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Map of England and Wales showing Lines of Equal Magnetic Declination for January 1, 1894. With a Reprint from the 'Colliery Guardian.' Two copies.  
Mr. W. Ellis, F.R.S., and The Editor, 'Colliery Guardian.'

"On Copper Electrolysis *in Vacuo*." By WILLIAM GANNON, M.A., "1851 Exhibition" Scholar, Queen's College, Galway. Communicated by ARTHUR SCHUSTER, F.R.S.  
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The following research upon the electrolysis of copper sulphate *in vacuo* was commenced nearly two years ago, at the suggestion of Dr. Schuster, and the experiments were made in the Physical Laboratory of the Owens College.

The electrolysis of copper salts is interesting, not only theoretically as affording a verification of Faraday's Law of Electrolytes, but also practically on account of its constant use in the graduation of current-measuring instruments, such as tangent galvanometers and ammeters. It is known that copper sulphate in solution does not conform rigorously to the simple form in which Faraday's law is generally expressed. Gray,\* who made a detailed examination of the electrolysis of copper sulphate, found that the weight of the deposit is very variable in neutral solutions for the same current and the same interval of time; and he also showed that, in solutions containing a little free sulphuric acid, this inconstancy was removed, but that the weight was a function of the temperature of the solution and of the current density at the cathode. His results with acid solutions are graphically represented by curves (partly reproduced at the end of

\* 'Phil. Mag.,' vols. 22 and 25 (1886-88).

this paper), an inspection of which shows that the deposit is heavier the higher the current density and the lower the temperature. ("Current density" is defined as the ratio of the value of the current in ampères to the total immersed surface of the cathode plate.) A very possible explanation of this anomaly is furnished by the work of Gore\* and Gray,† who independently found that copper dissolves to a very appreciable, though variable, amount in solutions of copper sulphate.

The secondary chemical reactions which follow—chiefly the formation of basic salts—complicate the electrolysis. This corrosion of copper plates in the sulphate solution is much diminished if a little free sulphuric acid is present, with the result that the electrolysis of acid solutions yields more consistent results than are obtainable with nearly neutral solutions. Now, Schuster‡ found that the loss in weight of copper plates in a solution of copper sulphate does not occur if the air be removed from the solution. It is therefore very probable that it is the oxygen of the air present in the solution that causes this chemical corrosion; and hence it was of interest to examine if any difference could be found between the weights of the deposits of two copper voltameters, one of which would be placed *in vacuo*. Schuster and Crossley§ showed that the silver deposit is slightly greater *in vacuo* than in air; and the experiments tabulated in this paper point out, with certain limitations, a similar result.

The plan of these experiments was simple. The same current passed through two voltameters connected in series, one being under the ordinary atmospheric pressure and the other in a partial vacuum. The voltameters, in most of the experiments, consisted of ordinary glass beakers, containing the solutions of copper sulphate, into which dipped three parallel copper plates of the same size, the centre one acting as the cathode, and the side ones forming a double anode. The plates were held in position by means of German silver clips pressing against vertical brass supports which were attached to an ebonite framework. One voltameter was placed in an inverted bell-jar, into the neck (lower part) of which was fitted an india-rubber cork. Through the cork, which was coated with Faraday cement, passed three glass tubes, one connected with an exhaust pump and the remaining two containing the leads. In some of the experiments another tube was introduced, through which was passed into the jar a stream of nitrogen gas previous to exhaustion; but as this did not give any better results, it was discarded. At the bottom of the bell-jar inside was a support for the beaker, and on the latter rested

\* 'Nature,' vol. 25, p. 473.

† 'Phil. Mag.,' vol. 22, p. 400, 1886.

‡ See "Note" at end of this paper.

§ 'Roy. Soc. Proc.,' vol. 50, pp. 344—353.

the framework with the three plates. In addition to the voltameter, the jar contained a small mercury gauge. The upper rim of the jar was ground, and previous to exhaustion was coated with grease, upon which pressed a ground-glass plate. The current was derived from storage cells, and was measured by a tangent galvanometer or a Thomson's magnetostatic centiampèremeter; it was adjusted to the proper value, and kept constant throughout an individual experiment by having in circuit a carbon rheostat and a set of specially prepared resistances of different values. The copper plates were made of commercial sheet copper (24 B.W.G.): they were cleaned with emery paper, nitric acid, caustic potash, tap water, and, finally, distilled water, and a deposit was laid on them before being weighed for an actual experiment. The deposit was treated in the way recommended by Gray; I found it advantageous to have the distilled water hot, as on removing the plate the deposit dries more quickly, and consequently the possibility of oxidation occurring is diminished. The plates, after being in the balance case for a variable period—never less than three hours, generally over night—were weighed on a 16-in. Oertling balance, which weighed accurately to 1 tenth-milligram. The solutions were made by dissolving ordinary commercial sulphate in distilled water and filtering; the solutions with no free acid added were used immediately, so as to conduct the electrolysis before the formation of basic salts; the acid solutions contained 1 per cent. free sulphuric acid. When all the joints were air-tight, by being closed with cement, no difficulty was experienced in retaining the partial vacuum constant throughout each individual experiment. Leakage of the current at either voltameter was tested for throughout the experiments, and this point was considered satisfactory when, both voltameters being under atmospheric pressure, the deposits did not differ by more than 1 or 2 tenth-milligrams. Particular attention was paid to the handling of the plates before and after each experiment, especially in the replacing in, or removal from, their clips. By means of a small rod, acting as a lever, friction was prevented between the clips and plates, and hence the slight danger of loss of copper prevented. Immediately after the current was stopped in each experiment, the framework holding the plates was quickly removed from the solution and plunged into distilled water so as to remove all solution from the plates—oxidation occurs very rapidly if any solution remains on the plates, even for a very short time.

My first object was to ascertain if any difference in the weight of the deposit was caused by placing one voltameter *in vacuo*, without any special regard to the current density (which throughout all the experiments was the same at both cathodes). The experiments arranged in Table I show an appreciable, though inconstant, differ-

Table I

Date.	Density of solution.	Current in amperes.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Difference.	Difference in 10,000 parts.	Remarks.
						Vacuum.	Air.			
1892.										
Jan. 26.....	1180	1·0	15·0	40	0·62	0·8589	0·8579	0·0010	+ 11	
" 28.....	1168	1·0	22·0	49	0·75	0·9770	0·9652	0·0118	+ 135	
Feb. 8.....	1168	1·0	13·9	40	0·62	0·8359	0·8342	0·0017	+ 20	
" 9.....	1178	1·0	17·5	41	0·62	0·8947	0·8915	0·0032	+ 36	
" 18.....	1177	1·0	15·0	40	0·62	0·8272	0·8282	0·0010	- 12	Deposits oxidised?
" 19.....	1171	1·0	16·6	40	0·62	0·8400	0·8370	0·0030	+ 35	
" 20.....	—	1·0	13·1	35	0·50	0·6768	0·6678	0·0090	+ 133	
Mar. 17.....	1070	0·9	14·6	39	0·75	0·6849	0·6844	0·0005	+ 7	} Some vacuum deposit lost.
" 18.....	1110	0·8	15·4	35	0·62	0·5600	0·5589	0·0011	+ 18	
" 22.....	1095	0·7	18·0	45	0·62	0·6345	0·6310	0·0035	+ 55	

The solutions in each experiment contained no free acid, and were not previously used in any experiments.

ence. In ten experiments, with the sulphate solution containing no free acid, nine gave a greater deposit *in vacuo* than in air, one giving a negative difference. In this experiment (February 18) the deposit was not of the usual colour, and it is possible it was oxidised. Great care was necessary in washing the vacuum deposit, as often the copper was deposited in a loose form at and near the edges; in the experiments of March 17 and 18 a little of the vacuum deposit was lost in drying between the folds of blotting paper. It was not to be expected that the experiments in this table would show very concordant results; as, even presuming that the deposit *in vacuo* is constant, the inconstancy of deposits in air from neutral solutions would cause an inconstant difference.

In order to get a constant deposit in air, I next added acid to the air solutions and compared the deposits from these with the deposits from a neutral solution *in vacuo*. Table II includes experiments conducted in this way: in the experiments of February 24 and 29 some of the vacuum deposit adhered to the blotting paper and was lost. I cannot account for the negative result of February 25. The remaining experiments show fairly concordant differences. It will be observed from Tables I and II that, with the exception of those experiments in which some of the deposit was mechanically lost, the percentage difference is greater with acid solutions in air than with neutral solutions, which agrees with Gray's observations that the deposit (in air) in neutral solutions is generally higher than in acid solutions.

I have brought together the experiments included in Table III, although the results are very inconsistent and puzzling. It will be seen that, if the neutral solutions have been used in previous experiments and acid added to them for a fresh experiment, the difference between the weights of the two deposits varies not only in amount but also in sign. An explanation of this may be that electrolysing a neutral solution changes its chemical constitution, and that adding acid afterwards does not remove all basic salts. Accepting this possible explanation, I abandoned for the present using neutral sulphate in either voltameter. In all the remaining experiments described in this paper, both solutions were freshly prepared, not previously used in any experiment, and contained 1 per cent. free sulphuric acid. The results I have obtained in this way are more concordant and very interesting. A deposit obtained from a neutral solution *in vacuo* shows the same looseness in deposition as in air; but the addition of a little free acid causes the copper to be deposited in a compact form, which is not liable to be lost in the washing or drying.

Table II.

Date.	Density of solution.	Current in ampères.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Difference.	Difference in 10,000 parts.	Remarks.
						Vacuum.	Air.			
1892.										
Feb. 24.....	1110	1.0	13.2	40	0.62	0.8122	0.8115	0.0007	+ 8	{ Some vacuum de- posit lost.
" 25.....	1091	1.0	14.6	49	0.62	1.0660	1.0684	0.0024	- 22	
" 29.....	1122	1.0	16.3	45	0.62	0.9802	0.9773	0.0029	+ 29	{ Some vacuum de- posit lost.
Mar. 24.....	1095	0.7	18.5	40	0.75	0.5768	0.5619	0.0149	+ 258	
" 25.....	1095	0.7	17.1	39	0.62	0.5557	0.5320	0.0237	+ 445	
" 28.....	1095	0.7	15.0	30	0.62	0.4852	0.4696	0.0156	+ 330	
" 29.....	1093	0.6	14.5	47	0.62	0.5959	0.5868	0.0091	+ 151	
" 29.....	1093	0.7	14.9	40	0.62	0.5719	0.5572	0.0147	+ 262	

Both solutions freshly prepared for each experiment; air solution with 1 per cent. free acid, vacuum solution neutral.

Table III.

Date.	Current in amperes.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Difference.	Difference in 10,000 parts.
					Vacuum.	Air.		
1892.								
Feb. 25.....	1.0	14.9	49	0.62	1.0181	1.0203	0.0022	- 20
" 26.....	1.0	15.0	40	0.75	0.8575	0.8554	0.0021	+ 22
" 29.....	1.0	17.0	49	0.62	1.1865	1.1859	0.0006	+ 5
Mar. 3.....	1.0	16.6	32	0.62	0.5878	0.5862	0.0016	+ 27
" 18.....	0.75	?	40	0.75	0.5781	0.5726	0.0055	+ 95
" 24.....	0.72	17.5	40	0.75	0.5429	0.5545	0.0116	-209
" 25.....	0.77	17.6	42	0.87	0.5799	0.5930	0.0131	-220
" 28.....	0.72	15.6	40	0.87	0.5705	0.5648	0.0057	+100
" 29.....	0.68	15.3	39	0.75	0.5235	0.5234	0.0001	+ 2

The solutions were used previously without any free acid; 1 per cent. acid added in these experiments.

The following tables are not arranged in the order in which the experiments were made.

Table IV includes four experiments in which the current density was approximately 0.007 ampère per square centimetre of "active" cathode, or 1 ampère to 135 sq. cm. All the experiments gave the vacuum deposit higher than the air deposit, and the percentage differences agree fairly. The mean value = 0.16 per cent. at a mean temperature of 18°1.

Table V includes three experiments in which the current density was 0.006 ampère per square centimetre. It will be seen the vacuum deposit is higher than the air deposit in the three experiments. Mean value of difference = 0.10 per cent. at a mean temperature of 16°5.

Table VI includes four experiments at a current density of 0.005 ampère per square centimetre. Again the vacuum deposit is higher than the corresponding air deposit. Mean value of difference = 0.14 per cent. at a mean temperature of 17°5.

Table VII includes five experiments at a current density of 0.004 ampère per square centimetre. All the vacuum deposits are higher than the corresponding air deposits. Mean value of the difference = 0.17 per cent. at a mean temperature of 19°.

Table VIII includes five experiments at a current density of 0.0033 ampère per square centimetre. Again deposit *in vacuo* is higher than the deposit in air. Mean value of difference = 0.14 per cent. at a mean temperature of 15°5.

Table IX includes seven experiments at a current density of 0.0027 ampère per square centimetre. The same results obtained here as in the preceding tables; but the experiments of April 12 and 13 do not agree very well with the others. Mean value of difference = 0.16 per cent. at a mean temperature of 16°6.

Table X includes nine experiments in which the strength of current was approximately 0.01 ampère per square centimetre. This table is very interesting, as showing that near this particular current density the previously observed differences cease to exist. The nine experiments never gave a greater difference between corresponding deposits than 1 tenth-milligram. The voltameters were carefully tested for leakage before and after these experiments; and the experiment of April 7 (Table IX), in which there was a percentage difference of 0.12, follows that of April 5, without any alteration in the arrangement of the apparatus. In addition, the experiments of December 2 and 3 were made with a different bell-jar and a different arrangement from that used in the previous experiments. It may be fairly concluded that at this density no difference in the deposit exists.

Table XI includes three experiments at a density of 0.02 ampère per square centimetre. It will be seen that there is practically no difference between the deposits.



Table IV.

Date.	Current in ampères.	Active area of cathodes in square centi- metres.	Current density.	Density of solution.	Temp. of room.	Time in minutes (approx.)	Vacuum in inches of mercury.	Deposit.		Differ- ence.	Differ- ence in 10,000 parts.
								Vacuum.	Air.		
1893.											
Aug. 26	0·676	96·6	{ 1 ampère to 135 sq. cm., or 0·007 ampère per sq. cm. }	1123	17·7	66	0·75	0·8517	0·8512	0·0005	+ 6
" 28	0·676	96·6		1123	18·2	69	0·75	0·8569	0·8562	0·0007	+ 9
" 29	0·676	96·6		1123	18·9	69	0·75	0·8541	0·8547	0·0006	+ 7
" 30	0·676	96·6		1123	17·5	72	0·75	0·8619	0·8625	0·0006	+ 7
				Mean temp.	18·1					Mean diff.	+ 7

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table V.

Date.	Current in amperes.	Active area of cathodes in square centimetres.	Current density.	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Difference.	Difference in 10,000 parts.
								Vacuum.	Air.		
1892.											
July 20	0.43	72	1 ampère to 166 sq. cm., or 0.006 ampère to each sq. cm.	1142	17.8	91	0.75	0.7618	0.7612	0.0006	+ 7
"	0.43	72		1142	15.6	93	0.75	0.7663	0.7654	0.0009	+ 12
"	0.43	72		1151	16.2	85	0.75	0.7217	0.7210	0.0007	+ 10
				Mean temp.	16.5					Mean diff.	+ 10

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table VI.

Date.	Current in amperes.	Active area of cathodes in square centi- metres.	Current density.  1 ampère to each 200 sq. cm. or 0·005 ampère per sq. cm.	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Differ- ence.	Difference in 10,000 parts.
								Vacuum.	Air.		
1893. Aug. 8	0·41	82	{ 1 ampère to each 200 sq. cm. or 0·005 ampère per sq. cm. }	1141	17°·6	105	0·75	0·8338	0·8329	0·0009	+12
"	0·41	82		1141	17·2	112	0·62	0·8413	0·8400	0·0013	+16
"	0·41	82		1141	17·8	104	0·62	0·8323	0·8312	0·0011	+13
"	0·41	82		1141	17·4	109	0·75	0·8407	0·8396	0·0011	+14
				Mean temp.	{ 17·5 }					Mean diff.	{ +14 }

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table VII.

Date.	Current in ampères.	Active area of cathodes in square centi- metres.	Current density.	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Differ- ence.	Differ- ence in 10,000 parts.
								Vacuum.	Air.		
1893.											
Aug. 21	0.386	96.6	{ 1 ampère to 250 sq. cm. or 0.004 ampère per sq. cm. }	1132	18.4	126	0.62	0.8966	0.8950	0.0016	+18
" 22	0.386	96.6		1113	20.0	115	0.75	0.8149	0.8136	0.0013	+17
" 23	0.386	96.6		1145	19.6	120	0.75	0.8665	0.8652	0.0013	+16
" 24	0.386	96.6		1145	18.2	120	0.75	0.8754	0.8739	0.0015	+18
" 25	0.290	72.0		1102	18.7	125	0.75	0.7996	0.7984	0.0012	+15
				Mean temp.	{ 19.0				Mean diff.	{ +17	

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table VIII.

Date.	Current in ampères.	Active area of cathodes in square centi- metres.	Current density.	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Differ- ence.	Differ- ence in 10,000 parts.
								Vacuum.	Air.		
1892. Apr. 29	0·24	74·0	1 ampère to 300 sq. cm., or 0·0033 ampère per sq. cm.	1132	15·0	170	0·75	0·8225	0·8214	0·0011	+ 14
May 3	0·24	74·0		1113	14·5	162	0·75	0·8199	0·8186	0·0013	+ 16
" 4	0·24	74·0		1113	16·7	161	0·75	0·8206	0·8194	0·0012	+ 15
" 5	0·24	74·0		1113	14·9	161	0·75	0·8213	0·8201	0·0012	+ 15
July 18	0·24	72·0	..	1145	16·5	160	0·75	0·8222	0·8213	0·0009	+ 12
Mean temp.										Mean diff.	+ 14

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table IX.

Date.	Current in amperes.	Active area of cathodes in square centi- metres.	Current density.	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Differ- ence.	Differ- ence in 10,000 parts.
								Vacuum.	Air.		
1892.											
Apr. 7	0.2	74	{ 1 ampère to 370 sq. cm., or 0.0027 ampère per sq. cm. }	1032	18.0	162	0.75	0.6406	0.6398	0.0008	+12
" 9	0.2	74		1032	15.3	147	0.62	0.5752	0.5744	0.0008	+14
" 11	0.2	74		1035	17.2	152	0.75	0.5674	0.5667	0.0007	+12
" 12	0.2	74		1035	16.0	154	0.75	0.5944	0.5929	0.0015	+25
" 13	0.2	74		1035	15.5	185	0.75	0.7104	0.7088	0.0016	+22
July 22	0.2	74		1124	17.4	180	0.75	0.6851	0.6842	0.0009	+13
" 24	0.2	74	1124	16.9	180	0.75	0.6736	0.6725	0.0011	+16	
				Mean temp.	{ 16.6				Mean diff.	{ +16	

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table X.

Date.	Current in ampères.	Active area of cathodes in square centi- metres.	Current density (approx.).	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Differ- ence.	Differ- ence in 10,000 parts.
								Vacuum.	Air.		
1892.											
Apr. 1	0.79	80	1 ampère to 100 sq. cm., or 0.1 ampère per sq. cm.	1130	15.7	41	0.62	0.6378	0.6378	0.0000	±0.00
" 1	0.80	80		1130	15.7	40	0.62	0.6279	0.6280	0.0001	-0.01
" 2	0.78	80		1130	15.9	40	0.75	0.6272	0.6271	0.0001	+0.01
" 2	0.79	80		1130	16.0	42	0.75	0.6367	0.6368	0.0001	-0.01
" 4	0.78	79		1115	16.5	40	0.62	0.6085	0.6084	0.0001	+0.01
" 4	0.79	79		1120	18.3	40	0.62	0.6148	0.6149	0.0001	-0.01
" 5	0.79	79		1120	17.0	45	0.62	0.6971	0.6971	0.0000	±0.00
Dec. 2	0.84	84		1067	11.0	47	0.75	0.7307	0.7307	0.0001	+0.01
" 3	0.84	84		1067	12.0	40	0.75	0.6186	0.6186	0.0000	±0.00
										Mean diff.	±0.00

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table XI.

Date.	Current in amperes.	Active area of cathodes in square centimetres.	Current density.	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Difference.	Difference in 10,000 parts.
								Vacuum.	Air.		
1893.											
Jan. 12	1.45	76.9	} 1 ampère to 53 sq. cm., or 0.019 ampère per sq. cm. {	1180	15.0	25	0.50	0.8762	0.8762	0.0000	±0.00
" 13	1.45	76.9		1180	16.3	28	0.50	0.9046	0.9046	0.0000	±0.00
" 14	1.45	76.9		1180	16.0	27	0.62	0.8943	0.8942	0.0001	-0.01
										Mean diff.	-0.01

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

Table XII.

Date.	Current in amperes.	Active area of cathodes in square centimetres.	Current density.	Density of solution.	Temp. of room.	Time in minutes (approx.).	Vacuum in inches of mercury.	Deposit.		Difference.	Difference in 10,000 parts.
								Vacuum.	Air.		
1893.											
Sept. 13	1.25	96.6	} 1 ampère to 75 sq. cm., or 0.013 ampère per sq. cm. {	1180	16.2	30	0.62	0.8222	0.8222	0.0000	±0.00
" 14	1.25	96.6		1180	17.4	30	0.75	0.8297	0.8296	0.0001	+0.01
" 15	1.25	96.6		1180	17.6	30	0.75	0.8314	0.8314	0.0000	±0.00
										Mean diff.	+0.01

The solutions were freshly prepared in each experiment, and contained 1 per cent. free acid.

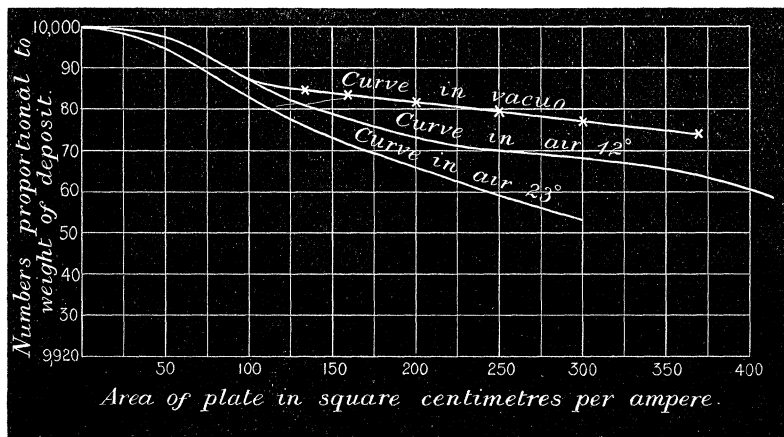


Table XII includes three experiments at a density of 0.013 ampère per square centimetre. The deposits show no difference in weight.

It would thus appear that, at current densities above 0.01 ampère per square centimetre, there is practically no difference in weight of the deposits obtained from solutions of copper sulphate (made acid), one of which is under ordinary atmospheric pressure, and the other under reduced pressure; but at densities below this there is a very appreciable difference, the deposit in a partial vacuum being *always* greater than the corresponding deposit in air. *No experiment with acid solutions ever gave the vacuum deposit less than the air deposit.* Why this difference should exist at certain densities and not at others is not very clear. The chemical corrosion above referred to will be more marked in the air solutions at weak current densities, where the duration of the experiments is three to four hours, but it would not be expected that it would be altogether missing at densities where the duration of the experiments is less than forty minutes and less.

My experiments do not completely reveal the cause of the relations existing between the deposit and current density. They clearly show, however, that the oxygen present in the solution has a certain diminutive action on the weight of the deposit, and that this action is prevented (partly or wholly) by conducting the electrolysis *in vacuo*. The removal of the oxygen of the solution prevents the copper plates, and more particularly the copper deposit, from dissolving in the solution; but it does not prevent (apparently) what some physicists speak of as an electrical corrosion, which occurs only when the current is passing through the solution.

It is of interest to draw a curve representing the deposits obtained *in vacuo* with different current densities. This I have done by



means of the data in Table XIII. In this table I have collected the chief results of my experiments. By means of Gray's values I have reduced the observed differences to a temperature of 15° C., and then calculated the values *in vacuo*. The curve thus obtained is more uniform in its course than the curves for air.

Table XIII.—Summary of Experiments with fresh Acid Solutions.  
(Tables IV—XII.)

Table.	Current density.		Mean temp. of experiments.	Difference in 10,000 parts.	Difference reduced to 15° C.	Gray's proportionate values (in air) at 15°.	Proportionate values <i>in vacuo</i> .
	Ampères per square centimetre.	Square centimetres per ampère.					
XI	0·019	53	..	± 0	± 0·0	9997	9997
XII	0·013	75	..	± 0	± 0·0	9992	9992
X	0·010	100	..	± 0	± 0·0	9986	9986
IV	0·007	135	18°·1	+ 7	+ 5·5	9979	9984
V	0·006	166	16·5	+10	+ 9·0	9974	9983
VI	0·005	200	17·5	+14	+11·0	9971	9982
VII	0·004	250	19·0	+17	+13·0	9967	9980
VIII	0·0033	300	15·5	+14	+13·0	9964	9977
IX	0·0027	370	16·6	+16	+13·0	9961	9974

The results of my experiments may be briefly summarised :—

1. With two copper voltameters containing freshly made neutral solution of copper sulphate, one of which is under reduced pressure, the copper deposit in the partial vacuum is higher (for the same current, current density, and temperature) than the deposit under the atmospheric pressure; but the percentage difference is not constant.

2. If a little free sulphuric acid be added to the air solution, the percentage difference is more constant and higher than in 1.

3. The addition of acid to both voltameters causes the percentage difference to be constant within experimental errors. The experiments conducted under this condition show that—

- i. For current densities above 0·01 ampère per square centimetre of active cathode, there is no practical difference between the two deposits.
- ii. For current densities below 0·01 ampère per square centimetre, the vacuum deposit is very appreciably higher than the air deposit.
- iii. A curve drawn representing the deposits obtained *in vacuo* at different current densities is more regular than the air curves, and for densities below 0·01 ampère per square centimetre is approximately a straight line.

