

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF
ELECTROLYTES.
IV. THE VALIDITY OF OHM'S LAW FOR ELECTROLYTES¹

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Introduction

Recently M. Wien² has published a paper entitled "On a Deviation from Ohm's Law for Electrolytes" in which he has recorded measurements of the conductance of electrolytes in very strong fields from about 30,000 volts per centimeter up to about 300,000 volts per centimeter. He reached the conclusion that a real increase in conductance with increase in field strength occurs at very high voltages. An increase in conductance of more than 50% above the conductance with low voltages was found in one case and smaller increases in many other cases. The feature most clearly established by his experiments is the great influence of the valences of the ions on the Wien effect. He made measurements on twenty-three different salts of varied valence types and concluded that the effect is proportional to the square of the product of the valences of the ions. The effect is greater for concentrated solutions than for dilute. For dilute solutions and for the lower range of voltages for which the effect was measurable he found that the increase in equivalent conductance appears to be proportional to the field strength, but at very high field strengths the conductance appears to approach a definite maximum. He says: "The observation of the limit of the effect as well as its theoretical interpretation is . . . extremely uncertain, and for the present it can only be inferred from the experiments that the limit of the effect agrees at least in rough order of magnitude with the decrease in equivalent conductance from the conductance at infinite dilution. . . . It is probable that the great velocity which the high field imparts to the ions completely or partially abolishes the cause for the change of equivalent conductance with the concentration."

This experimental paper of Wien stimulated the theoretical analysis of the problem by Joos and Blumentritt,³ based on the interionic attraction

¹ The earlier papers in this series are: (a) Grinnell Jones and R. C. Josephs, *THIS JOURNAL*, **50**, 1049 (1928); (b) Grinnell Jones and Giles M. Bollinger, *ibid.*, **51**, 2407 (1929); (c) **53**, 411 (1931).

² J. Malsch and M. Wien, *Wied. Ann. Physik*, [4] **83**, 305 (1927); M. Wien, *ibid.*, [4] **83**, 327 (1927).

³ G. Joos and M. Blumentritt, *Physik. Z.*, **28**, 836 (1927); G. Joos, *ibid.*, **29**, 755 (1928); M. Blumentritt, *Ann. Physik*, [4] **85**, 812 (1928); P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 425-426 (1928); M. Blumentritt, *Ann. Physik*, [5] **1**, 195 (1929); H. Falkenhagen and J. W. Williams, *J. Phys. Chem.*, **33**, 1124 (1929).

theory of Debye and Hückel. According to this theory the electric forces between the ions tend to maintain the ions in a space lattice distribution and oppose any displacement of the ions from their position in the lattice by an outside field. Since this braking effect of the interionic electric forces increases with the concentration it accounts for the decrease in mobility of the ions and hence of the equivalent conductance with increasing concentration. But when the solution is subjected to an outside electric field, the resulting motion of the ions tends to destroy the space lattice distribution and give a more random distribution, with the result that the mobility tends to rise until with sufficiently high field strengths it becomes the same as the mobility at infinite dilution.

Joos derived the expression

$$\Delta\Lambda = AX^2 - BX^4$$

where $\Delta\Lambda$ is the increase in equivalent conductance in a field, X (volts/cm.) and A and B are independent of the field strength but vary in a complicated but explicit manner with the temperature, and with the dielectric constant and viscosity of the solution, and with the valences, mobilities and concentrations of all of the ions.

These theoretical papers in turn stimulated Wien⁴ to a renewed experimental study of the problem with an improved technique which permitted the effect to be measured with field strengths as low as 3000 volts per centimeter. Although the precision attained in these difficult experiments is not great, they appear to support the theoretical deductions of Joos.

If, as seems probable, Wien's experiments are reliable, it means that Ohm's Law is not strictly valid for electrolytes over the entire range of voltages.⁵ The Wien effect must therefore be of interest and importance in the theory of solutions but it is not necessarily significant for the measurement of conductance by the Kohlrausch method, because the field strengths used by Wien were at least 1000 to 100,000 times as great as those commonly used in the Kohlrausch method. It may be inferred from Wien's data that the effect will be entirely negligible in the weak fields suitable for the Kohlrausch method. This is encouraging but not entirely conclusive because the form of the function as given by Joos is not well established nor can the value of the coefficients be precisely determined from Wien's experiments. A direct experimental test at low voltages is

⁴ M. Wien, *Ann. Physik*, [4] **85**, 795 (1928); [5] **1**, 400 (1929).

⁵ Incidentally it is of interest to point out that P. W. Bridgeman [*Proc. Am. Acad.*, **57**, 131 (1922)] has made experiments on the electric conduction of thin strips of gold and of silver at high current densities which he interprets as showing that Ohm's Law is not strictly valid for metallic conductors. "The maximum current densities were about 5×10^6 amp./cm.², and the deviations from Ohm's Law were of the order of one per cent." This interpretation of these experiments has, however, been challenged by H. M. Barlow, *Phil. Mag.*, [7] **9**, 1053 (1930).

therefore desirable—especially since there are also reports in the literature of an apparent variation in the resistance of electrolytes with variation of applied voltage as determined by the Kohlrausch method.

Comparatively few of the earlier experimenters on the conductances of electrolytes by the Kohlrausch method have purposely varied the voltage which they used and observed the effect, if any, on the apparent resistance. An apparent change of resistance with voltage (or with the current density, which amounts to the same thing) and which may be ascribed to polarization, has been observed by several experimenters, including Wien, Haworth, and Percy;⁶ but experiments in which the disturbing effect of polarization are avoided are more pertinent for our present purpose.

Early in his work on conductance, Kohlrausch,⁷ having first devised a technique which minimized polarization, tested the validity of Ohm's Law for electrolytes and found no variation of resistance with the voltage applied to the bridge greater than the errors in his measurements, although the precision attained in this early work was much below more modern standards.

More recently several experimenters have found a change in apparent resistance with change in voltage even when using conditions favorable for the elimination of polarization.

Taylor and Acree⁸ report variations in apparent resistance as large as 0.08% in unclean cells when the voltage was changed from 0.25 to 2 volts, but they state that no such effect was observed with clean cells.

Kraus and Parker⁹ do not accept the suggestion that lack of cleanliness is the sole reason for a variation in resistance with the voltage applied. They report that in their experiments a change in voltage from 0.2 to 7.0 volts caused a decrease of 0.02% in the apparent resistance when using iodic acid solutions and an increase of about the same magnitude with potassium chloride solutions. "It was not found possible to locate the cause of this effect in the limited time available. . . ."

This question has been further studied by Parker,¹⁰ who gives a curve showing the apparent percentage increase in resistance caused by varying the voltage applied to the bridge from 0.2 volt to 10 volts with numerous different solutions of potassium chloride covering the range from very low resistances up to nearly 10,000 ohms. He found that the higher voltage gave the higher resistance throughout the range so that the effect cannot be ascribed to heating. At low resistances variations up to 0.13% were

⁶ M. Wien, *Wied. Ann. Physik*, **58**, 44 (1896); H. F. Haworth, *Trans. Faraday Soc.*, **16**, 370 (1921); R. H. Percy, "Dissertation," Basel, 1922.

⁷ F. Kohlrausch and W. A. Nippolt, *Pogg. Ann.*, **138**, 280-298, 370-390 (1869); see especially pp. 370 and 378; F. Kohlrausch, *Wied. Ann.*, **6**, 9 (1879); **26**, 168 (1885).

⁸ W. A. Taylor and S. F. Acree, *THIS JOURNAL*, **38**, 2416 (1916).

⁹ C. A. Kraus and H. C. Parker, *ibid.*, **44**, 2438 (1922).

¹⁰ H. C. Parker, *ibid.*, **45**, 1370 (1923).

shown. Within the range from 1000 to 6000 ohms, the difference was about 0.02% and rose to nearly 0.04% at about 10,000 ohms. Parker concluded that there are two different causes for the variation, superimposed on each other. He ascribes the controlling influence at low resistances to polarization. With increasing resistance the polarization dwindles and yet the influence of change in voltage on the resistance passes through a minimum and then rises. This clearly indicates that there is some effect other than polarization influencing the results. Parker does not express an opinion as to the nature of the effect which predominates at the higher resistances, nor as to whether the results obtained with the high or the low voltage are more nearly correct. Morgan and Lammert, after referring to the papers of Taylor and Acree and of Kraus and Parker cited above, say: "In the present research no change in resistance with the change in impressed voltage has been observed when the electrodes were properly cleaned." The range used is not stated.¹¹

Experimental Part

Since we had available a new and improved bridge,¹ it became of interest to determine whether or not the deviations from Ohm's Law detected by Wien are detectable at voltages suitable for use in the Kohlrausch method and to endeavor to decide whether the apparent failure of Ohm's Law reported by Taylor and Acree, Kraus and Parker, and Parker is real or due to experimental error. With very low resistance (under 100 ohms) and a high voltage (4 volts or more) we have observed small changes in apparent resistance with change in voltage, but under these conditions the heating effect of the current on the cell is sufficient to make precise measurements difficult and polarization occurs, so that the apparent changes in resistance are not believed to be significant. In some of our earlier work, small voltage effects were detected which could not be ascribed to polarization or to heating and were traced to mutual inductance between the oscillator and the bridge^{1b} and the detector. It was shown that the results with the higher voltage were more nearly correct since the effect of mutual inductance had a relatively greater influence when the voltage impressed on the bridge was low. After the oscillator was moved to a safe distance, the influence of variation in voltage applied on the measured resistance disappeared entirely when measuring 300 ohms or more as is demonstrated by the data in Table I.

The cells designated by A, D and G are of the pipet type. Cells K, L, M and N are of our new type designed to minimize the effects of capacitance between parts of the cell and have been described and illustrated in the third paper of this series.^{1c} Cell Z is also of the new type. It has a capillary tube 70 cm. long and with a bore of about 0.9 mm., giving an

¹¹ J. L. R. Morgan and O. M. Lammert, *THIS JOURNAL*, **45**, 1704 (1923).

TABLE I
 EXPERIMENTAL RESULTS

Cell	Separation of electrode, cm.	Cell constant	Frequency, cycles per second	Spec. cond. of soln. used	Volts across bridge	Field strength, volts/cm.	Resistance, ohms
K	1.5	0.67	1090	0.0022	4.2	1.4	299.11
					0.01	0.003	299.11
M	11.5	11.7	1090	.011	4.2	.18	1,105.67
					0.4	.017	1,105.70
					.01	.0004	1,105.70
G	5	3.06	500	.0017	2.3	.23	1,770.25
					0.1	.01	1,770.28
D	12	12.38	2280	.0050	5.26	.22	2,468.96
					0.8	.03	2,468.97
N	16.5	126.7	3000	.022	5.0	.15	5,638.9
					1.0	.03	5,638.8
					0.1	.003	5,638.9
L	6	2.63	1090	.00021	4.2	.35	12,395.0
					0.6	.05	12,395.0
					0.01	.0008	12,395.0
Z	70	10600	1090	.51	4.2	.03	20,487.72
					.05	.0004	20,487.7
					0.02	.00014	20,488
N	16.5	126.7	3000	.0042	5.0	.15	29,712.5
					0.1	.03	29,712
N	16.5	126.7	4000	.0023	5.0	.15	55,307
					0.5	.015	55,306
A	16	144.6	1090	.0026	4.2	.13	56,097
					0.6	.02	56,098

exceptionally high cell constant. With some of these cells an appreciable variation of apparent resistance with frequency may be observed, whereas others are free from this fault. The electrolyte used was potassium chloride in all cases except the experiments with cell Z, which was filled with a solution of sulfuric acid having approximately the maximum specific conductance. The variations in measured resistance shown in the table might all be caused by a variation of 0.001°C . in the temperature and are regarded as insignificant. These data, selected from many others of like import in our notebooks, show that when suitable experimental precautions are taken to avoid heating and polarization, and when using a bridge properly designed to avoid complications inherent in working with alternating current, the voltage used is without effect on the measured resistance, over a wide range of frequencies and of resistances and with cells of widely varying design, throughout the range of voltages which are useful for the practical measurement of the conductance of electrolytes by the Kohlrausch method.

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Summary

Wien has shown experimentally that deviations from Ohm's Law amounting to more than 50% in some cases occur in electrolytes at very high field strengths (3000 to 300,000 volts per centimeter). It is demonstrated in this paper that if adequate experimental precautions are taken to avoid errors due to heating, to polarization, and to the secondary effects of inductance and capacitance, there is no measurable variation of the real resistance of electrolytes with variation of the applied voltage throughout the range of voltages and frequencies suitable for use in the Kohlrausch method of measuring electrolytic conductance. Ohm's law may, therefore, be regarded as valid for electrolytes under these conditions.

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THE STRUCTURE OF FERRIC THIOCYANATE AND THE THIOCYANATE TEST FOR IRON

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The usual explanation of the thiocyanate test for ferric ions assumes that the red color is due to the formation of un-ionized ferric thiocyanate, but there is no convincing evidence that dilute aqueous solutions of ferric thiocyanate are only very slightly ionized. Even if they were, it seems unlikely that the union of slightly colored ferric ion with colorless thiocyanate ion should produce a highly colored molecule, since simple ionic dissociation is usually not accompanied by marked color changes. On the other hand, it has been known for a long time that the action of an excess of ammonium or alkali thiocyanate on ferric salts leads to the formation of highly colored substances of the type $\text{Me}_3[\text{Fe}(\text{CNS})_6]$.² That the formation of the complex ion $[\text{Fe}(\text{CNS})_6]^-$ has not been generally accepted as an explanation of the reaction is due to two causes. In the first place, the solid salts do not appear to have a color exactly identical with that of the solutions in question. In the second place, these salts are not soluble in dry ether, which, as is well known, extracts the colored substance from

¹ This article is taken from a thesis presented by H. B. Van Valkenburgh to the Ogden Graduate School of Sciences in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Krüss and Moraht, *Ann.*, **260**, 193 (1890); Rosenheim and Cohn, *Z. anorg. Chem.*, **27**, 280 (1901).