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XLVIII. *On the Electrolysis of Silver and of Copper, and the Application of Electrolysis to the Standardizing of Electric Current- and Potential-meters.* By THOMAS GRAY, B.Sc., F.R.S.E.*

[Plate VII.]

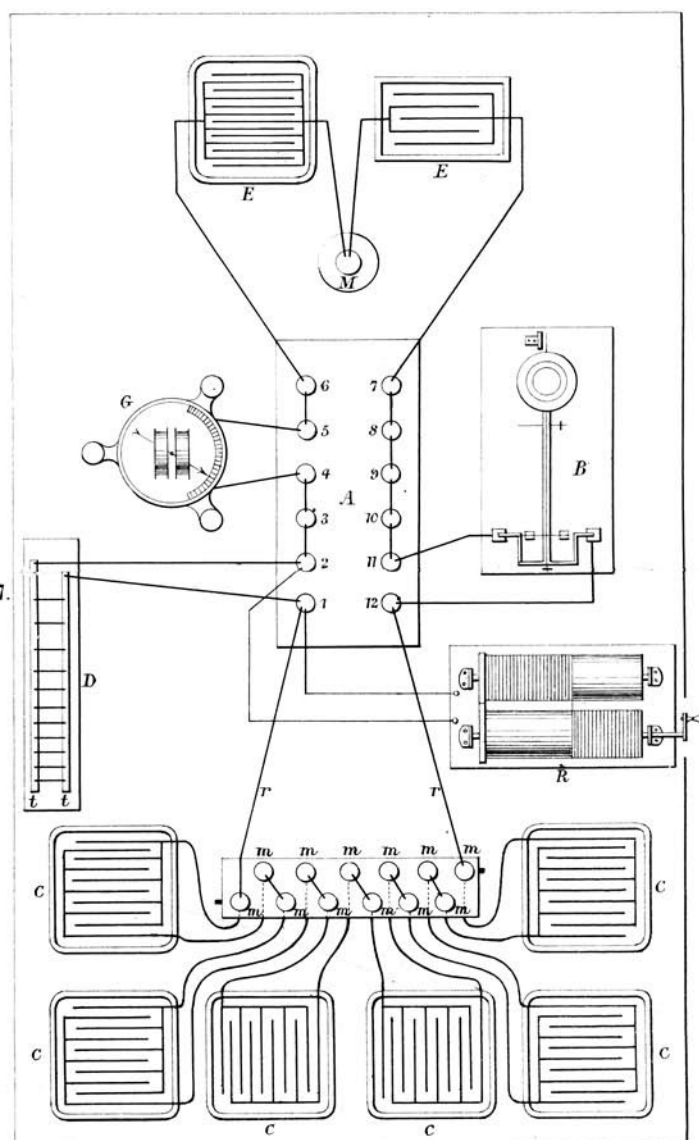
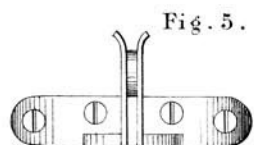
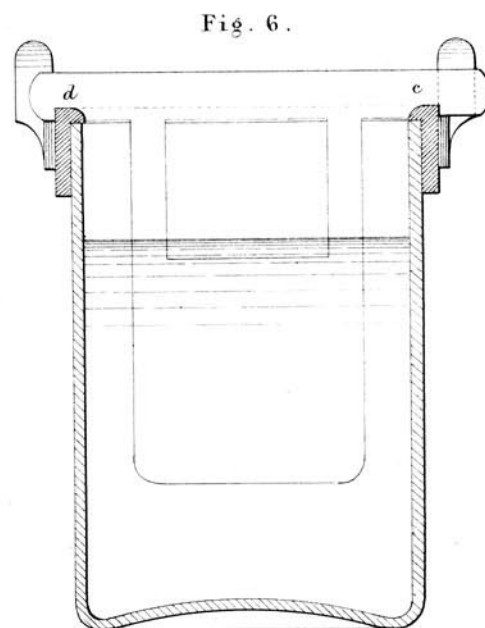
THE following paper contains an account of a large number of experiments on Electrolysis, and on its application to the standardizing of electrical measuring instruments, which have been made during the past year in the Physical Laboratory of Glasgow University: it forms a summary of the reports which have been from time to time made to Sir William Thomson on the subject. The primary object of most of the earlier experiments was to obtain the value, in absolute measure, of the indications of ampere- and volt-meters; but these experiments were always taken advantage of for the purpose of investigating the reliability of the method under various circumstances as to treatment, size of plates, density of solution, and so on. Many of the later experiments were made specially for the purpose of investigating points of interest suggested by the earlier experiments. It should be borne in mind, with regard to the conclusions put forward in this paper, that they have not been arrived at simply as the result of the experiments made personally by the writer, but that he has had the advantage of seeing the methods applied by several independent experimenters in this laboratory and of comparing the results they obtained.

The electrolysis of copper has for several years been occa-

* Communicated by Sir William Thomson, F.R.S.

sionally used by Sir William Thomson as a check on the graduation of galvanometers; but the question of its reliability had not been systematically attacked before the series of experiments here described were taken up. From a number of experiments made in the above laboratory about four years ago, I inferred that copper was capable of giving fairly uniform results; and I obtained as the electrochemical equivalent of copper $\cdot 003307$, or as the amount of copper deposited by a coulomb of electricity $\cdot 0003307$. This value has since been found to be too high; and recent experience indicates that there are at least two ways of explaining the discrepancy—namely, either that the measurement of the current was in error, or that the solutions were wrongly treated. The first of these needs no remark, it is impossible to tell now whether the current was measured with the needful accuracy or not; but the second will be referred to at some length in this paper. The solutions were in that case very carefully saturated with copper by shaking them up with, and filtering them through, copper oxide; and I bring the matter forward now because I believe that treatment was a serious mistake. It is easy to make a solution of copper sulphate which will give as high, and even a much higher, value for the electrochemical equivalent than that above stated; but once the cause of this is known, it is equally easy to avoid the error. In order to obtain good results it is necessary that the solution be distinctly acid. The ordinary commercial copper sulphate, or the sulphate ordinarily sold as pure, usually contains enough of acid; but the same solution cannot be repeatedly used with safety.

Following the results of the investigations of Kohlrausch, and of Lord Rayleigh and Mrs. Sidgwick, the substances used in the earlier of the present series of experiments were pure silver and pure silver nitrate. Sheet silver was used both for the gain and for the loss plates; it was supplied by Messrs. Johnson and Mathey as pure silver. The form of the cell used for the silver is illustrated in fig. 1 (Plate VII.); it consists of a glass vessel partially filled with a solution of silver nitrate, in which three plates of silver, arranged with their planes parallel, are suspended from spring clips of the form illustrated in figs. 2 and 3. This form of cell offers, in comparison with the platinum-bowl method recommended by Poggendorff and adopted by Lord Rayleigh, some advantages which, in my estimation, outweigh its disadvantages. The total weight of the plate is very small, and hence a light and very delicate balance can be used. The thorough polishing and cleaning of the plates is easier than when a bowl is used. The cleaning of the platinum bowls by dissolving off the



deposit in nitric acid and the satisfactory washing of a bowl generally is troublesome ; indeed the time spent in this operation is often more valuable than if the gain plate, deposit, and all were thrown away ; while, since the deposit is pure silver, the depreciation in value due to cutting up the sheet is small. When the deposit is good it may be rolled, beaten, or burnished down sufficiently to allow the plate to be again used, and thus the operation simply means a transfer of silver from the anode to the cathode. Another and perhaps more important reason for preferring the vertical plates is the fact that, if the plates be properly proportioned as to size and properly prepared, the loss plate can be used with perfect ease as a check on the result of the gain plate. This is a point of some importance in the case of silver, where the deposit is apt to be of such a nature that there is considerable risk of loss in the operation of washing. There is of course the objection to the use of vertical plates, that the density of the solution is apt to decrease at the cathode and increase at the anode. Such an action does take place, and the result is a slightly thicker deposit on the lower part of the plate, thus changing to a small extent the effective area ; but no difficulty has been experienced from this cause, even when the current is allowed to flow for three or four hours, when the current and the solution have the densities stated below.

In the later experiments copper has been almost exclusively used. It is found to be very much more easily managed than silver, and gives, over a wide range of size of plate and density of solution, deposits which are perfectly adherent and homogeneous, thus rendering it more generally convenient where currents of a considerable variety of strength are used. Besides, for large currents such as from 10 to 100 amperes and upwards, the use of silver is almost excluded on account of the expense of the necessary materials. When the highest accuracy is required, however, and when it is used in experienced hands, silver is decidedly superior to copper. It presents hardly any of the uncertainties which, as will be pointed out below, it is absolutely necessary to guard against in the case of copper ; but the fact must not be lost sight of that an expertness in manipulation and a degree of care are required which cannot always be obtained.

The objections which have been brought against the use of copper are its readiness to oxidize in the air, especially if moisture be present, and the fact that it loses weight in the liquid*. Both of these are of course legitimate objections,

* See a paper by G. Gore, LL.D., F.R.S., 'Nature,' March 16, 1882 ; and Lord Rayleigh and Mrs. Sidgwick, Trans. Roy. Soc. 1884, pp. 411-460.

and more might easily be added ; hence the point to be decided is whether the oxidation and loss in the solution can be avoided or their effects eliminated. As the result of a good deal of experience, it appears to me that the first objection is of very little weight indeed, as the plate need not be sensibly oxidized in the process of washing and drying if even ordinary care is taken in the operation. The loss by corrosion in the liquid leads to results which depend to some extent on the size of the plate and the temperature of the solution ; and a great many experiments have been made on the effect this may have on the apparent value of the electrochemical equivalent in different cases. Examples of such experiments are given below, and they are there discussed more in detail ; but it may be stated here that the effect can be fairly well allowed for if the size of the plate and the strength of the current, as well as the state of the solution, are known. The error due to this cause need never exceed a tenth per cent., and will generally be considerably less than that.

It appears from experiments on the loss of copper in solutions of sulphate of copper, that a strong solution of normal pure sulphate is at ordinary atmospheric temperature even more active in dissolving copper than the same solution when as much as 5 per cent. of acid has been added ; but that in the use of the normal solution there is a danger that the presence of the copper plates in the cell may render the solution saturated with copper, after which a rapid oxidizing action takes place which invariably causes the gain of weight in an electrolysis experiment to be too great. The deposit in such a case is of a darker colour than when the solution is kept sufficiently acid ; and indeed a bad plate can generally be detected by simple inspection, but it is well always to add such a quantity of acid (a very little is sufficient) as will prevent any uncertainty on the subject.

Electrolytic Cells.—Some of the arrangements which have been found convenient for the electrolytic cells are illustrated in figs. 1 to 6. They consist, in the smaller sizes, of round glasses into which three plates, arranged with their planes parallel and about one centimetre apart, are held by means of clips of stiff platinoid or brass wire of the form shown in figs. 2 and 3. The outer clips are connected together by a cross piece, *a* (fig. 1), at the top, but are insulated from the middle clip by a block of vulcanite, fixed in the cross piece, *b*, into which they are all tightly fitted. These clips are very convenient, and are easily made by taking a piece of stiff wire, bending it nearly close at its middle point, then winding each half two or three times round a rod of metal of suitable size

so as to form the springs, and after bending the two ends together soldering them to a stiff back-piece, as shown; care must be taken that the spring front presses firmly on the back before the two are soldered together. Several sets of clips are fitted into one cross piece *b*, so that one frame may serve for one or more cells, the double clips of any one set being connected permanently to the single clip of the next set. When the plates are being placed in the clips, the cross piece which holds them is lifted off the frame and the plates placed in position, the jaws of the clip being opened before the plate is introduced. Care is also taken to open the jaws of the clip before removing the plate, so as to obviate any risk of loss of metal by friction between the holding-points and the plate. This arrangement has been found very convenient for small cells, as it allows the plates to be quickly and almost simultaneously placed in, and removed from, the liquid, and avoids all risk of the plates touching each other or the sides of the vessel; but for cells to be used with currents of over 10 amperes the plates become rather too large, and the arrangement shown in figs. 4 to 6 is then found more convenient. In this form a frame of insulating material is fitted to the top of the cell, and two sets of spring-contact clips, one set on each of two opposite sides of the cell, are fixed to it. These clips may be of the form just described, or they may be simply flat strips of springy metal soldered to a stiff base piece, as in fig. 5, in such a way that they press firmly against each other. In the use of this form of cell the anode plates are placed in contact with one set of clips and the cathode plates with the other set, the number of anodes being always one greater than the number of cathodes. The form of the plates and the mode of placing them in the cells are illustrated in figs. 4 and 6, from which it will be seen that the surface of the plate above the liquid is made as small as possible by cutting away the plate so as to leave two narrow strips connected to a cross piece, *c, d*. The end *c* of the cross piece is held in the contact clip, while the other end, *d*, is kept in position by a shallow notch in the insulating rim. The insulating frame and attached clips are simply laid on the top of the vessel, and can therefore be lifted off and cleaned so as to insure perfect insulation.

Sizes of Plates and Densities of Solutions.—The size of the plate can be varied within moderate limits in the case of silver, and within very wide limits in the case of copper, without greatly interfering with the quality of the deposit. In the case of silver and silver nitrate the effect of making the plate either too small or too large is, as has been pointed

out by Lord Rayleigh, to make the deposit less adherent and more roughly crystalline. There is then a tendency for the deposit to grow out from the cathode towards the anode in long branch-like crystals. This tendency is increased by any sharp corner on the cathode-plates, and hence care must be taken to round the corners and smooth the edges thoroughly. The deposit also deteriorates as time goes on in consequence of the crystals presenting sharp protuberances, which tend to grow and become more and more prominent. It follows that a somewhat smaller plate or greater density of current can be used if the time be short; but I have generally found that when the density of the current is such that the deposit would deteriorate greatly during the first two or three hours, the adhesion to the plate is likely to be uncertain. The best results seem to be obtained with a solution containing about five per cent. by weight of nitrate of silver, and cathode-plates which present an area of not less than 200 nor more than 600 square centimetres per ampere of current. If this strength of solution and size of plate be used *and the plates be properly cleaned*, the deposit is very compact and finely crystalline, and adheres very firmly to the surface of the plate. When the strength of the solution is increased the size of the plate can be slightly diminished, but not by any means in the proportion of the increased quantity of silver in the solution; the deposit is then more roughly crystalline, will not bear lengthened application of the current, and adheres much less firmly to the plate. So far as these experiments have gone, it seems a mistake to use a solution containing more than, or even as much as, ten per cent. of silver nitrate. Solutions containing from three to thirty per cent. have been repeatedly tried; but the best results have always been obtained with solutions containing from four to ten per cent. There seems no reason for using strong solutions except a slight difference in the original cost of the plates; but as these may be of very thin metal, the cost is a small matter compared with the risk of either total or partial failure of the experiment.

When the loss or anode-plates are to be used simply to supply silver to the solution, they need not be larger than the gain or cathode-plates; and there is some advantage in making them smaller, so as to increase the distance of the edges of the cathodes from those of the anodes. When the plates are small the surface becomes very soft and spongy, and if the density of the current exceed a certain moderate amount they will blacken, and the resistance of the cell is apt to become variable, due to the liberation of gases. It is better to make the anodes a good deal larger than the cathodes, because in

that case the surface of the plate remains bright and moderately hard, so that the plate can be washed and weighed if that be thought necessary. The density of the current at the anode should not exceed one ampere to 400 square centimetres of surface, and should be even less if the plates are to be weighed. The action of the current in causing the solution of the anode is somewhat curious, especially if the plates be made of rolled sheet. If the plates be simply washed and placed in the cell with the bright polished surface still on them, it is seldom that the outside skin will be dissolved. The silver is taken from the interior of the plate, leaving a very thin skin lying loose on the surface, which is ready to fall off either when the plates are lifted out of the cell or when they are placed in water for the purpose of washing. Whether this is due to the mechanical state of the silver on the surface or to a peculiar difficulty in so cleaning the surface of the plate that it is properly wetted by the liquid, is not yet quite clear. A plate of silver when repeatedly used for an anode becomes soft and almost devoid of elasticity, due to the solvent action taking place deep into the interior of the plate; and it is well to heat the plates to about a red heat in a spirit flame between different experiments, so as to keep it hard and prevent loss of silver.

In the case of copper and copper sulphate, the size of the plate may be almost anything from twenty square centimetres to the ampere upwards; but for experiments which are to be continued for two or three hours, the cathode-plate should present about fifty square centimetres of surface per ampere of current. With plates of from this size upwards the current may be allowed to flow for almost any length of time without introducing the least difficulty as to loss of copper in the subsequent washing. At the higher limit of current-density here mentioned (one fiftieth of an ampere per square centimetre), there is a slight tendency for the deposit to thicken at the edges of the plate and become rough, but as the current-density diminishes this becomes less and less marked. It may be taken as certain that the aggregation of the deposit at the edges of the plate is due to the current-density becoming too great at the sharp edges, and thus causing the formation of sharp crystals, which in their turn intensify the action. If the plates are made large enough, this critical current-density is never reached, and the deposit is as smooth on the edges as elsewhere. It is mainly in the ease with which a perfectly uniform and solid deposit can be obtained that the great advantage of copper over silver for ordinary use in electrolytic measurements lies.

The anodes in the copper cell behave in a similar manner to

that above described for the silver anodes, with the exception that they show no tendency to become soft and inelastic. If the current-density at the anode exceed the fortieth of an ampere per square centimetre, the current is apt to be variable and may almost stop completely, even when an electromotive force of 25 volts is used to produce it*. This is due to excessive resistance at the surface of the anode. In some cases the current will, after a few minutes, resume nearly its former strength, and gases are then freely given off at the anode. When the current-density is small, from the two-hundredth of an ampere per square centimetre downwards, the plate can generally be washed, and used to show the loss of copper during the passage of the current. This loss does not in any case agree with the gain on the cathode, in consequence of the solution taking up copper during the experiment; some examples of the results which have been obtained, and some further remarks on this subject are given below. In almost all cases there remains on the surface of the anode more or less of a very fine brown powder, which increases in amount as the current-density is increased, and which also seems to depend somewhat on the nature of the plate. If, for example, a plate of electrolytic copper be used, the surface will be found to have become a dark red when the plate is removed from the cell, but no loose copper will be found. That is certainly the case at least so long as the current-density does not exceed the one hundred and fiftieth of an ampere per square centimetre. Currents of greater density were not tried with electrolytic copper. This result seems to point either to the mechanical state of the copper in the rolled sheet, or the presence of a somewhat insoluble oxide, as the cause of the loose powder being left on the plate. Local action, due to unequal quality of the plate itself, may have something to do with it; it is certainly greatly increased by frequent reversals of the current in the cell.

The effect of varying the density of the solution of copper sulphate is not great until the density falls to about 1.05, when the deposit begins to be less adherent. There is, however, greater danger of error due to oxidation of the deposit in weak than in strong solutions, when no acid is added, owing to the fact that the solution becomes more quickly saturated with copper. Any density between 1 and 1.18 will be found to answer perfectly, but it is not advisable to use a saturated solution because there is then a risk of crystals forming on the plates.

Preparation of Plates.—In all experiments on electrolysis the proper treatment of the plates previous to their immersion in the liquid is a most important consideration. The treat-

* See note on page 413.

ment which I have found to give the best results with silver is extremely simple. Suppose a new sheet of silver is to be used either for a cathode or anode—first make the corners and the edges round and smooth, and then polish the surface thoroughly with a soft clean pad, water, and fine silver sand, so as to remove the skin which has been in contact with the rolls in the manufacture; rinse the plate in clean water, or by holding it in a rapid stream of clean water from a water-tap, so as to remove the sand, and then wash it first with clean soap and water and afterwards with clean water; next place it for a few minutes in a boiling solution of cyanide of potassium, and after that wash it thoroughly in a stream of clean water, taking care not to touch the part of the surface which is to receive the deposit with anything. If the surface of the plate be touched with the fingers, even when they appear to be clean, the markings of the skin will be reproduced by the deposit leaving the parts of the plate bare which were in contact with it. The plate may be dried either in a current of dry air in front of a bright fire, or in any other convenient manner which will insure that the surface of the plate will remain clean, and then accurately weighed. One point about weighing should be mentioned, because it is apt to be overlooked, that is, that the plate must be allowed to assume the temperature of the air before it is weighed, as even a very slight difference of temperature between the plate and the air inside the case of the balance is sufficient to produce quite a sensible error in the weight.

For the preparation of copper-plates a very good plan, especially with large plates and powerful currents, where it is necessary to arrange the resistance of the circuit carefully when the electrolytic cell is included, is, after the edges and corners of the plates have been well smoothed and rounded, to proceed as follows:—Polish the plate thoroughly with silver sand, wash the sand off by holding the plate in a rapid stream of water and rubbing it with a brush or a piece of clean cloth; place the plate in the cell, as a trial plate, and deposit a thin coating of copper over it, at the same time adjusting the current to the proper strength; then remove the plate, wash it in clean water, and dry it, first in a clean blotting-pad, and then before the fire, taking care not to heat the plate sensibly. If the plate has not been properly cleaned, the deposit of copper will show any defect; and if it be found to be perfect, the plate may be weighed and the electrolysis continued. For small currents it is more convenient to use a battery of moderately high potential, say twenty or thirty volts, and to keep a resistance in circuit with the cells; and in

this case it is not necessary, after the first trial at least, to adjust the current with the plates in position, as the resistance of the cells can be nearly enough allowed for. In these cases the plates were simply polished either with silver sand and water or with clean sand-paper, then washed in clean water to remove the sand, placed in water slightly acidulated with sulphuric acid for a short time so as to remove any trace of oxide, then rinsed in clean water, and dried first in clean blotting-paper and afterwards in front of the fire or over a spirit-flame. If the plate be thickly oxidized on the surface but otherwise clean, as is often the case with new sheet copper, the quickest mode of cleaning is to wet the plates and then place them for a few seconds in strong nitric acid, rinsing them immediately afterwards in clean water, and putting them into water containing a few drops of sulphuric acid to prevent oxidation. The plates may then be lifted one by one out of the acidulated water, rinsed in clean water, and dried in the manner above described.

The method of drying here recommended is important, as the blotting-pad removes almost at once nearly the whole of the water, and hence the drying can be completed in a few seconds, either in front of a fire or over a spirit-flame, without the slightest oxidation taking place. A plate may be washed and dried in this manner over and over again without producing as much as the tenth of a milligramme of difference in its weight.

Washing the Deposit.—The operation of washing the deposit at the conclusion of the electrolysis is one on the importance of care in which Lord Rayleigh has laid great stress. The method adopted for silver in these experiments was to lift the bar *b* (fig. 1) with the plates attached, and either to dip them several times in clean distilled water contained in a clean glass vessel before removing them from the clips, or to remove them as quickly as possible from the clips, and dip them several times one by one into the water; in either case observing carefully whether any small crystals were removed in the operation. If there is danger of loss of silver from the anodes, it is better to remove the plates from the clips before they are dipped in the water. After this preliminary rinsing to wash off the greater part of the silver nitrate solution, the plates were laid in the bottom of a shallow glass tray containing distilled water, and the water made to flow backwards and forwards over them for a minute or two by raising and lowering one edge of the tray. The plates were then removed and placed in another similar tray containing clean, but not necessarily distilled, water, washed in a similar

manner, and allowed to soak for about fifteen minutes before being dried. It is important to bear in mind that the water used for the first rinsing and washing must be clean water which has been recently distilled, and which has not had an opportunity of absorbing any impurity, such, for example, as a minute quantity of common salt, by coming in contact with anything which has not been recently and thoroughly cleaned. The water supplied by the Glasgow Corporation for domestic purposes, although very nearly pure, clouds immediately on contact with silver nitrate, and throws down a considerable precipitate of silver chloride, no doubt due to the fact that the water contains an appreciable percentage of chlorides in solution. A plate which has been insufficiently washed will generally want brightness when dried, and will assume a somewhat brighter appearance and be found to lose slightly in weight if heated to redness. The comparatively simple washing indicated above will generally be found sufficient, and the plate may be heated without any sensible loss of weight; but it is well not to continue the electrolysis so long as to put a very thick coating of crystals on the plate, as this increases the difficulty in washing and gives no corresponding increase in accuracy from any other source.

The plates were dried by heating the end of the plate in a spirit-flame, the greater part of the water having been previously drained off by holding one corner of the plate in contact with a pad of blotting-paper.

The washing of the copper deposit requires much less care because, if the plate is large enough for the current, it is almost impossible by any ordinary washing to remove copper from the plate. The deposit is solid copper, and may be handled like any other piece of metal without risk of loss. One thing, however, must be attended to, and that is that the plate be not exposed to the air for a longer time than is absolutely necessary before the copper sulphate solution has been completely washed off. The reason for this is that a copper plate oxidizes very rapidly when wet with a solution of nearly neutral copper sulphate and exposed to the air.

The plates should be removed from the solution and at once dipped two or three times into clean water (it need not be distilled), containing two or three drops of sulphuric acid to the litre, and then laid in a tray containing similar water, and washed in the manner above described for the silver plates. The plates may then be lifted out of the acid water, rinsed in clean water containing no acid, and dried, first in a pad of clean white blotting-paper, and afterwards in front of the fire, or, if the plates be small, over a spirit-flame.

No copper will be left on the blotting-paper, and no oxidation will take place if the deposit is of average quality. If the plate has been too small for the current, the drying in the blotting-paper may have to be omitted; and in that case it will be found advantageous to dip the plate in alcohol or ether before drying, as it then dries more quickly and is less likely to be oxidized. The plate should never be raised to a temperature so high that it cannot be held comfortably in the fingers, and evaporation should be, if possible, promoted by holding it in a rapid current of dry air. This latter treatment is that best suited for the loss plates, as they can seldom be placed in a blotting-pad without removing copper; after a little practice, however, it is not difficult to dry without oxidizing them; at the same time it does not seem advisable to make use of the loss plates for ordinary purposes.

Loss of Weight in the Solution.—A number of experiments were made on the effect of leaving silver plates in solutions of silver nitrate, and copper plates in solutions of copper sulphate, for the purpose of finding the rate of loss of weight in these circumstances. The solutions of silver nitrate contained from five to thirty per cent. of the salt, and were in all cases pure with no acid added. The plates were pure silver sheet. There was no appreciable change of weight. The solutions of copper sulphate varied in density from 1.2 to 1.05, and were partly made from pure copper sulphate and distilled water with no acid added, and partly from this solution with from one to twenty per cent. of ordinary commercial sulphuric acid added. The copper plates were in some of the experiments ordinary "high conductivity" sheet copper, and in others thin sheet copper thickly covered with electrotypes copper. The results were generally somewhat irregular, but they all showed a considerable loss of copper from the plate to the solution*.

The results of a series of weighings of plates of ordinary copper sheet which were immersed in solutions of copper sulphate of varying density and acidity for a period extending in the aggregate to about seventy-one days are given in

* Dr. Gore, in the paper above quoted, describes experiments on this subject made by him both on the loss of copper in an acid solution of the sulphate, and on the loss of the anode and cathode plates in a copper-copper-sulphate electrolytic cell. Some of the results there given are in agreement with the results of my experience as given below—for example, the advisability of using high current-density for the measurement of the electrochemical equivalent; but the statement made to the effect that a copper anode loses less by direct chemical action when the current is flowing than when it is not, is not borne out by my experiments.

To face page 401.]

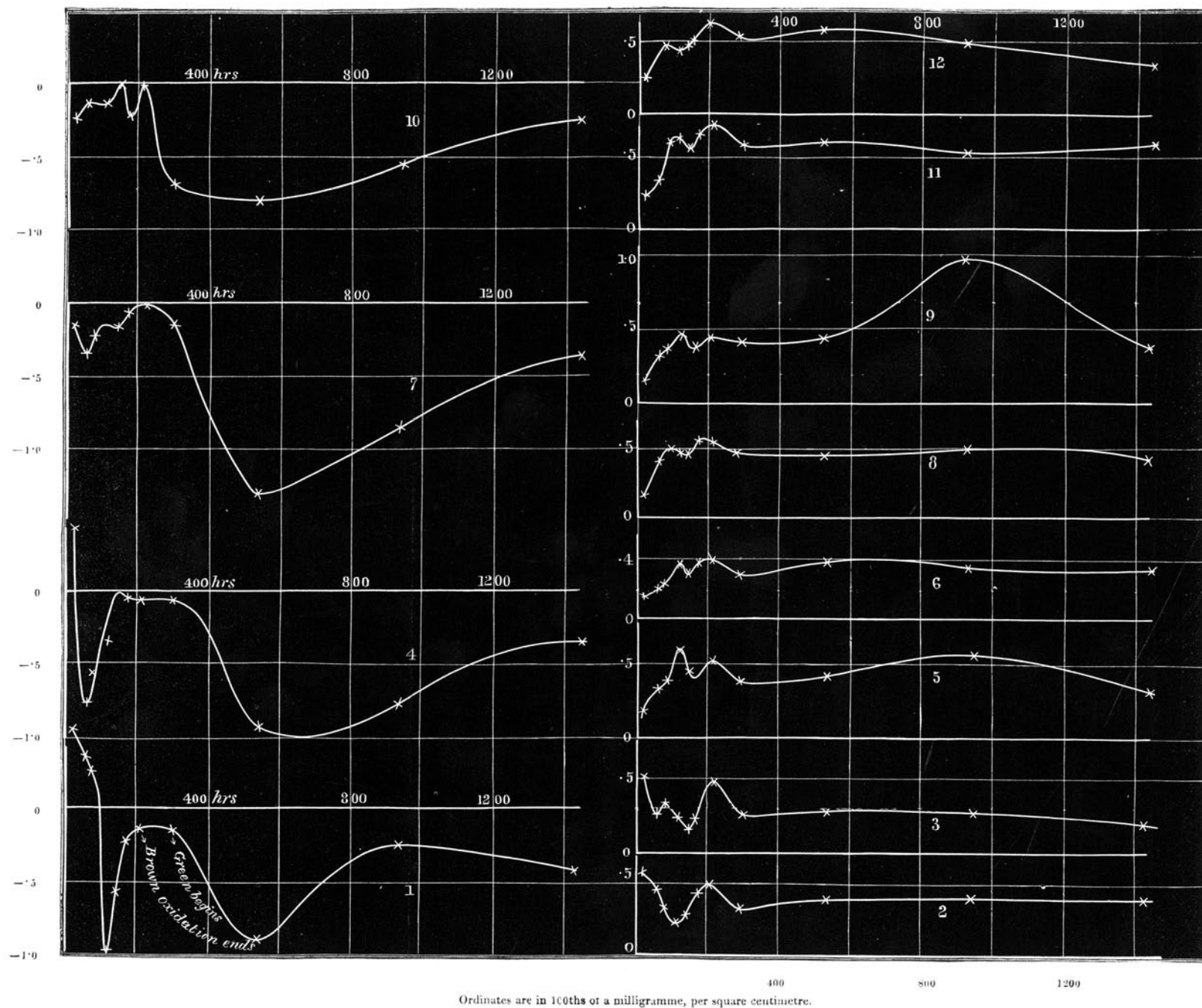


Table I., and are illustrated in the curves 1-12. The headings of the Table sufficiently explain the meaning of the different columns. The ordinates of the curves show the rate of loss of copper in hundred thousandths of a gramme per square centimetre of surface per hour. A glance at the Table, or at the curves, is sufficient to show how very variable the loss was, and also that it seldom exceeds the two hundredth of a milligramme per square centimetre per hour. For a plate of fifty square centimetres surface this would amount to a quarter of a milligramme, and the copper which may be deposited on this surface in the same time is, if fifty square centimetres to the ampere be chosen, about 1.2 gramme. Hence if the action be nearly the same during the passage of the current as when no current is passing, the error will amount to about one in three thousand. The actual difference, as will appear from the results discussed below, is greater than this, which seems to indicate a more rapid corrosion of the copper by the liquid when the current is flowing, a result agreeing with those obtained by Gore.

The rate of loss, as shown by the results given in Table I., is at first greater in the dense than in the weak solutions, but seems to reach a minimum between the density 1.10 and 1.15, a result which was confirmed by other experiments, extending over shorter intervals. The loss, however, although never great, is somewhat variable, and it is difficult to make out anything with certainty, unless a very much larger number of experiments are made. The effect of adding acid to the solution seems not to be great when the solution is dense, and seems, for densities between 1.15 and 1.10, rather to retard than to accelerate the action.

The result of subsequent experiments, made with saturated solutions containing different quantities of acid up to twenty per cent., and electrotype copper plates, showed that the effect of the addition of acid on the rate of corrosion was to diminish the rate of loss under these circumstances.

Perhaps the most interesting part of this series of results is that which gives the behaviour of the plates in the solutions to which no acid was added. The first action is a corrosion of the plate, but after a sufficient time has elapsed the corrosion ceases and the plates rapidly gain weight by oxidation. This action goes on until the plates are nearly completely covered with brown oxide, after which the weight remains nearly constant for a few days. Another change then takes place, the plates begin again to increase in weight rapidly, and on examination it is found that they have now begun to form hydrated oxide. This action continues until the plates

TABLE I.—Showing Rate of Loss of Weight of Copper in Solutions of Sulphate of Copper of different Densities, and containing different amounts of free Sulphuric Acid.

Initial densities. } ...	1-20.			1-15.			1-10.			1-05.		
	2-3869.	2-7556.	2-9777.	3-1445.	2-8367.	2-4508.	3-0917.	3-1793.	2-8144.	2-9177.	2-6875.	2-7225.
Number of plate ...	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
	Total loss per square centim. in grammes $\div 10^5$.	Rate of loss during successive intervals, in grammes per square centim. $\div 10^5$.	Total loss per square centim. in grammes $\div 10^5$.	Rate of loss during successive intervals, in grammes per square centim. $\div 10^5$.	Total loss per square centim. $\div 10^5$.	Rate of loss during successive intervals, in grammes per square centim. $\div 10^5$.	Total loss per square centim. in grammes $\div 10^5$.	Rate of loss during successive intervals, in grammes per square centim. $\div 10^5$.	Total loss per square centim. in grammes $\div 10^5$.	Rate of loss during successive intervals, in grammes per square centim. $\div 10^5$.	Total loss per square centim. in grammes $\div 10^5$.	Rate of loss during successive intervals, in grammes per square centim. $\div 10^5$.
Date, 1886.	June 17. 48	0-56	27	21	9	8-3	7	8	8	12	9-9	11
" 18. 70	0-36	37	31	4	16	13	15	17	15	15	17	13
" 19. 92	0-27	44	38	8	32	18	20	23	23	18	13	23
" 20. 140	1-00	54	49	25	44	37	28	50	46	25	60	53
" 21. 162	0-55	60	53	25	55	44	32	60	54	25	72	63
" 22. 184	0-23	69	58	26	64	52	34	72	62	30	86	74
" 23. 235	0-12	95	84	28	89	74	34	99	84	32	121	106
" 24. 275	0-13	141	120	36	140	129	37	162	143	130	202	178
July 1. 685	0-37	257	200	327	273	244	450	297	282	384	588	557
" 14. 1189	0-24	442	330	710	550	421	882	546	49	667	919	858
Aug. 4. 1189	0-42	632	438	888	727	592	1068	755	779	770	919	858
" 25. 1693	0-42	632	438	888	727	592	1068	755	779	770	919	858

have become completely coated with a thick green coating, when it gradually ceases. All the phases of this action are illustrated in curves 1 and 4; the first part, namely the loss of weight at the beginning, is not shown in curves 7 and 10, as the plates had already gained weight before the first weighings were made.

Electro-chemical Equivalent of Silver.—Some preliminary experiments were made on this subject, but owing to faults being discovered in the standard galvanometer the experiment was put aside and has not yet been resumed. The first trouble that was experienced with the galvanometer is perhaps worth recording here. It was a new instrument of the sine type, made almost wholly of brass, and had a short needle suspended at the centre of the coil, and a light index enclosed in a long rectangular box, the sides of which were made of thin brass, and the top and bottom of glass. The coil was forty centimetres in diameter, and consisted of one layer of silk-covered copper wire containing seventy turns, making up a breadth of about five centimetres. The constant of a second and more convenient instrument, of high sensibility, was determined by comparison with the sine galvanometer, and then used in accordance with the method described below for measuring the current passing through two silver-silver-nitrate electrolytic cells arranged in series. The magnetic field at the needle of this auxiliary galvanometer was produced by permanent magnets, and was so intense as to be hardly at all, certainly not to the extent of $\frac{1}{100}$ th per cent., influenced by variations of the Earth's magnetism. In the first three trials the constant of the second galvanometer was such that the current produced a deflection of about 20° on the sine galvanometer, an angle which could be measured with a fair amount of accuracy, but which of course did not take full advantage of the sine principle. These three measurements each gave the same result, namely $\cdot 0011185$ gramme as the amount of silver deposited by a coulomb of electricity. The constant of the second galvanometer was then changed so as to give a deflection of about 40° on the sine galvanometer, and then a difference amounting to about one sixth per cent. was discovered between the value now obtained and that previously got for silver. This seemed to indicate a departure from the law of sines, and suggested, as almost the only possible explanation, magnetic brass. A small Bottomley's reflecting-magnetometer was then set up, and the magnetic field at its needle made almost zero by means of a permanent magnet. The brass box enclosing the needle was unscrewed and, the needle

having been taken out, the box was brought up close to the back of the magnetometer. It was then found to have several magnetic poles, but particularly a north pole on one side and a south pole on the other side of the position where the galvanometer-needle was suspended. This polarity, although sensible enough to the test here made, was so small that it could not be detected with certainty by a magnetometer placed in the Earth's field. The frame of the galvanometer-coil when tested in a similar manner showed signs just perceptible of magnetism, but so small as to produce no sensible effect on the indications of the instrument.

The brass case was then replaced by a glass cell, and two other measurements taken with deflections of about 40° and 60° respectively, the results obtained being $\cdot 0011183$ and $\cdot 0011182$; but on continuing the experiment the indications of the galvanometer were found to have become uncertain, due apparently to some defect in the insulation, which has not yet been investigated. The results so far as they go seem to confirm the value given by Kohlrausch and Lord Rayleigh as closely as could be expected, but no great value can be put upon them. In subsequent work the value $\cdot 001118$ was assumed to be sufficiently accurate for our purpose.

RATIO OF SILVER TO COPPER.—A number of experiments were made for the purpose of determining the ratio of the electro-chemical equivalents of silver and copper. These involved the determination of the effect of density of solution, the effect of repeated use of the same solution, and the effect of current-density.

Effect of Density.—The effect of changing the density of the solution was only gone into sufficiently to show that no important error is likely to arise from this cause. The results of two experiments are given in Table II. They show a slightly smaller deposit from weak than from strong solutions; but the absolute difference of weight, only a fifth of a milligramme, if the somewhat doubtful result from the weakest solution be omitted, is too small to found any conclusion upon.

TABLE II.

Densities.	Comparative weight of deposit in grammes.		Current density in amperes per sq. cm.
	1.	2.	
1.20	·2352	·3519	0.02
1.16	·2350	·3418	0.02
1.12	·2351	·3517	0.02
1.08	·2350	·3518	0.02
1.05	·2347	·3512 (?)	0.02

The number 3512 has a note against it in my notebook stating that copper was lost in the washing, and generally that the deposits from solutions of this density are unsatisfactory with this size of plate and strength of current. It would appear, therefore, that the last line of the table should be struck out, but, as there is no note against the first result, I have quoted the complete numbers in both cases.

Effect of Acidity.—In the first experiments made on the relative value of the electrochemical equivalents of copper and silver the solution was made with pure sulphate of copper which had been supplied by Burgoyne Burbidges and Co. as very free from acid. The results obtained were at first very puzzling, the gain of weight being generally greater than the loss and very irregular. They are given in Table III., from which the general nature of the result will be readily gathered.

The ratio of the equivalents of copper and silver are not given in the table. They may be calculated from the results given; but as the early results are of no value for this purpose, and the area of the plate has not been recorded for the later ones, it has been thought unnecessary to give them.

The results with the nearly neutral copper sulphate were invariably too high, and this excess of weight was increased by leaving a copper plate in the solution. Repeated use of a solution which has been supersaturated with copper by leaving a copper plate in it seems to bring the solution back towards its normal state.

The addition of a very small percentage of acid causes different solutions to give perfectly accordant results.

One possible explanation of the peculiar action of the neutral solution suggested itself, namely the formation of subsalts of copper when the solution was placed in contact with metallic copper, the subsalt giving twice as much copper as the ordinary sulphate. The real explanation is, however, I believe, the oxidation of the deposit while in the electrolytic cell. In one or two cases the deposit was hammered so as to separate it from the sheet, and it was then found that the back of the deposit obtained with the neutral solution and the surface of the plate were completely oxidized, while those from the acid solution were bright.

Some further experiments were made with various specimens of copper sulphate, some of them obtained in Glasgow and others in London, with the view of finding whether any difference might arise due to a change from one sample of sulphate to another. These need not be quoted in detail, the result being entirely negative. Precisely the same gain of weight was obtained from a solution of the ordinary com-

TABLE III.

Number of experiment.	Silver gain in grammes.	Copper gain in grammes.	Copper loss in grammes.	Remarks.
1.	1.6084	{ .4774 .4836	.4747 .4748	
2.	0.8042	{ .2391 .2373	.2372 .2372	
3.	1.0059	{ .3053 .3073	.2967 .2969	
4.	.9042	{ .2688 .2728		
5.	1.2063	{ .3589 .3547	.3496 .3574	Solution of Nitrate. " Sulphate.
6.	1.2041	{ .3546 .3542 .3543	.3557 .3504? .3573	Different Sulphate. Same solution as before, with $\frac{1}{10}$ per cent. of sulphuric acid added.
7.	Accidentally lost.	{ .2359 .2361 .2360 .2374	Not weighed " " "	Ordinary pure sulphate, $\frac{1}{10}$ per cent. acid added. Burgoyne Burbidges as above, $\frac{1}{10}$ per cent. acid added. Ditto, stood for four days with a copper plate in it and no acid added.
8.	1.2067	{ .3550 .3549 .3549 .3549 .3560	" " " " "	Ordinary pure sulphate, no acid added. Ditto, ditto, with $\frac{1}{10}$ per cent. acid added. Burgoyne Burbidges with $\frac{1}{10}$ per cent. acid added. Ditto, with no acid added.
9.	.8053	{ .2368 .2368 .2367 .2369 .2371	" " " " "	Solutions the same as last, with the exception of the third, which had 5 per cent. of acid added.

mercial copper sulphate as from the various specimens of pure sulphate experimented on; and for the first few hours no difference was found, whether acid had or had not been added to the solution. If, however, the same solution is to be used for several successive experiments, acid should be added, as will be evident from the results given in Table IV. The first column of this table gives the numbers of the experiments in the order in which they were made; the second column the ratio of the electrochemical equivalent of copper to that of silver, obtained from the experiments when the current-density at the cathode was one fiftieth of an ampere per square centimetre; the third column the same ratio when the current-density at the cathode was one two hundred and fortieth of an ampere per square centimetre. Two or more silver cells were always in circuit with the copper cells, but as the differences between them, except in one or two cases where one of them was known not to be reliable because of silver lost previous to weighing, were never so great as to enter into the figures here given, it does not seem necessary to record the numbers in detail.

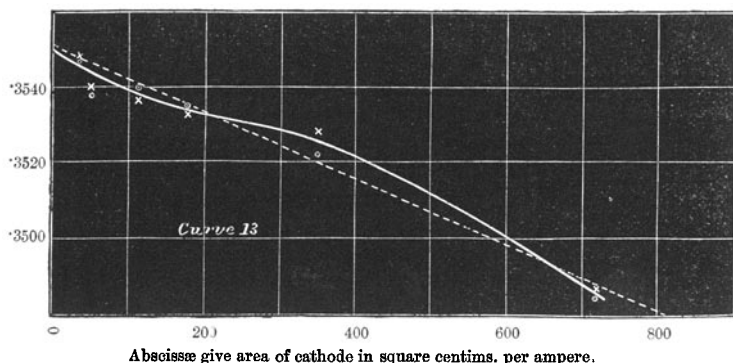
TABLE IV.

Number of Experiment.	Ratio of the Electrochemical equivalent of Copper to that of Silver.		Remarks.
	Area of plate 50 sq. cms. per ampere.	Area of plate 240 sq. cms. per ampere.	
1.	·2939	·2930	Fresh solutions.
2.	·2944	·2929	Solutions interchanged.
3.	·2941	·2935	Solutions as in 2.
4.	·2942	·2939	" "
5.	·2944	·2942	" "
6.	·2947	·2932	Solutions again interchanged.
7.	{ ·2940 ·2940 ·2941 }	{ ·2934 ·2930 ·2932 ·2929 }	New solutions once previously used.
8.	{ ·2941 ·2940 }	{ ·2930 ·2932 ·2929 }	Fresh solutions containing a little acid.

In all these experiments, with the exception of the 8th, no acid was added to the solution. The quantity of liquid contained in the cells for the experiments 1 to 6 was about 100 cubic centimetres and was the same for the large as for the small plates. The total area of copper plate, including both gain and loss plates, was about 30 square centimetres for the small plates and 60 square centimetres for the large plates.

These experiments show clearly a gradual increase in the ratio with successive experiments, and that in a more marked degree with the small current-density than with the large.

Omitting the results of experiments 2 to 6, the average ratio for the two current-densities here used are $\cdot 2940$ and $\cdot 2931$, and the ratio of these two numbers will be found to be in good agreement with the results of special experiments on the effect of size of plate given in Table V. and illustrated in curve 13.



Effect of Size of Plate or Current-Density.—The two experiments on the effect of the density of the current at the cathode, the results of which are given in Table V. and illustrated in curve 13, were made on the 25th and 28th of June respectively; the current, as measured by one of Sir William Thomson's galvanometers, was about $\cdot 0997$ ampere and was continued for three hours. The first column gives the area of the deposit, the second and third the amount of copper deposited.

TABLE V.

Area of plate in sq. cms.	Weight of deposit in grammes (first experiment).	Weight of deposit in grammes (second expt.).
3	$\cdot 3534$	$\cdot 3533$
5	$\cdot 3530$	$\cdot 3529$
11	$\cdot 3528$	$\cdot 3530$
18.5	$\cdot 3526$	$\cdot 3527$
36	$\cdot 3524$	$\cdot 3521$
73	$\cdot 3503$	$\cdot 3502$

The results given in Table IV. indicate a slightly greater difference between the results obtained with a current-density of a fiftieth of an ampere and those obtained with a two hundred and fortieth of an ampere per square centimetre of

the cathode; but both sets agree in indicating rather less than a tenth per cent. as the correction which has to be added to the results obtained with the denser of these currents, in order to arrive at the true value of the electro-chemical equivalent of copper.

The results of Table IV. give for the amount of copper deposited by a coulomb of electricity, when the cathodes expose a surface of fifty square centimetres to the ampere, '0003287 gramme, if we assume '001118 as the corresponding number for silver. They would thus indicate a value not differing much from '0003290 as the true value of this constant for copper. In the use of copper for the measurement of currents by electrolysis the absolute value of this latter number is not of much importance; what is wanted is the proper number to use for a certain current-density, and at ordinary temperature this number will not differ much from the number obtained by using '0003287 for cathodes of fifty square centimetres per ampere, and correcting for other sizes by the dotted line in curve 13.

A few experiments were made with very weak current-densities, the circuit being kept closed for about a week in each case. The results show that when the current-density is very small the rate of loss by direct action of the liquid is much the same as if no current were flowing. The deposit was patchy and did not usually cover all the surface of the plate, a result which was perhaps due to inequalities in the plate itself.

The difference between the gain and loss of weight by the plates in the electrolytic cell is usually very much greater than can be accounted for by the loss of similar plates placed in the same liquid when no current is flowing, a result which appears to be largely contributed to by the anode-plates losing very much more when the current is flowing than when it is not. If the difference between the gain and loss be divided by the sum of the areas of the anodes and cathodes, and the quotient, multiplied by the area of the cathode, be added to the gain, a result is obtained which is always too high to give the true electro-chemical equivalent, but which is very nearly constant for different cells, even when they begin to give uncertain results from the gain of weight taken by itself.

Arrangement of the Circuit.—For experiments with weak currents, such as those the results of which are given in the Tables II. to V., the circuit generally included a battery of twenty-four tray cells, the electrolytic cells, one of Sir William Thomson's improved rheostats, and a galvanometer. The galvanometer was in some of the earlier experiments one of Thomson's lever voltmeters, but in the later experiments one

of his "school galvanometers" arranged so as to have a "false zero," and having its needle suspended in a strong field produced by permanent magnets, was used. An ordinary index galvanometer when arranged in this way, with its zero well off the scale, gives ample sensibility, and is very compact and convenient. The current was adjusted by the rheostat until the index was exactly over a division of the scale, and it was kept there by turning the rheostat, if the current varied, all through the experiment.

Standardizing Arrangements.—The arrangement of the apparatus for standardizing instruments intended to measure strong currents such as *deca* and *hecto* ampere-metres is shown in figure 7, which may be taken as a plan of the arrangements on the top of the standardizing table, with the exception that the galvanometer *G* is, for convenience in the figure, shown much too close to the conductors. On one end of the table six of the Electric Power Storage Company's accumulators are arranged, and connected by means of thick copper rods to a mercury-cup commutator as shown. The mercury cups *m* are shown joined across by bridges which are of thick copper in such a way that the cells are in series, but for most purposes these are removed and the cells joined in parallel by means of two rods of copper, provided with teeth at the proper distances apart to fit into the cups *m*, and thus join all in each row together. The battery, when fully charged and joined in this way, is capable of maintaining a current of two hundred amperes for ten hours. The commutator is joined by means of two copper rods *r, r*, to a distributing board *A*, by means of which one or more instruments can be put in the same circuit. In the arrangement shown, a set of conductivity-bridges *D* and a rheostat *R* are introduced between the cups 1 and 2; a galvanometer *G* between the cups 4 and 5; a pair of large electrolytic cells, joined together by means of a moveable cup *M*, between the cups 6 and 7; and an electric-current balance between 11 and 12. The arrangement here shown, together with details of the conductivities *D* and the rheostat *R*, will be found described by Sir William Thomson in a recent patent specification. The following description will give a general idea of the apparatus and the mode of using it.

A perspective sketch of two of the conductivity-bridges *D* is given in figure 8, where one that is in the circuit is shown standing in the mercury troughs *t, t*, and another insulated. These conductivity-bridges consist of **U**-shaped pieces of platinoid rod or wire according to the conductivity required. The thick rods are bent into shape and the two limbs held at the proper distance apart by wooden blocks, while the thin wires are

supported all along their length by a strip of wood. The length of rod in each *U* must of course be sufficient for the metal not to become much heated by the potential of cell, one or two volts; the length actually used in the apparatus is four metres. The troughs *t* are partially filled with mercury and have thick copper bottoms, against which the ends of the plantinoid rods press by their own weight. The thin wires have thick terminal pieces fixed to the wooden strips for this purpose. The conductivities of the different bridges, beginning at the end *t*, *t*, fig. 7, are graduated so as to be nearly in the ratio 1, 1, 2, 4, 8, 16, &c.; so that any conductivity between the highest and the lowest can be put in by steps equal to the lowest conductivity in the set. To bridge over these steps and thus make the variation from the highest to the lowest perfectly continuous, the rheostat *R*, which has a minimum conductivity somewhat less than the lowest of the bridges, is introduced and forms in fact another bridge which can be readily varied. The wire of this rheostat is formed of a strand of fine copper wires, and is capable of carrying a current of ten amperes.

The galvanometer *G* and the current-balance *B* may be of any form which it is desired to standardize; they are simply put into the figure by way of illustration. The electrolytic cells *E* are rectangular earthenware vessels fitted in the manner illustrated in figs. 4-6, and described on page 392, above. The larger of these cells is fitted to receive plates the aggregate surface of which is sufficient for two hundred amperes, but when the current to be measured is smaller the plates are not all introduced. In this cell the plates are so large that there is considerable danger of their touching each other when they are left freely suspended in the liquid, and hence two *U*'s of thin glass rod are hung over each of the anode plates, so as to keep the cathodes from touching them. The small cell is convenient for currents of from 5 to 25 amperes.

All these operations connected with the treatment of the plates for these cells have been already described, and hence it only remains to indicate how the apparatus is generally used for standardizing instruments. Suppose, for example, a current-balance is to be standardized, and that it is known, by preliminary trials or by comparison with another instrument, to require about fifty amperes to bring its index to the zero mark when a certain weight is put on the beam. Arrange the electrolytic cell so that the cathode plates expose a surface of about twenty-five hundred square centimetres, and join up as shown in the diagram, fig. 7, putting a bridge across from 4 to 5. Introduce conductivity into *D* until the index of the

balance comes nearly to zero, and then adjust by the rheostat. Leaving everything in position, break the circuit and take out the cathode plates, wash, dry, and weigh them, in the manner already described. Again put the plates in the cell, and observing the time carefully on an accurate time-keeper, close the circuit. The current will at once assume almost the exact strength, and what little deviation there may be can be adjusted in a second or two by the rheostat. From five to ten seconds usually suffices to bring the current accurately to the proper strength, and the electrolysis is as a rule continued for an hour. Now suppose the average error during ten seconds amounts to as much as five per cent., the error on the total amount will only be about one-seventieth per cent., which may be neglected. The current is kept steady by means of the rheostat during the whole hour, and with most instruments this can be done with sufficient accuracy by observing the index of the instrument itself, but if the instrument is not sufficiently sensitive, or if the constancy of its indication is to be tested, a second instrument possessing the requisite sensibility and constancy is introduced into the circuit in the manner indicated at G, and the current kept steady by observing the index of it. The constant of this second instrument does not require to be known; it should be of such a kind that its constant can be readily changed so as bring its deflection to the proper amount, and the index exactly to a scale-division. The position of the index of the instrument being standardized may then be observed from time to time and the variations, if any, noted.

When instruments which are designed for the measurement either of very weak or very strong currents, as, for example, milliamperes- or hectoampere-meters, are to be standardized, it is generally more convenient to send a stronger current in the former case, and a weaker current in the latter case, through the electrolytic cell. Several methods involving the use of auxiliary galvanometers have been used for this purpose; but the method illustrated in fig. 9 is sufficient to indicate the general principle of divided circuits on which such methods are based.

Referring to the figure, r, r_1 is a set of resistances, supposed in this case to consist of eleven straight wires each of exactly the same resistance and as nearly as possible of the same length and thickness. These wires are soldered to thick bars of copper, b, b_1, b_2 , the resistances of which are negligible in comparison with that of the wires. In the case here considered the resistances are supposed to be arranged in two groups of ten and one respectively, but for general purposes it is more

convenient to solder separate terminal pieces to one end of each wire, so that the number in each group may be varied by putting the terminals in one or other of two mercury troughs. Between the bars b_1 and b_2 a zero galvanometer g is connected, and is used for the purpose of indicating when b_1 and b_2 are at the same potential. When this is the case, the current from b to b_1 is to the current between b and b_2 in the ratio of the resistance between b and b_2 to the resistance between b and b_1 . Two sets of resistances, or two rheostats, R and R_1 , are introduced into the branches for the purpose of adjusting the currents to the required strength. The electrolytic cells E and E_1 are placed in one or other of the branch circuits according as the instrument to be graduated is designed for weak or for strong currents, and the instrument is included in the other branch. The circuit is closed through a suitable battery, which must be of such a kind as will maintain a nearly uniform electromotive force. The current through the instrument G_1 is kept constant by means of the rheostat R_1 , and the difference of potential between b_1 and b_2 is kept at zero by means of the rheostat R . When the instrument G_1 is to be standardized by means of a standard galvanometer or a standard current-balance, the arrangement and mode of operation is precisely similar, the standard instrument taking the place of the electrolytic cells.

Note on the Effect of Excessive Current-Density at the Anode in the Electrolysis of Copper Sulphate.—On page 396 above, the effect of excessive current-density at the anode of a copper-copper-sulphate electrolytic cell is referred to, and it is there stated that, unless the anodes present a surface greater than 40 square centimetres per ampere, the current is apt to diminish greatly in strength after the first few minutes.

As the result of some special experiments on this subject I find that the requisite size of anode depends greatly on the degree of saturation of the solution. When the solution is nearly saturated, say above 1.18 in density, the current is apt to be almost entirely stopped on account of the anode plates becoming completely covered by a finely crystalline deposit of copper sulphate which dissolves in the liquid very slowly. A current of one-tenth of an ampere derived from a battery of 24 tray Daniells was passed through an electrolytic cell charged with a solution of sulphate of copper of density 1.18, and having two anode-plates made of round copper wires presenting a total surface of 3.8 square centimetres. The current remained nearly constant for 12 minutes, when it gradually diminished, became practically zero in a few seconds, and remained so for 20 minutes. At the end of this time the

circuit was broken, and the plates taken out of the liquid. The cathode was found to be covered with a good deposit of copper, but the anode was completely enclosed in a glacial sheath of copper sulphate.

Another cell, in which the anode had a surface of 4.4 square centimetres, was treated in the same way, and was found to carry a current of one-tenth of an ampere for 14 minutes. The plates were then found to be covered by a similar coating of copper sulphate.

A similar cell in which the anode had a surface of 7 square centimetres was found to carry one-tenth of an ampere for 30 minutes, when the current fell off as before from the same cause.

Experiments were then made in a similar manner with cells containing a solution the density of which was 1.11. When the current density at the anode exceeded one ampere per 20 square centimetres, the plate became covered with black oxide and the current diminished greatly in strength after a few minutes (about 7 minutes for a current-density of one ampere to 7 square centimetres, and 3 minutes for double that current-density). The current does not entirely cease, and will after a few minutes, if the battery be of sufficiently high potential, again assume nearly its former strength. The oxide then falls off and gases are liberated at the surface of the anode, forming a descending stream close to the plate and an ascending stream two or three millimetres further out. As the current-density is diminished, less and less oxidation takes place and it becomes a lighter brown in colour. With a current-density of one ampere to 30 square centimetres the anode became covered with brown oxide, which made the resistance of the cell high and variable, but little or no gas was generated.

No gas was, so far as could be observed, given off at the cathode during any of these experiments.

XLIX. *On certain Sources of Error in Connection with Experiments on Torsional Vibrations.* By HERBERT TOMLINSON, B.A.*

Introduction.

DURING a long series of researches on the torsional elasticity and internal friction of metals, I have come across certain sources of error in connection with torsional vibrations

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