THE ELECTROCHEMICAL EFFECTS PRODUCED BY SUPERIMPOSING ALTERNATING CURRENTS UPON DIRECT CURRENTS.

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Some curious effects have been observed when alternating currents are superimposed upon direct currents during electrolysis. Thus, O. Reitlinger¹ claims that this combination causes a diminution of the over-voltage. Whether or not this is the case, the fact remains that certain electrolytic reactions can be carried out at a lower voltage, with consequently modified products, by this means. S. G. Brown² found that voltaic action is stimulated by alternating currents and that the electrolytic corrosion of electrodes is much more marked than by direct current alone. Work of a similar kind has been carried out by J. S. Ghosh.³

More recently H. M. Goodwin and M. Knobel⁴ have discussed the effect of alternating currents on hydrogen over-voltage, and have given an explanation of the effects observed. This explanation does not seem to be in accordance with the facts, and although the present author is not prepared to give an alternative explanation he thinks that certain observations he has made, and which are here described, may lead to a clearer appreciation of the subject.

A general distinction may be drawn between low frequency and high frequency currents.

A further classification may be introduced depending upon the relative magnitudes of the alternating and direct currents. Three cases may be distinguished.

Case 1. The amplitude of the alternating current is smaller than the value of the direct current, as shown in Fig. 1. Here OA is the value of the direct current and the alternating current is indicated by the curve OCD. When the latter is superimposed on the direct current the resultant is given by the curve AEF, and the effect is the production of a fluctuating unidirectional current, or a direct current with a ripple upon it.

Case 2. If the amplitude of the alternating current is equal to the value of the direct current the resultant current falls to zero at each cycle as shown in Fig. 2. Assuming a sine wave this will be the case when 1·41

¹ *Zeits. für Elektrochem.*, 1914, vol. xx., p. 261.

² *Proc. Royal Soc.*, 1914, vol. xc., p. 26.

³ *Journ. Am. Chem. Soc.* 1914, vol. xxxvi., p. 2333 and 1915, vol. 37, p. 733.

⁴ *Trans. Am. Electrochem. Soc.*, 1920, vol. xxxvii., p. 617.

times the alternating current (as measured by an ammeter) is equal to the direct current.

Case 3. If the amplitude of the alternating current exceeds the value of the direct current there will be a reverse current once every cycle, as indicated in Fig. 3.

FIG. 1.—Amplitude of A.C. less than value of D.C.

Low Frequency Currents.

The arrangement used for experiments with low frequency currents is shown diagrammatically in Fig. 4. The cell C under observation is connected in series with a hot-wire ammeter A_1 , a moving coil ammeter A_2 , a

FIG. 2.—Amplitude of A.C. equal to value of D.C.

variable resistance R , a battery B (consisting of three lead accumulator cells of 30 ampere-hour capacity, with sometimes a fourth smaller cell, and the secondary of a double wound transformer T . The battery was also

FIG. 3.—Amplitude of A.C. greater than value of D.C.

used on a potentiometer resistance to obtain small currents. The primary of the transformer was supplied with current from the public mains at a frequency of 50. By this arrangement the value of the direct current could be varied by adjusting R . The resistance of the whole circuit could then

remain fixed and any adjustment of the superimposed alternating current could be effected by varying the distance of the secondary from the primary. This distance could be increased sufficiently to make the alternating current as small as desired. The hot wire ammeter indicated, of course, the sum of the currents, and it could be read down to 0.05 ampere, full scale deflection being obtained with 0.5 ampere, but the lower part of the scale is not open. The moving coil instrument indicated the direct current alone, so that the value of the alternating current could be found by difference.

It seemed open to doubt at first whether the apparent effect of alternating current could be due to some rectifying action. Consequently electrodes which were approximately equal, and both of the same metal, were generally used. No evidence of rectification was obtained, and the fact that the effect does not cease immediately on removing the alternating current (as will be shown later) proves that rectification does not afford an explanation.

S. G. Brown observed that when an alternating current was superimposed much greater corrosion effects were obtained. Although a positive result was not expected it appeared worth while to observe whether electro-deposition, or electrolytic corrosion, was affected by such currents in a case where polarisation was absent. For this purpose electrodes of ordinary

FIG. 4.—Arrangement for low frequency currents (frequency 50).

- A_1 = hot wire ammeter.
 A_2 = moving coil ammeter.
 B = battery.
 C = electrolytic cell.
 R = variable resistance.
 T = transformer with variable coupling.

pure copper sheet were used in a solution of copper sulphate rendered acid by the addition of about 5 per cent. of sulphuric acid. The electrodes were immersed to the extent of about 56 sq. cms. (on either side) and the direct current was about $\frac{1}{4}$ ampere. The electrolysis was carried on for half an hour in each case, but no great accuracy was attempted. The results are shown in Table I.

TABLE I.
ELECTRO-DEPOSITION OF COPPER.

	Superimposed A.C.	Cathode Gain.	Anode Loss.
Direct current alone	—	0.160 grs.	0.165 grs.
Alternating current alone (about $\frac{1}{4}$ ampere)	—	0.0015 „ loss	0.002 „
Both currents	0.26 amp.	0.162 „	0.165 „
„ „ „ „ „	0.11 „	0.161 „	0.164 „
High frequency alone	—	0.001 „	0.0005 „
Direct current + H.F.	—	0.168 „	0.1700 „

ALTERNATING CURRENTS UPON DIRECT CURRENTS 105

These figures are sufficient to show that no great difference is caused by superimposing low frequency alternating current under these conditions. One experiment was made with high frequency currents, as shown, and some difference is noticeable, but the conditions were not ideal and therefore it is not desired to lay stress upon this single result.

Numerous experiments were then made using platinum wire electrodes in dilute sulphuric acid. Assuming that the effect of alternating current depends in some way upon polarisation or over-voltage, it would be expected that the effect would be nil upon lead accumulator cells in which the depolarisation is very effective—at least so long as the current taken is small for the size of cell. It is obviously necessary to be certain upon this point, and therefore the arrangement was tested by replacing the electrolytic cell by a piece of resistance wire (about 0.54 ohm). The effect of superimposing alternating current was noticeable, but was small in comparison with the effect when an electrolytic cell was in circuit. For example, a direct current of 0.170 ampere increased to 0.173 ampere when an alternating current of 0.03 ampere was superimposed. As will be seen later, so small a change can be generally neglected, but it is none the less curious that it should be produced.

With regard to the three possible cases (defined by the relative magnitudes of the direct and alternating currents), it was found that a superimposed alternating current gave an increase irrespective of the relative values. The case where the amplitude of the alternating current is smaller than the value of the direct current seems the most interesting because it appears the least explicable. If an actual reversal of current takes place then it may well be argued that the polarisations are wiped out, more or less, by each reversal. This is the line taken up by Goodwin and Knobel,¹ who measured the variations in over-voltage, and who actually make the statement that :—

“No effect is observed until the alternating current is large enough to cause some reverse current to pass through the cell, and the rapid decrease in over-voltage which then follows corresponds closely with the quantity of oxygen theoretically liberated.”

It is surprising that the authors should have made a limiting statement of this kind, though perhaps this may be explained by the apparent limitation of their experiments to a direct current of 2.00 milliamperes and an alternating current *not less* than 2 milliamperes, though a curve is dotted in for lower values deduced from theoretical calculations.

The effect of alternating current for a given electrolytic cell varies with the values of both the direct and superimposed currents. The percentage increase may be much more with a small direct current than with one that is larger, as might be expected. Although for a given direct current the increase becomes greater as the alternating current is made greater the rate of increase soon falls off. This is shown in Fig. 5 which refers to a direct current of 0.075 ampere. Small platinum wire electrodes were used in dilute sulphuric acid, and time was allowed for the direct current to resume its original value substantially in each case before the alternating current was applied for a fresh observation. In this case an alternating current of 0.039 ampere gave an increase of 0.041 ampere (or 55 per cent.) and 0.080 ampere gave an increase of 0.55 ampere (or 73 per cent.).

The fact that the effect does not pass off at once when the alternating current is switched off is shown by the following figures. In this case a direct current of 2.2 milliamperes rose to 12.7 milliamperes when the al-

¹ *Loc. cit.*

ternating current (which was only just observable, but not readable, on the hot wire instrument) was superimposed for a very brief interval. The direct current fell after switching off the alternating current as follows :—

<i>Time in minutes.</i>	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	2	$2\frac{1}{2}$	3
<i>Current in m.a.</i>	12.7	3.5	3.2	2.9	2.7	2.7	2.5	2.4

FIG. 5.—Showing variation of direct current with superimposed alternating current. Low frequency. Electrodes 0.41 mm. platinum wire in dilute sulphuric acid.

These values are plotted in Fig. 6. This comparatively slow return to the original value presumably indicates a disturbance of the state of polar-

FIG. 6.—Fall of direct current after stopping the alternating current. Electrodes 0.41 mm. platinum wire in dilute sulphuric acid. Current originally 2.2 m.a.

isation and will be less marked the smaller the electrodes, or the larger the current. A current of as much as 0.1 ampere, however, took 2 minutes or more to become nearly normal.

FIG. 7.—Variation of the effect with applied voltage. Low frequency. Electrodes 0.41 mm. platinum wire, dipping about $\frac{1}{2}$ cm. into dilute sulphuric acid.

The greatest sensitiveness appears to be obtained when the voltage applied to the electrolytic cell is below that of decomposition. This is shown in Table II. and Fig. 7. The readings were taken in each case after the

ALTERNATING CURRENTS UPON DIRECT CURRENTS 107

direct current had become steady (*i.e.* after the polarisation had become complete, or practically so) which required intervals of several minutes in the case of the higher currents. The alternating current was small, as above, being estimated to be about 20 milliamperes. This was maintained just long enough to obtain a reading. The increase in most cases could only be read approximately because the current fell off rapidly to some extent, *i.e.* the continued application of the alternating current did not maintain the full effect. It should be noted that the applied voltage is the voltage in the whole circuit and therefore is not necessarily the same as the voltage on the cell terminals except for zero current, but the difference is small with the currents here used. The resistance of the secondary of the transformer was about 16.9 ohms.

TABLE II.

SHOWING VARIATION OF EFFECT WITH APPLIED D.C. VOLTAGE. (PT WIRE ELECTRODES 0.041 MM. DIAM.) LOW FREQUENCY.

Applied Volts.	Current through Cell.		Increase.
	No A.C.	With A.C.	
0.25	0 (not readable)	0.3 m.a.	0.3 m.a.
0.5	"	0.5 "	0.5 "
0.75	"	1.4 "	1.4 "
1.0	"	3.6 "	approx. 3.6 "
1.25	"	5.5 "	" 5.5 "
1.5	"	7.25 "	" 7.25 "
1.75	"	9 "	" 9 "
2.0	"	12 "	" 12 "
2.25	0.3	15.5 "	" 15.2 "
2.5	1.4	17 "	" 15.6 "
2.75	2.7	20 "	" 17.3 "
3.0	4.4	23 "	" 18.6 "
3.25	6.4	25 "	" 18.6 "

If an unsymmetrical arrangement is used, one electrode being a wire and the other a much larger surface, some differences are observed, but not of a very fundamental kind. For this purpose platinum foil was used as one of the electrodes, the area immersed (taken on one side only) being about $1\frac{1}{2}$ in. $\times$ $1\frac{1}{4}$ in. (say 12 sq. cms.). The sensitiveness, expressed as the percentage increase of current, seems to be somewhat higher with a small anode than with a small cathode, and the latter may be more sensitive than two small electrodes. For quick response, however, it is necessary that the condition of polarisation should reach a steady state quickly, and from this point of view two small electrodes are to be preferred.

The electrodes were also observed in a small cell under the microscope with a $\frac{1}{2}$ in. objective and illumination thrown on the front of the electrodes. Platinum wire 0.016 in. (0.41 mm.) was used and dipped into the acid, say, 3 to 5 mm. By this means it was found that the small alternating current used for Table II. was sufficient to cause a very slight evolution of gases at the electrodes apart from any direct current. The transformer was therefore adjusted until no gas appeared, and some of the observations were then repeated. The results were similar, but the effect somewhat reduced (*e.g.* a current of 4.2 m.a. rose to about 13 m.a.).

The electrodes during electrolysis were observed under the microscope to see if any light on the phenomena could be thus obtained. It was noticeable that the whole of the hydrogen was at times absorbed by the cathode although oxygen was being given off freely at the anode. In one particular case it was found that the current could be taken well over $1\frac{1}{2}$ milliamperes before hydrogen was noticeable. The application of high frequency current at once caused an evolution of hydrogen. In another case a current of about 0.2 milliamperes was maintained between these electrodes for over $3\frac{1}{2}$ hours. During part of this time half a dozen bubbles were seen clinging to the hydrogen electrode, but during the last two hours no bubbles of any kind could be seen, though a small stream of oxygen was readily apparent on the other electrode, notwithstanding the fact that the volume of oxygen is half that of the hydrogen involved in the decomposition. No experiment was made to determine how long this absorption will continue, and no special effect bearing on the liberation of hydrogen by superimposed currents was noticeable except, possibly, that the bubbles liberated seemed to be smaller on applying alternating current or high frequency currents.

A more convenient method of examination is to place a suitable cell in

FIG. 8.—Platinum wire electrodes as seen on the screen.

a lantern so as to throw a shadow of the electrodes on a screen. It is not, of course, possible in this way to see anything like so much detail, but there is a great advantage in having both electrodes in view at the same time, and any change is more readily watched. In this way the electrode appeared to be about $1\frac{3}{4}$ cm. in diameter, so that a magnification of about 45 was obtained.

The only noticeable feature on the screen in the electrolysis of sulphuric acid with platinum electrodes is the large size of the hydrogen bubbles which form on the cathode. The oxygen bubbles appear to get away so much more easily. This is shown to scale in Fig. 8, but this appearance was not always observed.

High Frequency Currents.

The arrangement used for superimposing high frequency current is shown in Fig. 9. It was not very satisfactory from the point of view of maintaining any fixed high frequency current. A potentiometer resistance was again used for obtaining small direct currents.

In one respect high frequency current gives simpler conditions in that

ALTERNATING CURRENTS UPON DIRECT CURRENTS 109

it does not itself cause decomposition to take place, even when the currents are considerable.

It was found when the applied D.C. voltage was below the decomposi-

FIG. 9.—Arrangement for high frequency currents.

tion voltage that the effect of high frequency current was much less than that of low frequency. This is shown in Table III., and Fig. 10 in which the conditions are similar to those in Table II. The H.F. current varied from 0.05 to 0.1 ampere.

TABLE III.

SHOWING VARIATION OF EFFECT WITH D.C. VOLTAGE (PT. WIRE ELECTRODES 0.41 MM. DIAM.). HIGH FREQUENCY.

Applied Volts.	Current through Cell.		Increase through H.F.
	No H.F.	With H.F.	
0.5	0 (not readable)	0	nil
0.75	"	0	"
1.0	"	just noticeable	"
1.25	"	"	"
1.5	"	"	"
1.75	"	"	"
2.0	"	0.2 m.a.	0.2 m.a.
2.25	0.1 m.a.	0.3 "	0.2 "
2.5	0.5 "	1.8 "	1.3 "
2.75	1.1 "	5.9 "	4.8 "
3.0	2.3 "	13.2 "	10.9 "
3.25	5.4 "	22.7 "	17.3 "

It will be noticed that the effect is not apparent until the applied voltage is much higher than in the case of low frequency (namely, 2 volts as against, say, $\frac{1}{4}$ volt), but when once the curve starts it rises much more steeply.

The appearance under the microscope, or on the screen, was the same as with low frequency currents. The same wire electrodes were used.

It is well known that the phenomenon here discussed is utilised in the electrolytic detector for wireless telegraphy, but in this case only one wire electrode is used, the wire being very fine, and only just dipping into the

electrolyte. These conditions were reproduced roughly (*i.e.* without going down to the small dimensions necessary in the electrolytic detector) by using a platinum wire 3 mils (0.076 mm.) in diameter as one electrode, the other being platinum foil of comparatively large area, and the electrolyte dilute sulphuric acid. The electrode was adjusted so as just to appear below the meniscus. If, under these conditions, the applied voltage is sufficient to cause a ready evolution of bubbles, the application of a small high frequency current is then seen to have the effect of scattering the bubbles, repelling them from one another as if they were electrified, and the direct current at the same time rises. Possibly the same effect, though less marked, takes place with the larger electrodes.

FIG. 10.—Variation of the effect with applied voltage. High frequency. Electrodes 0.41 mm. platinum wire, dipping about $\frac{1}{2}$ cm. into dilute sulphuric acid.

Further, a very curious phenomenon was observed, and one that is new so far as the author is aware. If the applied voltage is reduced until only one or two minute bubbles form upon the wire electrode, or even if the applied voltage is cut entirely out of the circuit, and a small high frequency current is passed momentarily (for example, by allowing merely a spark or two to pass across the gap), a large hemispherical bubble forms over the electrode. The most curious feature is that this bubble starts its formation, not from the electrode but from the body of the electrolyte. On the screen the formation appeared to start about 15 cm. below the electrode; that

FIG. 11.—Electrode and bubble (to scale).

is, actually about $\frac{150}{48}$ or, say, 3 mm. below the electrode in the electrolyte. It travels very fast and takes up its position with unerring accuracy. Another curious point is the very large size of the bubble compared with those formed by electrolysis, more particularly when regard is had to the small quantity of electricity involved, and to the fact that such a high frequency current does not cause electrolytic decomposition in the ordinary way. The relative sizes of the bubble and electrode are shown in Fig. 11. The result is the same whether the wire is anode or cathode. As far as the author is aware, an electrolytic decomposition of this kind at a distance from the electrode has not been previously observed. It seems to be due

ALTERNATING CURRENTS UPON DIRECT CURRENTS 111

to an electric discharge starting in the electrolyte. The discharge is audible, and in the dark it is luminous.

The effect generally seems to be closely connected with the absorption properties of platinum.

The direct current responded very readily to a high frequency impulse whether the wire was anode or cathode. Experiments with a larger wire electrode, similar to those already described with low frequency currents, showed that the sensitiveness, expressed as the percentage increase of the direct current, was greater with the wire as anode. This is the arrangement that is usual in the electrolytic detector.

Metals other than Platinum.

A few experiments were made with palladium wire as electrodes (0.5 mm. diameter). It was found that high frequency currents increased the direct current as in the case of platinum, and that the effect appeared quantitatively to be much the same, but only a few observations were made.

As was to be expected the absorption of hydrogen was more marked with palladium, and under the microscope the direct current could be taken considerably higher before any hydrogen appeared. This became still more marked if the polarity was reversed at any time.

In the case of mercury electrodes the effect was considerable, but with lead it was very small. With metals of this kind, however, there is the added complication of chemical combination at the anode.