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ELECTRICAL STANDARDS.

BY KARL E. GUTHE.

As soon as any commodity becomes of commercial value a system of practical units has to be established for its measurement. In the case of electrical energy we have fortunately been saved from the natural development of a system of units, a development which has, for example, given us our remarkably complex, incongruous, and unscientific collection of weights and measures. While by no means perfect the electrical units have at least the advantage of being consistent, and being worked out by scientists they have naturally been based upon the metric system. I do not wish to tire you with a lengthy description of the various methods which have been employed for the derivation of the different electrical, or to be more specific, electro-magnetic units, in terms of the fundamental units, the centimeter, gram, and second,—suffice it to state that of the three most important electrical units two, that of the resistance, the Ohm, and that of current, the Ampere, can be determined by so-called absolute methods, in which determinations only length, mass and time enter into the measurements, while the third, the unit of electromotive force, the Volt, is found from the other two by the use of Ohm's law.

All other electrical quantities can easily be derived from these three by the application of well-known mathematical relations.

As can be imagined determinations of the absolute or c. g. s. units are difficult and require a great deal of labor and time; so it is natural that an attempt was made to substitute for these theoretical units practical and wherever possible, concrete and easily reproducible units, standing in definite relation to the former. This is not difficult in the case of the unit of resistance, the Ohm. A column of mercury of definite mass and length at a specified temperature will always have the same electrical resistance to a constant current and by a series of classical experiments* it was determined some years ago that the Ohm which equals 10^9 c. g. s. units of resistance is represented with sufficient accuracy by the resistance, at the temperature of melting ice, of a column of mercury, 14.4521 grammes in mass, of a constant cross sectional area and of the length of 106.3 centimeters.

At the International Electrical Congress at Chicago, in 1893, this unit was adopted and thus replaced some of the older measures which did not as closely correspond to the theoretical value. For a perfectly satisfactory definition of the mercury ohm, it is, however, necessary to add to the already given data the method of filling the tube, the form of the

*Dorn, Zeit. f. Instr.—Kunde, 1893, APP.

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end vessels, the manner in which the current is led to the mercury column and the factor to be used for the calculation of the end correction. Under such conditions it is possible to reproduce mercury ohms with an accuracy of 1 in 50,000, i. e., an accuracy far surpassing that with which the ohm can be determined in absolute measure.

With the ampere and the volt the case is different. We cannot construct a standard of current but must make use of one of the effects of a current for its measurement. The best and most reliable method seems to be, to measure a current by means of the electrolysis of a silver nitrate solution, the silver to be deposited upon a planinum bowl. The Chicago definition of the ampere states that a constant current of one ampere will deposit in a voltameter or coulometer, as I shall in the following always call this instrument, 1.118 milligrams of silver in one second.

While we cannot construct a cell whose electromotive force is exactly one volt, there are standard cells which have a definite and constant electromotive force if properly constructed. In 1893 only one of these was known, the Clark Standard Cell, and it was selected as a practical standard, its electromotive force being assumed at that time to be 1.434 volts.

Here we have then the definitions of the three fundamental electrical units and they were recommended by the international congress for adoption by the Governments represented. In the United States, Great Britain, Canada, Germany, Austria and France government action was taken, but in some important points these legal definitions are not quite in accordance with those adopted in Chicago.*

It is apparent that it is not necessary to define all three units, but the third can always, by Ohm's law, be derived from the other two. The United States legalized all three, a procedure which was bound to lead to trouble if it should be found that one or two of them should be incorrect, because it is hardly to be expected that Mother Nature will change Ohm's law in spite of all congressional decisions. The first work which seemed to indicate that the value of the volt was incorrect was an investigation at the Reichsanstalt* in Germany; and at practically the same time two researches carried out at the University of Michigan fully confirmed the results obtained, and also proved that the electro-chemical equivalent of silver depends greatly upon the specifications of the silver coulometer.* Soon other scientists took up the subject and the above mentioned results have received confirmation. Prominent among the investigators of the silver coulometer is Professor Richards* of Harvard, who designed an apparatus which we may call a porous cup coulometer, for which he claimed a higher degree of accuracy than could be obtained by the usual form. I made an extended research* comparing the various forms which had been used by the different experimenters on the subject and found Richards' claim to be correct, and designed a form of

*Wolff, Bulletin, Bureau of Standards, 1, p. 39, 1904.
*Kahle, Zeit. f. Instr. K. 18, pp. 229 and 267, 1898.
*Patterson and Guthe, Phys. Rev. 7, p. 257, 1898.
Carhart and Guthe, Phys. Rev. 9, p. 288, 1899.
*Richards, Collins, and Heimrod, Proc. Am. Ac. 35, 123, 1899.
Richards and Heimrod, Ibid. 37, p. 415, 1902.
*Guthe, Phys. Rev. 19, p. 138, 1904.

porous cup coulometer which is somewhat more convenient for use than Richards' type. The main disturbing factor in silver coulometric work lies in the formation around the silver anode of a complex silver salt which on reaching the platinum cathode deposits too much silver. The introduction of a porous cup keeps the troublesome solution at least partly away from the cathode, if the current is not allowed to be closed for more than an hour. I use in my form a platinum bowl of the size recommended by the Chicago congress and a closely grained porous cup only a little smaller in diameter. At the bottom of this cup some granulated silver is placed and upon this a large plate of silver, forming the anode, is pressed. The granulated silver partly decomposes the heavy solution streaming from the plate and makes the use of a siphon (to keep the solution inside the porous cup at a lower level than the outside) unnecessary.*

Richards' and my results were corroborated by Van Dijk, namely that with a porous cup coulometer the silver deposit is about 3 in 10,000 smaller than in the usual form, and that such coulometers will give results which can be relied upon to 1 in 10,000.

While thus the silver coulometer was improved other investigators attacked the problem of perfecting the standard cell. The Weston standard cell with solid hydrated Cadmium sulphate has proved to be, in many respects, so far superior to the Clark cell that doubtless it will at the next international congress be selected as the standard cell and it is natural that the most recent work has been done with this type of cell instead of the Clark. Carhart, Hulett and Wolff* have by their researches upon the electrolytic preparation of Hg_2SO_4 enabled us to construct cells which, when made by different experimenters, will closely agree in their electromotive force. According to Hulett the Hg_2SO_4 should be prepared electrolytically from an acid solution of concentration larger than normal, so as to avoid hydrolysis.

By these researches we have now arrived at a point where we can rely with equal confidence upon as well the indications of the silver-coulometer as upon an accurate reproduction of Standard cells, and the next question of importance was to redetermine with improved apparatus the absolute values of the electrochemical equivalent as determined by the porous coulometer, and the electromotive force of the improved standard cells. I have just finished this work, the experimental part of which was done at the Bureau of Standards in Washington. The apparatus which I used was a large electrodynamometer, consisting of two coils, each of a single layer of wire. This allows an accurate measurement of the linear dimensions entering into the calculations. The large coil was wound upon a plaster of Paris cylinder while the smaller movable coil was wound upon Berlin porcelain. Two movable coils of different dimensions were used, and the small difference of the two final results served as a valuable check upon the whole work. The torsional

*Guthe, Bull. Bur. Standards, I, p. 349, 1905.
*Van Dijk, Ann. Phys. 19, p. 249, 1906.
*Carhart and Hulett, Proc. Am. Electroch. Soc. 5, p. 59, 1904.
Wolff, Proc. Am. Electroch. Soc. 5, p. 49, 1904.
Hulett, Zeitsch. Phys. Chem., 49, p. 483, 1894. Phys Rev. 22 p 321, 1906.

moment produced by the electromagnetic action between the two coils was balanced by an accurately measured angular twist of the suspending phosphor-bronze wire, i. e., by a torsional moment which may be determined in terms of centimeters, grams, and seconds. To obtain this moment a cylinder of known moment of inertia was vibrated when suspended from the same wire as the movable coil and the period of its torsional vibrations determined.

Let K be the moment of inertia, T the time of vibration of the cylinder, then the torsional moment for unit angle of twist of the suspension is given by the equation,

$$J = \frac{4\pi^2 K}{T^2}$$

The dimensions of the two coils of the electrodynamometer were so chosen that the field strength inside the stationary could be expressed by the simple equation,

$$H = \frac{4\pi N}{\sqrt{D^2+L^2}} I = C\,I,$$

where N is the number of turns of wire on the coil, D its diameter, L its length and I the current flowing through it; and the effective area of the movable coil by the equation

$$A = \pi r^2 n,$$

where r is the average radius of the movable coil and n the number of turns. The torsional moment produced by the current I flowing through the electrodynamometer is then, with the coils at right angles to each other $T' = ACI^2$; this was balanced by the torsional moment of the suspension when the torsion head was turned 90 degrees, or n over 2 radians. Solving for the current, we obtain as final formula:

$$I = \frac{1}{T r}\sqrt{\frac{\pi r \sqrt{D^2+L^2}}{2 N n}}$$

As you see, only measurements of length, mass and time enter into the calculation and this is therefore an absolute determination of the current.

This current was sent through resistance standards and the difference of potential produced compared by means of an accurately calibrated potentiometer with the electromotive force of a dozen standard cells.

The absolute value of the latter is then easily calculated from the current and resistance by means of Ohm's law.

The electrochemical equivalent of silver had been previously determined* by direct comparison between the electromotive force of one of the standard cells and the potential difference at the terminals of the same standard resistances when a constant silver depositing current passed through it.

The standard cells were kindly given to me by Professors Carhart and Hulett. Most of them were set up with electrolytically prepared Hg_2SO_4

It is needless to say that in the actual measurements a great many difficulties were encountered; but thanks to the valuable help of my

*Guthe, Phys. Rev. 19, p. 152, 1904.

colleagues at the Bureau of Standards, and due to the fact that the wonderful facilities of this institution were placed at my disposal, I was able to obtain results, which I consider accurate within 1 in 10,000, an accuracy which I believe has not been obtained before in measurements of this kind.

My final results are the following:

A. Standard cells with electrolytically prepared Hg_2SO_4.

Clark cells at 25° C.

E. M. F. = 1.42040 volts.

Cadmium cells at 25° C.

Acid solution stronger than normal,

(F series) E. M. F. = 1.01827 volts.

Acid solution weaker than normal,

(E, K and O series) E. M. F. = 1.01833 volts.

B. Standard cells with chemically prepared Hg_2SO_4.

Cadmium cells at 25° C. (C series)

E. M. F. = 1.01857 volts.

This shows that the cells with electrolytic Hg_2SO_4 have an electromotive force 0.0003 volt lower than those with chemically prepared Hg_2SO_4

Reducing to 20° C, we obtain for the Cadmium cells,

F. series, E. M. F. = 1.01847 volt.

E, K and O series, E. M. F. = 1.01853 volt.

C series, E. M. F. = 1.01877 volt.

Reducing to 15° C, we obtain for the Clark cells,

E. M. F. = 1.43296 volt.

By this investigation I have therefore fully corroborated the results of our former work, namely that the correct value of the Clark standard cell at 15° C is nearer 1.433 volt and not 1. 434 as legalized in the United States.

The electrochemical equivalent of silver as determined by the porous cup coulometer is 1.11773 milligrams per coulomb.

The following table gives a comparison of the results obtained by former investigations. The values of the electrochemical equivalent are reduced to the porous cup coulometer. The values of the E. M. F. of the Clark cell are given for 15°C, that of the Cadmium cell for 20°C.

A.

ELECTROCHEMICAL EQUIVALENT OF SILVER.

Observer	Date	Coulometer	Method	Found	Corrected
Mascart	1884	Usual type	Current balance	1.1156	1.1153
Fr. and W. Kohlrausch	1884	Usual type	Tangent galvanometer	1.1183	1.1177
Rayleigh and Sidgwick	1884	Usual type	Current balance	1.1179	1.1176
Gray	1886	Plate Coulom'r	Sine galvanometer	1.1183	1.1178
Koepsel	1887	Usual type	Current Balance	1.1174	1.1169
Pellat and Potier	1890	Usual type	Current Balance	1.1192	1.1189
Patterson and Guthe	1898	Sil'r-oxide type	Electro-dynamometer	1.1192	1.1177
Pellat and Leduc	1903	Leduc's type	Current balance	1.1195	1.1190
Van Dijk and Kunst	1904	Usual type	Tangent galvanometer	1.1182	1.1178
Guthe	1905	Porous cup	Electro-dynamometer	1.1177	1.1177

B.

ELECTROMOTIVE FORCE OF STANDARD CELLS.

Clark	1872	Clark at 15 degrees	1.4378
Rayleigh and Sidgwick	1884	Clark	1.4345
Kahle	1896	Clark	1.4322
Carhart and Guthe	1899	Clark	1.4333
Guthe	1905	Clark	1.43296
Guthe	1905	Cadium at 20 degrees	1.01857

Doubtless in the near future other determinations of the absolute value of these important electrical units will be made, some being carried on in the national physical laboratory in England, and some at the Bureau of Standards at the present time. It is to be hoped that in a couple of years steps may be taken for new international action looking towards a uniform legalization of electrical units throughout the civilized world and of units which agree more closely with those derived from absolute measurements. Certainly only two can be defined as fundamental, moreover, even if based upon c. g. s. units they should be concrete units unaffected by the possible discovery of slight errors to be found in future time in the absolute values. It is true they would not be prototypes in the same sense as the international Kilogram and the meter, but there is a certain advantage in the possibility of their reconstructions at any time by different observers. Whether, besides the ohm the ampere or the volt shall be chosen as the second fundamental unit can hardly be predicted at the present time; that depends upon the question which of the two will prove to be reproducible with the higher degree of accuracy. Under otherwise equal conditions preference should be given to the coulometer since the current is found in terms of the fundamental units alone, while in the present determinations of the volt, the ohm enters always as a factor and with it the error made in its measurement, or in other words, the present methods for the determination of the volt are not strictly absolute methods. Whatever decision may be reached it is certain that there will be a closer agreement than under the present law between scientific results and the system used in the commercial world.