CCCXLVII.—*The Electrolysis of Potassium Chloride Solutions by Alternating Currents.*

By Arthur John Allmand and Herbert Charles Cocks.

This subject has been studied by Coppadoro (*Gazzetta*, 1905, **35**, ii, 604), using 42-cycle current and $3N$-potassium or sodium chloride. With polished platinum electrodes and at room temperature, no electrolysis was noticed until a *C.D.* of 0·5 amp./cm.^{2} had been exceeded; above this threshold value, hydrogen was evolved and hypochlorite formed, oxygen also being detected after the electrolysis had been proceeding for some time. The electrodes were corroded, and to some extent went into solution as platinum compounds and as colloidal platinum; if the *C.D.* were not sufficiently high, they became platinised and electrolysis ceased. With graphite electrodes, no hypochlorite was formed below a *C.D.* of 10 amps./cm.^{2}, under which conditions the electrodes were considerably attacked. The hypochlorite current efficiencies were low, *e.g.*, 2% during a 30-minute run at 1 amp./cm.^{2}. After a time, a stationary hypochlorite concentration was reached, and further electrolysis produced chlorate. In a second paper (*ibid.*, 1906, **36**, ii, 321), Coppadoro reports experiments carried out at 50—70°, under which conditions chlorate, and not hypochlorite, is formed.

The work now recorded is a systematic study of the different factors which can affect this electrolysis when carried out at room temperature. In particular, the effects of frequency, current density, and concentration have been investigated. It may be said at once that, in so far as the conditions under which we have worked coincide with those of Coppadoro, our results are in agreement with his.

EXPERIMENTAL.

Apparatus.—The cell used in the great majority of the experiments consisted of a beaker of about 200 c.c. capacity, provided with a wooden lid. This carried (*a*) the capillary exit-tube of a glass hood of bell-jar shape, which dipped below the surface of the electrolyte to within 1—2 cm. of the bottom of the beaker, (*b*) a thermometer, and (*c*) the glass tubes into which the electrodes were sealed. These tubes were bent back twice through 90°, so as to project upwards below the edge of and into the hood. The electrodes, spaced vertically and parallel to one another about 2 cm. apart, were 1 cm. square, and were carefully polished and burnished before each experiment. The cell itself stood in a large vessel of water, in order to keep down the temperature during electrolysis. The capillary exit led to the three-way tap of a gas-burette, which could also be connected with a Hempel gas-pipette containing alkaline pyrogallol. About 90 c.c. of electrolyte were placed in the cell and, by manipulation of the burette, made to fill completely the hood, the capillary connecting tube, and one bore of the three-way tap. The gas-burette, the other tap-bore, and the second connecting tube were then filled with water, and the whole was attached to the pyrogallol pipette. After electrolysis for a definite period of time, the evolved gases were passed over to the burette (care being taken to transfer all bubbles adhering to the sides of the hood), measured, and the oxygen content was determined. No attempt was made to estimate or to allow for any gases dissolved either in the electrolyte or in the burette liquid. No chlorine was detected at any time, and consequently, after subtracting the oxygen present, the residue was regarded as hydrogen. Immediately after the transfer of the gases, the cell liquid was made up to a definite volume, and analysed by the usual methods for hypochlorite and for total available oxygen. The presence of platinum in the solution caused the iodine–starch end-point to be rather less definite than usual, but did not appreciably affect the accuracy of the analysis.

The current used was hand-regulated by a variable resistance, and measured by a calibrated hot-wire ammeter. It was produced by one of two machines (a G.E.C. 16-pole alternator, capable of being run between the limits of 5 and 240 cycles, and a 24-pole alternator of inductor type, made by the Crocker–Wheeler Company, and giving 350—500 cycles) which have been described elsewhere (*Trans. Faraday Soc.*, 1925, **21**, 1).

Preliminary Experiments.—When graphite electrodes, 3*N*-potassium chloride, and a *C.D.* of 1 amp./cm.^{2} were used, electrolysis was inappreciable with 18 cycles, and only very slight at a frequency of 6 cycles. (With this very low frequency, we made no attempt to use higher *C.D.*'s. This could only have been done by reducing the size of the electrodes, the output of our machine under these conditions being small.) With polished platinum electrodes and a frequency $n = 6$, there was considerable electrolysis even at 0·3 amp./cm.^{2}. If the electrodes were platinised, the results were as with graphite. These experiments also showed the importance of determining the hypochlorite immediately after conclusion of the electrolysis. In presence of the $3N$-potassium chloride, decomposition was fairly rapid, even in the absence of platinum and platinum compounds.

Effect of Frequency and Current Density.—The experiments described in this section were all carried out with $3N$-potassium chloride. The frequencies employed were $n = 5$—6, 21—22, 41, 50, 64, and 120 cycles per second. Depending on n (and therefore on the available output of the machine), the currents used varied between the limits of 0·1 and 2·5 amps. Low *C.D.*'s and high frequencies favoured platinisation of the electrodes. With $n = 6$, this was hardly perceptible, even with the lowest *C.D.*'s employed (0·1—0·3 amp./cm.^{2}); with $n = 22$, platinisation was appreciable with low *C.D.*'s, but very slight with 2—2·5 amps./cm.^{2}; with the higher frequencies, it was always very noticeable. In addition, a yellow deposit (probably potassium chloroplatinate) was sometimes found on the electrode; it was produced neither at the lowest nor at the highest *C.D.*'s, but usually at about 0·3—1 amp./cm.^{2}. It was less noticeable with high frequencies. Finally, with all except the lowest *C.D.*'s, the electrolyte became yellow or brownish-yellow and finally cloudy, and the more so as the electrolysis proceeded. On the assumption that the lessened tendency to formation of deposits of any kind on the electrodes at high *C.D.*'s is due to their being scoured by the rush of evolved gas, the facts mentioned are qualitatively consistent with the conception that ionisation of the normally passive platinum, like the other electrolytic processes (as will be seen), takes place the more readily during the anodic pulse the lower the frequency and the higher the *C.D.*; and that the reverse change takes place to a greater extent during the cathodic pulse the higher the frequency.

Only in one case ($n = 41$, $i = 2$ amps.) was any chlorate production noticed, and here there was definite local heating.

Table I contains a typical set of results. The current efficiencies are calculated, as throughout the paper, on a basis of actual coulombs passed, *i.e.*, assuming the current to have a sine wave form, the average current used for the calculation is 0·9 of the value in column 2, or $i_{\text{average}} = 2\sqrt{2}/\pi \,.\, i_{\text{effective}} = 0{\cdot}9\ i_{\text{effective}}$.

Fig. 1 shows the effect of *C.D.* on current efficiency for $n = 5$—6, 21—22, and 64. A remarkable feature in the curves for the lower frequencies is the abrupt changes in direction that occur at 0·3—0·4 and at about 1 amp., respectively. Fig. 2 exhibits the effect of frequency for currents of 1, 1·5, and 2 amps.

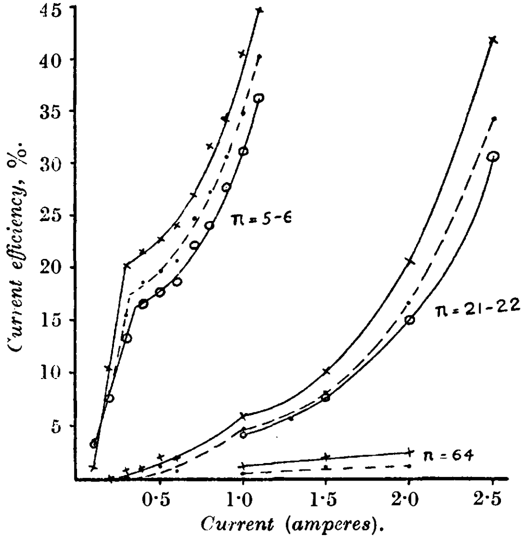
As Fig. 1 shows the current efficiency (for the lower frequencies) to be increasing very rapidly with the *C.D.*, a few experiments were carried out with very high *C.D.*'s and platinum wire electrodes. In

TABLE I.

Polished platinum electrodes, 1 cm.^{2}. Electrolyte, $3N$-KCl. Frequency, 5—6 cycles. Temperature, 10—20°.

Time (mins.).	Current (r.m.s.) (amps.).	Current efficiencies, %.			
		Hydrogen.	Hypochlorite.	Oxygen.	Total anodic.
120	0·1	1·1	3·3	0·22	3·5
60	0·2	10·7	7·8	0·56	8·3
40	0·3	20·3	13·3	2·3	15·6
30	0·4	21·6	16·7	2·1	18·8
24	0·5	22·9	17·8	2·1	19·9
20	0·6	24·2	18·7	2·1	20·8
17	0·7	27·1	22·3	2·7	25·0
15	0·8	31·8	24·2	3·2	27·4
10	0·9	34·4	27·8	2·9	30·7
10	1·0	40·6	31·3	3·6	34·9
6	1·1	44·9	36·4	3·9	40·3

FIG. 1.



× *Hydrogen.* · *Total anodic.* ⊙ *Hypochlorite.*

this case, the gases were not collected, and the cell used, of 35 c.c. capacity, was cooled externally by running water. Each electrode consisted of 8 mm. of platinum wire of 0·38 mm. diameter, and had therefore a total area of 0·09—0·1 cm.^{2}. They were spaced about 1·3 cm. apart. The results (Table II) show that the curves for these frequencies in Fig. 1 must soon bend over with increasing current and, from being convex, become concave.

C.D.'s exceeding 15 amps./cm.^{2} at 22 cycles caused the formation of sparks and arcs around the electrodes which remained quite clean

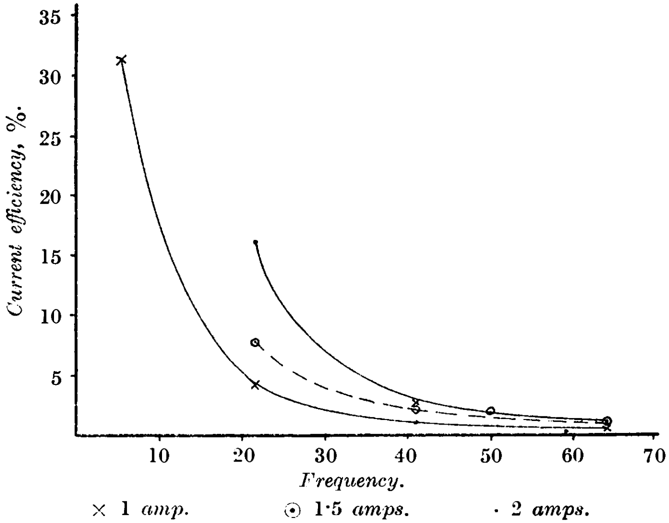
TABLE II.

Platinum wire electrodes, 0·1 cm.^{2}. Electrolyte, 3N-KCl.

Frequency.	Time (mins.).	Current (r.m.s.) (amp.).	Hypochlorite current efficiency, %.
5	15	0·4	65·6
6	30	0·3	64·4
22	5	1·0	61·1

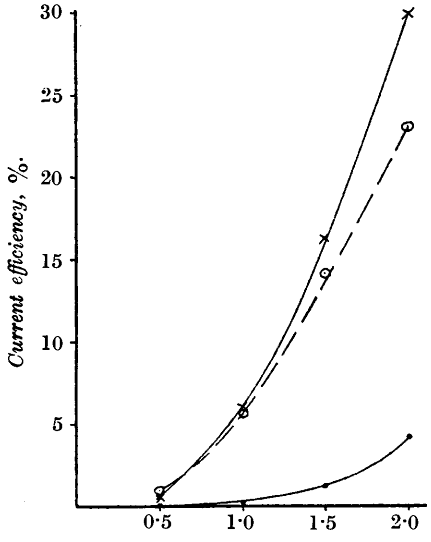
in every case. At 5—6 cycles, the electrolyte also remained clear at these high *C.D.*'s, but became pale yellow in colour, whilst, with 22 cycles, it became dark brown or black. In all cases, good thiosulphate end-points were obtained (sharp change from blue to colourless).

FIG. 2.



Whatever the *C.D.*, the total anodic current efficiency (hypochlorite plus oxygen) was less than the cathodic current efficiency (as in Table I, for $n = 6$). A determination of the quantity of platinum dissolved after one of the experiments indicated that about one-third of the usual deficiency could be accounted for in this way, assuming that the metal had dissolved in the quadrivalent state. In addition, the electrodes, carefully washed after electrolysis and then immersed in a colourless solution of acidified potassium iodide and starch, soon caused a slight colour to develop, showing that they contained traces of some oxidation product of platinum, the amount, however, being negligible in comparison with the "missing" oxygen. Formation of perchlorate was not tested for, but is very unlikely. As the products formed at the two electrodes were collected together, the cause could not be a slight rectification. With platinum electrodes of unequal size in sulphuric acid, this does take place to a certain extent (Mengarini, *Electrician*, 1891, **27**, 334; Gundry, *Phil. Mag.*, 1906, **11**, 329; Vaillant, *Compt. rend.*, 1919, **168**, 687), and it was also observed by Ayrton and Perry (*Electrician*, 1888, **21**, 299) when using an ordinary Hoffmann voltameter. In our work, it seemed negligible, judging from the results of experiments carried out with a variety of *C.D.*'s and frequencies, a hot-wire ammeter and a moving-coil ammeter being in series in the circuit.

FIG. 3.



× *Hydrogen.* ⊙ *Hypochlorite.* · *Oxygen.*

In some cases, indeed, we certainly noticed more gas coming off at one of the two apparently quite similar electrodes, but this does not necessarily indicate rectification.

Expressed in terms of oxygen gas, the maximum deficiency was of the order of 1 c.c. One possibility is that the missing gas had dissolved in the electrolyte or in the water in the measuring burette. Perhaps it was formed by spontaneous decomposition of the hypochlorite, and remained in a state of supersaturation, as is the case in the photodecomposition of chlorine water or of hypochlorous acid solutions (J., 1925, **127**, 822). It may be remarked that the alternating-current electrolysis of sulphuric acid between platinum electrodes has, on several occasions, been noticed to give a deficiency of oxygen (Manœuvrier and Chappuis, *Compt. rend.*, 1888, **106**, 1719; Marsh, *Proc. Roy. Soc.*, 1920, **97**, 124).

Effect of Concentration.—A series of experiments was carried out on N-potassium chloride solutions, with frequencies varying between 6 and 180, and currents up to 2 amps. The electrodes became platinised in every case, but there was no formation of yellow deposit. The electrolyte became increasingly turbid (yellow or brown) as the electrolysis proceeded. Fig. 3 contains graphs of the data for $n = 21$, whilst in Table III are the results for $n = 5$—6 and $n = 21$—22, compared with the corresponding figures given by 3N-potassium chloride.

TABLE III.

Frequency.	Current (r.m.s.) (amps.).	Cathodic current efficiency, %,		Hypochlorite current efficiency, %,	
		3N-KCl.	N-KCl.	3N-KCl.	N-KCl.
6	0·1	1·1	0·33	3·3	0·22
6	0·2	10·7	0·78	7·8	2·3
6	0·3	20·3	6·1	13·3	6·4
21	0·5	2·1	0·56	1·2	1·0
21	1·0	6·0	6·0	4·2	5·6
21	1·5	10·3	16·2	7·8	14·1
21	2·0	20·8	29·8	15·2	23·0

It will be noted that the curves for N-potassium chloride do not show the breaks which are such a marked feature in those for the 3N-solution. Like the latter, their slope must clearly become less at higher *C.D.*'s. Corresponding to their continuous nature, the current efficiencies are seen to be lower at lower, and higher at higher, current densities than is the case with 3N-potassium chloride. The effect of frequency is similar to that shown in Fig. 2.

A few experiments only were done with 0·1N-potassium chloride solutions, owing to the low conductivity and consequent tendency to temperature rise, with formation of chlorate. The results were of no particular interest.

Effect of Addition of Alkali.—These experiments, carried out with solutions of composition 3N-KCl + 0·1N-NaOH, were suggested by the well-known fact that hypochlorites are more stable in alkaline than in neutral or acid solution. The results, compared with those given by a neutral solution, are shown in Table IV.

It will be seen that, whilst the yield of hypochlorite is lowered, that of both hydrogen and oxygen is increased by the addition of alkali, whilst the deficiency in the total anodic yield still persists. This last result appears to dispose of the suggested possibility of the deficiency being due to supersaturated oxygen resulting from chemical decomposition of the hypochlorite, for this was found to be very low in the alkaline solution.

TABLE IV.

Polished platinum electrodes, 1 cm.^{2}. Frequency, 6.
Temperature, 10—20°.

	Current efficiencies, %.							
	Neutral solutions.				Alkaline solutions.			
Current (r.m.s.) (amp.).	Hydrogen.	Hypochlorite.	Oxygen.	Total anodic.	Hydrogen.	Hypochlorite.	Oxygen.	Total anodic.
0·5	22·9	17·8	2·1	19·9	27·1	17·0	8·0	25·0
0·8	31·8	24·2	3·2	27·4	34·4	22·0	8·3	30·3

Effect of Addition of Potassium Chromate.—It is well known that, in direct-current electrolysis of alkali-metal chlorides, the hypochlorite yield can be markedly increased by the addition of a chromate, its effect being to reduce considerably the cathodic reduction of hypochlorite ions which otherwise takes place, owing to the formation on the electrode of a film (" cathode diaphragm ") which is usually supposed to be chromium chromate. Experiments were consequently done with 3*N*-potassium chloride solutions containing, in addition, 1 g. of potassium chromate per litre. It is unnecessary to give the results in detail, as the effects were small. Quite definitely, however, there appeared to be a decrease in current efficiency at low, and an increase at high, current densities. This was observed with both 6- and 22-cycle current. The platinum also appeared to be less attacked. No platinum-black was formed, nor did the electrolyte become as cloudy as under similar conditions in the absence of chromate.

Effect of Stirring.—Experiments were carried out in the simple type of cell used for investigating the effect of high *C.D.*, a mechanically driven stirrer running at a fairly high speed being used. No attempt was made to collect the gases. The anticipated increase in current efficiency is seen to be marked (Table V).

TABLE V.

		Hypochlorite current efficiency, %.	
Frequency.	Current (r.m.s.) (amps.).	Without stirring.	With stirring.
6	0·2	7·8	14·8
6	0·5	17·8	25·0
6	0·8	24·2	36·0
6	1·0	31·4	38·7
42	1·0	2·4	6·2
42	1·5	2·1	8·3

Limiting Hypochlorite Concentration.—These experiments were carried out in the same simple cell. Stirring was not employed, but the cell was kept cool by a stream of water running over it. With 25 c.c. of neutral 3*N*-potassium chloride and a current of 1·2 amps.

at a frequency of 6, the hypochlorite concentration rose, first rapidly, then slowly, to about 0·27—0·28N after a run of 2½—3 hours. Further electrolysis led to no further increase—on the contrary, a slight decrease was observed after 5 hours, the concentration falling to 0·26N. Considerable amounts of a brown precipitate were formed, and the electrodes became covered with a (partly black) deposit. Gas evolution had almost ceased after 4 hours. An experiment with 3 amps. at 21 cycles gave very similar results—a concentration of 0·27N after 2½ hours, considerable electrode corrosion and precipitate formation, and gradual elimination of gas evolution. Before this ceased, it was noticed that much of it was taking place throughout the whole bulk of the electrolyte, not merely at the electrodes. In another experiment, after 4 hours' electrolysis with 1·2 amps. ($n = 6$), the solution was 0·32N with respect to hypochlorite. Chlorate was present to the extent of 0·095N. It was noticed that, in this case, gas evolution was much stronger at the end of the experiment than in the previous cases, and, at the same time, the electrodes were far cleaner. The addition of free alkali to the original electrolyte lowered the limiting hypochlorite concentration. On the other hand, the addition of 1 g./litre of potassium chromate raised it slightly, concentrations of 0·30—0·31N being obtained in three separate experiments, using 1·2 amps. and $n = 6$. Both results are in accordance with those recorded earlier.

Voltage Measurements.—Using the same apparatus, measurements were made of the r.m.s. voltage across the cell under varying conditions of electrolysis. In all cases, an unstirred 3N-potassium chloride solution was used, and the cell was cooled by running water. The electrodes were 1 cm. squares of polished and of platinised platinum, in addition to graphite electrodes of as nearly as possible the same area. In all cases, they were placed 1·2 cm. apart. The measurements were made by means of a Duddell thermo-galvanometer, previously calibrated by means of a standard *D.C.* voltmeter. Readings were taken immediately on switching in the current, and repeated at 10-minute intervals during 1 hour. With polished platinum, there was generally a fall during the electrolysis, varying from 1 or 2 centivolts up to several decivolts, comparatively rapid at the start, most noticeable when electrolysis was considerable, and obviously connected with the corrosion or platinisation of the electrodes. With platinised platinum and graphite, at which little or no electrolysis took place, the decreases in voltage noticed were correspondingly less. Occasionally a rise in voltage was observed. Under identical conditions of current and frequency, the cell voltage decreased in the order : polished platinum>platinised platinum>graphite, represented by (A), (B), and (C) respectively in Table VI, which contains typical figures.

TABLE VI.

Time (mins.) after start.	Voltage across electrodes.								
	$n=6$; $i=0{\cdot}12$ amp.			$n=6$; $i=1$ amp.			$n=48$; $i=1$ amp.		
	(A).	(B).	(C).	(A).	(B).	(C).	(A).	(B).	(C).
0	1·60	1·04	1·10	3·77	3·08	3·23	3·05	2·42	2·22
10	1·58	1·27	1·04	3·63	3·04	3·06	2·95	2·36	2·07
20	1·60	1·32	1·00	3·58	3·02	2·97	2·78	2·34	2·08
30	1·60	1·32	0·98	3·56	3·02	2·97	2·78	2·36	2·08
40	1·60		0·96	3·53		2·97	2·74		2·08
50	1·60		0·83	3·51		2·99	2·59		2·07
60	1·59		0·94	3·51		2·96	2·50		2·06
Electrolysis	Slight	Nil	Nil	Much	Slight	Slight	Slight	Nil	Nil

Owing to the time effect, the data are, in general, unsuited for exact comparison. It is clear, however, that the cell voltage increased both with increased *C.D.* and with diminished frequency. If the last factor were kept constant, more or less linear voltage–current density plots were obtained, which, on extrapolation to zero current, cut the voltage axis at some distance from the origin. These intercepts, which must be regarded as indicative of residual polarisation at the electrodes, were smaller the higher the frequency. But, even with 480 cycles, they corresponded to about 0·5 volt with polished and 0·2 volt with platinised platinum. This last figure must be regarded as showing the linear extrapolation to be unjustified.

Depolarisation by Chlorine at Platinum and Graphite Cathodes.—The lower r.m.s. voltages obtained with graphite as compared with polished platinum electrodes are in agreement with the much smaller degree of electrolysis found when using graphite, and suggest that, in this case, the electrode processes occurring during the anodic and cathodic pulses to a great extent simply reverse one another. The direct-current chlorine over-voltage is known to be greater, during the early stages of electrolysis, at graphite than at smooth platinum (Knobel, Caplan, and Eiseman, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 55), which argues for a slower rate of the reaction $2\mathrm{Cl} \longrightarrow \mathrm{Cl}_2$, and for a relatively great heaping up of chlorine atoms in the graphite surface layers. Under the conditions of alternating-current electrolysis, these might be expected to ionise during the cathodic pulse, whereas, with a platinum anode, hydrogen ions would be discharged. If, however, the reaction $2\mathrm{Cl} \longrightarrow \mathrm{Cl}_2$ is slow, so will also be $\mathrm{Cl}_2 \longrightarrow 2\mathrm{Cl}$, and consequently a graphite cathode depolarised by chlorine should be more easily polarised under the same conditions of *C.D.* than a similar smooth platinum cathode.

Experiments were done to test this view. The cell consisted of a U-tube of wide bore, partly filled with N-hydrochloric acid. In one limb was a platinum anode, in the other a 1 cm.-square cathode of either polished platinum or graphite, half immersed in the electrolyte. Against the cathode pressed the tip of a Luggin capillary, sealed in through the wall of the U-tube, and making connexion, through a bridge of $3N$-potassium chloride, with a normal calomel electrode. By means of a jet sealed into the bottom of this limb, a stream of chlorine gas could be bubbled round the cathode. After the electrolyte had been saturated with chlorine, the static cathode potential was measured, and then a series of continuously increasing small measured currents was passed through the cell, and the potential again observed after each alteration in current. The results are contained in Table VII. The differences observed are very marked, and of the nature anticipated.

TABLE VII.

	Polished platinum cathode.		Graphite cathode.	
Polarising current (milliamps.).	Potential (π_H) (volts).	Change in potential (millivolts).	Potential (π_H) (volts).	Change in potential (millivolts).
0·0	+1·392	—	+1·378	—
0·2	1·390	− 2	1·378	0
1·0	1·383	− 9	1·367	− 11
2·0	1·376	−16	1·350	− 28
3·0	1·371	−21	—	—
4·0	1·366	−26	1·322	− 56
10·0	1·321	−71	1·212	−166

Average Electrode Potentials during Alternating-current Electrolysis.—These measurements were carried out with currents of frequency 20, polished platinum electrodes in $3N$-potassium chloride being used, and a normal calomel electrode. Prior to them, readings were taken with 1 cm.-square electrodes of platinised platinum in N-sulphuric acid, a normal mercurous sulphate electrode being used as reference electrode, and currents of 17 and of 480 cycles being employed. The results indicated that, whilst a static platinised platinum electrode in N-sulphuric acid acts as an air electrode with a potential of about $\pi_H = + 0·97$ volt, its oxygen content increases and its average potential becomes more positive as electrolysis proceeds. When the current is cut off, the static potential slowly returns to the original air value. Typical results are contained in Table VIII.

Similar observations on the behaviour of the potentials of platinum electrodes in sulphuric acid under the influence of alternating currents have been made by Ghosh (*J. Amer. Chem. Soc.*, 1914, **36**, 2333) and by Vaillant (*Compt. rend.*, 1919, **168**, 768).

TABLE VIII.

Electrode potentials (π_H), volts.

Conditions of measurement.	$n = 480$; $i = 0{\cdot}11$ amp.		$n = 17$; $i = 0{\cdot}15$ amp.	
	π_H.	Change.	π_H.	Change.
Static.	+0·9739	—	+0·9695	—
A.C. on for 0·5 min.	0·9940	+0·0201	1·0211	+0·0516
,, ,, 10 mins.	1·0014	+0·0275	1·0512	+0·0817
,, ,, 20 ,,	1·0046	+0·0307	1·0663	+0·0968
,, ,, 30 ,,	1·0071	+0·0332	1·0749	+0·1054
A.C. off for 10 ,,	1·0046	+0·0307	1·0511	+0·0816
,, ,, 30 ,,	—	—	1·0468	+0·0773
,, ,, 18 hrs.	0·9695	−0·0044	—	—
	No electrolysis.		Traces of gas evolved.	

The behaviour of polished platinum electrodes in 3*N*-potassium chloride was, however, different, as is shown in Table IX.

TABLE IX.

Polished platinum electrodes, 1 cm.^{2}. Electrolyte, 3*N*-KCl.
Frequency, 20 cycles.

Electrode potentials (π_H), volts.

Conditions of measurement.	$i = 0{\cdot}2$ amp.		$= 0{\cdot}3$ amp.		$i = 0{\cdot}5$ amp.	
	π_H.	Change.	π_H.	Change.	π_H.	Change.
Static.	+0·5482		+0·5050		+0·5345	
A.C. on for 2 mins.			0·2443	−0·2607		
,, ,, 10 ,,	0·0424	−0·5058	0·2307	−0·2743	0·3486	−0·1859
,, ,, 20 ,,	0·0481	−0·5001				
A.C. off for 5 ,,			0·7052	+0·2002	0·9540	+0·4195
,, ,, 30 ,,	0·5884	+0·0402	0·7303	+0·2253	0·9832	+0·4487
,, ,, 60 ,,			0·7448	+0·2398		
,, ,, 75 ,,	0·5674	+0·0192				
,, ,, 80 ,,					0·9931	+0·4586
,, ,, 18 hrs.	0·5737	+0·0255				

The average potential measured during electrolysis is seen to be less positive than the static air potential, but to increase with increasing *C.D.* As oxygen is liberated during the electrolysis (although only in traces at those *C.D.*'s used in this series of experiments) and in amounts increasing with, and more rapidly than, the *C.D.*, it is reasonable to assume here also, as with platinised platinum in dilute sulphuric acid, that the average electrode potential corresponds to the average oxygen charge in the electrode during the complete cycle. When the current is cut off, the potential rapidly rises, owing to the hypochlorite in the solution, and to an extent determined by the concentration of the latter. Slow decomposition of the hypochlorite will be accompanied by an ultimate gradual potential fall to the air value. It may be mentioned that Ghosh (*loc. cit.*), using platinum electrodes in hydrochloric acid solutions, also found the potentials to become more negative on polarisation with alternating currents. In this case, however, as no oxidising agent is formed in solution, the electrode potentials, after electrolysis, simply return gradually to the limiting air potential figures.

Discussion.

The main results of this work are in general agreement with the "fundamental laws" of alternating-current electrolysis formulated by Mengarini (*Electrician*, 1891, **27**, 304), *viz.*, that the current efficiency (1) decreases with decreasing *C.D.* and falls to zero below a threshold *C.D.* value, and (2) decreases with increasing frequency and becomes zero above a threshold frequency—these threshold frequencies and *C.D.*'s being functions of one another and also of the particular electrolysis in question. The most interesting feature of Figs. 1 and 3 is the discontinuity shown by the $3N$-potassium chloride curves at low frequencies when compared with the N-potassium chloride curves. These breaks could not be correlated with changes in the electrode surface, and they seem difficult of explanation. Systematic measurements of electrode polarisation, best with the aid of an oscillograph, appear necessary. An increase in *C.D.* also increases the current efficiency of *direct-current* hypochlorite production; but, whereas the favourable effect is here probably connected with the more ready formation of an acid diffusion layer, free from hypochlorite ions, around the anode, in the case of alternating currents it is a question of a relative diminution in the extent to which the anodic and cathodic pulses merely neutralise one another's effects, as a result of discharged ions remaining in or on the electrodes.

The addition of *alkali*, obviously owing to the primary discharge of hydroxyl instead of chlorine ions, has been seen to lower the efficiency of hypochlorite production. This is also the fact in direct-current electrolysis; but, in that case, where higher hypochlorite concentrations are encountered, the cause is rather the destruction of the acid "diffusion layer" mentioned above, and the consequent facilitated anodic discharge of hypochlorite ions. The small effect of the addition of *chromate*, compared with its influence on the course of the direct-current electrolysis, results from the fact that the hypochlorite ions are produced inside, or in the pores of, and not outside, the "cathode diaphragm." For similar reasons, stirring increases the current efficiency, whereas the best results are obtained with direct currents when an undisturbed electrolyte is used.

The limiting hypochlorite concentration observed (about $0{\cdot}3N$) is, of course, far lower than that given by a direct current under similar conditions of concentration, current density, and temperature. It corresponds, in fact, roughly to the equilibrium concentration obtained at room temperature with $1{\cdot}7N$-sodium chloride, and a *C.D.* of 1·7 amps./dcm.^{2} (Foerster and Müller, *Z. Elektrochem.*, 1903, **9**, 196) whereas, in the present experiments, $3N$-potassium chloride and a *C.D.* of 1·2 amps./cm.^{2} (at 6 cycles) were employed. As mentioned, chlorate was found to be present, and there is no doubt that, with alternating as with direct currents, the limit reached in the hypochlorite concentration is due to hypochlorite-ion discharge.

The electrode potential data have already been discussed. We will only add that oscillographic measurements appear necessary for their more detailed elucidation.

Summary.

(1) The alternating-current electrolysis of solutions of potassium chloride at room temperature, with polished platinum electrodes, has been investigated.

(2) The influence on the hypochlorite current efficiency of changes in concentration, current density, and frequency have been studied, as have also the effects of adding free alkali or a chromate.

(3) The maximum hypochlorite concentration possible under the conditions of electrolysis has been determined.

(4) Measurements have been made of the average electrode potentials during electrolysis under different conditions.

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