THE CONDUCTIVITY OF LIQUIDS: METHODS, RESULTS, CHEMICAL APPLICATIONS AND THEORETICAL CONSIDERATIONS

OLIN FREEMAN TOWER

THE CONDUCTIVITY OF LIQUIDS: METHODS, RESULTS, CHEMICAL APPLICATIONS AND THEORETICAL CONSIDERATIONS

Trieste

=====The=====

Conductivity of Liquids

Methods, Results, Chemi-
cal Applications and ❧ ❧
Theoretical Considerations

By
Olin Freeman Tower, Ph.D.,
Assistant Professor of Chem-
istry, Western Reserve
University.

Nº

THE CONDUCTIVITY OF LIQUIDS.

CHAPTER I.

UNITS. METHODS FOR DETERMINING CONDUCTIVITY.

THE KOHLRAUSCH SYSTEM OF UNITS.—Conductivity is always determined by measuring its reciprocal resistance. Conductivity is, therefore, always defined in terms of units of resistance. Until recently the Siemens mercury unit has been the basis of the unit of conductivity of solutions, and, in fact, of all liquid conductors. This, in turn, has been very generally reproduced from the conductivities of various standard solutions, which values, as given by different authorities, have not always been identical. Within a few years, however, Kohlrausch and associates[1] have proposed a standard unit of conductivity based on the ohm and have determined with great care the conductivities of many standard solutions in terms of this unit. It is, consequently, very easy to reproduce and has now been very generally adopted by both physicists and chemists.

This **unit of conductivity** is defined as the conductivity of a column of liquid 1 cm. in length and 1 sq. cm. in cross section, which has a resistance of 1 ohm. Conductivity expressed in terms of this unit is called the **specific conductivity** and is designated by κ. The conductivity of a solution, which depends almost entirely on the dissolved substance, is, however, best expressed by means of the equivalent conductivity, which takes into account the concentration.

The **equivalent concentration** η is the fraction of a gram-equivalent of the solute in 1 cc. solution. The **dilution** φ is the reciprocal of this, that is $\varphi = \dfrac{1}{\eta}$ and is the number of cubic centimeters in which a gram-equivalent of the solute is dissolved. Since in most cases η and φ are rather cumbersome numbers, it is customary in referring to the concentration of a solution to give

[1] Kohlrausch, Holborn, and Diesselhorst: *Wied. Ann.*, **64**, 417 (1898).

in their stead m and v, respectively. These quantities are based on 1 liter of solution, so that $m = 1000\eta$, and $v = \dfrac{\varphi}{1000}$. m and v sometimes refer to gram-molecules per liter instead of gram-equivalents. When they are used thus in this book, it will be so stated.

The **equivalent conductivity** $\varLambda$ equals the specific conductivity divided by the equivalent concentration or multiplied by the dilution, that is,

$$\varLambda = \frac{\kappa}{\eta}, \text{ or } = \varphi\kappa.$$

The **molecular conductivity** M is sometimes given. This is equal to the specific conductivity divided by the molecular concentration. For monobasic substances the equivalent conductivity and the molecular conductivity are, of course, equal.

UNITS FORMERLY EMPLOYED.—Until recently the specific conductivity k was the conductivity of a column of liquid 1 m. long and 1 sq. mm. cross section, referred to the conductivity of a column of mercury of the same dimensions (Siemens unit) as unit. The ohm equals 1.0630 Siemens unit. This unit of conductivity is, therefore, $100 \times 100 \times 1.0630$ times the new one, so that $\kappa = 10630k$. Occasionally specific conductivities are met with expressed in units in which the conductivity of a column of liquid 1 cm. long and 1 sq. cm. cross-section is referred to the Siemens unit. Conductivity, expressed in this way, will be designated by l,[1] consequently

$$\kappa = 1.0630l.$$

The equivalent conductivity, when based on the Siemens unit, has been commonly designated by λ and the molecular conductivity by μ. Since concentrations were formerly almost invariably expressed in liters instead of cubic centimeters, it was convenient to multiply the small numbers obtained by 10^7, so that

$$\lambda = 10^7 \frac{k}{m};$$

and, therefore,

[1] The symbols which have been used by different authorities to indicate conductivities referred to the Siemens unit have been very much at variance. See preface.

$$A = 1.0630\lambda, \text{ and } M = 1.0630\mu.$$

In Kohlrausch's earlier work $\lambda = 10^8 \dfrac{k}{m}$, and consequently here

$$A = 0.1063\lambda.$$

Although 1.0630 is theoretically the factor for converting conductivities expressed in units based on the Siemens unit into those expressed in the new units, the factor actually required is, in most cases, a little greater than this. It is 1.0690 for most of the work which has originated with Kohlrausch and his associates. The last equation in the preceding paragraph should, therefore, really be

$$A = 0.1069\lambda, \text{ or } = 0.1069\dfrac{k}{m}.$$

The factor is 1.066 for most of the work from Ostwald's laboratory. More exact information concerning this factor can be found in the paper by Kohlrausch, Holborn and Diesselhorst, referred to above. The conductivities of the more important solutions have been recalculated by Kohlrausch and Holborn and are given, expressed in the new units, in their *Leitvermögen der Elektrolyte*. Most of the recent conductivity results will be found in the appendix to this book.

ABSOLUTE UNITS.—Absolute electromagnetic units (C. G. S.) are sometimes employed, especially in formulating certain theoretical relations. In this system the unit of current strength $= 10$ amperes, the unit of potential $= 10^{-8}$ volts and the unit of resistance $= 10^{-9}$ ohms. If K represents the electrical conductivity of a liquid when the unit is the conductivity of a cubic centimeter whose resistance is 10^{-9} ohms, then

$$K = 10^{-9}\kappa.$$

RESISTANCE CAPACITY.—Since the vessel in which the conductivity of a liquid is measured is never of standard dimensions, it is always necessary to introduce a factor to reduce the resistance actually measured to conductivity expressed in the proper units. The factor is called the **resistance capacity**, or sometimes simply the **capacity**, of the vessel and is designated by C. The

resistance R of a column of liquid 1 cm. in length and 1 sq. cm. in cross section is, according to definition, equal to $\frac{1}{\kappa}$ ohm. If the column is l cm. long and s sq. cm. cross-section and the electrodes entirely fill the cross-section, obviously

$$R = \frac{1}{\kappa} \frac{l}{s} \text{ ohm,}$$

or

$$\kappa = \frac{l}{s} \frac{1}{R}.$$

The resistance capacity C is, therefore, equal to $\frac{l}{s}$, that is,

$$\frac{l \text{ cm.}}{s \text{ cm.}^2} = C \text{ cm.}^{-1}$$

Consequently the dimensions of the resistance capacity are reciprocal centimeters. In general for any vessel

$$\kappa = \frac{C}{R}.$$

Since C is expressed in reciprocal centimeters, and R in ohms, the dimensions of the specific conductivity are $\frac{1}{\text{cm.} \times \text{ohm}}$.

TEMPERATURE.—The conductivity of most solutions changes about 2 per cent. for each degree of temperature, and the temperature coefficient of many pure liquids is even greater than this. It is, therefore, essential when determining conductivity that the temperature remain constant and that it be expressed in terms of some fixed standard. The hydrogen scale is the standard commonly employed, and all temperatures given in this book are based on that scale. At 18° an accurate mercury thermometer of Jena normal glass registers about 0.1° too high (see Chapter IX).

METHODS FOR DETERMINING CONDUCTIVITY.

CLASSIFICATION.—Methods for determining the conductivity of solutions are simply methods for measuring resistance applied to liquid media. They are of three classes: (1) Methods in which a direct current traverses the solution; (2) methods in which an

alternating current traverses the solution; (3) indirect method in which no electrodes are used, the solution being simply exposed to the influence of a strong electromagnetic field[1]. This last method has only become of theoretical interest, so it will not be further considered.

When a direct current is passed through a solution, polarization takes place upon the electrodes, and unless this can be eliminated it seriously interferes with the accurate determination of the conductivity. Various means have been employed to try to compensate this polarization, but very few of the methods so devised for determining conductivity compare in accuracy and rapidity with those in which alternating currents are employed. Recently, however, a method of this class has been described by Stroud and Henderson,[2] for which certain advantages are claimed over methods of the second class.
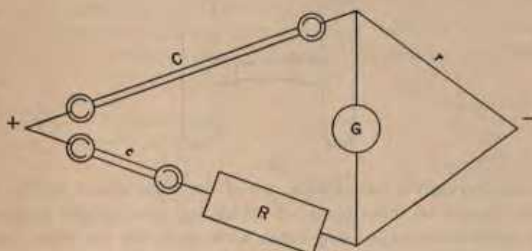

Fig. 1.

STROUD AND HENDERSON'S METHOD.—The method depends on the elimination of polarization on the electrodes by the employment of two electrolytic cells of similar form, but of different resistance capacity in two adjacent branches of a Wheatstone bridge and balancing the difference of resistance between them by means of suitable known resistances. This principle was not new at this time, but the value of Stroud and Henderson's application of it lies in the simplicity of their apparatus and in the accuracy with which measurements can be made.

[1] Guthrie and Boys: *Phil. Mag.* (5), 10, 328 (1880).
[2] *Phil. Mag.* (5), 43, 19 (1897).

The apparatus is arranged as in Fig. 1. C and c are two electrolytic cells of different capacity; r and r' are equal resistances of 1000 ohms each; R is a rheostat containing resistances up to 20,000 or 30,000 ohms; G is a D'Arsonval galvanometer.

Resistance is introduced at R until the resistance of $c + R$ is, as nearly as possible, equal to that of C. Then, since r and r' are equal, equal currents are traversing C and c, and, therefore, the polarization in each cell should be equal. These polarizations are opposed and in theory eliminated. It was found, as a matter of fact, that more than 99 per cent. of the polarization could be eliminated in this way. The rest could be drowned or at least reduced to insignificance by using high resistances and high voltages. With cells having a difference of resistance of about 20,000 ohms and with a resistance in the galvanometer of 300 ohms, good results were obtained with an electromotive force of 30 volts.
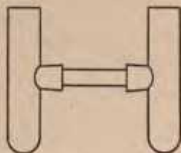

Fig. 2.

Cells giving the best results are of the form shown in Fig. 2. They consist of three parts, of which the two upright portions are small thick-walled test tubes with necks on the side. Into these necks fit the well-ground ends of a tube of, as nearly as possible, uniform bore. The diameter of the upright portions in Stroud and Henderson's apparatus was 1.2 cm. and the height 6 cm. The external diameter of the horizontal tube was 0.6 cm. The internal diameter was suited to the resistance of the electrolyte. In cell C this tube was about 30 cm. long, and in c, 5 cm.

The relative resistance capacity of the two cells can be determined from the following data:

Length of horizontal tube in C	29.70 cm.
Weight of mercury to fill same, plus watch glass.	29.836 grams.
Length of tube in c	4.89 cm.
Weight of mercury plus watch glass.............	11.481 grams.
Density of mercury at temperature of experiment	13.558