[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF McGILL UNIVERSITY]

THE DIELECTRIC CONSTANT OF WATER AND ITS TEMPERATURE COEFFICIENT AS DETERMINED BY A RESONANCE METHOD. II

BY E. P. LINTON[1] AND O. MAASS

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In the following a new modification of a dielectric cell is described which makes possible a more accurate determination of the dielectric constant of water by the resonance method than the cell previously used for this purpose.[2]

This cell was also used for the redetermination of the dielectric constants of several liquids and for the measurement of the temperature coefficient of the dielectric constant of water.

New Type of Variable Condenser.—Figure 1 gives a diagrammatic sketch of the new type of cell. It consists of two cylindrical tubes B (closed at each end) and D which are insulated from each other by the glass plates K and C. The outer cylinder D is about 5.2 cm. in diameter and 50 cm. high. By varying the radius of the inner rod a condenser of any desired capacity can be made. In the following measurements two inner tubes were used, one 0.5 cm. and the other 4.4 cm. in diameter.

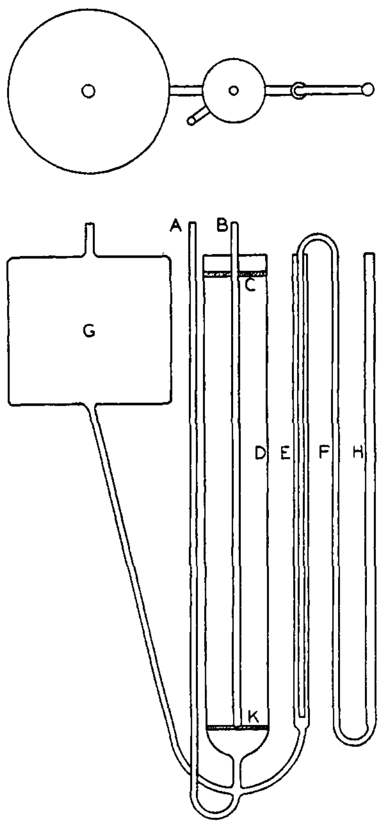

Fig. 1.—The dielectric cell: above, plan; below, elevation.

A maximum of 700 cc. of liquid is necessary to fill the cell. By applying suction or pressure to G the height of the liquid in the cell can be varied as desired, G acting as a reservoir. The position of the liquid in D is measured by means of the glass tube H, which is 2 cm. in diameter. The glass tube F completely filled with liquid is connected through E to D so that the height of the liquid in H is the same as that in D. A, B, E and H are open to the air. A, B, D, G and E are made of pure block tin, and the construction is such that no glass to metal joint is needed in the apparatus.

The purpose of tube A is to drain the liquid from the cell by the application of suction. The cell is dried out by means of a stream of air. As a further precaution the whole apparatus is then rinsed with the liquid whose dielectric constant is to be measured.

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[2] Linton and Maass, THIS JOURNAL, **53**, 957 (1931).

The apparatus can therefore be cleaned without dismounting or removal from the thermostat. This enables one to measure a series of liquids without removing the inner tube B. The cell is in convenient form for thermostating. An oil- or water-bath can be used in the thermostat, but the outer cylinder of the condenser must be grounded. Since the capacity of the cell is dependent on the ratio of the radii of the inner and outer tubes, a change in temperature does not alter the capacity of the cell for a fixed height. With the procedure used the cell is therefore admirably adapted for the measurement of a temperature coefficient of a dielectric constant of a liquid over a large range of temperature.

Furthermore, in this cell, since the capacity is dependent on the position of the liquid and not on any setting of condenser plates, complete reproducibility is possible. The capacity of the cell was found to vary in a linear manner within the accuracy to which the height of the liquid in the tube could be read, *i. e.*, to within 0.1%.

Then if ϵ_1 and ϵ_2 are the dielectric constants of two liquids and $C_1 - C_1^1$ and $C_2 - C_2^1$ the corresponding changes of capacity for equal changes in position of the liquids in the cell then

$$\frac{\epsilon_1 - 1}{\epsilon_2 - 1} = \frac{C_1 - C_1^1}{C_2 - C_2^1}$$

These changes in capacity are measured by the tuning condenser as previously described.

To eliminate the influence of conductivity in the case of water at the higher temperatures, the power tube described previously was used. With the above cell the "dead space" was found to be negligible and the linear relationship was given by all intermediate settings of the cell.

Experimental Results

In order to determine the dielectric constant of water it was necessary this time to start with a standard liquid, and benzene was chosen. Smyth evaluates the dielectric constant at 25° as 2.273. The authors have found the value of 2.271. It is considered better, however, to use Smyth's value.

Only two stages are required to determine the dielectric constant of water. In the first, benzene and ethylene dichloride and the 4.4-cm. inner tube was used; in the second, ethylene dichloride and water with the 0.5-cm. inner tube.

The average of five determinations, each of which started with benzene, gave 79.2 as the dielectric constant of water at 25°. The greatest deviation from this mean was one in four hundred. The following dielectric constants for carefully purified liquids were found: ether, 4.23; ethylene dichloride, 10.46; nitrobenzene, 34.9.

Temperature Coefficient of the Dielectric Constant of Water.—A large number of determinations of the dielectric constant of water at various temperatures were made. The procedure was as follows. After filling the cell with pure water the capacity height slope at 25° was determined. Then the cell was brought to a different temperature and the new slope determined. The cell was filled with fresh conductivity water for each measurement. Occasionally the slope at 25° was redetermined after the temperature change and was always found to be the same. From a series of twenty measurements between 0 and 50°, a smooth curve relating temperature and dielectric constant was drawn. The equation to this curve was found to be

$$\epsilon_t = 79.2(1 - 0.00428(t - 25) + 0.0000212(t - 25)^2 - 0.00000041(t - 25)^3)$$

This equation follows the curve from 0 to 25° with an accuracy of one part in one thousand, from 30 to 50° the accuracy is one in five hundred.

Conclusion

The dielectric constant of water now found is the same as that previously determined by the authors, although the dielectric constants of some of the intermediate liquids are not the same. This difference is due to the greater care taken this time in the purification of the liquids. The purity of the liquid, of course, does not alter the absolute value obtained for the dielectric constant of water as long as the first medium in the series of steps (air or benzene) is pure.

The dielectric constant of water as determined by the authors gives good agreement with the Debye–Hückel theory of ions.[3]

In the Debye–Hückel theory of the heats of dilution of strong electrolytes, the dielectric constant of water and the temperature coefficient of the dielectric constant give much closer agreement with the experimental values found by Lange and Messner[4] than the values obtained by Kockel and Drude. On the basis of Kockel's values, 41 calories, on the basis of Drude's, 33 calories are the calculated values for the heat of dilution of a potassium chloride solution. The authors' value gives 26 calories, which is in fair agreement with 23 ± 3 found by Lange.

The cell as described can be modified as far as dimensions are concerned so as to be available for much smaller quantities of liquids.

Summary

The new type of variable condenser is described which has a greatly increased accuracy as far as setting is concerned. The dielectric constants of water, nitrobenzene, ethylene dichloride, ether and benzene have been measured at 25°. The dielectric constants of water have been measured over the temperature range 0 to 50°. The new values obtained for water were found to be in better agreement with the calculations involved in Debye's theory.

MONTREAL, CANADA

[3] Williams and Brönsted, THIS JOURNAL, **50**, 1342 (1928).

[4] Lange and Messner, *Z. Electrochem.*, **33**, 431 (1927).