

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Measurement of Dielectric Constants by the Comparison Method. The Dielectric Constant of Carbon Tetrachloride from 15 to 40°

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The comparison method is the most common method of measuring dielectric constants of liquids. This paper will apply to that method a scheme of capacity measurement recently proposed by the author.¹ Specifically, the application will involve the determination of the dielectric constant of carbon tetrachloride, but will be equally useful in work with all non-conducting liquids such as are used in dipole moment determinations.

In the comparison method, the measuring cell is calibrated by its capacities when filled in turn with two different standards whose dielectric constants are known with high accuracy. From these capacities, C_A and C_B , and the respective dielectric constants, ϵ_A and ϵ_B , of the standards (usually air and benzene) the replaceable capacity of the cell, C_R , and the fixed capacity, C_O , are determined.

$$C_R = \frac{(\epsilon_B C_R + C_O) - (\epsilon_A C_R + C_O)}{\epsilon_B - \epsilon_A} = \frac{C_B - C_A}{\epsilon_B - \epsilon_A} \quad (1)$$

$$C_O = C_B - \epsilon_B C_R = C_A - \epsilon_A C_R \quad (2)$$

The capacity of the measuring cell, C_C , when filled with a third substance is then used as a measure of the dielectric constant, ϵ_C , of that material.

$$\epsilon_C = (C_C - C_O)/C_R \quad (3)$$

Throughout these calculations it is assumed that C_R and C_O are constants. The principal objection to the method is caused by this assumption, since the construction of the plates, spacer blocks, and leads might be such that C_R and C_O change appreciably with change in the liquid filling the cell. However, if reasonable care is taken in designing the cell, these changes are negligible, especially if the liquids being measured have nearly the same dielectric constant as the standards. This is the case with non-conducting liquids; the largest source of error in such measurements is the determination of the capacity of the cell.

This determination is usually based on parallel substitution measurements at high frequencies. In order to obtain results the accuracy of which is limited only by the accuracy of the readings of the precision condenser in parallel with the cell,

it is well recognized that the circuit must be carefully arranged. In dealing with non-conducting liquids, the principal difficulty is caused by the leads connecting the cell to the precision condenser. Their various capacities, to ground and to other parts of the circuit, as well as their inductances may have an important effect upon the measurement.

The capacities of the leads are difficult to measure accurately since they vary in a complex manner with change in position such as that during connection and disconnection of the cell as required for determination of the absolute capacity of the cell.² A large part of the error to be feared in absolute methods of determining dielectric constant may be due to the capacities of the leads.³

Error due to the manner in which the leads are moved during connection and disconnection will also occur in the comparison method if absolute values of the cell capacity are estimated and used for the calculation of dielectric constants by the customary equations written above. It is more convenient, as well as more accurate, to avoid the use of absolute values of the cell capacity, making measurements only with the cell connected, and making calculations based only on those differences of the precision condenser readings which are due to differences in the cell contents. In this practice, the leads can be more readily arranged in a stable, reproducible position to ensure constancy of their various capacities so that these are safely eliminated from the calculations. While eq. (1) shows that only the difference of C_B and C_A , and not the absolute capacities need be known to evaluate C_R , it appears that the absolute value of C_B or C_A as well as that of C_C must be known to obtain C_O and ϵ_C by eqs. (2) and (3). This is deceptive, however, since C_O need not be evaluated for the determination of ϵ_C . Assuming C_O and C_R constant, we may calculate ϵ_C from either the difference of C_B and C_C or that of C_A and C_C . For example

(2) Field, *General Radio Experimenter*, **12**, 1 (Jan., 1938).

(3) (a) Hartshorn and Oliver, *Proc. Roy. Soc. (London)*, **A123**, 664 (1929); (b) Sugden, *J. Chem. Soc.*, 768 (1933).

(1) Miller, *THIS JOURNAL*, **60**, 42 (1938).

$$C_R = \frac{(\epsilon_B C_R + C_0) - (\epsilon_C C_R + C_0)}{\epsilon_B - \epsilon_C} = \frac{C_B - C_C}{\epsilon_B - \epsilon_C}$$

$$\epsilon_C = \epsilon_B - (C_B - C_C)/C_R \quad (4)$$

The effect of the inductances of the leads and the rest of the measuring circuit can be eliminated from parallel substitution measurements by calculations based on determinations made at varying frequency. It has been shown¹ that if C is the capacity of the precision condenser with the leads attached but the cell disconnected, and C' that maintaining constant parallel circuit capacity when the cell is connected, then the true value of the absolute capacity of the cell, C_x , can be obtained from $C - C'$ by either of the two equations

$$C - C' = C_x + k_1 f^2 \quad (5)$$

$$C - C' = C_x/(1 - k_2 f^2) \quad (6)$$

where k_1 and k_2 are constants for any value of C_x and f is the frequency.

This scheme of capacity determination can be applied to the present problem in the form of eq. (5) which shows that $C - C'$ is a linear function of f^2 such that C_x is the intercept in a plot of $C - C'$ against f^2 . If the circuit is arranged so that C is independent of the frequency, then the frequency variance of $C - C'$, the apparent capacity of the cell, is due to variance in C' alone and a plot of $-C'$ against f^2 will have the same slope as the $C - C'$ plot. Therefore, if we want only the differences in true capacity caused by change in the cell contents, we may obtain those differences simply as the differences in the intercepts of the $-C'$ lines; that is, we may use only those measurements made with the cell connected. Finally, we are not troubled with the necessity of using the absolute values of C' . If the dial of the precision condenser is calibrated to read directly in capacity decrements, then the dial readings will replace $-C'$. Due to this convenience and the ease with which C can be made independent of the frequency, this scheme of varying frequency measurements can be applied advantageously to the determination of dielectric constants.

Experimental

The radio frequency capacity bridge and cell described previously¹ were modified slightly to ensure a maximum of stability in the circuit, and to maintain exact matching of the impedances of the measuring and balancing arms at all frequencies. The entire measuring assembly, with the exception of the cell, was mounted in a single housing. The singly-shielded air core transformer coupling the detector to the bridge across the matched ratio arms was adjusted so that the small leakage impedances between its

windings were made exactly equal with respect to their terminals. With such adjustment, those capacities which are shunted to ground across the balancing and measuring arms of the bridge are matched, and the power factor balance remains constant with change in frequency, especially if the self-contained capacities of those arms are matched. Thus, only a small resistance (less than 0.02 ohm) was needed in the balancing arm and this remained essentially constant for all measurements. The balancing condenser was locked so that its capacity was constant at about 1000 $\mu\mu\text{f}$. Inductance symmetry was obtained by choosing the lead connecting the precision condenser rotor in the bridge such that the precision condenser balance reading (C , above) was exactly the same at all frequencies when the leads to the cell were attached and the cell disconnected.

The leads to the cell were 0.25 inch bare brass rods led out to the cell in parallel positions 0.75 inch apart in a horizontal plane. These rods were drilled near their ends to fit 0.125 inch brass rods which could be lowered vertically into the mercury cups of the cell and could be fixed in position by set-screws tapped into the ends of the horizontal rods. This arrangement of leads was designed to fix their positions firmly, and also to shield the high potential lead in a way that made the lead capacities constant to within 0.02 $\mu\mu\text{f}$ for all separations of the high potential lead from the high potential terminal of the cell between 0.25 and 0.875 inch when the ground terminal was connected. This was of great convenience in checking the constancy of the leads and the C readings, since without such arrangement the condenser reading is very sensitive to the manner in which the cell is disconnected.²

The cell was also held firmly in reproducible position for all measurements. A long glass rod was joined to the bottom of the cell and fitted snugly into a brass cylinder soldered to the bottom of the thermostat. The upper part of the glass housing of the cell was ground to fit a glass holder which had three long arms reaching to the sides of the thermostat where they were clamped. The thermostat was filled to constant level with 50 gallons of General Electric No. 10 Insulating Oil. Each temperature used was maintained constant within 0.01° by the thermostat and was known with an accuracy of $\pm 0.01^\circ$ by use of a thermometer calibrated against a standard platinum resistance thermometer. The room temperature was kept at $24 \pm 3^\circ$.

The oscillator was calibrated with a wavemeter and against the signals of several broadcasting stations. The series of seven frequencies used ranged from 0.548 to 1.500 megacycles in such a way that the spacing of their squares was approximately constant. The precision condenser was freshly calibrated by the General Radio Company, who supplied the corrections to be applied to the direct reading of the dial at every ten worm divisions. The dial readings were made as precisely as possible with the aid of a lens mounted on the panel in front of the drum of the condenser. Each dial reading value used in the calculations reported below was the mean of several determinations. These mean values were rounded off to the nearest 0.05 $\mu\mu\text{f}$, the limit of disagreement between any determination and the mean being 0.05 $\mu\mu\text{f}$.

The cell was calibrated with dry air and benzene. The air was passed over calcium chloride and then filtered

TABLE I

f^2	R_A	S_A	R_B	S_B	R_C	S_C
0	345.406 \pm 0.015	566.570 \pm 0.018	558.643 \pm 0.026
0.300	345.60	345.609	567.80	567.756	559.80	559.766
0.650	345.85	345.847	569.10	569.139	561.05	561.075
1.000	346.10	346.084	570.50	570.523	562.35	562.385
1.350	346.30	346.322	571.90	571.906	563.70	563.695
1.700	346.60	346.559	573.30	573.290	565.05	565.004
2.050	346.80	346.796	574.70	574.673	566.25	566.314
2.250	346.90	346.932	575.45	575.463	567.10	567.062

through cotton. After the purifications described below the benzene was refluxed over sodium and distilled directly into the cell. It was found that Baker C. P. benzene could be purified adequately by distillation through an all-glass column of the type described by Tongberg, Quiggle and Fenske⁴ and packed to a height of 17 inches with 3/16 inch glass helices. This material had a density of 0.8737 g. per cc. and a refractive index, n_D , of 1.4980 at 25°. As a check on the purity of this material, Baker thiophene-free benzene purified for precision freezing-point determinations was found to have exactly the same dielectric constant. This benzene had been purified⁵ by successive washing with concentrated sulfuric acid, water, 1 *M* potassium hydroxide, and water, followed by fractional freezing and distillation.

The carbon tetrachloride was Merck C. P. grade and was distilled through the same column used to purify the benzene. The material was then refluxed over sodium and distilled directly into the cell. The dielectric constant was exactly the same when the material from the first distillation was further purified by washing with concentrated sulfuric acid, water, 2 *M* sodium hydroxide, and water, followed in this case by drying over sodium sulfate and phosphorus pentoxide. The density and refractive index, n_D , were 1.5846 g. per cc. and 1.4575, respectively, at 25°.

Results and Discussion

The series of seven dial readings obtained from each varying frequency determination was treated by the method of least squares to evaluate the zero-frequency dial reading, D , for that filling of the cell. This method was used instead of a graphic extrapolation because it permits a more exact estimate of the error in the value obtained. Some of the data were treated by the method of Merriman⁶ which is more legitimate for calculation of the constants of linear formulas to fit the values of variables both of which are subject to error; the results were identical with those of the least squares calculations, showing that the error in the frequency values was relatively negligible. Probable error was used as the index of precision

(4) Tongberg, Quiggle and Fenske, *Ind. Eng. Chem.*, **26**, 1213 (1934).

(5) The author is indebted to Mr. John A. Davison for the purification of this benzene, and to Mr. Edgar L. Eckfeldt for the column used in the other purifications.

(6) Scarborough, "Numerical Mathematical Analysis," Johns Hopkins Press, Baltimore, Md., 1930, p. 380.

of all values, to conform with the practice followed by most workers in this field. The dielectric constants of air and benzene were calculated by the equations $\epsilon_A = 1 + (0.159/T)$ and $\epsilon_B = 2.2925 \pm 0.0005 - (0.00198 \pm 0.00003)(t - 15)$, respectively. In the former equation, which is sufficiently accurate for these calculations,⁷ T is the absolute temperature. In the latter,^{8a} which is widely accepted, t is the centigrade temperature.

Typical data are presented in Table I which lists the dial readings, R_A , R_B , R_C , observed at the various frequencies with air, benzene and carbon tetrachloride, respectively, at 30°. The frequencies, in megacycles, are expressed as their squares, f^2 . In columns adjoining the R values are listed the corresponding values, S_A , S_B , S_C , according to the least squares lines for the series. The value of S at zero frequency is D , the probable error of which was calculated by the method of Gauss.⁸ This table shows that eq. (5) provides adequate treatment of such data. The superiority of eq. (6) would be quite overcome by the fact that it requires knowledge of both C and C' .

Table II lists the values of C_R calculated from the values of D_A , D_B , ϵ_A and ϵ_B at the different temperatures by eq. (1)

$$C_R = \frac{C_B - C_A}{\epsilon_B - \epsilon_A} = \frac{D_B - D_A}{\epsilon_B - \epsilon_A} = \frac{\Delta D_{(B-A)}}{\Delta \epsilon_{(B-A)}}$$

The necessity of applying calibration corrections which are accurate only to $\pm 0.1 \mu\mu\text{f}$ causes the large errors in D_A and D_B and is largely responsible for the errors in C .

Table III presents the values of the dielectric constant, ϵ_C , of carbon tetrachloride calculated from D_B , D_C , C_R , and ϵ_B , according to eq. (4).

$$\epsilon_C = \epsilon_B - \frac{C_B - C_C}{C_R} = \epsilon_B - \frac{D_B - D_C}{C_R} = \epsilon_B - \frac{\Delta D_{(B-C)}}{C_R} = \epsilon_B - \Delta \epsilon_{(B-C)}$$

In these calculations the error in C_R is of small effect since C_R is large compared with $\Delta D_{(B-C)}$

(7) Goss, *J. Chem. Soc.*, 730 (1935).

(8) Whittaker and Robinson, "Calculus of Observations," 2nd ed., Blackie and Son, London, 1937, pp. 243-247.

TABLE II

$t, ^\circ\text{C.}$	D_A	D_B	$\Delta D(B-A)$	$\Delta\epsilon(B-A)$	C_R
15	345.36 \pm 0.10	571.84 \pm 0.11	226.48 \pm 0.15	1.29195 \pm 0.00050	175.30 \pm 0.14
20	345.36 \pm .10	570.15 \pm .11	224.79 \pm .15	1.28205 \pm .00052	175.34 \pm .14
25	345.36 \pm .10	568.44 \pm .11	223.08 \pm .15	1.27216 \pm .00058	175.36 \pm .14
30	345.31 \pm .10	566.77 \pm .10	221.46 \pm .14	1.26227 \pm .00067	175.45 \pm .14
35	345.33 \pm .10	565.06 \pm .11	219.73 \pm .15	1.25238 \pm .00078	175.45 \pm .16
40	345.29 \pm .10	563.47 \pm .10	218.18 \pm .14	1.24249 \pm .00090	175.60 \pm .17

TABLE III

$t, ^\circ\text{C.}$	D_B	D_C	$\Delta D(B-C)$	$\Delta\epsilon(B-C)$	ϵ_C
15	571.638 \pm 0.039	563.693 \pm 0.022	7.945 \pm 0.045	0.04532 \pm 0.00026	2.24718 \pm 0.00056
20	569.951 \pm .037	561.998 \pm .029	7.953 \pm .047	.04536 \pm .00027	2.23724 \pm .00059
25	568.240 \pm .034	560.327 \pm .017	7.913 \pm .038	.04512 \pm .00022	2.22758 \pm .00062
30	566.570 \pm .018	558.643 \pm .026	7.927 \pm .032	.04518 \pm .00019	2.21762 \pm .00070
35	564.862 \pm .033	556.971 \pm .024	7.891 \pm .041	.04498 \pm .00024	2.20792 \pm .00082
40	563.272 \pm .029	555.342 \pm .025	7.930 \pm .038	.04516 \pm .00022	2.19784 \pm .00093

TABLE IV

f^2	R_A	R_B	R_C	C_R	ϵ_C
0.300	345.50 \pm 0.11	568.00 \pm 0.11	560.00 \pm 0.11	176.27 \pm 0.16	2.2174 \pm 0.0011
0.650	345.75 \pm .11	569.30 \pm .11	561.25 \pm .11	177.10 \pm .16	2.2173 \pm .0011
1.000	346.00 \pm .11	570.70 \pm .11	562.55 \pm .11	178.01 \pm .16	2.2170 \pm .0011
1.350	346.20 \pm .11	572.10 \pm .11	563.90 \pm .11	178.96 \pm .16	2.2170 \pm .0011
1.700	346.50 \pm .11	573.50 \pm .11	565.25 \pm .11	179.83 \pm .16	2.2169 \pm .0011
2.050	346.70 \pm .11	574.90 \pm .11	566.45 \pm .11	180.79 \pm .16	2.2161 \pm .0011
2.250	346.80 \pm .11	575.65 \pm .11	567.30 \pm .11	181.30 \pm .16	2.2168 \pm .0011

which is the result of a close subtraction and is the large source of error in the $\Delta\epsilon$ term. Fortunately, the inaccuracy of the calibration corrections did not cause any difficulty in the ΔD term for the following reason. The calibration chart showed that not quite the same correction applied to both D_B and D_C , yet the corrections differed by amounts beyond the limits of accuracy guaranteed by the chart. Referring to the least squares calculations which dealt with R values covering this dial range completely, there appeared no irregularities such as would surely have occurred if the corrections were not exactly the same throughout this range; therefore, these corrections cancelled exactly. If a real difference had existed in these corrections, it could have been evaluated rather precisely from the least squares data. It is a distinct advantage of this scheme that it can improve the accuracy of the measurement in this manner.

The values of the dielectric constant of carbon tetrachloride so determined owe most of their error to the error feared in the dielectric constant of the standard, benzene. This error is magnified at the higher temperatures by the error in the temperature coefficient of the standard value. It is interesting that no improvement in the values of this standard has been made since 1929.

The dielectric constant of carbon tetrachloride has a temperature coefficient, $d\epsilon/dt$, of -0.001976 ± 0.000013 , calculated as a mean of the values for the five separate temperature intervals studied. This is almost identical with that of benzene and is more accurate than the values previously published.⁹

The advantages of the method can be shown by the data in Table IV, which presents the values of the dielectric constant of carbon tetrachloride at 30° which would have resulted from calculations based on the separate frequency values of R listed in Table I. The considerable errors in R which are carried over to ϵ_C are due to the necessity of applying the calibration corrections in such calculations. The effect of inductance is shown by the decrease in these apparent values of ϵ_C with increase in frequency, but is barely appreciable in the presence of the other errors. It can be concluded that the advantage of the varying frequency scheme in such measurements is not so much due to the removal of the inductance effect as to the elimination of the precision condenser calibration errors. This scheme could be used with great advantage in polarization studies of dilute solutions, especially if more frequencies

(9) Davies, *Phil. Mag.*, **21**, 1 (1936); Goss, *J. Chem. Soc.*, 730 (1935).

were employed and the precision condenser readings were made more precise by methods such as suggested by Hobbs, Jacokes, and Gross.¹⁰

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Summary

1. A scheme of capacity measurements at varying frequency has been applied to the com-

(10) Hobbs, Jacokes and Gross, *Rev. Sci. Instruments*, **11**, 126 (1940).

parison method of dielectric constant determination. The principal advantage of this scheme in the case of low dielectric constants is the elimination of certain calibration inaccuracies apt to be present in precision condenser readings made at fixed frequency.

2. The dielectric constant of carbon tetrachloride has been determined at six temperatures from 15 to 40°. The values owe most of their error to the uncertainty in the values of the standard, benzene.

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The Oxidation of Cellulose by Nitrogen Dioxide*

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Since the work of Witz¹ on the action of oxidizing agents on cellulose, a vast literature concerning oxidized cellulose has accumulated. A summary of this literature to 1922 has been compiled by Clifford and Fargher.² The oxidizing action on cellulose of numerous oxidants has been studied under widely varying conditions of temperature, pH, time of reaction and concentration. Space does not permit a summary of this phase of the subject, but the investigations of Hibbert and Parsons³ and of Heuser and Stöckigt⁴ illustrate the methods employed. Recently periodic acid has been studied as an oxidant for several carbohydrates.⁵

A rigorous comparison of the various oxidized celluloses reported in the literature is difficult because they are not definite chemical entities. However, two general types are recognized.⁶ One of these, the "methylene blue" type, has a high methylene blue absorption, a low copper number and a low alkali solubility; while the other, the "reducing type," has a low methylene blue number, a high reducing value and a high alkali solubility. An excellent and concise sum-

mary of the present status of the oxidation of cellulose has been given by Heuser.⁷

The major problem in studying oxidized celluloses is the difficulty of producing materials which are homogeneous in chemical and physical properties. Several of the oxidants employed are apparently not selective as to the particular hydroxyl groups of the anhydro-glucose unit in the cellulose molecules which are attacked. Many methods of oxidation are topochemical. When the oxidation is mild, the products usually consist of an oxidized portion and an unchanged residue of unreacted or only slightly modified cellulose. More drastic oxidation produces a larger proportion of oxidized material accompanied by increased degradation. Physical degradation accompanying the oxidation breaks up the cellulose fibers and usually the material is friable and powders easily.⁷

We have found that, under suitable conditions, cellulose may be readily oxidized by nitrogen dioxide to produce a new type of oxidized cellulose.⁸ This method of oxidation is readily controlled to produce oxidized celluloses of various carboxyl group contents. When the degree of oxidation is sufficiently high, the products dissolve rapidly and completely in dilute aqueous alkalis, for example, 2% aqueous sodium hydroxide. Even with high degrees of oxidation, the cellulose remains fibrous and is not friable.

(7) E. Heuser, "Organic Chemistry," H. Gilman, Editor, John Wiley and Sons, New York, N. Y., 1938, Vol. II, pp. 1556-1559.

(8) See U. S. Patent 2,232,990, E. C. Yackel and W. O. Kenyon, February 25, 1941.

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(1) G. Witz, *Bull. Soc. Ind. Mulhouse*, **43**, 334 (1883).

(2) P. H. Clifford and R. G. Fargher, *Shirley Inst. Mem.*, **1**, 118 (1922), and *J. Text. Inst.*, **13**, 189T (1922).

(3) H. Hibbert and J. L. Parsons, *J. Soc. Chem. Ind.*, **44**, 473T (1925).

(4) E. Heuser and F. Stöckigt, *Cellulosechemie*, **3**, 61 (1922).

(5) E. L. Jackson and C. S. Hudson, *THIS JOURNAL*, **59**, 2049 (1937); **60**, 989 (1938).

(6) J. T. Marsh and F. C. Wood, "An Introduction to the Chemistry of Cellulose," D. Van Nostrand Co., New York, N. Y., 1939, Chapter 8, pp. 153 *et seq.*