[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of the Conductance of Electrolytes. VI. Galvanic Polarization by Alternating Current

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Introduction

This study of galvanic polarization with alternating current of audio frequencies was undertaken as a part of a comprehensive investigation of the measurement of the conductance of electrolytes.[1] The original incentive was to determine the wisdom and adequacy of the various experimental precautions which may be used as a means of avoiding or minimizing errors due to polarization in the measurement of conductance. For this purpose it seemed desirable to obtain a better understanding of the phenomena, which are of considerable interest for their own sake. A detailed review of the extensive earlier literature must be omitted for the sake of brevity. Only a brief outline of the conflicting ideas and conclusions in a few of the more important of the earlier papers can be given as a means of stating the problem before us.

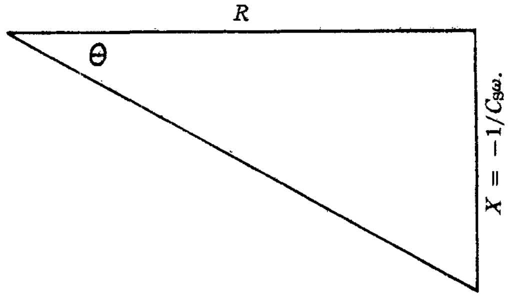

Fig. 1.

Kohlrausch[2] believed that when an alternating current is passed between inert platinum electrodes, hydrogen and oxygen gases are deposited on the electrodes alternately in every cycle and that the electrolysis is strictly reversible both chemically and thermodynamically at all frequencies. This reversible transformation of electrical energy into chemical energy would be electrically equivalent to a large electrostatic condenser, whose capacitance may be designated as C_S, in series with the resistance of the electrolyte. It would cause a reactance, $X = -1/C_S\omega$ which although small is not zero, and a phase displacement across the cell, $\theta = \tan^{-1}(-1/RC_S\omega)$. This point of view is shown in the conventional vector diagram used in alternating current theory.

If these views of Kohlrausch really represent the whole truth accurately the effects of this polarization capacitance and reactance on the measurement of the conductance of electrolytes with a Wheatstone bridge could be compensated completely by the introduction of a corresponding capacitative reactance in an adjacent arm of the bridge or a compensating inductive reactance in the same arm of the bridge so that polarization would cause no error in the measured resistance. For this purpose Kohlrausch[3] connected an electrostatic condenser in parallel with the resistance box in another arm of the bridge and this device helps so much that it is now almost universally used and is considered an essential part of the Kohlrausch method.

However, Kohlrausch found that this device was not by itself sufficient to prevent errors due to polarization in resistance measurements and adopted the following experimental devices which he found empirically to be necessary to obtain consistent results, (a) the platinization of the electrodes, (b) an increase of the frequency to 1000 cycles per second or more, (c) the use of large (1 sq. cm. or more) electrodes, (d) the design of the cell so that the resistance to be measured would be high (100 ohms or more). Kohlrausch's[4] practice was better than his theory. Although none of these devices should be needed if his theory were correct, he defended his theory and experimental technique against criticisms by his contemporary, Wien.

Max Wien[5] demonstrated experimentally that with nickel, or silver, or smooth platinum, or mercury electrodes, polarization causes an increase in apparent or measured resistance, ΔR

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(1) Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928); Grinnell Jones and G. M. Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411, 1207 (1931); Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

(2) F. Kohlrausch, *Pogg. Ann.*, **148**, 143 (1873); Jubelband, 290 (1874); F. Kohlrausch and W. A. Nippolt, *ibid.*, **138**, 280 (1869). A clearer statement of Kohlrausch's views is given in the book by Kohlrausch and Holborn, "Leitveermögn der Elektrolyte," published by Teubner, Leipzig, 1898, pp. 56, 65.

(3) F. Kohlrausch, *Wied. Ann.*, **49**, 249 (1893); **56**, 182 (1895).

(4) F. Kohlrausch, *ibid.*, **58**, 514 (1896); **60**, 315 (1897).

(5) Max Wien, *ibid.*, **58**, 37 (1896); **59**, 267 (1896); *Drude Ann Physik*, **8**, 372 (1902).

which cannot be eliminated by the use of a condenser. He found the polarization resistance, ΔR, to be inversely proportional to the area of the electrodes, and independent of the current density up to about 0.0015 amp./sq. cm., and independent of the frequency between the limits $f = 64$ and 256 cycles per second. He found the polarization capacitance, C_S, to be proportional to the area of the electrodes, and independent of the current density and nearly independent of the frequency, although C_S decreased slightly with increasing frequency. He believed that the incomplete reversibility of the electrode processes is responsible for the polarization resistance. Wien's views may be represented diagrammatically in Fig. 2.

γ may be regarded as the phase displacement across the electrodes, which should not be confused with the phase displacement across the complete cell, θ. If ΔR were zero, γ would be $-90°$; ψ the complement of γ therefore represents the change in the phase displacement across the electrodes due to the irreversibility of the electrode processes, or as Wien expresses it to "spontaneous depolarization." The product, $\Delta RC_S\omega = \tan\psi$, was found to be independent of the area of the electrodes, the current density, and the frequency, and nearly independent of the concentration of the solution but greatly dependent on the particular metal and on the electrolyte used.

Warburg[6] suggested and developed the idea that diffusion is responsible for the incomplete reversibility of the electrode reactions. By the integration of Fick's law of diffusion with suitable boundary conditions he reached the conclusion that polarization causes a capacitance in series with the resistance of the cell and that the capacitance varies inversely with the square root of the frequency and that there is a phase displacement of 45° at the electrodes. According to this theory $\tan\psi = \Delta RC_S\omega = 1$.

Warburg's theory was extended somewhat and tested experimentally by his pupil, Neumann,[6a] who pointed out that if ψ is 45°, $\Delta RC_s\omega = 1$; and if C_S is inversely proportional to the square root of the frequency, then ΔR must also be inversely proportional to the square root of the frequency. The experimental tests of these relationships using mercury and silver electrodes indicated that they are only valid as rough approximations but are obeyed better when the polarization is small than when it is great. The contrasting views of these men are summarized in the table.

SUMMARY OF VIEWS AS TO ALTERNATING CURRENT POLARIZATION

Writer	Phase displacement at electrodes, γ	Series capacitance due to polarization, C_S	Series resistance due to polarization, ΔR
Kohlrausch	$-90°$	Independent of frequency	0
Wien	less than $-90°$, independent of frequency, $\Delta RC_S\omega = k$	Nearly independent of but decreases slightly with frequency	Positive, greatly dependent on metal, varies inversely with frequency, $\Delta R\omega = k$
Warburg	$-45°$ $\Delta RC_S\omega = 1$	Varies inversely as square root of frequency, $C_S\sqrt{\omega} = k$	Positive, greatly dependent on metal, varies inversely as square root of frequency, $\Delta R\sqrt{\omega} = k$

The issues presented here have not been definitely and generally settled by later work. Most of the experimenters have been industrialists interested in the design and construction of electrolytic condensers for use in radio sets or for controlling the phase displacements in telephone or power lines, or physicists who were interested mainly in the capacitance and have devoted little attention to the polarization resistance. The latter is of greater interest to chemists because it probably depends on the incomplete reversibility of the electrode reactions. Among the more important of these investigations are those of Reichinstein,[7a] who introduced the use of an

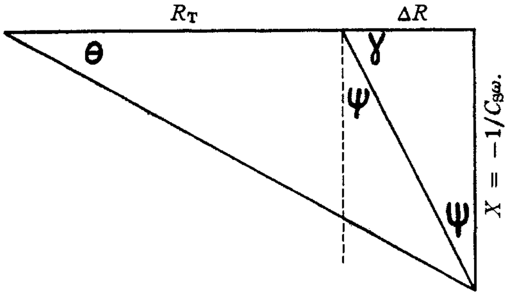

Fig. 2.

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[6] E. Warburg, *Wied. Ann.*, **67**, 493 (1899); *Drude Ann. Physik.* **6**, 125 (1901).

[6a] E. Neumann, *Wied. Ann.*, **67**, 500 (1899).

[7] (a) D. Reichinstein, *Z. Elektrochem.*, **15**, 734, 913 (1909); **16**, 916 (1910); **17**, 85, 699 (1911); **18**, 850 (1912); **19**, 384, 518, 520 (1913); (b) T. R. Rosebrugh and W. Lash Miller, *J. Phys. Chem.*, **14**, 816 (1910); (c) W. Lash Miller and A. R. Gordon, *ibid.*, **35**, 2785 (1931).

oscillograph; Rosebrugh and Miller,[7b] and Miller and Gordon,[7c] who improved Warburg's mathematical analysis but stopped short of the goal.

In addition to the references cited below the work of the following authors should be consulted: Krüger, Günther-Schulze and Shipley.[8]

Carl Miller[9] devised an ingenious new experimental method of attack on the problem. He attached the two electrodes of his cell to a micrometer caliper which made the distance between the electrodes variable and also accurately measurable. When the resistance was plotted against the separation of the electrodes a straight line was obtained which did not pass through the origin. Miller regarded the intercept on the resistance axis as a measure of the polarization resistance, ΔR. Miller also computed the phase angle between the voltage and current at his electrodes and found that this phase angle was nearly independent of the frequency and concentration of the solution, but was not 45° as predicted by the theoretical analyses referred to above. But although Miller has a good idea for a new experimental method, his apparatus had many defects and his data are meager and lacking in precision.

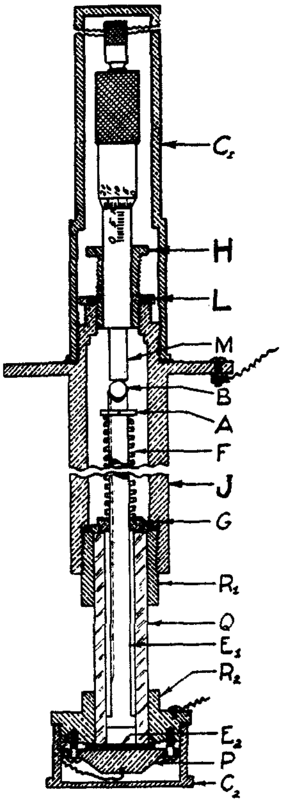

Fig. 3.—Conductance cell with movable electrode.

Experimental

The final form of the cell used for most of our measurements is shown in Fig. 3. The idea of using a micrometer caliper to control and measure the separation of the electrodes was suggested by Miller's paper, but Miller's design was greatly modified to overcome the defects of his cell. A tube of fused quartz, Q, was ground and polished internally to a true cylinder, of internal diameter 0.89 cm., and length 7.5 cm. At each end a threaded brass ring, R_1 and R_2, has been permanently attached by a cement of litharge and glycerol. The lower electrode, E_2, consists of a plate of the desired metal (silver, nickel, platinum, etc.) firmly pressed against the quartz tube by the plate, P, and screws shown. This joint was made perfectly tight by wetting the end of the quartz tube with a solution of rubber in an organic solvent (tire patching cement) and allowing the solvent to evaporate, which gave a tight seal when the metal electrode is pressed against the end of the quartz tube. A threaded cap, C_2, with leather washer protects the electrode from contact with the oil of the thermostat.

The movable electrode, E_1, made of the desired metal (Ni, Ag, Pt) was carefully machined so that the clearance between the electrode and the cylinder was about 0.003 cm. and the end was machined to make it parallel with the lower electrode. The electrode was pushed upward by a coiled spring, F, against the spindle of a Brown and Sharpe precision micrometer caliper, M. The steel ball, B, made it unnecessary to have perfect alignment between the electrode and the caliper and permitted the spindle to revolve without requiring the electrode to revolve. After putting the desired solution into the tube, Q, the electrode was inserted and held in alignment by screwing the nut, G, into the ring, R_1. Then the brass cylinder, J, carrying the micrometer, M, was screwed onto R_1, the joint being made oil-tight by means of a thin leather washer. The upper electrode was then forced downward by turning M until the electrodes were separated by the maximum amount desired for the series of measurements (usually about 3 cm.), and the reading of the scale observed. The brass cap, C_1, was then screwed onto J, the joint being made oil tight by means of a leather washer. The whole was then completely submerged in an oil thermostat, at 25.00°, being supported by a ring under the flange of J. Wires connected J and R_2 (which are in metallic contact with E_1 and E_2) to the bridge. The resistance and reactance were then measured with several different frequencies. Readings of either resistance or capacitance made immediately after filling the cell were often erratic and variable, but on standing the readings became more definite. The cell was sometimes left in the thermostat for twenty-four hours before taking the final readings. In other cases satisfactory constancy was attained in one hour after filling. Many other experimenters report a similar experience.

The cell was then lifted out of the thermostat, the cap, C_1, removed, the electrode, E_1, adjusted to a new position and the separation read on the scale and the measurements repeated. Finally the upper electrode was lowered until it made contact with the lower electrode, which gave the effective zero point of the micrometer scale. The separation of the electrodes could be determined with a precision of about 0.002 cm.

This instrument, although using the fundamental idea suggested by Miller, has been greatly modified to make it a precision instrument. It has been improved in the following respects: (1) the temperature can be controlled by immersion in an oil thermostat; (2) the solution cannot change during an experiment by evaporation or by contact with anything except quartz or the metal of the electrodes; (3) the cross section of the cell is uniform; (4) the

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[8] F. Krüger, *Ann. Physik*, [4] **21**, 701 (1906); *Z. physik. Chem.*, **45**, 1 (1903); Günther-Schulze, *Z. Physik*, **6**, 237 (1921); J. W. Shipley and C. F. Goodeve, *Trans. Am. Electrochem. Soc.*, **52**, 375 (1927); *Trans. Roy. Soc. Can.*, [3] **21**, Sect. 3, 395 (1927).

[9] C. W. Miller, *Phys. Rev.*, [2] **22**, 622 (1923).

separation of the electrodes can be varied from 0 to 3 cm. and can be measured with precision.[10]

Resistances and reactances were measured on the bridge built by R. C. Josephs.[1] Since the object of this investigation was to study polarization, the conditions were selected to magnify the effects. The capacitative reactance of the cell due to polarization was much greater than usual, which caused some difficulties in the measurements. In some of the preliminary work the capacitative reactance in the cell was compensated and measured by means of inductors in the same arm of the bridge. However, serious experimental difficulties of this method induced us to abandon it in favor of the use of condensers in parallel with the resistance box in the other arm of the bridge. Corrections were applied for the dielectric loss in the insulator and for the shunting effect of the parallel capacitance by the methods explained in the first paper of this series.[11]

The oscillator used was of the vacuum tube type which would give many different fixed frequencies by merely turning two rotary switches. An auxiliary variable air condenser was connected in parallel with the condensers of the oscillator which made it possible to adjust the frequency to definite round frequencies of 500, 1000, 2000, 3000 and 4000 cycles per second. These frequencies were determined and controlled by means of a General Radio Company wavemeter, type 434B. It seems probable that the error in the determination of the frequency did not exceed 0.5%.

The results obtained with silver electrodes having an area of 0.62 sq. cm. each in a 0.1 N silver nitrate solution are shown in Table I. The symbols not already explained in the text have the following meanings: R_P is the resistance in ohms of the box in the adjacent arm of the bridge, with a correction applied for the parallel resistance of the imperfect condenser connected in parallel with the box. C_P is the capacitance in microfarads which is required in parallel with the box to obtain a balance. R_S and C_S are the resistance and capacitance of the cell, which when in series are equivalent to the parallel combination of R_P and C_P in the other arm. R_S is computed from R_P and C_P by the equation $R_S = R_P/(1 + R_P^2C_P^2\omega^2)$.

It is a well-known relationship in alternating current theory that

$$\tan\theta = \frac{X_S}{R_S} = \frac{R_P}{X_P} = \frac{1}{R_SC_S\omega} = R_PC_P\omega$$

and therefore $C_S = 1/R_SR_PC_P\omega^2$.

If polarization causes an extra resistance, ΔR, having its seat at the electrodes, and if this resistance is independent of the current density, it should also be independent of the separation of the electrodes, l, and therefore we should expect the following relationship to hold

$$R_S = R_T + \Delta R = (l/a\kappa) + \Delta R$$

Therefore, if we plot R_S for any particular frequency against the separation of the electrodes, l, we should obtain a straight line with the value of ΔR given by the intercept on the resistance axis. The slope is $l/a\kappa$, where a is the area of the cross section of the cell and κ is the specific conductance of the solution. The slope should be independent of the frequency. Figure 4 gives a plot of R_S against the separation, l, for silver electrodes in 0.1 N silver nitrate at 500 and 4000 cycles Similar lines have been drawn for 1000, 2000 and 3000 cycles but are not shown in the figure because they would cause confusion on the small scale which can be printed The equations of each of these lines as determined by the method of least squares are for

$f =$ 500 $R_S = 109.81\,l + 21.10$
1000 $R_S = 109.84\,l + 14.57$
2000 $R_S = 109.84\,l + 10.22$
3000 $R_S = 109.85\,l + 8.36$
4000 $R_S = 109.81\,l + 7.39$

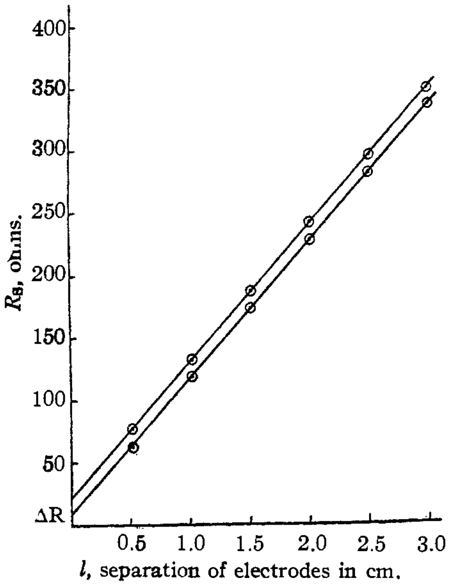

Fig. 4.—Silver electrodes in 0.1 N $AgNO_3$ solution: upper line, f = 500; lower line f = 4000 cycles/seconds.

As will be seen from the figure and equations, all of these lines are straight and parallel and do not pass through the origin. The average difference between the observed values of R_S and the values computed by these equations is less than 0.05 ohm

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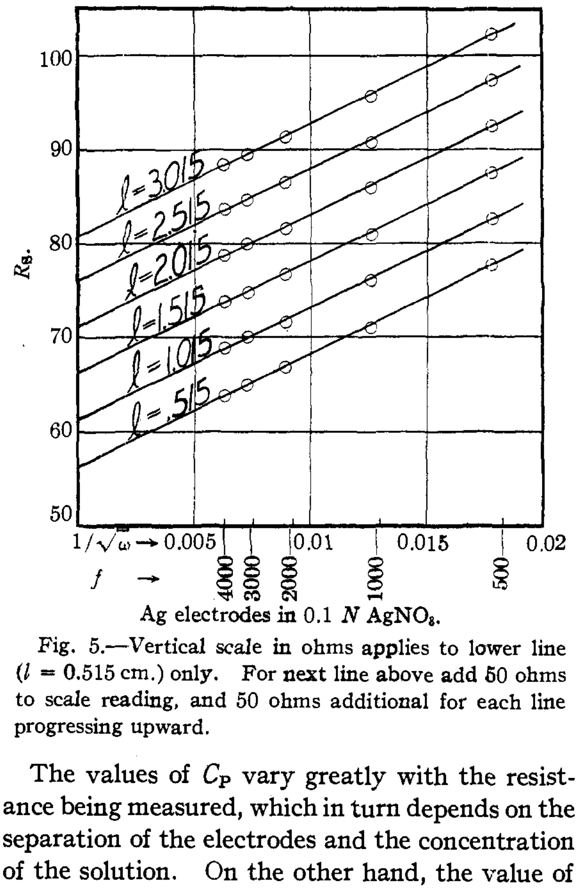
[10] The first step in the evolution of this instrument was made by Mr. R. C. Josephs, who built a cell of this type and made some measurements with it in this Laboratory. These results were not published because the experimental difficulties were not fully overcome. This experience was, however, helpful in the design of the cell used in this research.

[11] Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1075–1076 (1928).

which is within the limit of error of these measurements. These data, therefore, give definite evidence that polarization causes a positive resistance which is not located in the body of the solution but is one aspect of the phenomena which occur at the electrodes. This method gives a reliable measure of polarization resistance. In this case the polarization resistance is a substantial fraction of the total resistance and would cause a gross error if the measured resistance were taken as the true electrolytic resistance without allowance for the polarization resistance.



Ag electrodes in 0.1 *N* $AgNO_3$.

Fig. 5.—Vertical scale in ohms applies to lower line (l = 0.515 cm.) only. For next line above add 50 ohms to scale reading, and 50 ohms additional for each line progressing upward.

The values of C_P vary greatly with the resistance being measured, which in turn depends on the separation of the electrodes and the concentration of the solution. On the other hand, the value of C_S is independent of the separation of the electrodes between the limits of 1 and 3 cm., within the limit of error of the capacitance measurements. The value of C_S at 0.5 cm. is larger in all cases but whether this increase is real or due to some experimental error is not clear. In spite of this minor deviation, the contrast between the great variation in C_P with the resistance being measured and the constancy of C_S demonstrates clearly that the actual capacitance due to polarization is really in series with the resistance of the electrolyte.

The data recorded in Table I show that Kohlrausch, Wien and Warburg are all wrong as to the influence of variation in frequency on the series capacitance due to polarization. Warburg's prediction that $C_S\sqrt{\omega}$ should be a constant is verified approximately but not rigorously. In this case $C_S\sqrt{\omega}$ varies systematically with the frequency and changes by about 15% from 500 to 4000 cycles. Warburg's theoretical prediction that $\Delta R\sqrt{\omega}$ should be independent of the frequency is verified much better, the deviations in this case being no greater than the experimental error and not systematic. The value of $\tan \psi = \Delta R_S C_S \omega$ is not unity and is not independent of the frequency as predicted by Warburg, but decreases with increasing frequency and becomes close to unity at 4000 cycles. Tan ψ is independent of the separation of the electrodes except at the closest setting (l = 0.515 cm.).

The fact that ΔR is inversely proportional to the square root of the frequency suggests that the variation of resistance with the frequency may be used to estimate ΔR. We may write $R_S = R_T + \Delta R = l/a\kappa + k/\sqrt{\omega}$. Therefore, if we plot R_S for any given value of l against $1/\sqrt{\omega}$, we should get a straight line whose intercept on the resistance axis would be the true resistance, $R_T = l/a\kappa$ and whose slope would be $k = \Delta R\sqrt{\omega}$. These plots have been drawn from the data in Table I for each of the separations, and are shown in Fig. 5. In order to show all of these plots on one figure it was necessary to shift the origin of the vertical scale for the different curves. The equations of these lines as determined by the method of least squares are

For l = cm.

0.515 $R_S = 56.15 + 1198/\sqrt{\omega} = 109.03\,l + 1198/\sqrt{\omega}$
1.015 $R_S = 111.21 + 1189/\sqrt{\omega} = 109.56\,l + 1189/\sqrt{\omega}$
1.515 $R_S = 166.13 + 1190/\sqrt{\omega} = 109.65\,l + 1190/\sqrt{\omega}$
2.015 $R_S = 221.14 + 1187/\sqrt{\omega} = 109.75\,l + 1187/\sqrt{\omega}$
2.515 $R_S = 275.97 + 1191/\sqrt{\omega} = 109.73\,l + 1191/\sqrt{\omega}$
3.015 $R_S = 330.75 + 1193/\sqrt{\omega} = 109.70\,l + 1193/\sqrt{\omega}$

The experimental points lie approximately on straight lines, although there is an indication that the curves connecting the points have a small positive curvature. The deviations between the experimental points and the values of R_S computed by these equations are 0.11 ohm on the average, and have a systematic character indicating that the lines are slightly curved instead of straight. We are doubtful whether this apparent curvature is real or due to some systematic experi-

TABLE I

POLARIZATION AT SILVER ELECTRODES IN 0.1 N SILVER NITRATE SOLUTION

Area of electrodes 0.62 sq. cm. each

l, cm.	C_P, μf	R_S, ohms	C_S, μf	$C_S\sqrt{\omega}$, $\times 10^6$	$\Delta R C_S \omega$ = tan ψ
$f = 500$, $\Delta R = 21.10$, $\Delta R\sqrt{\omega} = 1183$					
3.015	0.06174	352.13	13.174	738.4	0.873
2.515	.08646	297.31	13.171	738.2	.873
2.015	.1295	242.43	13.180	738.7	.874
1.515	.2154	187.45	13.170	738.2	.873
1.015	.4240	132.54	13.165	737.9	.873
0.515	1.14	77.64	14.745	826.4	.977
$f = 1000$, $\Delta R = 14.57$, $\Delta R\sqrt{\omega} = 1155$					
3.015	0.02152	345.67	9.829	779.1	0.900
2.515	.03043	290.84	9.809	777.5	.898
2.015	.04615	235.98	9.810	777.6	.898
1.515	.07805	181.02	9.825	778.8	.899
1.015	.15898	126.07	9.863	781.8	.903
0.515	.47581	71.07	10.039	795.8	.919
$f = 2000$, $\Delta R = 10.22$, $\Delta R\sqrt{\omega} = 1146$					
3.015	0.007464	341.34	7.274	815.4	0.934
2.515	.010615	286.51	7.257	813.5	.932
2.015	.01622	231.60	7.262	814.1	.933
1.515	.02783	176.63	7.268	814.5	.933
1.015	.05819	121.68	7.291	817.4	.936
0.515	.18686	66.79	7.406	830.2	.951
$f = 3000$, $\Delta R = 8.36$, $\Delta R\sqrt{\omega} = 1148$					
3.015	0.003992	339.48	6,114	839,3	0.963
2.515	.005716	284.67	6.070	833.4	.957
2.015	.008742	229.82	6.087	835.7	.959
1.515	.01514	174.76	6.070	833.4	.957
1.015	.03194	119.84	6.103	837.9	.962
0.515	.1067	64.91	6.152	844.6	.969
$f = 4000$, $\Delta R = 7.39$, $\Delta R\sqrt{\omega} = 1171$					
3.015	0.002607	338.35	5.302	840.5	0.984
2.515	.003718	283.58	5.291	838.8	.982
2.015	.005716	228.76	5.287	838.2	.982
1.515	.00988	173.80	5.294	839.3	.983
1.015	.02113	118.91	5.277	836.6	.980
0.515	.07170	63.81	5.355	849.0	.994

mental error in the measurement of the frequency. On account of this curvature this method of determining R_T and ΔR is probably not quite as reliable as the first method described above for cases in which the polarization resistance is a substantial fraction of the electrolytic resistance. The best straight line drawn through the points of the R_S–$1/\sqrt{\omega}$ plots gives values for R_T which are slightly lower than the values of R_T given by the other method, and therefore gives values of ΔR which are slightly higher.

However, if modern oscillators and wavemeters are available, it is far easier experimentally to vary the frequency while using a cell with fixed electrodes than it is to vary the separation of the electrodes at a constant frequency.

We have carried out similar experiments in eight other cases but only publish the results in a condensed form in Table II to save space in printing, although the calculations have been carried out in full detail and analyzed and in general show the same relationships which have been pointed out in the case presented in detail in Table I. Three of these experiments were carried out with the same silver electrodes but with a different electrolyte. Decreasing the concentration of the silver nitrate from 0.1 to 0.01 N caused a slight but definitely measurable increase in ΔR and a decrease in tan ψ and in C_S at all frequencies, indicating greater polarization. The use of 0.02 N potassium nitrate more than doubled the polarization resistance and greatly reduced the series capacitance but had little effect on tan ψ. This would seem to indicate that when the electrolyte contains an ion which may be formed from the electrode the phenomena of electrolysis are more perfectly reversible and therefore the polarization is reduced. On the other hand, the use of 0.01 N potassium iodide caused a substantial reduction in the polarization resistance. In this case the values of C_S show a definite decreasing trend with increasing separation of the electrodes which is not shown in Table II on account of the condensed form of presentation and which was not found in the other cases. With potassium iodide as electrolyte, tan ψ is smaller and much more variable with the frequency and separation than when silver electrodes are immersed in the other electrolytes studied.

The substitution of nickel electrodes caused a great increase in polarization. Thus, for example, at 500 cycles nickel electrodes in 0.01 N nickel nitrate gave a polarization resistance of 491 ohms and a value of 0.35 microfarad for the polarization capacity, compared with 23.50 ohms and 10 microfarads for silver electrodes in 0.01 silver nitrate. All of the relationships noted in describing the first case are valid for nickel electrodes. The plots of R_S against l gave straight lines which were used to determine the values of ΔR given in Table II. The values of C_S were independent of the separation of the electrodes (except for l = 0.515 cm.) but decreased with increasing frequency. $C_S\sqrt{\omega}$ increased with the frequency relatively more than was found for silver electrodes. Tan ψ is clearly not unity and is dependent on the frequency. The positive curvature in the plots of R_S against $1/\sqrt{\omega}$ is more plainly evident than it was for the silver electrodes, but the curves are so nearly straight that this method of determining R_T and ΔR is useful, although not so precise as the results obtainable with our cell with movable electrodes, in cases where the polarization resistance is substantial. These cases confirm the conclusion of Wien, Warburg and others that polarization depends on the nature of the electrodes more than on any other factor.

With nickel electrodes the use of 0.01 N nickel nitrate gave a greater polarization resistance and lower capacitance than 0.01 N potassium nitrate, which is surprising in view of the contrary results obtained with silver electrodes. This shows that more extensive experimentation is needed before attempting to generalize from these data.

The polarization resistance at the smooth platinum electrodes was greater than for our silver electrodes in 0.1 N silver nitrate and the polarization capacitance was less than for silver which is contrary to Wien's experience. In this case the value of C_S decreased about 40% when the frequency was varied from 500 to 4000, which is a greater relative change than was observed in the other cases. The distinguishing feature of the experiments with smooth platinum electrodes is that the phase displacement due to spontaneous depolarization, ψ, is much smaller than was found for silver and nickel electrodes. At 500 cycles tan ψ = 0.33 and at 4000 cycles tan ψ = 0.60. Evidently Warburg's theoretical prediction that tan ψ should be unity at all frequencies is incorrect.

TABLE II

SUMMARY OF RESULTS ON POLARIZATION

Area of electrodes 0.62 sq. cm. each

Frequency...... N	500	1000	2000	3000	4000	500	1000	2000	3000	4000	500	1000	2000	3000	4000
	ΔR ohms					$C_S \mu f$					tan $\psi = \Delta R C_S \omega$				
Ag–0.1 $AgNO_3$	21.10	14.57	10.22	8.36	7.39	13.2	9.8	7.3	6.1	5.3	0.87	0.90	0.94	0.96	0.98
Ag–0.01 $AgNO_3$	23.5	19.0	11.9	9.7	8.4	10.0	7.5	5.3	4.4	3.6	.74	.90	.79	.80	.76
Ag–0.02 KNO_3	57.2	38.0	26.1	21.6	19.0	4.6	3.5	2.7	2.3	2.0	.83	.84	.89	.94	.83
Ag–0.01 KI	16.9	10.6	7.4	6.2	5.8	8.4	7.2	5.9	5.0	4.8	.45	.48	.55	.58	.70
Ni–0.01 $Ni(NO_3)_2$	491	326	220	184	163	0.35	0.30	0.25	0.23	0.21	.54	.61	.69	.80	.86
Ni–0.01 KNO_3	398	273	192	158	139	.55	.43	.34	.29	.25	.69	.74	.82	.86	.88
Pt-smooth 0.015 KCl	63.6	40.2	27.6	23.8	21.5	1.66	1.50	1.29	1.19	1.09	.33	.38	.45	.52	.59
Pt-smooth 0.01 KCl	57.7	37.2	25.9	22.0	20.7	1.9	1.7	1.45	1.3	1.2	.34	.40	.47	.53	.62
Pt-platinized 0.01 KCl	1.29	0.84	0.67	0.57	0.47	100	80	50	30	20	.40	.42	.42	.32	.24

The other relationships noted with silver and nickel electrodes are repeated in this case.

The last experiment recorded in Table II demonstrates the marked reduction in polarization resistance caused by platinization. With platinized electrodes the values of C_P were so small that they were not measurable with precision and therefore the values of C_S and tan ψ are only approximate. In this particular case the variation of the resistance with frequency and the values of the C_P, which were comparatively high for platinized electrodes, show that the quality of the platinization was poor. It will be shown in a later paper that much lower values of ΔR and higher values of C_S can be obtained by better platinization. An analysis of this case shows that where the polarization is small the method of determining ΔR based on the use of movable electrodes at constant frequency is not as good as the other method based on determining the variation of resistance with variation of frequency at constant separation.

A critical examination of all of the evidence from these experiments shows that ΔR invariably decreases with rising frequency and that Warburg's rule that $\Delta R\sqrt{\omega}$ is independent of the frequency and separation of the electrodes and of current density holds more accurately and generally than any of the other generalizations which have been suggested.

We have considerable additional experimental data obtained with cells having fixed electrodes. The polarization resistance can be computed from the variation of the resistance with the frequency by the use of Warburg's rule. We first confirmed the observation of Oberbeck[12] and of Wien[13] that both polarization resistance and capacitance are independent of the current density. We used cells in which polarization was substantial as shown by the variation of the resistance with frequency but found no measurable change of resistance or capacitance with variation of applied voltage and therefore with current density throughout the range of voltages and current densities which are important for the measurement of the conductance of electrolytes by Kohlrausch's method. Since these data prove nothing new they are omitted for the sake of brevity although the point is of fundamental importance for the development of the method described above which uses the micrometer caliper cell.

Wolff[14] states, "When two harmonic alternating currents of differing frequencies are simultaneously impressed on a cell, the polarization capacity measured by means of either one is independent of the other." However, he does not give the experimental data in support of this conclusion. We have carried out a similar experiment to determine the effect on the polarization resistance of superimposing another current of a different frequency from that used to balance the bridge. For this purpose two oscillators were used operating at different frequencies with the secondary coils of their output transformers in parallel with each other. The balance was obtained as usual with 500, 2000 or 4000 cycles per second while a current of 200 or 10,000 cycles per second was simultaneously passing through the cell, but the sound of this other frequency, although heard in the telephones, was easily ignored in obtaining the balance. The electrodes were of smooth platinum and the electrolyte was 0.1 N nickel nitrate. The results are given in Table III and show that the effective resistance and capacitance when measured with 500, 2000 or 4000 cycles are not influenced by a current of 200 or of 10,000 cycles passing simultaneously through the cell. Since the polarization was substantial in these experiments, it is clear that the polarization resistance and capacitance at a given frequency are not influenced by a superimposed current at a different frequency. This means that overtones do not necessarily cause an error in conductance measurements even when polarization is present, provided the overtones are not of sufficient intensity to cause heating effects. A single frequency pure sine wave oscillator is nevertheless desirable because of the psychological disturbance by the overtones, which may diminish the sharpness of the setting of the bridge.

TABLE III

EFFECT OF SUPERIMPOSED CURRENT ON RESISTANCE AND CAPACITANCE

	Resistance		
Frequency	No current superimposed	10,000 cycles superimposed	200 cycles superimposed
500	327.146	327.146	327.148
2000	324.997	324.996	324.998
4000	324.505	324.504	324.500
	Parallel capacitance $\mu\mu f$		
500	24,010	24,015	24,025
2000	2,170	2,160	2,170
4000	640	638	639

The Effect of Temperature on Polarization

Some incidental observations on the influence of temperature on polarization have been made by Haworth[15] with platinum electrodes, by Günther–Schulze[16] with tantalum electrodes, and by Sun[17] with platinum electrodes. The most extensive investigation of this question has been carried out by Zimmerman.[18] He found that with smooth platinum electrodes in sulfuric acid the temperature coefficient of the capacitance was about $+1\%$ and the temperature coefficient of polarization resistance was about -0.9% and that both were almost independent of the frequency and of the concentration of the acid. With gold electrodes in sulfuric acid he found that the temperature coefficients were smaller and more variable with the frequency than for platinum.

We have carried out one series of measurements on temperature coefficients using a cell designed to avoid capacitative shunts having smooth circular platinum electrodes of 2 cm. diameter immersed in 0.1 N nickel nitrate. At 25° the cell was mounted as usual in an oil thermostat, but at 0° the cell was enclosed in a solid block of paraffin which was immersed in an ice-bath for twenty-six hours before the measurements were taken.[19] The paraffin block was thick enough to prevent errors in the capacitance and resistance measurements due to the presence of a conductor surrounding the cell. The results are shown in Table IV.

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[12] A. Oberbeck, *Wied. Ann.*, **19**, 625 (1883); **21**, 139 (1884).

[13] M. Wien, *loc. cit.*

[14] I. Wolff, *Phys. Rev.*, [2] **27**, 755 (1926).

[15] H. F. Haworth, *Trans. Faraday Soc.*, **16**, 378 (1920).

[16] A. Günther–Schulze, *Z. Physik*, **6**, 237 (1921).

[17] K. F. Sun, *Phys. Rev.*, [2] **23**, 617 (1924).

[18] E. E. Zimmerman, *ibid.*, [2] **35**, 543 (1930).

[19] Grinnell Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1789 (1933).

TABLE IV

EFFECT OF TEMPERATURE ON POLARIZATION RESISTANCE AND CAPACITANCE, SMOOTH PLATINUM ELECTRODES IN 0.1 N $Ni(NO_3)_2$

f	C_P $\mu\mu f$	R_S	C_S, μf	ΔR	$C_S\sqrt{\omega} \times 10^6$	$\Delta RC_S\omega = \tan\psi$	$\frac{dC_q}{C_{S25}dT}$	$\frac{d\Delta R}{R_{25}dT}$
		0°						
500	10,073	579.33	29.96	4.89	1679	0.460		
1000	2823	577.72	26.88	3.28	2131	.554		
2000	820	576.75	23.22	2.40	2603	.700		
3000	388	576.42	21.83	1.98	2997	.812		
4000	231	576.25	20.64	1.81	3272	.939		
		25°						
500	24,010	326.91	39.46	3.81	2212	0.472	0.0096	−0.011
1000	7232	325.77	33.00	2.67	2616	.554	.0074	− .009
2000	2171	324.94	27.62	1.84	3096	.639	.0064	− .010
3000	1055	324.65	25.31	1.55	3475	.740	.0055	− .011
4000	640	324.50	23.49	1.39	3724	.821	.0049	− .012

These results are satisfactorily expressed by the equations $R_S = 574.44 + 269/\sqrt{\omega}$, at 0°, and $R_S = 323.10 + 212/\sqrt{\omega}$, at 25°.

In this case the temperature coefficient of the polarization resistance is negative and about 1% per degree and independent of the frequency. The temperature coefficient of the capacitance is positive but varies from about 1% at 500 cycles to about 0.5% at 4000 cycles.

Summary

1. A new form of cell suitable for measuring the resistance and the capacitance due to galvanic polarization with alternating current has been devised and used for a series of measurements with silver, nickel and platinum electrodes.

2. Polarization resistance is inversely proportional to the square root of the frequency. Another method of measuring polarization resistance based on this law is described.

3. Polarization causes a capacitance in series with the resistance which decreases with increasing frequency.

4. Both polarization resistance and polarization capacitance are greatly dependent on the metal used for the electrodes, and dependent to a lesser degree on the electrolyte and temperature, but independent of the current density and the separation of the electrodes and uninfluenced by another superimposed current of a different frequency.

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[CONTRIBUTION FROM THE BYERLY CHEMICAL LABORATORY OF RADCLIFFE COLLEGE]

The Measurement of the Conductance of Electrolytes. VII. On Platinization[1]

BY GRINNELL JONES AND DOROTHY M. BOLLINGER

Introduction

Kohlrausch[2] discovered that errors due to polarization in the measurement of the conductance can be minimized by covering the electrodes by a deposit of finely divided black platinum. He recommended deposition of the platinum by electrolysis from a solution of chloroplatinic acid (H_2PtCl_6) to which a trace of lead acetate has been added. Nearly all later investigators in this field have used platinized electrodes prepared as recommended by Kohlrausch except when using very dilute solutions or when there was a danger that the platinum black might catalyze an undesired reaction in the solution. A detailed review of the earlier studies[3] of the effect of platinization must be omitted for the sake of brevity.

The purpose of this investigation was to develop a convenient and reliable quantitative test of the quality and sufficiency of the platinization and to use it for a critical study of the procedure of platinization. The adequacy of platinization has been judged by the earlier investigators by one or more of the following tests: (1) the sharpness of the minimum of sound in the telephones and the identity of pitch on opposite sides of the minimum; (2) intercomparisons of two or more cells with a series of identical solutions; (3) the magnitude of reactance due to polarization, or some related quantity such as the capacitance or

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(1) The earlier papers in this series are: Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928); Grinnell Jones and Giles M. Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411 (1931); **53**, 1207 (1931); Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933); Grinnell Jones and S. M. Christian, *ibid.*, **57**, 272 (1935). This investigation was started in the laboratory of Bowdoin College by the late Giles M. Bollinger with the aid of Dorothy M. Bollinger. After the death of Professor Bollinger the work was transferred to Radcliffe College.

(2) F. Kohlrausch, *Wied. Ann.*, **60**, 315 (1897); F. Kohlrausch and L. Holborn, "Das Leitvermögen der Elektrolyte," published by Teubner, Leipzig, p. 9, 1898.

(3) M. Wien, *Wied. Ann. Physik*, **58**, 46, 56 (1896); *Drude Ann. Physik*, **8**, 373 (1902); Whetham, *Phil. Trans.*, **194**, 321 (1900); P. Schönherr, *Drude Ann. Physik*, **6**, 116 (1901); E. Warburg, *Drude Ann. Physik*, **6**, 125 (1901); W. A. Taylor and H. L. Curtis, *Phys. Rev.*, [2] **6**, 61 (1915); W. A. Taylor and S. F. Acree, THIS JOURNAL, **38**, 2409, 2421 (1916); E. W. Washburn, *ibid.*, **38**, 2456 (1916); H. C. Parker, *ibid.*, **45**, 1366 (1923); Grinnell Jones and Giles M. Bollinger, *ibid.*, **53**, 411 (1931); Grinnell Jones and S. M. Christian, *ibid.*, **57**, 278 (1935).