DISCUSSION PUBLISHERS
Research Center · Open Access Edition

Dielectric constant of water from 0 to 100 C

C Malmberg, Arthur A. Maryott

Discussion Research ID	DPR-2026-1293
Year	1956
Field	Engineering
DOI	10.6028/jres.056.001
Licence	PUBLIC-DOMAIN
Original source	Journal of research of the National Bureau of Standards
Permanent link	https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59
Publisher	Discussion Publishers discussionpublishers.com

Abstract

An equal ratio arm, capacitance-conductance bridge, operated at frequencies below 100 kilocycles per second, was med to measure the dielectric constant of water with an accuracy of better than 0.1 percent at 5-degree intervals over the range .0 to 100 C. At 25 C the dielectric constant was found to have the value 78.30, which is about 0.3 percent lower than t hat usually accepted.The data fit the equation E= 87.740 -0.400081+ 9.398(10-4) tL 1.410 (10-6)13, with a maximum deviation of 0.01 unit in dielectric constant.The experimental method and sources of error are considered in some detail.

Republished by Discussion Publishers under the original PUBLIC-DOMAIN licence. Copyright remains with the original authors; please cite the original work.

Cite as: C Malmberg, Arthur A. Maryott (1956). Dielectric constant of water from 0 to 100 C. Discussion Publishers, DPR-2026-1293.

Dielectric Constant of Water from 0° to 100° C

C. G. Malmberg and A. A. Maryott

An equal ratio arm, capacitance-conductance bridge, operated at frequencies below 100 kilocycles per second, was used to measure the dielectric constant of water with an accuracy of better than 0.1 percent at 5-degree intervals over the range 0° to 100° C. At 25° C the dielectric constant was found to have the value 78.30, which is about 0.3 percent lower than that usually accepted. The data fit the equation

$$\epsilon = 87.740 - 0.40008t + 9.398(10^{-4})t^2 - 1.410(10^{-6})t^3,$$

with a maximum deviation of 0.01 unit in dielectric constant. The experimental method and sources of error are considered in some detail.

1. Introduction

Numerous determinations of the dielectric constant of water have been reported in the literature during the past half century. [1] However, much of this work was not conducted with sufficient accuracy to provide data adequate for reference purposes. Several of the more recent investigators [1,2,3,4,5],[2] employing varied experimental techniques in which the accuracy was stated or has been inferred to be of the order of 0.1 percent, report values that are in close agreement at room temperature but not at higher and lower temperatures. Discrepancies amounting to a percent or more exist at higher temperatures.

This investigation was undertaken to redetermine the dielectric constant of water over the range 0° to 100° C with an accuracy better than 0.1 percent. A low-frequency bridge method with a Wagner earth to permit the use of three-terminal dielectric cells was employed. The various methods of measurement, generally some form of bridge or resonance method, are all more or less subject to errors associated with the residual impedances of the network that are enhanced when the medium possesses appreciable conductivity. The present assembly has the advantage of facilitating the minimization, ready control, and accurate evaluation of these residual errors, and of simplifying certain problems regarding the design of cells suitable for accurate absolute measurements.

The values of dielectric constant reported in this investigation are significantly lower than previously assigned values [6], about 0.3 percent at 25°, but the variation of dielectric constant with temperature is substantially the same as reported by Wyman and Ingalls [5] except at the lowest temperatures.

2. Apparatus

The a-c bridge is of the equal-ratio arm, capacitance-conductance type, with a Wagner earth. The Wagner earth permits use of either two- or three-terminal cells, and in conjunction with proper shielding, either eliminates or fixes the influence of ground admittances and interbranch couplings. A schematic diagram of the circuit is shown in figure 1. The basic network and its components, with the exception of the unknown arm and standard capacitor, are substantially the same as those described previously [7].

The unknown arm contains a shielded 3,000-ohm resistor, R, and a small capacitor, C, in parallel with the guarded capacitance, C_x, of the test cell in order to provide convenient "zero" settings for the standards, C_m and R_4, of the measuring arm. The capacitance of the test cell is measured in terms of C_m by connecting the cell in parallel first with C and then with Z_5 of the Wagner earth by means of the switch, K. In the latter case the cell is effectively removed from the main bridge circuit because its earth-potential electrode is connected to ground, and admittances from any corner of the bridge to ground do not affect the conditions of balance.

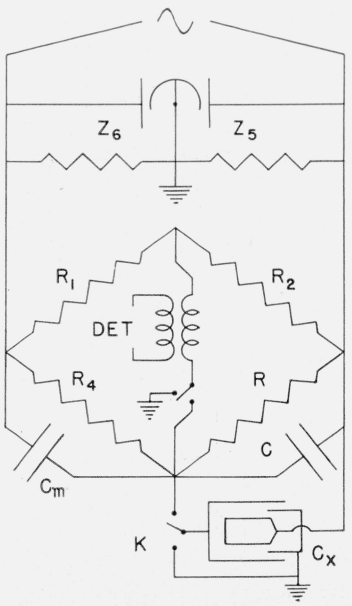


FIGURE 1. *Schematic diagram of the bridge circuit.*

[1] For an extensive compilation and comparison of data prior to 1937, see N. E Dorsey, Properties of ordinary water substance, ACS Monograph, (Reinhold Publishing Co., New York, N. Y., 1940).

[2] Figures in brackets indicate the literature references at the end of this paper.

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59

The three cells used were designed for "absolute" measurements, the insulating supports being located where they should not affect the desired interelectrode capacitances. Intercomparisons between the three cells, using media of various dielectric constants, indicated that these capacitances varied linearly with the dielectric constant of the medium. Because accurate measurements become increasingly difficult as the conductivity of the medium increases, the materials of construction of the two cells, *A* and *B*, used with water, were selected to minimize electrolytic contamination. Cell *C* was used only for intercomparisons with liquids of lower dielectric constant and conductivity.

Cell *A* is a fixed, three-terminal, cylindrical capacitor. A schematic drawing is shown in figure 2. The base material is copper, with the electrode surfaces coated with pure tin. The central, or high-potential, electrode, *H*, is supported by the grounded guard electrode, *G*. Electrical insulation and a liquid-tight seal are provided by 0.01-in. Teflon gaskets on each side of the silvered copper spacer, *F*, and by a Bakelite bushing on the upper side. The high-potential terminal is electrostatically isolated from the case by the removable shield, *S*. The guard electrode is supported on the outer case, which, in part, serves as the earth-potential electrode *D*, by means of a Pyrex-glass ring and 0.01-inch Teflon gaskets, and held by six bolts insulated from the guard electrode by Bakelite bushings. To prevent the trapping of gas in the annular space between the guard and the earth potential electrodes when the cell is being filled with liquid, four 1-mm holes were drilled through *G* at level *E*. A Pyrex-glass reservoir is attached to a silvered copper tube extending from the bottom of the cell, as shown at the left of figure 3, to facilitate the introduction and manipulation of fluids. Coaxial cable, with the outer conductor grounded, connects the cell to the appropriate bridge terminals. Coupling between the exposed, earth-potential electrode and other components of the network is prevented by proper shielding. As lead, shield, and guard capacitances are all effective directly to ground, only the capacitance between the test electrodes, *D* and *H*, is measured. This capacitance in air is about 34 $\mu\mu$f.

Cell *B*, shown at the right in figure 3, is of the differential type. It was constructed from a General Radio type 568–D variable air capacitor modified in several respects. The number of plates was reduced to give a replaceable capacitance of about 28 $\mu\mu$f, and all metal surfaces were tinned. The steatite insulators were replaced with Pyrex glass and partially shielded to minimize any effect of the insulation on the differential capacitance. The unit was mounted in a gold-plated brass case. The rotor control handle is variable between fixed stops mounted on the cover. The high-potential stator plates bracket the earth-potential rotor plates when interleaved to avoid varying the stray fields through the insulating supports. Both are isolated from the case except when the cell is used as a two-terminal capacitor. Then the rotor plates and the case are connected together. A comparison (table 1) of the values of dielectric constant obtained for a given medium when the cell is used as both a two- and a three-terminal capacitor provides a check of the linearity of its replaceable interval of capacitance with respect to dielectric constant. Any nonlinear effects associated with the insulating supports should differ in the two cases.

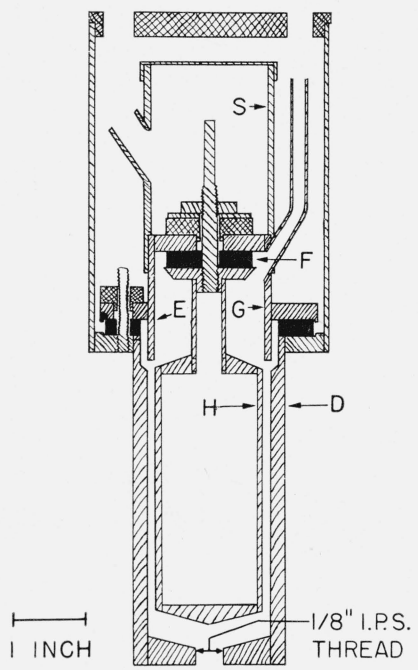


FIGURE 2. *Sectional view of cell A.*

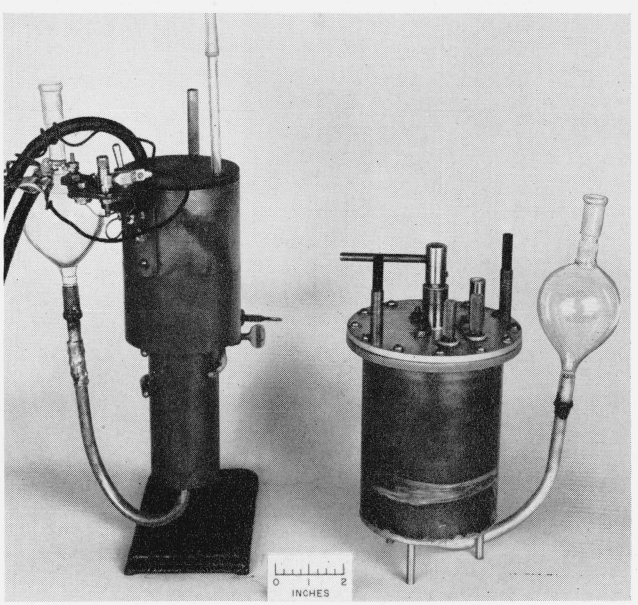


FIGURE 3. *Cell A (left) and cell B (right).*

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59

Cell C is also of the differential type, and similar in design to cell B. It consists of a General Radio type 539–J variable air capacitor, mounted in a brass container, and has a replaceable capacitance of about 500 $\mu\mu$f. Both electrodes are insulated from the case to permit use as either a three- or a two-terminal capacitor.

The standard capacitor, C_m, is a General Radio type 722–D variable precision capacitor with the following modifications: The original wood case, lined with sheet copper, was replaced by a metal case to improve the stability of capacitance; in addition, an external worm and gear drive was mounted on the panel to expand the scale and to allow a precision of setting of 0.01 $\mu\mu$f on the 100 to 1,100 $\mu\mu$f range. The capacity of this interval was assumed to be exact and was calibrated internally in the conventional stepwise manner, using the replaceable air capacitances of cells A and B and other larger and smaller fixed increments. Calibrations made several times during the course of the measurements on water and with the different increments were consistent to 0.05 $\mu\mu$f or better throughout the range of the precision capacitor. The total backlash associated with the setting of this capacitor amounts to about 0.005 $\mu\mu$f on the 100 to 1,100 $\mu\mu$f range and about one-tenth of this value on the 25 to 110 $\mu\mu$f range. Mica capacitors, General Radio type 505, were plugged to the terminals of the precision capacitor to extend its range as needed. These were calibrated in terms of the standard capacitor at the required frequencies, and over a period of a year their capacitances were found to remain constant to better than 0.01 percent.

The apparatus was contained in a constant-temperature room maintained at 23° C. The cells were placed in a grounded oil bath controlled to better than 0.01 deg and the temperatures determined with a platinum resistance thermometer. Cell A was immersed to within 1 inch of the top and the exposed portion provided with adequate thermal shielding. Experimental evidence showed that without such shielding, significant thermal gradients existed within the cell at the higher temperatures. Cells B and C were immersed so that the oil just covered the lids and were used only for measurements at 25° C.

3. Water

Distilled water was obtained as required from the regular supply piped to the laboratory. This supply is free of ammonia and has an average conductivity of 0.5 micromho/cm at 25°, due mainly to dissolved CO_2. Each sample was boiled in the test cell prior to measurement. This procedure was effective in removing dissolved air in order both to eliminate the tendency for bubbles to form between the electrodes and to reduce the CO_2 content, thereby decreasing conductivity. An atmosphere of hydrogen was thereafter maintained in the cell. After thorough cleaning and leaching of the cell, it was possible to keep the conductivity of the water in the range 0.1 to 1.7 micromho/cm at all temperatures and to avoid rapid drifts, which would interfere with the precision of capacitance balance.

4. Procedure and Errors

If C_x is the true interelectrode capacitance of the fixed, guarded cell, A, when filled with a medium of dielectric constant, ϵ_x, then

$$\epsilon_x = C_x/C_v = \epsilon_k C_x/C_k, \tag{1}$$

where C_v is the capacitance in vacuum, C_k the capacitance in air, and ϵ_k the dielectric constant of air. If the residual impedances associated with the bridge network are negligibly small, the interelectrode capacitance is obtained directly as the difference in capacitance of the standard capacitor, $C_m - C_m'$, where C_m and C_m' are the capacitances measured with the cell connected to the appropriate bridge terminals and with the earth-potential electrode connected directly to ground, respectively. In practice, errors that may seriously limit the accuracy of the measurements of dielectric constant can arise from the effects of residual impedances associated with the leads and components of the bridge circuit. Although these errors can be minimized by careful design of the network and the selection of components, by optimum choice of frequency and cell capacitance, and by avoiding excessively high conductivities resulting from electrolytic contamination of the medium, it is often not feasible to reduce these errors to negligible proportions, and procedures must be devised for their evaluation.

If the admittances between each test electrode and the guard electrode of the cell are neglected for the moment, the actual network can be simulated by that shown in figure 4. The effective capacitances of the ratio arms are represented by C_1 and C_2, the self-inductance of the standard condenser and its leads by l_m, the effective series inductance of the

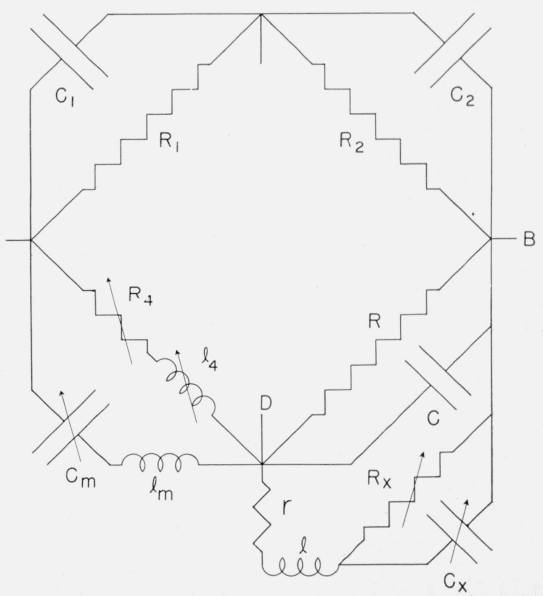


FIGURE 4. *Schematic circuit showing the distribution of residual impedances in the bridge network.*

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59

resistance box by l_4, the cell resistance by R_x, and the inductance and resistance of the leads to the cell by l and r. The residual impedances associated with the fixed 3,000-ohm resistor, R, and small condenser, C, of the unknown arm are neglected, as they do not alter the error analysis to follow. The cell capacitance is given by

$$C_x=(C_m-C_m')+C_a+C_b+C_c+C_d+C_e, \qquad (2)$$

where, neglecting terms of higher order,

$$C_a=(C_1-C_2)(R_1/R_4-R_1/R_4'),$$
$$C_b=l/R_x^2+l_4'/R_4'^2-l_4/R_4^2,$$
$$C_c=-2rC_x/R_x,$$
$$C_d=\omega^2 l_m(C_m^2-C_m'^2)-\omega^2 l C_x^2\cong\omega^2(l_m-l)C_x^2.$$

C_e, the capacitance due to electrode polarization, varies approximately as ω^{-n}, where ω is the angular frequency and n generally lies between 1.5 and 2 but is virtually constant for a given experiment and temperature. The unprimed symbols refer to the case where the cell is connected in the normal manner, and the primed symbols to the case where the earth-potential electrode is connected directly to ground.

The errors attributable to C_d and C_e, being functions of the frequency, were eliminated in the following manner. In each instance values of C_m were obtained at 3, 6, 12, 24, 48, and 96 kc. A representative plot of such data is shown by the solid line of figure 5. At the lower frequencies the variation of C_m is due predominately to electrode polarization, and the error associated with the lead inductances is negligible or greatly minimized, whereas the converse is true at the higher frequencies. The unbalance in lead inductances, l_m-l, which amounted to 1.2 μh, was determined experimentally and the appropriate correction made, as indicated by the broken line of figure 5. Extrapolation of this latter curve to infinite frequency then gives the cell capacitance, corrected for the frequency-dependent errors. Determinations of l_m-l were made both during the normal course of the measurements on water at the lowest temperatures, where electrode polarization was negligible at all but the lowest frequencies, and by plugging sufficient capacitance in the form of the mica standards across the empty cell and standard condenser to cause a readily measurable change of capacitance balance with frequency. The uncertainty in the value of the dielectric constant of water associated with these corrections is definitely less than 0.01 unit.

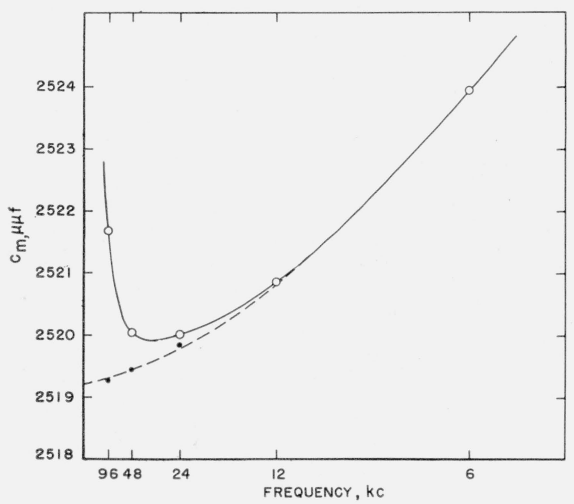


FIGURE 5. *Capacitance C_m plotted on an inverse frequency scale.*

_____ measured values, _ _ _ _ _ after correction for C_d.

Of the remaining terms in eq (2), C_c is not significant in the present case as long as good electric contacts are maintained. The sum of the errors C_a+C_b, which depend upon the resistance balance, was obtained by a modification of the procedure previously described [7]. The dielectric cell was replaced by a conductivity cell of negligible capacitance, with l kept very nearly the same. The resistance of the cell filled with distilled water was then decreased in small steps by the addition of a solution of KCl. The change in C_m required to rebalance the bridge was observed at about 10-ohm intervals. The entire range of R_4 required for the measurements on water, namely, 1,000 to 3,000 ohms, was calibrated in this manner, using a frequency sufficiently high to avoid any effects of electrode polarization. The range 1,000 to 2,600 ohms was also calibrated directly, using cell A. In this case the resistance was changed by the addition or removal of small amounts of CO_2. Both calibrations were in satisfactory agreement. The correction for C_a+C_b, which, in the extreme case, amounted to about 0.07 unit in dielectric constant, should not lead to an uncertainty greater than 0.005 unit.

Determination of the replaceable capacitance of the cell when filled with dry air, C_k, was made as part of the procedure employed for calibrating the standard capacitor. Thus, C_k was equal to the total interval of capacitance that could be covered in integral steps of C_k divided by the number of steps. Four determinations of C_k, made at various times during the measurements on water, gave an average deviation of 0.007 percent. The variation of C_k with temperature was obtained from measurements at a number of temperatures in the range 0 to 100°, using the low range of the standard condenser, where a precision of setting of 0.001 $\mu\mu$f was possible. When C_k is corrected to vacuum, using adequate values for the dielectric constant of air [8], the vacuum capacitance, C_v, is given by

$$(C_v)_t=33.76_1[1+1.8_0(10^{-5})(t-25)]\mu\mu\text{f}.$$

The change with temperature is very nearly the same as predicted from the linear coefficient of expansion of copper.

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59

Determinations of the dielectric constant of water were made in cell A at 5-deg intervals, using two or more samples of water at each temperature. As a further check on the correction for C_a+C_b, the use of samples of corresponding conductivity was avoided. Without exception, the values of dielectric constant obtained at each temperature agreed to 0.01 unit or better with respect to their mean.

As an over-all check on the accuracy of the measurements with cell A, some additional experiments were made at 25° C, using auxiliary cells B and C both as two- and as three-terminal cells. The nature of the residual errors and the procedures used in their evaluation are similar to those discussed above for cell A. However, as these cells are of the differential type, they require twice as many measurements of capacitance and associated corrections. The dielectric constant of water was redetermined in cell B, whereas ethylene chloride and 2-ethylhexanol were measured in cell C. The latter materials were of technical grade. The degree of purity was immaterial as the sample was used for intercomparison in cell A. The values of dielectric constant obtained with the three cells are listed in table 1. The differences are quite negligible except in the case of water, where cell B gives a value about 0.03 percent larger than cell A. However, as the experimental uncertainties associated with cell B are at least twice those of cell A, this difference is hardly significant.

TABLE 1. *Intercomparison of values of dielectric constants measured at 25° C with the different cells*

Cell	Dielectric constant		
	Water	$C_8H_{18}O$[a]	$C_2H_4Cl_2$[a]
A	78.30$_1$	6.831$_6$	10.376
B 2-terminal	78.32$_5$		
B 3-terminal	78.32$_7$		
C 2-terminal		6.831$_2$	10.377
C 3-terminal		6.831$_4$	10.378

[a] Technical grade, unpurified.

It was assumed in the previous analysis that the test cell and its leads are adequately represented by the series-parallel combination of r, l, and C_x, and R_x, shown in figure 4, for which the equivalent parallel capacitance is given to a sufficient approximation by

$$C_p=C_x(1+\omega^2 lC_x-2r/R_x)-l/R_x^2. \tag{3}$$

A more rigorous consideration of its properties as a three-terminal impedance with associated leads results in the equivalent circuit of figure 6. D, B, and G are the points of connection to the bridge and to ground, and D', B', and G' are the corresponding electrodes of the cell. Analysis of this circuit was made by using the star-mesh transformation [9]. The equivalent parallel capacitance is given to a sufficient approximation by

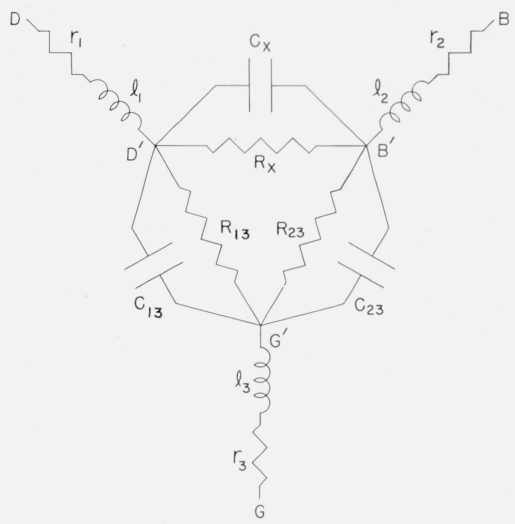


FIGURE 6. *Schematic circuit for the three-terminal cell.*

$$C_p=C_x\left[1+\omega^2 l_2(C_{23}+C_x)+\omega^2 l_1(C_{13}+C_x)-\frac{r_2(R_{23}+R_x)}{R_{23}R_x}\right.$$
$$\left.-\frac{r_1(R_{13}+R_x)}{R_{13}R_x}\right]-\frac{l_2(R_{23}+R_x)}{R_{23}R_x^2}-\frac{l_1(R_{13}+R_x)}{R_{13}R_x^2}-\frac{r_2(C_{23}+C_x)}{R_x}$$
$$-\frac{r_1(C_{13}+C_x)}{R_x}+\frac{r_3(C_{13}R_{13}+C_{23}R_{23})+l_3(1-\omega^2 C_{13}C_{23}R_{13}R_{23})}{R_{13}R_{23}}. \tag{4}$$

It is evident from this relation that significant lead impedances can seriously limit the utility of a three-terminal cell unless the admittances from each of the test electrodes to the guard electrode are kept small compared to the direct admittance between the test electrodes. The procedures described previously for evaluating the residual errors are not entirely valid when the effective capacitance is calculated by eq (4) rather than eq (3). In the present measurements, however, where the admittances to the guard electrode were comparatively small, computations indicate that the use of eq (3) should not lead to an error in dielectric constant greater than 0.01 unit in any case. In fact, if any difficulty had arisen from this simplification, it would have become evident at various stages during the course of the measurements, as, for example, in a discrepancy in the calibrations for C_a+C_b when the conductivity and dielectric cells were used.

5. Results

The values of the dielectric constant of water measured over the range 0.1° to 99° C fit the equation

$$\epsilon=87.740-0.4008t+9.398(10^{-4})t^2-1.410(10^{-6})t^3, \tag{5}$$

where t is the temperature in degrees Celsius. The

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59

values computed from this equation are listed in table 2, together with the differences between these values and those actually measured at each of the specified temperatures. The maximum difference does not exceed 0.01 unit. The last two columns list the values of $d\epsilon/dt$ and the temperature coefficient $(1/\epsilon)(d\epsilon/dt)$. It is interesting to note that the temperature coefficient is remarkably constant over the entire range. In fact, the alternative relation

$$\log_{10}\epsilon = 1.94315 - 0.0019720t, \qquad (6)$$

fits the data nearly as well as eq (5). In this case the maximum deviation is 0.02 and the average deviation 0.01 unit in dielectric constant.

It is estimated that the over-all accuracy of the tabulated values of dielectric constant is ± 0.05 unit or better, and that the temperature coefficient is determined to 1 percent or better at all temperatures.

TABLE 2. *Dielectric constant of water and related data at various temperatures*

t	ϵ eq (5)	ϵ eq (5) $-\epsilon$ obs.	$-d\epsilon/dt$	$-\frac{1}{\epsilon}\frac{d\epsilon}{dt}$
°C				
0	87.740	----------	0.4001	4.560×10^{-3}
0.1	87.700	+0.004	----------	----------
5	85.763	−.001	.3908	4.557
10	83.832	−.002	.3817	4.553
15	81.946	−.004	.3729	4.550
20	80.103	+.003	.3642	4.547
25	78.304	+.003	.3557	4.543
30	76.546	+.006	.3475	4.539
35	74.828	−.004	.3395	4.537
40	73.151	+.002	.3317	4.534
45	71.512	+.004	.3241	4.532
50	69.910	−.007	.3167	4.530
55	68.345	.000	.3095	4.529
60	66.815	−.005	.3025	4.528
65	65.319	+.002	.2958	4.528
70	63.857	−.002	.2892	4.529
75	62.427	+.009	.2829	4.531
80	61.027	+.008	.2768	4.535
85	59.659	+.001	.2709	4.541
90	58.319	+.005	.2652	4.547
95	57.007	−.001	.2597	4.555
99	55.977	−.008	----------	----------
100	55.720	----------	.2544	4.566

6. Discussion

A comparison of the present data with those reported, over a wide range of temperature, by certain investigators in the last quarter century is shown in figure 7. The differences between the values of dielectric constant obtained in the earlier work and the present investigation are plotted as a function of the temperature. Smooth curves are shown where the data were fitted to empirical relations. With respect to the variation of dielectric constant with temperature, only the data of Wyman and Ingalls [5], which were obtained in terms of Wyman's [1] value at 25° C, are in satisfactory agreement with the present measurements over an extended interval of temperature. Although their values are consistently higher, the temperature coefficient derived from the two sets of data agrees to better than 1 percent at all temperatures above 20° C.

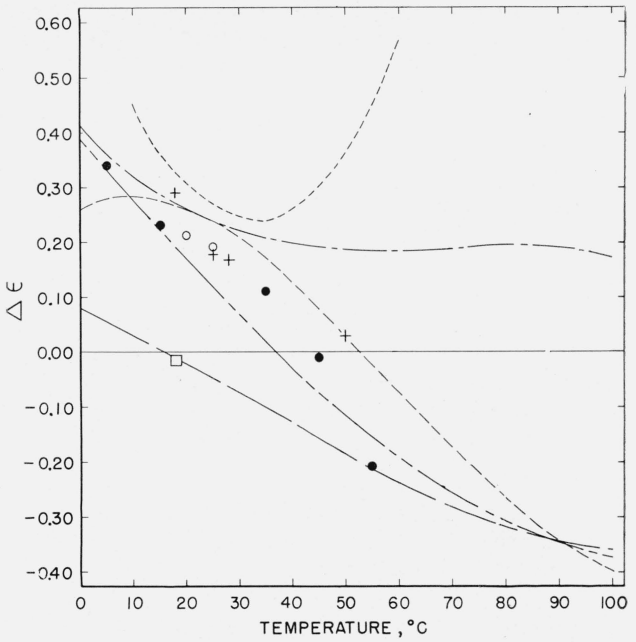


FIGURE 7. *Comparison of the differences in the values of the dielectric constant of water obtained by various workers.*

$\Delta\epsilon = \epsilon$ literature $-\epsilon$ present work.
- Drake, Pierce, and Dow (1930).
- Wyman and Ingalls (1938).
- Wyman (1930).
- Åkerlöf and Oshry (1950). [11].
- Lattey, Gatty, and Davies (1931).
- + Albright (1937).
- ● Albright and Gosting (1946).
- ○ T. T. Jones and R. M. Davies (1939).
- □ Mean of 17 values selected from literature, Lattey, Gatty, and Davies (1931).

Various reported values of the dielectric constant at 25° C are compared in table 3. The value of Lattey, Gatty, and Davies [10] resulted from a survey of the literature prior to 1930. Although this value is closest to that obtained here, the agreement is not significant because of the wide scatter in the individual results (mean deviation ± 0.4 unit). The remaining values, each obtained by a different experimental procedure and considered to have an accuracy of the order of 0.1 percent, are roughly 0.3 percent higher than that reported in this investigation. The close agreement between these earlier values at 25° C would appear to be rather fortuitious in view of the sizable discrepancies existing at other temperatures, as shown by figure 7.

TABLE 3. *Comparison of values of the dielectric constant of water at 25° C*

ϵ_{25}	Method	Frequency	Authors
78.25	Mean of 17 reported values prior to 1930.	----------	Lattey, Gatty, Davies (1931).
[a]78.54	Resonators suspended in medium.	4 to 81 Mc	Wyman (1930).
78.57	Standing waves in coaxial line.	12 to 77 Mc	Drake, Pierce, Dow (1930).
[a]78.48	Bridge	570 kc	Albright (1937).
[a]78.49	Voltage resonance	670 kc	Jones and Davies (1939).
78.30	Bridge	3 to 96 kc	Present work.

[a] Values apparently relative to air rather than to vacuum.

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59

Although the work of Jones and Davies [4] was of high precision and conducted with unusual care and attention to possible sources of error, the method was a comparative one in which benzene was employed as the primary standard. Consequently, any error in the assumed value for the dielectric constant of benzene would result in a percentage error nearly twice as large in the value for water. Furthermore, direct comparisons of water and benzene in the same cell were not feasible, so that additional cells and liquids of intermediate dielectric constant were required. The number of operations upon which the value for water was dependent was thereby increased and the over-all uncertainties of the method somewhat enhanced. In view of these limitations the difference between this and the present work does not appear to be excessively large. In fact, if the data of Jones and Davies are corrected for the value of benzene recently recommended [6], this difference is reduced to about 0.1 percent.

The remaining values in table 3 were obtained by methods essentially absolute in that no standard medium other than air was needed. Because of the lack of experimental detail pertinent to the possible sources of error in the report of Albright [3], no detailed comment on this work is possible. The experimental methods of Wyman [1] and of Drake, Pierce, and Dow [2] were comparatively direct and simple in principle. Although the experimental precision was less than that obtainable with conventional bridge and resonance methods, this disadvantage was seemingly offset by the reduction or avoidance of troublesome residual errors. In both cases the value reported at 25° C was the mean of a number of values obtained at various frequencies which had a spread of more than 0.3 percent.

The method of Wyman involves the determination of the resonant frequencies of fixed, metallic resonators suspended in the medium. Seven resonators of several different designs and of varying frequencies were employed. Exclusive of the value obtained with the resonator of lowest frequency, which was about 5 percent too high, the values of dielectric constant, when corrected to 25° C, ranged from 78.42 to 78.70. It was assumed that these resonators behaved as idealized lumped circuits of inductance L and capacitance C, so that the resonant frequency $f=1/[2\pi(LC)^{1/2}]$. Then $\epsilon=f_0^2/f^2$, where f_0 is the resonant frequency in vacuum, and f is the corresponding frequency in the medium. The strict validity of this relation is questionable because of the effect of conductance of the medium on the properties of resonant circuits and the dependence of the inductance and resistance of metallic conductors upon frequency through the "skin effect." A change in inductance due to the skin effect would lead to a high value for the dielectric constant. Although the magnitude of this error is difficult to evaluate without more specific details regarding the construction of the resonators, estimates based upon simple U-loops, which simulate the form of inductance in some of the resonators, indicate that an error of the order of several tenths of 1 percent is plausible. From a study of the behavior of several resonators when the ionic conductivity of the water was increased by the addition of small amounts of KCl, Wyman showed that the resulting error also gave high values for the dielectric constant, but concluded that the error was not significant in the case of pure water. However, estimates based upon the data presented, after making allowance for the small but significant contribution to the conductivity arising from dielectric loss, indicate a remaining error of the order of 0.1 percent in most instances.

The procedure of Drake, Pierce, and Dow involved, in essence, the determination of the half wavelength of the standing waves set up by a source of known frequency in a 4-m, vertical, coaxial pipe filled with water. Except for factors computed to be of negligible proportions, the dielectric constant was given by $\epsilon=c^2/(f^2\lambda_m^2)$, where f is the frequency, λ_m the wavelength in the medium, and c the velocity of light. The precision obtained in determining the values of dielectric constant was governed primarily by the limitations in measuring half wavelength and temperature, about 0.2 mm and 0.2° C, respectively, and varied from 0.3 to 0.15 percent, depending upon the frequency. Inasmuch as the presence of systematic errors of comparable magnitude would hardly be detected, the difference noted between their value and the present value is not unreasonable.

The magnitude of the disagreement shown in figure 7 indicates that, in general, the accuracy of these data can hardly approach 0.1 percent. This is not too surprising as the reproducibility obtained was only rarely better than 0.1 percent.

For the present investigation, the uncertainty due to any known source of error seems to be limited to ± 0.01 unit. Summation, without regard to sign, of the individual uncertainties associated with the recognized sources of error, leads to a possible uncertainty of ± 0.05 in the values of ϵ or ± 0.1 percent at the highest temperature. The over-all reproducibility of separate determinations at any single temperature, ranging in number from 2 to 10, was such that the largest deviation from the mean for any given temperature was never worse than ± 0.015 unit, which occurred with both cells at 25° C ($4+6=10$ observations); and the average of all 69 deviations from the individual means for 21 temperatures was ± 0.005 unit. This agreement indicates the absence of significant cumulative error and should provide a reasonable basis for an estimation of the accuracy attained. As a consequence, the assignment of an accuracy of ± 0.05 unit to all these data seems entirely justified.

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59

7. References

[1] J. Wyman, Phys. Rev. **35**, 623 (1930).
[2] F. H. Drake, G. W. Pierce, and M. T. Dow, Phys. Rev. **35**, 613 (1930).
[3] P. S. Albright, J. Am. Chem. Soc. **59**, 2098 (1937); P. S. Albright and L. J. Gosting, **68**, 1061 (1946).
[4] T. T. Jones and R. M. Davies, Phil. Mag. **28**, 307 (1939).
[5] J. Wyman and E. N. Ingalls, J. Am. Chem. Soc. **60**, 1182 (1938).
[6] A. A. Maryott and E. R. Smith, Table of dielectric constants of pure liquids, NBS Circular 514 (1951).
[7] C. G. Malmberg and A. A. Maryott, J. Research NBS **45**, 299 (1950) RP2137.
[8] A. A. Maryott and F. Buckley, Tables of dielectric constants and electric dipole moments of substances in the gaseous state, NBS Circular 537 (1953).
[9] B. Hague, Alternating current bridge methods, 5th ed. (Sir Isaac Pitman & Sons, Ltd., London, 1943).
[10] R. T. Lattey, O. Gatty, and W. G. Davies, Phil. Mag. **12**, 1019 (1931).
[11] G. C. Åkerlöf and H. I. Oshry, J. Am. Chem. Soc. **72**, 2844 (1950).

WASHINGTON, October 6, 1955.

Discussion Publishers edition DPR-2026-1293 https://discussionpublishers.com/research/49293a79-7d6e-47d4-939d-d066ab3acf59