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POLARIZATION AND INTERNAL RESISTANCE OF ELECTROLYTIC CELLS.

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BESIDES Kohlrausch's alternating-current method and its modifications for measuring the resistance of an electrolytic cell, numerous direct-current methods have been proposed and are largely in use in determining the resistance of voltaic batteries. The latter methods, though polarization is prevented as much as possible, show more or less a characteristic decrease of the apparent resistance of the cell with increasing current. In many cases well defined curves were obtained. (Streintz, Wied. Ann., 49, p. 571, 1893 ; Carhart, PHYS. REV., II., p. 392, 1895.) Even in the alternating-current methods this was observed in a less pronounced degree. (Uppenborn, Electrotech. Ztschr., 1891, p. 157 ; Greeff, Dissert., Marburg, 1895.) Greeff found the curves obtained by the two methods to be practically parallel to each other, but the one obtained with the alternating current somewhat below the other. Haagn (Zeitschr. für Phys. Chem., 23, p. 97, 1897) has lately modified Kohlrausch's method and claims to obtain a practically constant resistance ; but it must be borne in mind that he used cells with large electrodes and rather large currents, in which case the change in the internal resistance is small even when measured by the constant-current methods.

The peculiar behavior of the cells has led to the belief that we have here, at least in cells with small electrodes, a so-called resistance of transition (the German " Uebergangswiderstand ") which

increases rapidly with decreasing current. Of interest in this respect are especially the investigations of Richarz (Wied. Ann., 47, p. 567, 1892) and Koch and Wüllner (Wied. Ann., 45, pp. 475 and 759, 1892).

On the other hand, it has been frequently asserted that all this change is due to the fact that polarization in the cells was not entirely prevented. Numerical calculations have never been undertaken to show that these changes in internal resistance can be represented by a formula taking the polarization into account. Out of the numerous theories, and in many cases empirical formulæ for galvanic polarization, I have selected Wiedeburg's theory as the one which represents the facts best and is supported by a number of experimental data. (Wiedeburg's Habilitationsschrift, Leipzig, 1893.)

It is based on the following few suppositions :

The two kinds of ions are urged by the current towards the electrodes. The change in density of the solution produces a counter e. m. f., which, in combination with the impressed e. m. f., determines the current according to Ohm's law. Not all ions collect on the electrodes in the active state, but only a part, while the rest are neutralized and will not influence the difference of potential between electrodes and the liquid. The number of the collecting ions which remain in the ionic state at any instant is proportional to the difference between a certain limiting value and the state of condensation at the electrodes.

From these fundamental suppositions, Wiedeburg obtains as the value of the polarization of a voltameter

$$p = \frac{P_1}{2}\left(1 - e^{-\frac{\beta_1}{s_1} q}\right) + \frac{P_2}{2}\left(1 - e^{-\frac{\beta_2}{s_1} q}\right), \tag{1}$$

i. e., the sum of the polarizations on the two sides ; P denotes a limiting value, β a constant, depending on the electrode, s the surface of the electrode and q the quantity of electricity that has passed through the voltameter.

In a voltameter whose electrodes are of the same size, this formula simplifies to

$$p = P\left(1 - e^{-\frac{\beta}{s} q}\right). \tag{2}$$

Besides this polarization proper, there is an absorption of the ions in the metal of the electrodes, which has been studied by Jahn and Schönrock (Zeitschr. f. Phys. Chem., 16, p. 45, 1895), and the convection currents. Both these influences are of a rather sluggish nature, and can, by proper arrangement of the apparatus, be reduced to almost nothing.

In the following I shall show that Wiedeburg's theory demands a curve for the internal resistance decreasing with increasing currents.

If we arrange our experiments now in such a way as to take a set of observations always with the same interval of time, we get the formula

$$E' - P(1 - e^{-KI}) = rI. \tag{3}$$

The formula from which the resistance is usually calculated is simply

$$\rho = \frac{E'}{I}. \tag{4}$$

ρ will, therefore, always be too large.

Writing formula (3) in the following form,

$$\rho - r = \frac{P}{I}(1 - e^{-KI}), \tag{5}$$

we see immediately that $\rho = r$ for very large currents and that $\rho - r$ is infinitely great for zero current.

I made use of the pendulum apparatus (see Phys. Rev., II., 392, 1895) which works, while swinging, four keys, the first of which closes the circuit, the second and third charge and discharge a condenser, the fourth opens the circuit again. By this means the time, during which polarization takes place, is kept constant: moreover, it is so short that the disturbing influences of absorption and convection do not in general appear.

The arrangement of the apparatus is given in the following sketch :

Keys *I* to *IV* denote the keys in the order they are knocked down. *B* is the electrolytic cell, *bbb* the source
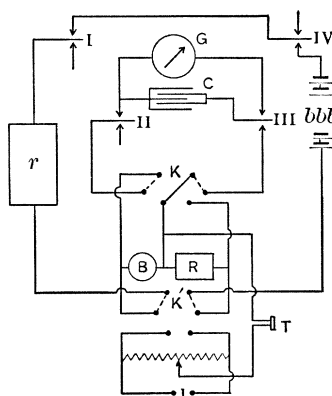

Fig. 1.

of the current, r a resistance by means of which the current may be varied, R a resistance nearly equal to the resistance of the electrolytic cell, C the capacity, G the ballistic galvanometer, whose constant was found by using a standard cell.

By means of the commutator K we are able to measure either the Potential Difference at the terminals of the cell (ε') or at the terminals of the resistance R (ε''). $\dfrac{\varepsilon''}{R}$ gives us the current.

The commutator K' can connect the cell and resistance R either in series with the pendulum apparatus or to a Kohlrausch bridge in such a way that they form two arms of a Wheatstone bridge.

The resistance can then be found by means of a small induction coil (I) and telephone (T).

The following experiments are given only as preliminary results, since the investigation is being continued. They will however show how well the calculated and observed curves coincide.

In the first column is given the capacity of the condenser, in the second the deflection due to the cell, in the third the deflection due to the fall of potential over the resistance R, and in the fourth the current calculated from the latter. The following column containing ρ shows the characteristic increase of the apparent resistance, while

TABLE I.

Copper sulphate solution between small copper electrodes.
Temperature $= 23.9°$.　$R = 10$ ohms.

Cap.	dc	dR	I	ρ	$(1 - e^{-KI})$	r
.25	240	283	.2218	8.48	1	8.33
	183	214	.1677	8.54	1	8.38
.5	256	297	.1163	8.62	1	8.39
	194	222	.0869	8.73	.99926	8.42
1.0	319	362	.0709	8.81	.99722	8.43
	162	177.8	.0348	9.11	.94434	8.38
	110	118	.0231	9.32	.85300	8.33
	84	'88	.0173	9.55	.76210	8.36
3.2	215	223	.0136	9.64	.69080	8.27
	138	138	.0084	10.00	.50203	8.38
	111	110	.00673	10.09	.42798	8.38

$K = 83$;　$P = .027$.

TABLE II.

Copper sulphate solution between large Copper electrodes.   R = 4 ohms.

Cap.	dc	dR	I	ρ	$(1 - e^{-KI})$	r
.8	247	383	.2344	2.58	.99813	2.36
1.0	237	359	.1758	2.65	.99101	2.36
	164	236.6	.1159	2.77	.95522	2.35
	128	176	.0863	2.91	.90102	2.37
3.2	340	452	.0692	3.00	.84348	2.36
	182	222	.0340	3.28	.59797	2.36
	125	146.8	.0225	3.41	.45284	2.36
	95	109.5	.0167	3.47	.36082	2.35
	76	87	.0133	3.47	.29985	2.30

$K = 26.8$; $P = .052.$

the real resistance r, calculated from my formula, is practically constant; its small variations do not exceed the errors of observation.

In Fig. 2 the observed and calculated values of ρ are plotted as functions of the current. The curves show the close agreement
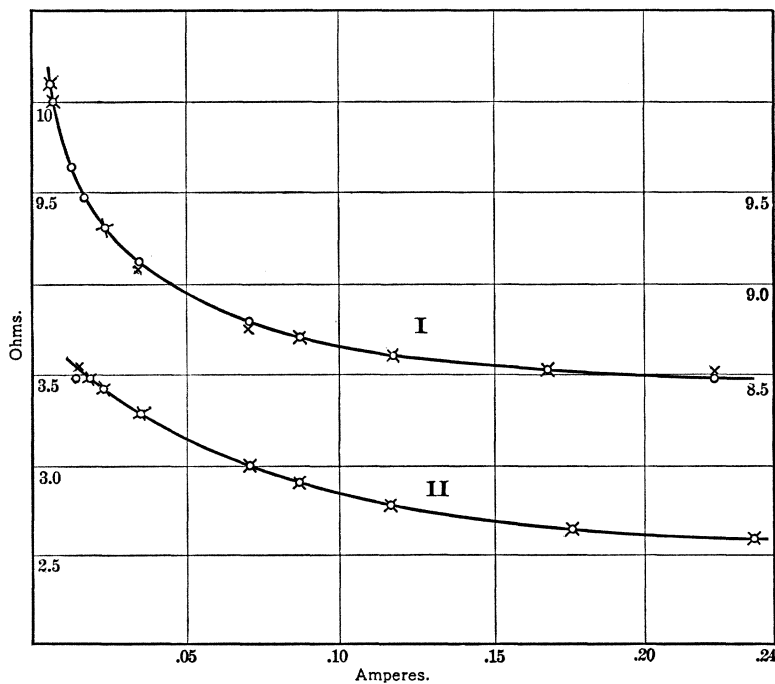

Fig 2.

between the two values, the circles marking the observed, the crosses the calculated values of ρ.

Kohlrausch's method gave for the first cell 8.32 ohms and for the second 2.17 ohms; in both cases it was rather difficult to determine the position for minimum sound. We see, therefore, that Kohlrausch's method gives a smaller result than the constant results calculated from my formula. But this is easily explained by the capacity effect of the cell, which is the more apparent, the smaller the resistance. It is doubtful whether Kohlrausch's method will give accurate results with ordinary cells, *i. e.*, with cells of small resistance.

Electrolytic cells with H_2SO_4 between Pt electrodes gave fair results, though the variations in the resistance calculated reached 2%; this is larger than could be expected from the errors of observation, which do not exceed 1%. I explain this by the fact that I used large platinized electrodes and could not prevent the disturbing influence of absorption. This showed itself in the experiment by the creeping up of the deflection from the cell from an orginally small value to a final value, sometimes 10% higher than the original. These experiments will be repeated with thin, bright electrodes.

An application of this method to the calculation of the resistance of a simple voltaic cell or cells without depolarizer is apparent. The action of the depolarizer or any chemical reaction will complicate the formula, though it is well known that the curves obtained from these cells have the same general appearance as those studied in this article.

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