

## DISCUSSION.

Professor Ernest Wilson gave the following *résumé* of his Paper (together with some additional matter) on "Alternate Current Electrolysis," which had been taken as read at the previous Meeting.

TABLE I.—Experiments (*Roy. Soc. Proc.*, vol. 54, p. 407) made with platinum plates in dilute sulphuric acid show that of the total energy supplied to the cell in a given time, more is returned to the source when the frequency is high than when it is low—the maximum coulombs being of the order '0006 per sq. cm. in each case. If the quantity of electricity be plotted co-ordinately with the E.M.F. of electrolysis it is found that at the higher frequency, for about the same maximum coulombs, the curve has relatively a smaller area, such reduction being probably brought about by

TABLE I.  
*Influence of Frequency upon Electrolytic Action.*

Metal.	Electrolyte.	Frequency.	Percentage in Total Energy Returned.	Max. Amperes per sq. cm.	Max. Coulombs per sq. cm. in. 10 <sup>3</sup> .	Max. Volts across cell.	Max. Volts. of Electrolysis.		Remarks.
							O <sub>2</sub>	H <sub>2</sub>	
Platinum...	Dilute H <sub>2</sub> SO <sub>4</sub>	142.5	40.8	.436	.474	1.77	.78	.68	See Roy. Soc. Proc., vol. 54, p. 407.
"	" "	2.4	13.6	.013	.800	1.37	.72	.66	
"	" "	100	23	.288	.432	2.7	Ergs per cycle per sq. cm. 17,900		
"	" "	"	24	.116	.180	2.4	3,000		
"	" "	"	34	.067	.109	2.38	—		
"	" "	"	—	.038	.059	1.93	—		Correction not made for Conductivity at 100 frequency.
"	" "	"	32	.019	.032	1.61	—		
"	" "	"	43	.014	.020	1.3	2,000		
"	" "	88.4	24	.0038	.0066	.232	20		
"	" "	88.7	54	.0018	.00226	.50	0.67		
"	" "	51.2	36	.0039	.0115	.45	32		Correction for Conductivity negligible.
"	" "	51	57	.0019	.0058	.41	8.4		
"	" "	51.8	48	.00097	.0029	.17	2.3		
"	" "	25.2	58	.00188	.0115	.29	21		
"	" "	25.5	44	.00098	.0061	.186	8.4		

Metal.	Electrolyte.	Frequency.	Percentage of Total Energy Returned.	Max. Amperes per sq. cm.	Max. Coulombs per sq. cm. in 10 <sup>-3</sup> .	Max. Volts across cell.	Max. Volts of Electrolysis.	Remarks.
Aluminium	{ Soda Alum { dilute }	43·2	26	·0042	—	35·0	—	Correction not made for Conductivity.
		10·5	3·2	·0032	—	31·3	—	
	{ Ammonium { Alum dilute }	41·3	22	·0042	—	47·6	—	
"		10·5	4·0	·0032	—	49·1	—	
"	{ Potash { Alum dilute }	41·3	14	·0042	—	45·0	—	
		10·5	2·6	·0032	—	44·4	—	

the greater reversibility. Further experiments have been made at different frequencies when the maximum coulombs were smaller, and give in some cases still higher values for the proportion of the total energy which is returned to the source—demonstrating that the magnitude of the maximum coulombs has an important effect, as the above explanation suggests.

Further experiments (*Ibid.*, vol. 63, p. 346) made with aluminium plates in dilute potash-, soda-, and ammonia-alum solution showed a similar effect.

TABLE II.—Judging from the above experiments, one might be led to expect that when a metal is dissolved in an electrolyte by alternate current electrolysis, the amount dissolved in a given time at a given current density would be smaller at high than at low frequency. This is found to be the case, as the experiments in the present Paper (*Faraday Soc. Trans.*, vol. 1, August, 1905) show.

TABLE II.  
*Influence of Frequency upon Electrolytic Action.*

Exp.	Metal.	Electrolyte.	Milligrammes per hour per sq. cm.	Frequency.	R M S Amperes per sq. cm.
1	Lead	Dilute H <sub>2</sub> SO <sub>4</sub>	6·29	21·5	·0236
2	"	" "	3·44	92·5	·0236
4	Zinc	Dilute H <sub>2</sub> SO <sub>4</sub>	5·30	25·5	·024
8	Amalgamated	" "	3·37	32·0	·031
5	"	" "	1·89	92·0	·025
17	Iron	{ Strong Ferrous Sulphate {	0·787	32·0	·034
13	"		0·462	92·0	·027
20	Iron	{ Strong Sodium Chloride {	0·100	32·0	·031
18	"		0·017	92·0	·026
14	Copper	{ Strong Sodium Chloride {	0·278	32·0	·034
23	"		0·028	92·0	·024

TABLE III.—Besides this chief conclusion there remain indications of other important effects. So great is the number of variables, and so great

the difficulty of keeping all but one constant during an experiment, that from the few experiments performed it is dangerous to attempt a generalisation.

All the experiments in Table III. were made at frequency 92. The weight of lead dissolved in dilute  $\text{H}_2\text{SO}_4$  increases with the current density. Amalgamated zinc is difficult to deal with, as the degree of amalgamation influences the result. Iron is dissolved in ferrous-sulphate at a greater rate the greater the current density when the respective experiments are started with fresh solutions. This is not the case when a new experiment is started in a solution whose density has been increased by electrolytic action in a previous experiment. Compare Experiments 13, 14, 16. A difficulty with ferrous-sulphate solution is its known tendency to oxidise. In sodium chloride more iron is dissolved at the higher current density. A complete investigation would need to take account of the density and temperature of the electrolyte, and possibly of other conditions.

TABLE III.

*Influence of Current Density upon Alternate Current Electrolysis.*

Exp.	Metal.	Electrolyte.	Milligrammes per hr. per sq. cm.	R M S Amperes per sq. cm.
2	Lead	Dilute $\text{H}_2\text{SO}_4$	3.44	.0236
3	"	" "	32.3	.0847
5	Zinc Amalgamated.	Dilute $\text{H}_2\text{SO}_4$	1.89	.0253
6	"	" "	6.95	.0923*
7	"	" "	1.66	.0889
13	Iron	Strong Ferrous Sulphate	.462	.0273
14	"	" " "	.457	.0979†
16	"	" " "	.445	.0929
18	Iron	Strong Sodium Chloride	+ 0.017	.0262
19	"	" " "	+ 0.121	.0929

\* Same solution and plates as in Experiment 5.

† Same solution as used in Experiment 13.

**Mr. A. P. Trotter** said he could not add much that was of any scientific interest to the subject under discussion, but there were one or two practical points bearing on corrosion of gas and water pipes by stray currents from alternating supply circuits, to which he would like to draw attention, and about which he would like to obtain advice from members. Stray alternating currents had not, he thought, done any mischief yet in this country, and he did not fear that any such currents would leak from high-pressure electric mains, for any appreciable leak on a high-pressure cable immediately resulted in a breakdown, but if alternating currents were used for traction, stray currents would have to be reckoned with.

The electrolyte generally concerned in this case was known as "humus." What "humus" was he could not say, but it appeared to be what was left after picking out the dead leaves, sand, and gravel from ordinary earth. Besides this were gravel, clay, and sand moistened with saline solutions. The electrodes were either of lead or of iron. As far as lead is concerned, the fact that an insoluble salt was formed probably tended to

reduce, but not to stop, further attack. With iron the case was different, the salt appeared to be soluble, resulting in the wasting away of wrought iron; and of pitting, with a deposit of graphite in the holes, in the case of cast iron.

In 1902 he had made some experiments with lead and alternating currents. These experiments were fully described in *Proc. Civ. Eng.*, CLI., pp. 96, 97. He buried two pieces of  $1\frac{1}{4}$  in. lead pipe in a box of moist earth. The pipes were about 4 in. apart, and an alternating current at a frequency of 83 was passed between them for six weeks. Considerable corrosion was found to have taken place on the sides of the pipes facing each other. He understood that the white crust was carbonate, and he would be glad of information on this point. The pipes were passed round the meeting for inspection. It was remarkable that the corrosion stopped at a definite line and the backs of the pipes were untouched. This pointed to a minimum current density or minimum difference of potential below which no corrosion took place. Under the circumstances there could hardly have been any appreciable difference of potential at different parts of the pipes, but having regard to the natural lines of current flow through the earth, it is probable that the current density differed considerably at different points on the pipes. The area corroded was about 40 square inches.

He made another experiment to investigate the minimum current density by burying four lead plates in moist earth through which a current was passed for one month. The plates were partially coated with varnish, so as to vary the areas exposed. The first plate had a current density of  $\frac{1}{40}$ th of an ampere per square inch, or 0.00387 ampere per square centimetre. On the back of the same plate 1 square inch was exposed, the current density was  $\frac{1}{180}$ th of an ampere per square inch, or 0.00097 ampere per square centimetre. The current density was reduced on each plate until on the last it was  $\frac{1}{3500}$ th part of an ampere per square inch, or 0.00006 ampere per square centimetre. When the plates were fresh the corrosion appeared to be proportional to the current density and was clearly visible on the last plate, but after being exposed to handling this could not be clearly seen on the plates which were passed round. It appeared to him that it was very important that this question of minimum current density should be settled both for lead and for iron with continuous and with alternating currents. He would suggest that such experiments should be carried out at the National Physical Laboratory.

The results of such experiments, by whomever they were made, would be of great practical value, but he desired to emphasise the need for caution in applying results of experiments, whether obtained in the laboratory or elsewhere, to practical engineering. When laboratory experiments are adduced in connection with this subject it is always asserted that a given current passing from an electrode into the soil must inevitably dissolve away a certain quantity of metal; but it is well known to tramway men that the South Staffordshire Tramways, which were started before the Board of Trade regulations were made, have been working for nearly twelve years with a very large drop of potential on the rails, and with a leakage current far exceeding the Board of Trade limits, which have never been imposed on that tramway. Electrolysis has often been looked for, and he had made repeated inquiries on the subject, but no trace of injury had been found on any pipes in the district. It was evident, therefore, that ordinary scientific experiments needed to be supplemented by further investigations which took into account all the circumstances that obtained in practice before the exact condi-

tions could be known under which destructive electrolysis was brought about in buried pipes by stray currents whether alternating or continuous.

**Dr. F. Mollwo Perkin** referred to experiments made by Le Blanc with copper electrodes, which bore out Professor Wilson's results regarding the effect of frequency in alternate-current electrolysis. He himself had made some experiments with platinum electrodes in a 50-60 per cent. solution of sulphuric acid, and also in alkaline solutions, using a current density of about 1 ampere per sq. dcm., and had found more corrosion to take place at low than at high frequencies. A colloidal solution of platinum seemed to form, and the electrodes presented the crystalline appearance peculiar to etched plates.

**Mr. W. R. Cooper** (*communicated*): If there are any conditions under which a change of frequency would be expected to have no effect on the amount of electrochemical action, and under which the decomposition might be the same as with direct current of equal quantity, it is in the case of non-polarisable electrodes. But on referring to Professor Wilson's experiments with copper plates in copper sulphate, a considerable difference is noticeable. The author, however, does not mention whether the electrolyte was acidified; since an acid electrolyte is necessary if oxidation of the electrodes is to be avoided, as in voltameter measurements, it might be desirable in this case also. If a definite quantity of electricity  $P$  per alternation is used up in polarisation, one would expect the amount of decomposition  $A$  per alternation to differ from that caused by an equal quantity in the shape of direct-current  $D$ : in its simplest form it might, perhaps, be supposed that  $D - A = aP$  (where  $a$  is a constant), so that when the frequency is high enough for coulombs per alternation to be equal only to the quantity used in polarisation, the decomposition would be nil. At different frequencies there would be a constant difference from the direct-current value.

The word *maximum* when applied to coulombs per half period seems rather confusing if the author means the total coulombs per half period.

**Mr. J. Swinburne** said it might be well to look at Professor Wilson's results from another point of view. By showing curves each for a period at widely different frequencies, the wide differences of frequency were put in the background. If instead of thinking of the electrical quantity per period, or energy per period, you consider the current or the power, it is to be expected the current would fall off more on a long period, owing to polarisation. The power would, therefore, be less on a long period, and would increase with the frequency until polarisation practically played no part, and the cell behaved like a resistance. The energy per cycle would thus be greater with a low frequency, but would not vary as the length of the period, or anything like it. This seemed to be what Professor Wilson's experiments showed, and it was just what was to be expected. Mr. Cooper's curves bore out the explanation.

As there was an irreversible loss, it could not be due to any reversible chemical action, and the chemical actions themselves seemed reversible. The irreversibility must, therefore, be the result of diffusion, so that the reverse current does not find itself under the same conditions as the original; and the time element would thus come in.

Referring to Mr. Trotter's remarks about insoluble and irreducible lead salt, probably no lead salts are really irreducible if good contact is made. In the early days of the secondary cell, when it was found that lead sulphate was formed, it was supposed that a cell would only last until all the paste had been acted on once, and thus turned into sulphate, the said sulphate being irreducible. Pure sulphate was tried and seemed to be irreducible. How-

ever, it was soon found that if a little litharge were mixed with the sulphate it could be reduced ; and even plain crystalline sulphate was reduced when good contact was made by pressure.

In the earth, chlorides, or a series of brown compounds, would be formed. These are non-adherent, and do not protect the lead. A lead anode can be eaten through very quickly in a chloride solution.

**Professor E. Wilson** (*communicated*) : It is interesting to hear from Mr. Trotter that he has obtained qualitative indications of limiting conditions.

Mr. Swinburne does not state the controlling conditions under which energy is supplied to the cell when he discusses the effect of variation of frequency. If the current is rigidly controlled and kept constant (as in my experiments) by employing a large non-inductive resistance in circuit with the cell, and a sufficiently large potential difference, constant for different frequencies, the maximum coulombs, and hence the polarisation, will diminish with increase of frequency. What will happen when the frequency is sufficiently increased is difficult to say, but Mr. Swinburne imagines the cell would "behave like a resistance." If Maxwell's electro-magnetic theory of light be true, one would expect that at sufficiently high frequency the electrolyte would act as though it were an insulator, in which case the cell would behave as though it were a condenser. As the frequency is increased the conduction effects become smaller and the capacity effects become more prominent, until ultimately conduction ceases and the coulombs are the result of oscillating charges on the plates of the condenser. Mr. Swinburne says the chemical actions in the experiments seemed reversible. This is not the case, for instance, with lead sulphate under the conditions of the tests. The possibility of chemical reversibility depends upon the stability of the products of electrolysis. He then concludes that the irreversibility is the result of diffusion. The maximum E.M.F. of polarisation is governed by the maximum coulombs of the conduction current. If the current is rigidly controlled, the phase of the E.M.F. of electrolysis is a dependent variable, and must be such that in a complete cycle the integral of the E.M.F. and the current is equal to the energy dissipated by electrolytic hysteresis. It remains, then, to determine in what directions energy is dissipated. The curves show that part of the gross energy delivered to the cell is returned to the source. This must imply reversibility. If electrolytic as well as mechanical diffusion is irreversible, and so far as I know this has not yet been proved in the case of the former, they cannot be the only factors in the exchange of energy. If there were no energy returned per cycle, the loops (coulomb-volt) would have quite a different shape.

Mr. Cooper does not specify the controlling conditions under which he supposes the current to be supplied to the cell at various frequencies. I fail to see how his equation,  $D - A = aP$ , can represent the facts when  $a$  is a constant, nor can I reconcile this with his statement that "at different frequencies there would be a constant difference from the direct-current value." The copper sulphate employed in the experiments was not acidified. When I speak of maximum coulombs I refer to the maximum ordinate of the curve of coulombs.

With regard to Dr. Perkin's remarks, I may say that an examination of the platinum plates employed revealed no material corrosion.

I wish to thank Mr. A. E. O'dell for the assistance he has given me in the latter part of the work.