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A CONDUCTIVITY CELL FOR ELIMINATING ELECTRODE EFFECTS IN MEASUREMENTS OF ELECTROLYTIC CONDUCTANCE

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The electrolytic conductivity of a solution is ordinarily determined by measuring its resistance, with alternating current, in a cell previously calibrated with a solution having a known specific conductance. The product of this specific conductance and of the corresponding cell resistance is the "cell constant." Values of the specific conductance of other solutions are obtained by dividing the cell constant by the resistance measured in the cell.

Parker[1] has compared measurements on solutions of potassium chloride and hydrochloric acid, obtained in several cells over a range of concentrations. He found that determinations with different cells would lead to somewhat different conductance values. That is, there seemed to be an apparent variation in "cell constant" when the nature or concentration of the measured solutions was varied. Randall and Scott[2] found similar variations on measuring in two cells the conductance of solutions of several substances. These workers found very surprising variations, which in some cases were as high as 0.5%. Such large variations evidently make precision work impossible, and the following study was made with the purpose of eliminating them.

We have made a number of intercomparisons between several cells and have also observed apparent variations in cell constants, although considerably smaller ones than those found by the above investigators. In our work the variations were never greater than 0.2% with bright platinum electrodes, and were always under 0.1% with platinized electrodes. This smaller variation is due, we believe, to the fact that our measurements were made with a bridge[3] which gave readings free from certain sources of error possible in the arrangements these workers used.

Parker has suggested that the variations of cell constants are due to adsorption at the electrode. However, adsorption would be less on bright electrode surfaces, which, as we have just seen, give the largest variations. Therefore, adsorption cannot entirely account for the observations. In addition, the bridge readings with bright electrodes showed fluctuations of a nature suggesting variable polarization effects. Such fluctuations disappeared when the electrodes were lightly platinized, but it is quite pos-

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[1] Parker, THIS JOURNAL, **45**, 1366, 2020 (1923).

[2] Randall and Scott, *ibid.*, **49**, 636 (1927).

[3] Shedlovsky, *ibid.*, **52**, 1793 (1930).

sible that such polarization was made constant by this procedure, rather than eliminated.

In this paper is described a cell which was designed for studying means of eliminating any effects at the electrodes which would disturb conductance measurements. The results of test measurements with the cell are also reported. To anticipate the conclusions, these results indicate that cell constant variations disappear if electrode effects are completely eliminated.

The Cell

The cell is shown diagrammatically in Fig. 1. It is provided with two end, or conducting, electrodes O and D, and the three loop, or detector, electrodes a, b and c. The electrodes O and D are hollow cones of platinum foil, made as nearly alike as possible, and a, b and c are loops of platinum wire. All the electrodes are sealed directly to the inner surface of the cell and are very lightly platinized. The cell is constructed from Jena glass 16^{III}, which may be sealed directly to platinum. This glass also has a very low solubility.

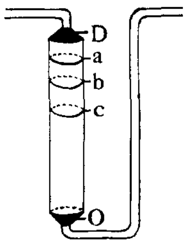

Fig. 1.

Such a cell may be connected into the Wheatstone bridge circuit in a number of different ways. For instance, measurements may be made in the ordinary manner between various electrode pairs. We have used the pairs OD, ab, bc, and ac in this way. This is obviously equivalent to an intercomparison between four ordinary cells. One of the purposes of this investigation was to see whether variations of the cell constant would disappear if similar electrodes were included in two arms of the bridge during measurement. The arrangement is shown in Fig. 2. It was hoped that the disturbing variations would be eliminated if measurements were made with one of the loop electrodes (a, b or c) connected to the detector, electrode O to one end of the current source, and the electrode D to a resistance box in the other arm of the bridge. Thus, for example, the portion of the cell (aO) with the electrode effect from O is balanced by the resistance box in series with the electrode effect from D, and the portion of the cell (aD) K is the condenser for balancing the resistances in the two arms, and the two 1000-ohm coils are the ratio arms. This particular arrangement we have called [a]. [b] and [c] are similar arrangements with the detector connected to (b) or (c) instead of to (a).

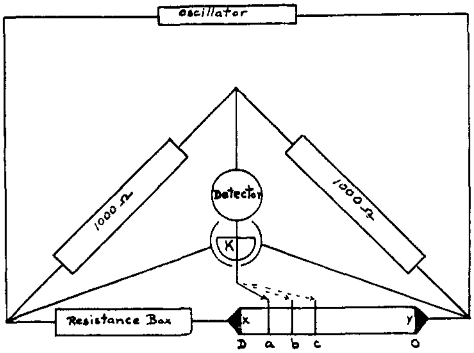

Fig. 2.

Parker,[1] who has made some excellent determinations of absolute conductance values for potassium chloride solutions, partially corrected for electrode effects by subtracting measurements made in two different cells provided with similar electrodes. He hoped that the electrode effect would be eliminated from the measurements if all determinations were made with the same two cells and the difference between the two readings were always taken as the resistance value. This would be so if the electrodes in the two cells behaved in exactly the same manner in all measurements. The method of making measurements by arrangements [a], [b] and [c] was chosen for obtaining directly the results given by Parker's two cell scheme. The difference between two of our measurements, ab, ac, bc, using the various pairs of loop electrodes as ordinary cells, corresponds to Parker's actual scheme. In Table II these arrangements are represented by (ac)–(ab) and (ac)–(bc).

Referring once more to Fig. 2, let us call x the effect on the resistance due to the electrode D, and y the effect due to the electrode O. The current density at these electrodes depends on whether the detector is connected to a, b or c; that is, on the resistance between the detector electrode and the current source terminals, other things being equal. We found that a ten-fold change in current density attained by altering the voltage supplied to the bridge had no effect on the value of a particular measurement, so that it is fair to assume that x and y remain essentially the same whether the detector is connected to a, b or c. Let us call R_a, R_b, R_c the resistance box readings for the arrangements [a], [b] and [c], respectively. Since the loop or detector electrodes draw no current when the bridge is balanced, it seems plausible to assume that there is no effect at such electrodes that influences the readings.

We can write the following equations representing the conditions of balance in our bridge for the arrangements [a], [b] and [c]

$$\begin{array}{ll}
[\mathrm{a}] & R_{\mathrm{a}} + x + \rho_{\mathrm{Da}} = \rho_{\mathrm{oa}} + y;\ R_{\mathrm{a}} = \rho_{\mathrm{oa}} - \rho_{\mathrm{Da}} + y - x \\
[\mathrm{b}] & R_{\mathrm{b}} + x + \rho_{\mathrm{Db}} = \rho_{\mathrm{ob}} + y;\ R_{\mathrm{b}} = \rho_{\mathrm{ob}} - \rho_{\mathrm{Db}} + y - x \\
[\mathrm{c}] & R_{\mathrm{c}} + x + \rho_{\mathrm{Dc}} = \rho_{\mathrm{ao}} + y;\ R_{\mathrm{c}} = \rho_{\mathrm{ac}} - \rho_{\mathrm{Do}} + y - x
\end{array}$$

where ρ_{Da} is the resistance of the solution between D and a, etc. The actual reading observed, for instance R_a, corresponds to the difference between the two fixed portions of the solution Oa and Da, modified by the effects from the electrodes. If $x = y$, this method of measuring conductances is free from these electrode errors. However, if x and y are not equal, the electrode effects can be entirely eliminated by taking the difference between any two of the measurements [a], [b] and [c]. Thus

$$\begin{array}{ll}
[\mathrm{a}] - [\mathrm{b}] & R_{\mathrm{a}} - R_{\mathrm{b}} = \rho_{\mathrm{oa}} - \rho_{\mathrm{ob}} + \rho_{\mathrm{Da}} + \rho_{\mathrm{Db}} = 2\rho_{\mathrm{ab}} \\
[\mathrm{a}] - [\mathrm{c}] & R_{\mathrm{a}} - R_{\mathrm{c}} = 2\rho_{\mathrm{ac}} \\
[\mathrm{b}] - [\mathrm{c}] & R_{\mathrm{b}} - R_{\mathrm{o}} = 2\rho_{\mathrm{bo}}
\end{array}$$

Thus, for instance, the difference $R_a - R_b$ is equal to twice the resistance of the solution between a and b, without error due to effects at the conducting electrodes.

The Measurements

Measurements were made with the cell described in the various ways discussed above. Four series were carried out at 1000, 2000 and 3000 cycles. First the cell was filled with potassium chloride solution (approx. 0.005 *N*) and then with three different concentrations of hydrochloric acid (approx. 0.001, 0.002 and 0.004 *N*). The cell was immersed in an oil thermostat which maintained a temperature regulation accurately to ±0.001°. The temperature was measured with a platinum resistance thermometer sensitive to about 0.0002°. A shielded bridge, described in another paper,[3] supplied with current from a balanced vacuum valve oscillator, and a detector amplifier was the measuring apparatus. The resistance box used in the measurements was calibrated to 0.01%.

The data are summarized in Tables I and II. The figures shown in Table I represent the resistances corresponding to the various arrangements when the cell was filled with approximately 0.005 *N* potassium

TABLE I

RESISTANCES WITH (APPROX.) 0.005 *N* POTASSIUM CHLORIDE

	1000 cycles	2000 cycles	3000 cycles
OD	8118.9	8118.9	8118.8
ab	1161.0	1160.6	1160.4
bc	1206.9	1206.6	1206.5
ac	2030.0	2029.6	2029.4
ac − ab	869.0	869.0	869.0
ac − bc	823.1	823.0	822.9
[a]	6064.3	6064.0	6063.6
[b]	4414.6	4414.4	4413.9
[c]	2705.8	2705.5	2705.1
[a] − [b]	1649.7	1649.6	1649.7
[a] − [c]	3358.5	3358.5	3358.5
[b] − [c]	1708.8	1708.9	1708.8

TABLE II

RESISTANCE RATIO VALUES

	$\frac{\text{Resistance HCl (concn.)}}{\text{Resistance KCl (approx. 0.005 }N)}$				Top value, 1000 cycles; middle value, 2000 cycles; bottom value, 3000 cycles	
	C = approx. 0.004 *N*	% error	C = approx. 0.002 *N*	% error	C = approx. 0.001 *N*	% error
	0.42605	−0.03	0.83440	−0.01	1.6763	−0.02
OD	.42605	− .03	.83437	− .02	1.6760	− .04
	.42604	− .03	.83437	− .02	1.6756	− .07
	....	....	.83437	− .02	1.6755	− .07
ab	.42618	+ .01	.83448	....	1.6759	− .05
	.42620	+ .01	.83454	....	1.6760	− .04
	....	....	.83429	− .02	1.6760	− .04
bc	.42616	....	.83441	− .01	1.6762	− .03
	.42619	+ .01	.83448	....	1.6763	− .02
	....	....	.83439	− .01	1.6760	− .04
ac	.42612	− .01	.83445	− .01	1.6762	− .03
	.42613	....	.83439	− .01	1.6764	− .02

TABLE II (*Concluded*)

	C = approx. 0.004 N	% error	C = approx. 0.002 N	% error	C = approx. 0.001 N	% error
	....	....	0.83437	−0.02	1.6767	....
ac − ab	0.42602	−0.03	.83437	− .02	1.6772	+0.03
	.42591	− .06	.83414	− .04	1.6768	....
	.42604	− .03	.8345	....	1.6761	− .04
ac − bc	.42604	− .03	.8345	....	1.6761	− .04
			.8342	− .03	1.6765	− .01
	.42599	− .04	.83438	− .01	1.6774	+ .04
[a]	.42601	− .03	.83440	− .01	1.6763	− .02
	.42604	− .03	.83442	− .01	1.6762	− .03
[b]	.42591	− .06	.83437	− .02	1.6762	− .03
	.42593	− .05	.83436	− .02	1.6761	− .04
	.42595	− .05	.83439	− .01	1.6760	− .04
	.42579	− .08	.83425	− .03	1.6760	− .04
[c]	.42584	− .07	.83426	− .03	1.6758	− .05
	.42590	− .06	.83428	− .03	1.6755	− .07
	.42618	+ .01	.83446	....	1.6767	....
[a] − [b]	.42618	+ .01	.83445	....	1.6767	....
	.42618	+ .01	.83448	....	1.6767	....
	.42615	....	.83450	....	1.6767	....
[a] − [c]	.42615	....	.83451	....	1.6767	....
	.42615	....	.83450	....	1.6767	....
	.42611	− .01	.83456	....	1.6767	....
[b] − [c]	.42611	− .01	.83452	....	1.6767	....
	.42610	− .01	.83454	....	1.6767	....
Correct value taken	.42615		.83450		1.6767	

chloride. Table II gives the corresponding resistance ratio, *i. e.*, $R_{\text{HCl (c)}}/R_{\text{KCl (0.005 }N\text{, approx.)}}$ for the three hydrochloric acid solutions measured.

These values are, therefore, proportional to the specific resistance of the three hydrochloric acid solutions as obtained from the various types of measurements, after calibrating with a potassium chloride solution.

It is evident that the arrangements [a] − [b], [a] − [c], [b] − [c], which are free from conducting electrode effects, as shown above, give the most consistent values. These figures show practically no variations with frequency, nor of "cell constant," the average deviation being within 0.01%, which is the precision to which the resistance box is calibrated. We have, therefore, assumed as correct the values obtained by making measurements in this manner. The percentage error of the values obtained from the other arrangements on this basis is indicated in Table II to the nearest 0.01%.

Discussion

Since electrodes O and D were made as nearly alike as possible both in construction and in the subsequent platinizing, we should expect smaller variations in the arrangements [a], [b] and [c] in which these two electrodes are in opposite arms of the bridge than in the ordinary arrangement OD, if the cause of the variations is due to simple adsorption. This does not seem to be generally true, which suggests that besides adsorption there is superimposed another effect. Referring to the equations [a], [b] and [c], the results seem to indicate that x and y may have opposite signs, so that their effect on the measurements may increase instead of decreasing when they appear in opposite branches of the bridge. Such may be the case if there is a definite difference between the rates of building up and decaying of the e. m. f. at the electrode surfaces for the oxidation and reduction parts of the current cycle.

It appears from our results that conductance values, free from errors due to effects at electrodes which tend to change the apparent cell constant, can be obtained with a four electrode cell. The measurements for the arrangements [a] — [b], [a] — [c] and [b] — [c] represent a comparison between three such four electrode cells and lead to consistent conductance values.

Cells of the ordinary type (with two electrodes), which may be more convenient for routine work, can be calibrated by comparison with a four electrode cell.

Summary

1. A multiple electrode cell for studying the elimination of electrode effects in conductance measurements is described.

2. Data obtained with one potassium chloride solution and three hydrochloric acid solutions of different concentrations, using various measuring arrangements of electrodes, are given for three frequencies.

3. The assumption of adsorption at the electrodes does not entirely explain the variations in "cell constant" which are observed.

4. A four electrode arrangement is found to give consistent results at the three frequencies without variations in "cell constant."

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