrease in potential at the anode due to the alternating current is almost counter-balanced by a simultaneous increase at the cathode.

TABLE XXVI.

Two cathodes (1 sq. cm.) and two anodes (3 sq. cm.) in 0.5 *N* H<sub>2</sub>SO<sub>4</sub>. The alternating current only plays between the cathodes.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0254	0.0325	-1.050	-0.650	+1.660	+1.660
2.....	0.0178	0.0250	-1.040	-0.620	+1.650	+1.670
3.....	0.0135	0.0225	-1.020	-0.500	+1.630	+1.660
4.....	0.0100	0.0185	-0.980	-0.470	+1.610	+1.640
5.....	0.0060	0.0135	-0.890	-0.450	+1.590	+1.630
6.....	0.0036	0.0095	-0.800	-0.420	+1.560	+1.610
7.....	0.0012	0.0060	-0.750	-0.390	+1.520	+1.600
8.....	0.0010	0.0040	-0.570	-0.370	+1.500	+1.580
9.....	0.0009	0.0013	-0.340	-0.280	+1.470	+1.510

The effect of the alternating current is far more marked at the cathode than at the anode. The cathode discharge potential diminishes very considerably while the anode discharge potential increases, during the play of the alternating current between the cathodes.



TABLE XXVII.

Two cathodes of Pt (1.25 sq. cm.) two anodes of Pt (1.5 sq. cm.) 0.5 M H<sub>2</sub>SO<sub>4</sub>. The alternating current passes through the cathodes as well as the anodes.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0205	0.0332	-1.140	-0.600	+1.650	+1.500
2.....	0.0140	0.0240	-1.020	-0.580	+1.630	+1.500
3.....	0.0108	0.0198	-0.940	-0.560	+1.600	+1.490
4.....	0.0065	0.0158	-0.930	-0.520	+1.590	+1.490
5.....	0.0038	0.0110	-0.830	-0.490	+1.570	+1.490
6.....	0.0022	0.0072	-0.820	-0.470	+1.550	+1.490
7.....	0.0010	0.0045	-0.630	-0.420	+1.520	+1.480
8.....	0.0008	0.0020	-0.450	-0.390	+1.460	+1.450

Some peculiar points could be noticed in Table XXVII. The anode potential diminishes, on the passage of an alternating current only down to a definite value, *viz.*, 1.49 volt. The cathode discharge potential diminishes continuously and the diminution is much larger in amount.

TABLE XXVIII.

Two cathodes of Hg (0.75 sq. cm.), two anodes of Pt (2 sq. cm.) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The alternating current only passes through the cathodes.

	Strength of current. Amp.		E. P. at cathode. Volts.		E. P. at anode. Volts.	
	DC.	DC+AC.	DC.	DC+AC.	DC.	DC+AC.
1.....	0.0110	0.0210	-1.560	-1.020	+1.770	+1.820
2.....	0.0045	0.0130	-1.400	-0.870	+1.710	+1.740
3.....	0.0022	0.0082	-1.230	-0.700	+1.610	+1.680

The results obtained are quite analogous to those recorded in Table VII, where the alternating current passes along with the direct current in a cell having mercury as cathode and Pt as anode.

In Tables XXIX and XXX, in the experiments marked (a) only the direct current passes; in those marked (b), an alternating current plays between the cathodes; in those marked (c) the alternating current passes through the anodes only and in (d) through both.

The effect on the value of the direct current is greatest when the alternating current passes both through anodes and cathodes. The effect is least when the alternating current passes through the anodes only. In the former case, there is at first a diminution in the discharge potentials at both the electrodes but under conditions of very low current density produced by diminishing the voltage of the electrolytic current, the diminution in the anode discharge potential continues; but the cathode discharge potential remains constant or even increases. In the latter case, the discharge potential at the anode diminishes while that at the cathode increases from the very beginning. Similarly, by the passage of an alter-

nating current through the cathodes only, the discharge potential at that electrode only diminishes.

TABLE XXIX.

Two cathodes of Pt (2 sq. cm.) and two anodes of Pt (2 sq. cm.), in 0.5 *M* Na<sub>2</sub>SO<sub>4</sub>.

	Strength of current. Amp.				E. P. at cathode. Volts.			
	a.	b.	c.	d.	a.	b.	c.	d.
1.....	0.0195	0.0255	0.0240	0.0280	-1.980	-1.860	-2.040	-1.913
2.....	0.0095	0.0140	0.0125	0.0160	-1.910	-1.810	-1.950	-1.850
3.....	0.0055	0.0088	0.0081	0.0115	-1.760	-1.690	-1.850	-1.750
4.....	0.0040	0.0060	0.0041	0.0065	-1.590	-1.520	-1.650	-1.580
5.....	0.0030	0.0030	0.0030	0.0030	-1.230	-1.200	-1.330	-1.250

	E. P. at anode. Volts.			
	a.	b.	c.	d.
1.....	+1.850	+1.880	+1.700	+1.780
2.....	+1.670	+1.700	+1.570	+1.620
3.....	+1.630	+1.640	+1.500	+1.530
4.....	+1.550	+1.570	+1.480	+1.510
5.....	+1.540	+1.570	+1.430	+1.520

TABLE XXX.

Two cathodes of Pt (2 sq. cm.) two anodes of Pt (2 sq. cm.) in 0.1 *N* NaOH.

	Strength of current. Amp.				E. P. at cathodes. Volts.			
	a.	b.	c.	d.	a.	b.	c.	d.
1.....	0.0240	..	0.0275	0.0330	-2.010	...	-2.080	-1.830
2.....	0.0128	0.0220	0.0175	0.0252	-1.910	-1.550	-1.950	-1.630
3.....	0.0073	0.0155	0.0120	0.0178	-1.810	-1.460	-1.900	-1.600
4.....	0.0038	0.0095	0.075	0.0122	-1.590	-1.310	-1.760	-1.410
5.....	0.0028	0.0058	0.0045	0.0083	-1.360	-1.210	-1.600	-1.300

	E. P. at anode. Volts.			
	a.	b.	c.	d.
1.....	+1.520	...	+1.350	+1.430
2.....	+1.350	+1.500	+1.190	+1.330
3.....	+1.230	+1.390	+1.010	+1.170
4.....	+1.110	+1.240	+0.870	+1.070
5.....	+1.080	+1.140	+0.810	+0.990

The results obtained with caustic soda solution are quite similar to those obtained with the sodium sulfate solution. Solutions of several other electrolytes were examined in the same way. The following relations seem to hold good generally: When the alternating current passes through cathodes, the cathode discharge potential diminishes, while there is a simultaneous increase in the anode discharge potential; when the alternating current passes through anodes, the reverse phenomenon happens; when the alternating current passes through both, the discharge potential at both the electrodes at first diminishes, but at very low current densities such is not always the case.

### Conclusions.

From the above results it is quite obvious, that the alternating current need not be impressed on an electrolytic cell in conjugation with a direct current, in order to produce its marked effect on the discharge potentials at the electrodes. The alternating current acts primarily on the surfaces of the electrodes. Of course it is very difficult to suggest how it facilitates the liberation of the ions at the electrode surface, since we have not got very definite views as to the cause of the overvoltage phenomenon. It is not easy to imagine how an alternating current can destroy the supersaturation on the electrode surface, which is generally ascribed to be the cause of the overvoltage. The hypothesis that the alternating current somehow alters the nature of the electrode surface appears to be most reasonable. Ruer<sup>1</sup> has observed that platinum passes into solution when it is acted upon simultaneously by a direct and an alternating current. Under the conditions, in which the experiments described in this paper were carried out, such was not found to be the case. The weight of a platinum foil which had been used in the course of many of the above experiments remained absolutely constant.

Newbury, in his very recent work,<sup>2</sup> holds that the ions first penetrate into the interior of the electrodes and there get discharged. The molecules thus produced from the ions, have not, like the ions, got free passage through the material of the electrodes. They accumulate inside the electrode, and only at very high pressures they come out by boring tunnels through the electrode surface. Now any process which facilitates this disruption of the electrode surface, will diminish the discharge potential on the electrodes. An alternating current of considerable intensity could easily be imagined to brush aside all the mechanical resistances offered to the passage of the molecules out of the electrode surface. The liberation of the ions are thus greatly facilitated and hence the discharge potential sinks.

### Summary of this Paper and the Previous Communication.<sup>3</sup>

1. When an alternating current of high frequency, about 30000 per minute, passes through a cell consisting of two platinum electrodes dipped in any electrolyte, the electrode potentials change, thus indicating that some chemical action at the electrode surface takes place in that short amount of time.

2. When an alternating current passes through a reversible voltaic cell, there is no change in the electrode potential. If, however, one of the electrodes consists of a metal covered with its insoluble salts, the alternating current has pronounced effect on that electrode.

<sup>1</sup> *Z. physik. Chem.*, 44, 81 (1903).

<sup>2</sup> *J. Chem. Soc.*, 1419 (1914).

<sup>3</sup> THIS JOURNAL, 36, 2333 (1914).

3. A greater amount of current could be supplied by a cell with one reversible and another irreversible electrode, when an alternating current plays in the circuit.

4. In cells like Cd-ZnCl<sub>2</sub>-Hg, Cd-ZnCl<sub>2</sub>-Pt, etc., the E. M. F. of Hg or Pt electrode approaches the value of the zinc electrode on the passage of the alternating current.

5. In perfectly reversible electrolytic cells the alternating current has no action when impressed on the cell along with a direct current.

6. But if the electrolytic cell be irreversible, the alternating current greatly increases the current strength through the circuit.

7. This increase in current strength is due to the diminution in the back electromotive force of polarization.

8. This diminution in the discharge potential is also observed, in electrolytic cells consisting of two cathodes and two anodes, the alternating current playing between the anodes or the cathodes, but not passing through the whole circuit.

In conclusion, my best thanks are due to Professors P. C. Rây, and J. B. Bhaduri, for their interest and encouragement.

CALCUTTA, INDIA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

## PROPERTIES OF SILVER IODIDE INTERPRETED IN RELATION TO RECENT THERMODYNAMIC CONCEPTIONS.

BY GRINNELL JONES AND MINER LOUIS HARTMANN.

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This paper presents the results of an experimental study of the most important thermodynamic properties of silver iodide, interpreted in the light of Richards' Theory of Compressible Atoms. These results have also furnished a quantitative test of the so-called Nernst Heat Theorem. They support the former theory, but not the latter.

The mathematical physicists who developed the kinetic theory of gases and liquids, in order to simplify the exceedingly complex mathematical analysis, were forced to assume that atoms are incompressible. Theodore William Richards<sup>1</sup> has, however, presented an array of facts and arguments which show that atoms and molecules are, in reality compressible, or, in other words, that the volume of the atoms is changeable, and dependent on the pressure exerted upon them, whether due to (1) external force, (2) the attraction between molecules of the same kind, which is manifested in cohesion, (3) the attraction of the atoms within the

<sup>1</sup> Professor Richards, in a Presidential Address for the American Chemical Society, "The Present Aspect of the Hypothesis of Compressible Atoms" (*THIS JOURNAL*, 36, 2417 (Dec., 1914)), gives a summary of the results obtained and a complete bibliography.