of standard potassium iodate solution (approximately 0.1 N); such a volume (between 10 and 20 ml.) of approximately 4.0 N potassium hydroxide that the solution remains alkaline after completion of the reaction; 10 ml. of approximately 0.25 F disodium hydrogen phosphate; 25 ml. of standard vanadyl sulfate solution, approximately 0.1 N in vanadium and 1.5 N in sulfuric acid; the required volume of approximately 1.2 N sulfuric acid, which is usually between 10 and 20 ml. The volume of standard thiosulfate solution (approximately 0.1 N) is in every case between 20 and 30 ml.

From the results of Expts. 8 and 9 it is seen that, on the average, approximately 1% of the tetravalent vanadium used is oxidized by the oxygen present in the vanadium solution alone. If oxygen is excluded from all solutions, the results obtained are, on the average, within 0.1% of those calculated.

Summary

It has been shown that iodate and tetravalent vanadium react completely in hot alkaline solutions. Phosphate has been found to catalyze this reaction.

A method of determining vanadium by means of this reaction has been described. The results check on the average within 0.1% of the calculated if oxygen is excluded during the reaction.

Los Angeles, California

[Contribution from the Physical Chemical Laboratory, McGill University]

THE DIELECTRIC CONSTANTS OF WATER AT VARIOUS TEMPERATURES

By A. C. Cuthbertson and O. Maass

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As a step in the measurement of the dielectric constant of hydrogen peroxide it was found necessary to use water for purposes of comparison. A large divergence exists in the values of the dielectric constant given for water and little attention has been paid to the measurement of the temperature coefficient over a wide range. This led to the development of the method described below in which measurements were carried out between 0 and 75°. This method offers no originality in its main principles but in the details of procedure improvements have been made which lead to consistent results.

Experimental

General Outline.—The method employed involves the resonance principle for the measurement of capacity in the ingenious set-up described by Williams and Krchma.[1] The distinguishing feature from that used

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[1] Williams and Krchma, This Journal, **48**, 1892 (1926).

by them lies principally in the design of the dielectric cell and the insertion of an invariable capacity in series with the dielectric cell and tuning condenser.

A diagram of the apparatus is shown in Fig. 1. As the source of oscillations two Hartley oscillators were employed designated as A and B in the figure. The inductances in both cases consisted of 75-turn honeycomb coils. A tap taken off at 50 turns was connected to the filament lead of the vacuum tube. In the case of A the inductance was shunted by a General Radio Condenser of the type used in wavemeters. In order to increase the accuracy of the readings a mirror was mounted vertically at the center of the dial so that the scale readings could be read by reflected light on a circular millimeter scale 4 feet in diameter. This type of condenser was supplied with a vernier control. The small composition knob was removed and a 1-inch brass pulley substituted. By means of a cord belt and another pulley 5 feet distant it was possible to tune the condenser without being sufficiently close to introduce body capacity effects. In the plate circuit a choke coil F was inserted to act as an impedance, which prevented radio frequency currents from passing through the plate circuit.

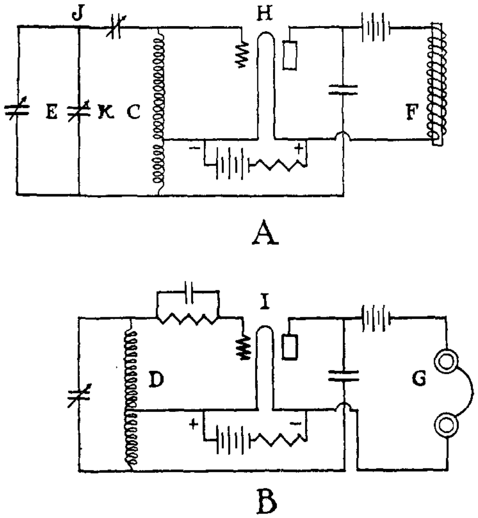

Fig. 1.—A, Variable oscillator; H, 171A. radiotron; F, impedance coil; C, inductance; J, series condenser; K, tuning condenser; E, dielectric cell; B, fixed oscillator; I, U. v. 199 Radiotron; G, phones; D, inductance.

The fixed oscillator B was shunted with a variable condenser whose capacity could be varied to suit the measurement, but it was of course fixed at a definite value for any one. The telephones G used to indicate the point of resonance between the two circuits occupy the same position in B that the impedance F does in A.

A 171A Radiotron tube was found satisfactory for the circuit in which the dielectric cell was connected, *i. e.*, A. In this circuit the oscillations have to be forced through substances which have a measurable conductivity and which show a tendency to absorb, and therefore it was necessary to place a capacity J in series with the variable tuning condenser and dielectric cell. Measurements could be made up to a conductivity of 10^{-5}. In the fixed oscillator B a U. v. 199 Radiotron was used.

Dielectric Cell.—The success of the method was found to depend very largely on the construction of the dielectric cell. The ordinary type of two fixed plates has disadvantages, one of the most important being "capacity lead effects." The one to be described was constructed on the principle of a variable condenser the plates of which could be immersed in the liquid. The container of the liquid acted as a support for the cell. It consisted of two sets of semicircular plates. One set was fixed and may be designated as the stator plates. These were bolted by means of brass rods to an insulating frame of hard rubber. The other set, known as the rotor, was fitted to a brass axle. The vertical position of the axle was so adjusted that the rotor plates would mesh with the stator plates. In order to fix rigidly the position of the two sets, the axle supporting the rotor one passed through two bearings, one through the insulating frame, the other a short distance above the plates. The latter was attached to but insulated from the brass rods supporting the stator plates. A vernier dial was fixed by means of a set screw to the brass axle and bolted by two screws to the same frame which supported the stator plates. This dial served to hold the rotor plates in position and also provided a means of setting the plates to a given capacity value. The liquid to be measured was placed in the container and the plates of the cell were immersed in it. A lid fastened to the insulating frame held it in position.

This type of cell removed any capacity lead effects. In actual use it was permanently connected in the circuit and set at a definite capacity value as given by the dial reading. Tuning of the variable condenser to which it was connected in parallel brought the oscillator A to resonance with B and the scale reading was noted. Readings were taken at two resonance positions of the variable condenser, first when the cell was filled with air, or a substance of known dielectric constant, second with the substance whose value was to be determined. The ratio of the differences in readings on the tuning condenser gives the ratio of the dielectric constants. This eliminates the end effects in the condenser, provided that the capacity setting is neither too small nor too large. Under these conditions the capacity varies in a linear way.

The dielectric constants of various substances vary from about unity to one hundred. It is not always practical to compare the liquid in question to air. The reason for this is that either the accuracy in the determination of air or the substance possessing a large dielectric would have to be sacrificed. With water as the dielectric the capacity of the cell is approximately 80 times that when air is present. If a large enough capacity were used to give a large scale reading for air then, using the same tuning condenser, the capacity of the same cell with water would be too large to measure.

In order to avoid sacrificing the accuracy of the air or water measurement, a "step-by-step" method was adopted. The flexibility in design of the cell permitted this to be accomplished easily. The stator plates were held in position by means of nuts threaded to the supporting brass rods. Separation was accomplished with machined brass washers. The capacity of such a condenser could be altered in one or both of two ways. In the first place the stator plate separation could be increased or decreased by a thickness of one or more washers. A corresponding alteration was of course made in the rotor plates. In the second place the number of stator and rotor plates could be increased or decreased, *i. e.*, a 3, 5, 7, 9, etc., plate condenser was readily constructed, depending on the magnitude of the constant to be measured.

The scheme is exemplified in the following way. A 9-plate condenser made possible an accurate determination of chlorobenzene relative to air. A 5-plate condenser allowed a comparison to be made between chlorobenzene and nitrobenzene, while 3 plates served to establish the relationship between nitrobenzene and water. The vernier dial was divided into 100 divisions corresponding to 180°. Instead of merely taking a reading at 20 and re-setting the dial at 80, resonance points were obtained at 20, 30, 40, 50, 60, 70 and 80—or whatever range was most convenient. In order to illustrate the experimental procedure, results are given for this particular series and are tabulated in Table I and plotted in Fig. 2.

Results

Curves 1 and 2 represent the relative capacity of air and chlorobenzene using a 9-plate condenser; 3 and 4 that of chlorobenzene and nitrobenzene with a 5-plate condenser, while 5 and 6 represent the relationship between nitrobenzene and water, the comparison being made in a 3-plate condenser.

The values of the dielectric constants can be computed easily from the

TABLE I

RESONANCE READINGS FOR VARIOUS SETTINGS OF DIELECTRIC CELL. TEMPERATURE, 25°

Cell settings	Readings at resonance	Cell settings	Readings at resonance	Cell settings	Readings at resonance
Air, 9-plate condenser		C_6H_5Cl, 9-plate condenser		C_6H_5Cl, 5-plate condenser	
20	5.90	20	11.50	20	5.20
30	6.80	30	16.30	30	7.50
40	7.70	40	21.60	40	10.30
50	8.60	50	26.80	50	12.80
60	9.50	60	31.30	60	15.30
70	10.40	70	36.60	70	17.90
80	11.30	80	41.30	80	20.45
$C_6H_5NO_2$, 5-plate condenser		$C_6H_5NO_2$, 3-plate condenser		Water, 3-plate condenser	
20	11.25	20	3.10	20	11.50
25	19.50	30	7.50	25	16.55
30	27.70	40	12.10	30	21.35
35	35.50	50	16.70	35	26.40
40	43.15	60	21.60	40	31.40
		70	26.30	45	36.50
		80	30.70	50	42.00
				55	46.90

above data as in every case they are inversely proportional to the slope of the line which is obtained by plotting the setting of the condenser against the capacity. As a result the dielectric constants for chlorobenzene, nitrobenzene and water based on air as unity are found to be 5.61, 35.20 and 75.40, respectively.

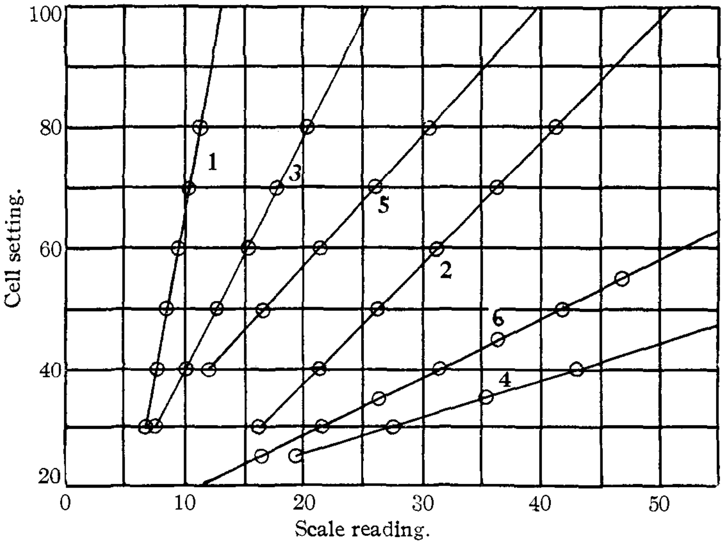

Fig. 2.

In order to check the value for water a 5-plate condenser made possible a comparison between air and ether, a 3-plate between ether and water. The results gave 4.02 and 75.5 as the dielectric constants of ether and of water at 25°.

A direct comparison was made for benzene. The value obtained was 2.28. All substances mentioned above had been carefully purified by standard methods. It may be pointed out that the value obtained for water will be independent of the purity of the substances used in the intermediate steps.

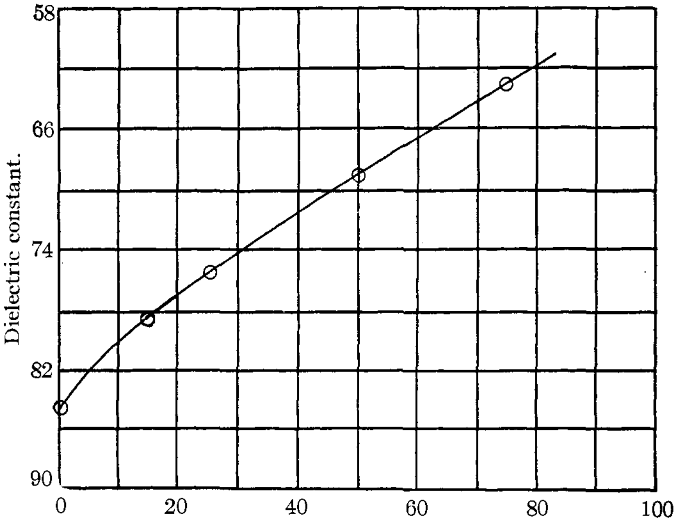

Fig. 3.

The Temperature Coefficient of Water.—From the above results the dielectric constant of water at 25° is 75.4. The effect of temperature was then investigated over the range 0 to 75°. Using the same 3-plate condenser which gave the value for water at 25°, the others were obtained at 0, 15, 50 and 75°. The values obtained at 0, 15, 50 and 75° were 84.4, 78.5, 69 and 62.9, respectively, all based on the value 75.4 at 25°. The above values were obtained repeatedly; especially the one at 0° was measured often. The values checked with one another within 1%, of which the above values are the mean.

The relationship between the dielectric constant and temperature is shown in Fig. 3.

Discussion of Results

From 25 to 75° the relationship between the dielectric constant of water and temperature is approximately linear, the temperature coefficient being −0.258. From 0 to 15° the average value is −0.390, while the intermediate value between 15 and 25° is −0.310. The temperature coefficients[2] over a narrow range found by various observers vary from −0.28 per °C. to −0.495; the lowest value, −0.28, obtained by Nernst[3] is in best agreement with the value obtained by the authors.

The most thorough investigation of the temperature coefficient of the dielectric constant is that carried out after the above compilation was made by Lattey. L. Kockel[4] made measurements over the range 0 to 100°. The resonance method with the particular set-up used did not give results on account of the conductivity of the water. The Nernst bridge method was then resorted to and the results were based on the absolute value of the dielectric constant of toluene. At 50° the value obtained by L. Kockel agrees with that of the authors, below the values are greater and above less. At 0° the difference amounts to 4%. The average temperature coefficient over the range 0 to 15° is 0.30 as compared to 0.35 above.

As to the value of the dielectric constant at 18°, the mean of the values obtained by various observers is 81.05, while that of the authors is 77.0 (the wave length used was 200 meters).[2]

The dielectric constants of benzene, chlorobenzene and nitrobenzene check well, however, with the accepted values. That of Isnardi,[5] 2.273, is usually taken as standard, so that the value 2.28 is probably accurate to 0.5 of 1%. In the case of chlorobenzene the constant 10.95 of Veley in Landolt-Börnstein's Tables is in error, as pointed out by Williams and Krchma[1] and Smyth, Morgan and Boyce.[6] The value 5.61 is in good agreement with their values. For nitrobenzene the values in Landolt-Börnstein's Tables are reasonably close to 35.2.

The Polarizability of Water at Various Temperatures.—The molecular polarizability P of a substance is given by

$$P = \frac{E-1}{E+2}\cdot\frac{M}{d}$$

E = dielectric constant
M = molecular weight
d = density

The values of P at various temperatures were calculated and the results tabulated in Table II.

TABLE II

POLARIZABILITY OF WATER

Temperature, °C.	0	15	25	50	75
Polariz., $(E-1)/(E-2)\cdot M/d$	17.38	17.35	17.36	17.45	17.62

For a substance having a large dielectric constant, the polarizability will vary less with the temperature than for a substance having a small one. Consequently, when the dielectric constant reaches a large value,

[2] Lattey, *Phil. Mag.*, **41**, 829 (1921).

[3] Nernst, *Z. physik. Chem.*, **14**, 622 (1894).

[4] Kockel, *Ann. Physik*, **77A**, 417 (1925).

[5] Isnardi, *Z. Physik*, **9**, 153 (1922).

[6] Smyth, Morgan and Boyce, THIS JOURNAL, **50**, 1536 (1928).

as is the case in water, variation in density will largely govern the variation in the polarizability. Furthermore, water in the liquid state is a substance in which the molecules show a great tendency toward association, which doubtless varies with the temperature. The Debye equation which would apply when the molecules are free to assume a random orientation, has no significance for a substance of this kind. An attempted calculation of the electric moment only serves to make this evident.

Any significance which may be attached to the above values is best left until more data are obtained.

Acknowledgment is made to the National Research Council of Canada for a bursary and studentship held by one of us, during the tenure of which the above work was carried out.

Summary

A resonance method for the measurements of the dielectric constant of pure liquids is described, involving the use of a variable dielectric cell in which lead and end effects are eliminated and the dimensions of which can be altered over wide limits.

The dielectric constants of ether, benzene, chlorobenzene and nitrobenzene were measured at 25°. The dielectric constant of water was determined between 0 and 75°. The step-by-step method used made it possible to make absolute determinations based on air as unity.

The polarizability of water was calculated from the dielectric constant data. The futility of applying the Debye equation for this substance was pointed out.

MONTREAL, CANADA

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY, MCGILL UNIVERSITY]

HYDROGEN PEROXIDE. VII. THE DIELECTRIC CONSTANTS, REFRACTIVE INDICES AND IONIZING POWER OF HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS

BY A. C. CUTHBERTSON AND O. MAASS

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Dielectric Constants.—The measurements referred to in the title may most conveniently be taken up in separate sections.

The determination of the dielectric constants of hydrogen peroxide and its aqueous solutions presents two difficulties: the tendency of the peroxide to decompose and conduction of the solutions due to impurities. The first of these was very largely overcome by constructing a cell similar to the one described elsewhere[1] but made of tin. The second difficulty was eliminated by paying particular attention to the purification of the peroxide. It was found that of all metals very pure tin showed the least

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[1] Cuthbertson and Maass, THIS JOURNAL, **52**, 483 (1930).