TRANSACTIONS

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I.—On the Measurement of the Resistance of Electrolytes.—By F. J. A. McKittrick, Physical Laboratory, Dalhousie College, Halifax.

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During the present session at Dalhousie College, I wished to make a series of experiments, determining the electrical resistance of certain electrolytes. Not having the apparatus necessary for Kohlrausch's method at my disposal, I employed that used by Ewing and MacGregor (Trans. R. S. Edin., Vol. XXVII (1873) p. 51), which, according to the tests applied to it by Prof. MacGregor (Trans. R. S. Can., Vol. VIII (1890), Sec. III, p. 49), seemed capable of giving results sufficiently accurate for my purpose.

Since this method, for its most successful application, especially if used in the way suggested by Prof. MacGregor in the latter of these two papers, requires some training of the eye in observing the motions of a spot of light, I undertook a series of preliminary experiments. In the course of these experiments, certain improvements suggested themselves to me. These improvements and their effect on the working of the method, this paper attempts to point out.

As the above method has been fully described by Prof.

MacGregor in the paper already referred to, I need give but a short sketch of it here. The electrolytic conductor is introduced by Platinum electrodes as one of the arms of Wheatstone's Bridge, and the process of determining its resistance is the same as in the case of a metallic conductor, viz., by a gradual adjustment of the arms. The indications of the Galvanometer, however, will not be the same as in that case, owing to the fact that the electrodes become polarized through the passage of the current. The effect of this polarization on the Galvanometer is the same as if, during the passage of the current, the resistance of the electrolytic cell gradually increased.

Imagine the arms of the bridge so adjusted that, on the passage of the current, the light spot of the Galvanometer moves off to the right and remains there, such a deflection having been ascertained to mean that the resistance being measured, if metallic, was too small to give zero deflection. If we gradually change the adjustment of the arms in such a way as to diminish this deflection to the right, it will not be found possible to obtain an adjustment making the deflection zero, but an adjustment will be reached with which the light spot moves first to the right, stops, moves back and off to the left, showing that though at the beginning of the flow of the current, the resistance of the cell was small enough to give a deflection to the right, it has been virtually increased by the polarization until it is so large as to give a deflection to the left. We have thus a double deflection. As we continue changing the adjustment so as to diminish the initial deflection to the right, the double deflection will grow less and less until finally we shall have only the deflection to the left.

If we had a magnet and mirror of indefinitely small moment of inertia, hung by a fibre offering no resistance to torsion, so that it would, at any instant, indicate the direction of the current flowing through it, this double deflection would only just vanish when the adjustment of the arms indicated the exact resistance of the cell, *i. e.*, when the resistance of the cell, calculated in the ordinary way from the resistances in the other arms, would be its exact resistance.

With an actual mirror and magnet of finite moment of inertia, no appreciable motion can be observed till the current has acted for some time If the adjustment of the arms be such as to indicate a resistance for the cell only slightly greater than its real value, the first current flowing through the Galvanometer will be very weak, and, before it will have had time to produce an appreciable deflection of the mirror, the electrodes will have become polarized, and our only deflection will be one to the left If, then, we take the resistance of the cell to be that indicated when the double deflection has just vanished, we make an error, and conclude the resistance to be greater than it really is. Whether, with any magnet and mirror yet manufactured, this error can be made small enough to be neglected, can be determined only by experiment.

In their experiments, Ewing and MacGregor assumed that the light mirror and magnets of Lord Kelvin's Dead-Beat Galvanometer would give a close approximation to accurate results. In order to reduce polarization, they used as current generator only one Grove cell, and introduced large resistances into the arms of the bridge. Their determinations, however, when compared with those given by more elaborate and accurate methods, were found to be too large, differing from Kohlrausch's, in some cases, by as much as 12 per cent.

As their experiments were made when they were students and had acquired little experience in experimental work, the discrepancy may have been due to other causes than the defects of the method. Hence Prof. MacGregor, in order to test the method, made a series of experiments, described in the paper cited above, comparing the resistances of solutions of zinc sulphate as given by this method and by the use of non-polarizable electrodes. To reduce polarization, he also used weak currents and, in addition, electrodes of large area. He found that, if the mere vanishing of the double deflection were taken as the test of adjustment, the resistances determined would be too much greater than their real values to be regarded as a sufficiently close approximation. He noticed, however, that, when he could no longer observe a double deflection, he yet could notice a distinct hesitation at the beginning of the single deflection. That this should be so is evident. For, after the double deflection has just vanished, the first current passing through the Galvanometer still tends to cause a deflection to the right, but is overpowered by the polarization current. Hence the mirror does not begin to move as soon as contact is made but, for a short time, remains at rest. Clearly then, if the adjustment of the arms be changed until we can observe not only no double deflection, but also no hesitation, we shall get more nearly accurate results. By observing the vanishing of the hesitation, Prof. MacGregor was able to get results which, in the case of high resistances, differed from their true values only by from 0.1 to 0.4 per cent.

I began, therefore, by endeavoring to observe the vanishing of this hesitation, testing my results in the same way as Prof. MacGregor had done in the paper cited above.

The electrolytic cell which I used consisted of strips of window glass cemented together with marine glue. Its length was about 16 cm., breadth, 8 cm., depth, 9 cm. It was divided transversely into two equal compartments by a glass partition cemented in so as to be water tight. Passing through the centre of this partition, and cemented at right angles to it, was a glass tube with its ends open. It length was 1 cm., the diameter of its bore 0.3 cm. At each end of the box I placed my platinum or amalgamated zinc electrodes, as the case might be. They were each about 7 cm. square and had narrow strips projecting above the box. To these strips of the zinc electrodes thick copper wires had been soldered without the use of acid ; to the platinum electrodes, thick platinum wires had been welded. By these wires the cell could be joined up as an arm of the bridge.

The electrodes were, in all cases, placed as close as possible to the ends of the box. Since, however, the resistance of the column of liquid in the tube was about 1,000 times that of a cross section, 1cm. in length of the liquid in the box, slight differences in placing the electrodes made no appreciable difference in the resistance of the box.

The part of the box above the surface of the liquid (especially that of the glass partition) was kept clean and dry, and, during the experiments, except where the narrow strips of the electrodes projected upwards, the box was kept covered.

With this cell (1) it was the same liquid, whose resistance was measured whether the platinum or zinc electrodes were used, and (2) the tube being in the centre of a large mass of liquid, that liquid being approximately at the temperature of the laboratory, and the time intervening between two measurements, one by platinum the other by zinc electrodes, being small, any change in the resistance due to change in temperature might be neglected.

The box of resistance coils used was a small one. The coils were arranged so as to form three arms of a Wheatstone's Bridge. Two of them contained two coils each, 10 and 100 Siemens units respectively. The third contained a number of coils ranging from 500 to 1 Siemens units, together with a rheochord for measuring fractions of a unit. The coils had been accurately calibrated in Legal Ohms by White, of Glasgow.

The Galvanometer used was a "dead beat" one of Lord Kelvin's, having a resistance of 400 ohms. The mirror, with magnets attached, weighed 0.035 grms.

For making and breaking contact I used a "rocker," like that described by Ewing and MacGregor in the paper referred to above. It was so designed that the battery wire was joined up a small fraction of a second before that of the Galvanometer.

I found that I was unable with any certainty to detect the vanishing of the hesitation. To my eye it did not seem to vanish even when the adjustment of the arms indicated less than the actual resistance of the cell. The motions of the magnet certainly became quicker then, but none the less did I think I could detect a hesitation. Nor is this other than we would expect. The current must always act for a certain time before any appreciable motion of the mirror occurs. The length of this time will vary with the strength of the current. With a weak current the magnet always starts slowly, while with a strong current it may seem to start almost instantaneously. With a certain current and a certain resistance of our cell, there will be a particular hesitation corresponding to the adjustment of the arms indicating the exact resistance of the cell. With considerable practice we may train the eye to recognize this particular hesitation, so that, within a short range of this resistance of the cell, we may be able to make almost perfect measurements. This was the only way in which I was able to use Prof. MacGregor's method and the result was unsatisfactory. For when the resistance of the cell was changed to any extent, the strength of the current changed and I found that my familiar hesitation was no longer that which corresponded to the adjustment of the arms indicating the resistance of the cell.

In my experiments I noticed, however, what is clearly evident, that, the stronger the currents, the greater was my double deflection, that if, for certain resistances of the arms, with a certain current I could get a double deflection, then with a stronger current I would get a larger deflection, and, what to me was more important, if, in the former case, the double deflection had just vanished, in the latter case it was distinctly visible. I immediately tried still stronger currents and found that in every case the stronger the current the nearer would the adjustment of the arms, when the double deflection had just vanished, indicate the true resistance of the cell. It appeared, therefore, that I had merely to increase the strength of the current to make my error as small as I pleased.

In attempting this, however, difficulties arose:

(1.) As the battery current was increased, so was the polarization current. To lessen this my electrodes were made as large as possible. As I have stated above, they were about 7 cm. square. I might have platinized them, after the manner of Kohlrausch; but as the method under consideration, owing to the simplicity of apparatus required, is especially useful for measuring resistances of electrolytes in ordinary laboratory work, I was more interested in knowing what degree of accuracy was attainable by it with apparatus which is always at hand.

(2.) Since the motions of the mirror are indicated by those of the spot of light reflected from it to a screen, in proportion as the double deflection gets smaller and smaller, the difficulty in observing it gets greater and greater. Especially is this so if the current be strong, for then the motions of the spot become so rapid that, unless the double deflection is distinctly made, we are not able to observe it. This difficulty I completely removed by placing a rectangular sheet of zinc three or four inches in front of, and hiding from my eye, the left side of the screen. It was easy to place this so that, on looking past its right edge, I could just see the faintest glimmer of the spot of light. Since I always sent the current in such a direction that the double deflection was to the right, it is evident that even the least tremble of the spot to the right could be at once observed. More especially was this so, as the sheet of zinc was much nearer to the spot of light than to my eye. It is necessary, of course, that the edge of the spot of light that we are observing should be very clearly defined, and that no motion of the head should be made at the instant of observation.

(3.) With strong currents electrolysis of the solution goes on at a rapid rate, and, again, there is danger of the coils becoming heated. During the final measurements, then, when we are using the strongest currents, contact in the battery wire must last only for a small fraction of a second. The "rocker," thus, became too slow a means of making and breaking contact. By joining up the Galvanometer first and by a separate key (a method to be justified later) the solution of this difficulty became easy, for then we have only to make and break contact rapidly in the one wire. This I accomplished by slightly flattening a piece of thick copper wire, and sinking it into a board till its flattened surface was only slightly above that of the board. This wire I connected with one of the battery wires. The end of the other battery wire I flattened, and by simply drawing it over the board and across the wire, contact could be made and broken as rapidly as desired.

I found it quite impossible, as did Ewing and MacGregor, and Professor MacGregor, to obtain platinum electrodes which, in themselves, did not constitute a voltaic cell. In every case my electrolytic cell was found to be a voltaic cell with a small and, apart from polarization, practically constant E. M. F. It is evident that, with this method, the adjustment of the arms which would give no double deflection, would not be exactly the same as if the electrolytic cell were not behaving as a voltaic cell.

Both Ewing and MacGregor, and Prof. MacGregor overcame this difficulty in this way. Call *e* the E. M. F. of the cell. Pass a current through the cell in such a direction as to produce a polarization current greater than, and opposite in direction to, that produced by *e*. Then, as this polarization slowly dies away, there will be a short time during which it will neutralize *e*. During that time they considered that the test could be made without error due to *e*.

To this procedure there are objections. In order to produce the necessary polarization so that it will die away slowly, the current must pass for a certain time, and thus a certain amount of electrolysis goes on—the more, the stronger the current. Then there is the great difficulty in making the test at the instant at which *e* is exactly neutralized. In my very many trials, I am not certain that I succeeded in making one test with which I was perfectly satisfied. In any case we do not entirely eliminate error due to *e*. For we have neutralized *e* only by covering our electrodes with gas, which must make the resistance of our cell appear greater than it really is. Since, however, *e* can always be made very small, this error is, in practice, negligible.

In his paper, Prof. MacGregor pointed out one result of which he made no use, but which suggested to me an easier solution of this difficulty. What he showed was, in effect, that if the Galvanometer wire be joined up first and the spot of light be allowed to take up a new position due to *e*, and if the adjustment of the arms corresponds to the exact resistance of the cell, then, on making contact in the battery wire, the current through the Galvanometer due to *e* will remain unaltered. It seems reasonable to suppose therefore that, if the adjustment of the arms nearly corresponds to the exact resistance of the cell, and if *e* be very small, then, under these circumstances, any change in the current due to *e* flowing through the Galvanometer, which occurs when contact is made in the battery wire, will be very small. If then we should join up the Galvanometer wire first and make our measurements as if *e* had the value zero, would the error be negligible ?

To test this, I simply made several measurements, first by this method, and then by neutralizing *e*. I varied both the size and the direction of *e*, but, in no case, was I able to notice any difference in the two measurements.

To proceed in this way, however, the Galvanometer must be joined up first. Rigorously this will not give accurate results; for the principle on which measurement of resistances by Wheatstone's Bridge rests, requires that the current shall have attained a steady value. Whether, practically, with circuits such I was using, any error would be introduced by this method, could be decided only by experiment. To test this, I simply measured the resistance of a solution of zinc sulphate, using amalgamated zinc electrodes, first joining up the battery wire before the Galvanometer wire, and then *vice versa*. The experiments that I made perfectly satisfied me, that the error, if there was one at all, was clearly negligible.

During my experiments the resistance of my cell varied from 100 to 10,000 Legal Ohms. The accuracy with which I could determine the resistance is shown in the following table, which gives a few average results:—

No. of Grove's Cells used.	Resistance as determined by		Error.
	Amal. Zn. Electrodes.	Pt. Electrodes.	
1.	6360 Legal Ohms.	6430 Legal Ohms.	1.1 %
2.	6360 "	6420 "	.94 %
3.	6360 "	6407 "	.74 %
8. of low internal resistance.	177.3 Legal Ohms.	178.2 Legal Ohms.	.51 %
	634.9 "	637.8 "	.46 %
	1893 "	1900 "	.37 %
"	4585 "	4595 "	.22 %
"	7439 "	7450 "	.15 %
"	9139 "	9151 "	.13 %

As stated above, Professor MacGregor's error in the measurements of high resistances varied from 0.1 to 0.4 per cent. With low resistances, however, his error was as great as 6 or 7 per cent. The first three entries of the above table show, then, that, with a comparatively weak battery as current generator, the errors in the resistances determined by employing the vanishing of the double deflection as test of adjustment, are comparatively large, considerably larger than they would be according to Professor MacGregor's experience, if the vanishing of the hesitation were taken as the test. The last seven show that, with a strong current, the employment of the vanishing of the double deflection as test of adjustment gives results which, in the case of high resistances, are considerably more accurate, and in the case of low resistances very much more accurate than those given by a weak battery with the vanishing of the hesitation as test.

It would thus appear that the above modifications render this method capable of measuring all resistances with increased accuracy and low resistances with greatly increased accuracy, while they render it also capable of application without any previous training of the eye, and diminish very materially the time required for its application. The error in the measurement of high resistances is still greater than that of Kohlrausch's method, viz., 0.05 per cent. The only mirror, however, which was available for my experiments, though it weighed but 0.035 grms, was much heavier than some which I believe are now manufactured. With a lighter mirror the inevitable error would doubtless be still further diminished.