METHODS USED IN DETERMINING THE ELECTRIC CONDUCTIVITY OF SOLUTIONS.*

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In making a study of the permeability of bacterial membranes it was thought advisable to look into the principles of the methods used in determining electric conductivity of solutions, since they applied to the study of suspensions of bacteria. The method generally used requires an alternating current, Wheatstone bridge, and telephone for detecting the current. The solution is placed in a conductivity cell containing two metallic plates or electrodes. Since the electrodes are usually made of platinum, and platinum salts are absent from the solution, polarization occurs at the electrodes and no considerable current can pass in one direction without a potential difference across the phase boundary equal to the decomposition potential of the water or salts composing the solution. Since the decomposition potential of water is 1.7 volts and potentials of various salts fluctuate around this figure, a counter E. M. F. of about 1 or 2 volts is added to the passive resistance of the solution and prevents the estimation of the latter. In order to obtain correct results, no current should be allowed to pass between the electrodes and the solution. The electrode surface and solution surface constitute an electric condenser of enormous capacity, since the capacity of a condenser varies inversely with the distance between the plates and this distance is very small, being the thickness of the electric double layer at the metal-water surface. By increasing the frequency of the alternating current and increasing the surface area of the electrodes a point may be reached at which the impedance caused

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by the phase boundary is so small as not to interfere with results of considerable accuracy. Alternating currents of high frequency may be produced by means of Vreeland oscillators, and by vacuum tube oscillators as used in wireless transmission. The electrode surface may be increased by enlarging the electrode or roughening it. An extremely rough electrode surface may be obtained by rapid electroplating in a solution of platinic chloride containing a trace of basic lead acetate. This platinized surface is so rough that it does not reflect light into the eye and hence appears black. Platinized electrodes have an enormous capacity when freshly prepared, but the capacity may decrease with use. This decrease is probably due to the interposition of a poorly conducting layer between the metal and the solution due to adsorption of colloids, or to stoppage of the pores in the surface, thus decreasing the area acting as a condenser. The capacity of a dirty electrode may sometimes be restored by cleaning it with a saturated solution of a bichromate in concentrated sulfuric acid. If this fails, the electrode must be platinized again.

In some of our experiments the electrodes decreased in capacity while the bacterial suspension remained in the conductivity vessel, and cleaning or platinizing of the electrode would necessitate complete change in experimental procedure. In such cases, not only is the impedance greater than the resistance that it is desired to measure, but a tone silence in the telephone cannot be obtained owing to the fact that the current is not in phase with the voltage across the conductivity cell. In recent years, a compensation method for obtaining a tone silence or sharp tone minimum in the telephone has been widely advocated in this country. The method usually consists in the placing of a variable condenser in parallel with the resistance box in the ordinary Wheatstone bridge apparatus (in which the two other resistances are represented on a meter wire with sliding contact). This method enables the operator to obtain a sharp tone-minimum and express his results in figures with five decimal places. It is one of the objects of this communication, however, to emphasize that such figures may be incorrect in the second place.

Our experiments have been made with frequencies varying continuously from 60 to 500,000 cycles per second produced by a Vreeland oscillator and a vacuum tube oscillator made of a Western Electric, VT 2, bulb. At radio-frequencies, we have had to simplify the apparatus in order to obtain currents in phase with the voltage and have had to eliminate much of the Wheatstone bridge apparatus. Furthermore, we used a crystal detector and galvanometer and have never achieved the accuracy possible with the lower frequencies and telephone. This paper will be confined, therefore, to work with the Vreeland oscillator and telephone receiver.

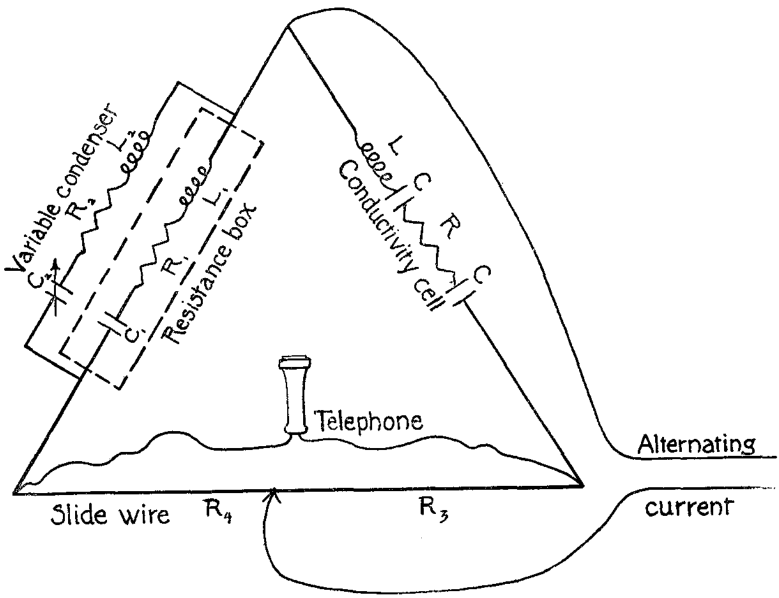

FIG. 1.

Our Wheatstone bridge is diagramed in Fig. 1, in which resistance is denoted by R, capacity by C, and inductance by L. In the conductivity cell, the resistance, R, is the solution; the total capacity is one-half the capacity of one electrode surface, C; and the inductance, L, is in the connecting wires. By straightening these wires, the inductance may be reduced to a small figure. The resistance box has a variable resistance, R_1, a small capacity in parallel but an infinite capacity in series, C_1, and a small inductance, L_1. In parallel with the resistance box is a variable condenser with variable capacity, C_2, small resistance, R_2, and small inductance, L_2. In the cell arm of the bridge, given the resistance in ohms, the capacity in farads, and the inductance in henries, the impedance, Z, to the flow of alternating current of frequency, f, is

$$Z = \sqrt{R^2 + \left(2\pi f L - \frac{1}{2\pi f C}\right)^2}$$

In the resistance box arm of the bridge the calculation is a little more complicated and will be given in greater detail.

The impedance, Z, may be resolved into two components, the resistance, R, and the reactance, X, such that

$$Z = \sqrt{R^2 + X^2}$$

where the reactance

$$X = 2\pi f L - \frac{1}{2\pi f C}$$

The admittance, Y, is the reciprocal of the impedance, Z; the conductance, G, is the reciprocal of the resistance, R; and the susceptance, B, is the reciprocal of the reactance, X, and

$$Y = \sqrt{G^2 + B^2}$$

or for the parallel circuit

$$Z = \frac{1}{Y} = \frac{1}{\sqrt{G^2 + B^2}} = \frac{1}{\sqrt{\left(\frac{R_1}{Z_1^2} + \frac{R_2}{Z_2^2}\right)^2 + \left(\frac{X_1}{Z_1^2} + \frac{X_2}{Z_2^2}\right)^2}}$$

But if the inductance and capacity of the resistance box are disregarded as well as the resistance and inductance of the variable condenser, and if the latter is so constructed to be of negligible dielectric loss, the equation may be simplified and reduced to the following.

$$Z = \frac{1}{\sqrt{\frac{1}{R_1^2} + (-2\pi f C_2)^2}}$$

In case the self-inductance of the conductivity cell is negligible, the resistance, R, of the solution may be found from the following proportion.

$$\sqrt{R^2 + \left(-\frac{1}{2\pi fC}\right)^2} : \frac{1}{\sqrt{\frac{1}{R_1^2} + (-2\pi fC_2)}} = R_3 : R_4$$

Example.—The following determination was made on 1 per cent NaCl in water in a conductivity cell containing bright gold electrodes 25 mm. square, at 25°. $R_1 = 20$ ohms, $C_2 = 1.06 \times 10^{-6}f$, $R_3 = 478$ and $R_4 = 522$, and f = 5,000. The impedance of the arm of the bridge containing resistance box and variable condenser was

$$\frac{1}{\sqrt{\frac{1}{20^2} + (6.2832 \times 5{,}000 \times 1.06 \times 10^{-6})^2}} = 16.67 \text{ ohms}$$

and the impedance of the cell: 16.67 = 478: 522, therefore the impedance of the cell = 15.28.

Since the difference in phase between the current and voltage is the same in the two arms of the bridge, the following ratio holds.

$$\frac{1}{R_1} : \frac{1}{16.67} = R : 15.28$$

therefore $R = 16.67 \times 15.28 \div 20 = 12.73$ ohms

It should be emphasized that if the usual method of disregarding the reactance of the bridge is followed the calculation is

$$R : 20 = 478 : 522$$

therefore

$$R = 18.314$$

in other words, the resistance of the solution is 12.73 ohms, whereas the uncorrected calculation gives 18.314 ohms, or 28 per cent too high a value.

A Method of Procuring Sharp Tone-Minimum with Bright Electrodes without the Necessity of Complicated Calculations.

If the variable condenser, $C_2R_2L_2$, is removed from the Wheatstone bridge, a tone-minimum of great sharpness may be secured with the aid of a variable inductor, L, in series with the conductivity cell. With bright electrodes, 25 mm. square, we found the General Radio Variometer 107 *C*, with a range of about 0.02 to 0.5 millihenries sufficient, and the cost was a small fraction of that of the variable condenser necessitated by the previous method. Since there is loss of power due to dielectric hysteresis in a paraffined paper condenser, a high grade condenser of maximum capacity of 10 microfarads had to be used in the previous method and hence the high cost.

If the reactance of the resistance box is negligible, the reactance of the conductivity cell plus variometer is zero when the variometer is adjusted for sharp tone silence, as follows:

$$\text{Reactance} = 2\pi f L - \frac{1}{2\pi f C}$$

and tone-minimum is not secured until the inductance, L, is so adjusted that it compensates the capacity, *C*, of the cell so that the reactance becomes zero.

With the elimination of the reactance from the equation, the calculation involves only the resistances in the four arms of the bridge and the subtraction of the resistance of the variometer from the resistance of the arm of the bridge containing it, in order to obtain the resistance of the conductivity cell. The variometer is made of two coils rotating on an axis in the plane of the coils, and hence the current passes through the whole length of wire no matter what the setting for inductance. Therefore, the resistance of the variometer does not change except at frequencies high enough to produce skin effect. The resistance of the variometer may be determined once for all. Its resistance was 1.095 with coils connected in series and 0.2855 with coils connected in parallel for low inductance.

The use of the variometer eliminates the necessity of platinizing the electrodes, and allows the use of smaller electrodes, thus adapting the conductivity method to a wider range of usefulness in biochemistry. Sufficient current must be used in order to work the telephone diaphragm, but, if the conductivity of the solution is high enough, very small electrodes may be used without danger of reaching current saturation. An inductance has been used by Taylor and Acree,[1] but their results were reduced to infinite frequency.

[1] Taylor, W. A., and Acree, S. F., *J. Am. Chem. Soc.*, 1916, xxxviii, 2403.