LXXX.—*Notes on the Determination of the Electrical Conductivity of Solutions.*

By HAROLD HARTLEY and WILLIAM HENRY BARRETT.

IN a series of experiments preliminary to the determination of the temperature-coefficients of the electrical conductivity of dilute salt solutions, the resistance of a solution was measured both with a commutator of the pattern described by Whetham (*Phil. Trans.*, 1900, *A*, **194**, 321) and with a telephone and induction coil. As the latter method appeared to give a lower value for the resistance, a careful comparison of the two methods has been made. The results show that they do not yield the same value for the resistance, and that the ratio of the resistances found by them varies (1) with the construction of the commutator, (2) with the rate at which the commutator is driven, (3) with the magnitude of the resistance to be measured, (4) with the form of the cell.

In the course of the work a new form of conductivity cell was devised for use with dilute solutions, which possessed several advantages over the usual patterns, and has since been found most useful in the investigation of both aqueous and non-aqueous solutions.

Comparison of the Values found for the Electrical Resistance of a Solution by the Commutator and Telephone Methods.

The resistance of solutions of potassium chloride (approx. 0.001*N*) was measured between three pairs of platinum plates: (*a*) a pair of small plates (area 2.5 sq. cm.) coated with platinum black, and placed close together in a cell of the Arrhenius pattern; and (*b*) and (*c*) two separate pairs of platinum plates of a larger size (area 6 sq. cm.) coated with grey platinum obtained by heating platinum

black to dull redness (Whetham, *loc. cit.*, p. 329) in a large cell containing 1500 c.c. of solution. The solutions being so dilute, special precautions were taken to protect them from contamination with impurities during the measurements, and the resistance of the solutions was tested at the end of each experiment by the method in use at the beginning, in order to see that it had not varied.

In the first set of experiments the results obtained with a double pole Bell telephone of the ordinary pattern and a small induction coil were compared with those obtained with a rotating commutator with eight sectors and insulated strips separating each pair. The commutator was driven by a small motor, and the speed was altered by varying the resistance in the motor circuit. A Nalder galvanometer was used as a current detector. The bridge consisted of three metres of wire wound on a marble drum, with extensions which increased its effective length to 30 metres. An accumulator was used as the source of current with the rotating commutator, a resistance of 2000 ohms being placed in the battery circuit.

TABLE I.
Resistances in Ohms.

Electrodes.	By telephone.	By commutator.		r_2/r_1 .	r_3/r_1 .
		High speed.	Low speed.		
A. Black Pt ...	237.51	238.77	238.60	1.0053	1.0046
B. Grey Pt ...	1391.6	1401.2	1399.4	1.0069	1.0056
C. „ Pt ...	2264.7	2277.6	2274.3	1.0057	1.0042

These results show that the telephone gives a lower value for the resistance than the commutator, and that the value of the resistance found by the latter depends to a small extent on the rate at which the commutator is driven. An increase of speed, that is, an increase in the number of alternations per minute and a decrease in the length of time during which a direct current flows through the solution, leads to a lower value for the resistance.

In some further experiments, in which the largest resistance measured was 2200 ohms, it was found (1) that if the electrolytic resistance is measured by a telephone and induction coil, the result is independent of the note the telephone is giving, and does not vary with different telephones and coils, and (2) that if two wire resistances not exceeding 4000 ohms are compared with a rotating commutator, the result is independent of the rate at which the commutator is driven, and is identical with the result obtained with a telephone.

A further comparison was made with the same pairs of electrodes in solutions of potassium chloride of nearly the same strength by three independent observers (Mr. T. S. Moore and the authors), in order to eliminate the effect of personal error; individual results never differed from one another by more than five parts in ten thousand, and usually agreed more closely. To increase the value of the comparison, a different pattern of commutator, kindly lent by Mr. B. Lambert, was also used. It was made with only two sectors. The number of alternations was determined by means of a revolution counter. The resistance in the battery circuit in all the commutator measurements was 700 ohms. The results are given in the following tables:

TABLE II.
Resistances in Ohms.

	By telephone, r_1 .	By commutator (two sectors).		By commutator (eight sectors).			
		2200 alts. r_2 .	2750 alts. r_3 .	2640 alts. r_4 .	3200 alts. r_5 .	5700 alts. r_6 .	6500 alts. r_7 .
A.	236.94	238.65	238.69	238.24	—	—	237.74
B.	1388.6	1400.6	1399.0	1395.6	1394.8	1394.0	1392.2
C.	2260.9	2277.5	2275.6	2271.4	—	—	2266.2

Ratios of Resistances Determined by Telephone and Commutator.

	r_2/r_1 .	r_3/r_1 .	r_4/r_1 .	r_5/r_1 .	r_6/r_1 .	r_7/r_1 .
A.	1.0072	1.0074	1.0055	—	—	1.0034
B.	1.0086	1.0075	1.0050	1.0045	1.0039	1.0026
C.	1.0073	1.0065	1.0046	—	—	1.0023

These results agree with those obtained in the preliminary series. Using the eight-sector commutator at 2600 revolutions per minute, the resistance with each kind of plate is, roughly, 0.5 per cent. higher than that found with the telephone. As the number of revolutions increases, the resistance appears to diminish, and its value approaches that found with the telephone. The higher the resistance the more closely does the resistance measured by the commutator agree with that found by the telephone. However, in some later experiments with Mr. Bourdillon, when higher electrolytic resistances (up to 250,000 ohms) were measured by both methods, large differences, amounting in some cases to 5 per cent., were observed.

Conductivity Cell for Use with Dilute Solutions.

In order to determine the conductivity of aqueous solutions more dilute than 0.001*N*, when the conductivity of the solvent under the best conditions amounts to 1 or 2 per cent. of the conductivity of

the whole solution, it is necessary to start with a considerable quantity of the solvent (compare Whetham, *loc. cit.*; Kohlrausch and Maltby, *Wiss. Abh. Phys. Tech. Reichsanstalt*, **3**, 157) in a cell which protects it from contamination with the air, and to add to it from weight- or volume-pipettes successive small quantities of a solution of the electrolyte under examination.

It must be possible to make these additions and to stir the contents of the cell without any risk of introducing impurities from the air. These conditions are fulfilled by the cell shown in the figure. It is made entirely of boro-silicate glass, and holds about 300 c.c. of solution. The tubes carrying the platinum are fused through

the cap of the cell, and the electrodes are held firmly together by small rods of glass fused on at the corners. They are covered with grey platinum (obtained by heating platinum black to redness) to avoid occlusion by platinum black (compare Whetham, *loc. cit.*, p. 329). The water or solution can be stirred by rotating the cap of the cell; the holes in the electrodes shown in the figure ensure the stirring of the solution between the plates even when they are within a few mm. of one another. The tap *A* admits a current of air freed from carbon dioxide and ammonia by passing through sulphuric acid and over soda-lime, and then through water to saturate it with water vapour.

At the beginning of an experiment the cell is cleaned with

conductivity water and dried, and a current of purified air passed through for some minutes. It is then weighed, and conductivity water is run in through the opening *B* until the surface reaches an etched mark on the cell. The mark is placed at such a height above the electrodes that the cell constant does not vary when small quantities of solution are added to the solvent. The cell is then weighed again to ascertain the weight of water it contains, and put into the thermostat. The water is stirred, and its resistance measured from time to time. Any change in the resistance that may have taken place after the temperature of the water has reached the temperature of the bath is due either to the solubility of the glass, to the solution of electrolytes absorbed by the electrodes, or to the exchange of volatile impurities with the air in contact with the water. If the resistance is falling, it is a good plan to pass in a little purified air, the cap at *B* being removed for a few seconds; this will often stop the fall and cause the resistance to rise. When the resistance of the solvent water is steady, small measured quantities of a solution of the electrolyte to be studied are run in from a weight- or volume-pipette, a slow current of purified air being admitted at *A* so as to prevent atmospheric impurities from entering the cell while the addition of solution is being made.

The following series of measurements show that the constancy of the solvent resistance can be maintained for a considerable time with water which has a specific conductivity of approximately 1 gemmho (1×10^{-6} reciprocal ohms).

Time, hrs. mins.	Resistance, in ohms.	Time, hrs. mins.	Resistance, in ohms.
— —	30400	19 —	30800
— 20	30500	19 30	30800 X
— 22	30500 X	20 —	30900
— 25	30500	21 —	30900 X
— 28	30600	22 —	30900 X
— 30	30600	23 —	30800

At points marked X the cap *B* was removed, and a slow current of air admitted at *A*, in order to show that portions of solution could be added without changing the resistance of the solvent.

Using water with a conductivity as low as 0.11 gemmho, Mr. Bourdillon found that the average rise per hour was 0.004 gemmho when the electrodes had not been in contact with a salt solution for some time, and 0.01 gemmho when they had been soaked for twelve hours in pure water after use with 0.05*N*-solution of potassium chloride.

In order to allow the cap of the cell to rotate easily and to ensure good stirring, the ground joint is lubricated with a little vaseline

previously purified by being heated with conductivity water to remove traces of organic acids. Care must be taken always to set the cap of the cell in the same position; for this purpose marks are etched on the edge of the cap and on the neck of the flask, and these are brought into coincidence. Since the cap is ground on outside the neck of the flask, there is no fear of dust falling in while the cap is being rotated.

The authors have pleasure in acknowledging their indebtedness to a grant from the Research Fund of the Royal Society, from which much of the cost of the apparatus used in this work was defrayed.

PHYSICAL CHEMISTRY LABORATORY,
BALLIOL COLLEGE AND TRINITY COLLEGE,
OXFORD.