## 190. The Dielectric Constants of Some Organic Liquids.

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At present, there are few absolute measurements of dielectric constant which have an accuracy of a few parts in a thousand; the most important are those of Hartshorn (*Proc. Roy. Soc.*, 1929, A, 123, 664) on benzene, and of Ball (J., 1930, 570) on benzene, chloroform, benzonitrile, and nitrobenzene. The work described below was undertaken to confirm these measurements. Since Hartshorn and Ball both used a bridge method of measurement at audio-frequencies it seemed desirable to use some other method at higher frequencies. The simple resonance method at radio-frequencies was therefore used and found to be capable of sufficient accuracy and flexibility.

Method of Measurement.—The arrangement of apparatus is shown in Fig. 1. The valve  $V_1$  generates oscillations whose frequency is determined by the capacity of the condenser  $C_3$  and the inductance of the associated coil. Instead of the "Dynatron" oscillator shown, a magnetically coupled triode oscillator, and a triode oscillator controlled by a quartz crystal were also used. Both gave good results, but the dynatron was found to give as steady a frequency as the quartz oscillator and could readily be arranged to give a wide range of frequencies. With a triode oscillator a marked drift of frequency with time was found and the valve had to be run for an hour before the frequency was steady enough for measurements to be made. The dynatron gave a frequency which was independent of small changes in filament and anode voltages and showed no appreciable drift. A Mullard P.M. 12 valve was used for the dynatron circuit and gave sufficient amplitude of oscillations when the grid was connected to the positive end of the filament. To ensure steadiness, the anode and screening grid potentials were obtained from a 60-volt battery of accumulators.

The oscillator valve and its associated apparatus were completely screened in an earthed tinned-iron box as shown by the broken line in Fig. 1. The resonance coil was also screened, and a light fixed coupling between the oscillator coil and the resonance coil provided by means of one or two turns of wire wound about 1 cm. from the end of each coil and connected as shown.





The resonance coil was tuned by the variable condensers  $C_4$  and  $C_M$ ;  $C_4$  was an inexpensive variable condenser used chiefly to adjust the position of resonance to a suitable point on the scale of the measuring condenser  $C_M$ . The latter was a standard laboratory pattern supplied by Messrs. H. W. Sullivan, of maximum capacity 1200 micro-microfarads ( $\mu\mu$ F); it was fitted with a degree scale and vernier which could be read by a lens to 0.02°. The measuring condenser was calibrated by taking readings with a small fixed air condenser at various points on the scale; its capacity was found to be accurately a linear function of the scale reading between 40° and 165°, and the corrections were determined outside these limits.

The attainment of resonance was detected by means of the valve voltmeter  $V_2$ . This consisted of an Osram H.L. 210 valve, the grid of which was biassed to -3.0 volts through a resistance of 100,000 ohms. The alternating potential built up across a portion of the resonance coil was applied to the grid of this valve through a small fixed condenser and the resultant rectified anode current was measured by the microammeter G. This arrangement gave ample sensitivity, as an applied grid potential of 1.5 volts gave a full scale deflexion of the microammeter. The voltmeter was calibrated by applying known steady potentials between grid and filament; since the resistance of the microammeter (500 ohms) is small compared with the anode-filament resistance of the valve (ca. 30,000 ohms), this static characteristic could be used if necessary to convert microammeter readings into grid volts.

The method of measurement used was to find two points on the measuring condenser which gave the same reading of the microammeter at some point on the steep part of the resonance curve. Switch S (Fig. 1) was then closed and a similar pair of points found on the new resonance curve. The mean of the second pair of condenser readings was subtracted from the mean of the

first pair to obtain the capacity of the experimental cell. This method of working gives very accurate readings because of the steep slope of the resonance curve; in most of the observations, the limit of accuracy was imposed, not by the setting of the microammeter, but by the reading of the measuring condenser, which might with advantage have had a more finely divided scale.

The quantity measured by the thermionic voltmeter is the potential developed across the parallel condensers in the resonance circuit; hence the curve can be taken as accurately symmetrical except very near the tip (see Moullin, "Radio Frequency Measurements," Griffin & Co., 1931, p. 373). The mid-point of the curve is displaced very slightly from the true resonance capacity, but this introduces no error if the two resonances curves have the same shape. Liquids which possess appreciable conductivity give marked damping when the cell is placed in circuit; by making the total capacity in circuit large, this damping can be considerably diminished, and it was found possible to make observations at frequencies of 100 kc./sec. with liquids possessing a specific conductivity up to 10<sup>-6</sup> mho. With the most conducting liquid used, the error

introduced by the slight shift of the resonance curve was computed from Moullin's equation to be less than 1 part in 2000 and can therefore be neglected.

Design of the Experimental Cell.—The cells used were all of the type introduced by Sayce and Briscoe (J., 1925, 127, 315) and used later by Ball (*loc. cit.*), in which the liquid is placed between two films of silver deposited on concentric glass tubes. The pattern used is shown in Fig. 2; it differs from that of Sayce and Briscoe only in the arrangement for making contact with the inner silver layer. Several cells were made of sizes suitable for use with liquids of a range of dielectric constants. Those used in the final series of measurements had the following approximate capacities when filled with air :

| Cell.             | А. | В.  | E.  | F. | G. |
|-------------------|----|-----|-----|----|----|
| Air capacity, µµF | 30 | 100 | 190 | 20 | 18 |

The switch which puts the cell in and out of circuit consisted of a central glass tube, the lower half of which contained a copper wire that made contact with the inner silver film through a pool of mercury and a platinum wire sealed through the glass as shown in Fig. 2. The upper end of the copper wire passed through a small plug of sealing wax and was covered by a few drops of mercury into which dipped a fine wire leading to the high-potential terminal of the measuring condenser. The circuit was broken by raising this wire until the end was 1 cm. above the mercury. This arrangement allowed the position of the make-and-break to be adjusted to a suitable position with respect to the upper end of the silver layers (see p. 772).

Some difficulty was experienced at first owing to a gradual disintegration of the silver films, which, in bad cases, became detached from the glass. The first symptom of this change was the appearance of white patches on the bright surface; these attained a considerable size before any measurable change was observed in the capacity of the cell. This difficulty was overcome by modifying the silvering solution. The process described below has given very durable films; one cell has survived 2 years without developing any blemishes and without any measurable change in capacity.

To 6 g. of silver nitrate in about 100 c.c. of water, aqueous ammonia was added until the precipitate redissolved; 70 c.c. of 3% sodium hydroxide solution were added (potassium hydroxide gives less stable films) and more ammonia until the solution was just clear; this solution was diluted to 500 c.c. 8 G. of glucose in 150 c.c. of water and 0.5 c.c. of nitric acid were boiled for 2 minutes, cooled, and 150 c.c. of methylated spirit added. The cell was cleaned with a hot mixture of chromic and nitric acids, washed thoroughly with water, and finally rinsed with spirit. 10 Parts of the silver solution were mixed with 1 part of the glucose solution and poured into the cell through the tube b. After  $\frac{1}{2}$  hour, a dense adherent film was formed. The spent solution was withdrawn through b, and fresh solution introduced. After three such treatments the cell was rinsed with benzene and dried by a current of air. In subsequent cleaning operations, the cell was rinsed with benzene and dried by a current of air. The use of ether was avoided, as it attacked the silver film. Cells thus prepared showed very small damping when introduced into a resonant circuit; from the amount of damping the total resistance of the leads and the silver films was calculated to be less than 0.5 ohm.



End and Lead Corrections.—The chief advantage of the Sayce-Briscoe type of cell lies in the fact that there is no solid dielectric between the silver plates and very little in the neighbourhood of their edges. The distance between the plates can also be made small compared with their linear dimensions, and, since the outer plate is earthed in the arrangement of apparatus shown in Fig. 1, it provides an almost complete screen. The cell thus approximates closely to an absolute condenser, *i.e.*, one in which the capacity is strictly proportional to the dielectric constant of the liquid between the plates. There is, however, a small end effect to be evaluated, which is caused by the capacity of the upper end of the inner layer to earthed objects other than the outer film, and a second, rather smaller, error dependent on the position of the make-and-break.

The end effect became evident when the capacity of a cell containing air was measured (a) remote from conductors and (b) immersed in an earthed water-bath. Condition (a) was realised by mounting the cell on a wooden stand and removing all conductors to a distance of more than 30 cm. from the upper end of the silver films. For cell B the change from (a) to (b) gave an increase in capacity of  $0.62 \ \mu\mu$ F or about 0.6%. Following Ball (*loc. cit.*), an attempt was made to eliminate this effect by using a guard ring. A special cell C was constructed with the necessary extra platinum contact and, by careful silvering, a guard ring was deposited which approached to within  $1.5 \ mm$ . of the main pair of plates. This cell showed, however, a difference in capacity of the same order of magnitude when measured under conditions (a) and (b). This behaviour becomes explicable when the dimensions of the cells are considered. The increase in capacity is equivalent to an increase in length of the cell of less than 1 mm.; also the distance between the silver films is about 1 mm. Hence, a guard ring, to be effective, should approach to within  $0.1 \ mm$ . of the main pair of films, and it is quite impracticable to construct such a guard ring using silver films.

It is not sufficient to subtract the measured end effect with air as dielectric from observations on other dielectrics. The main part of the end effect must be the capacity of the upper end of the inner film to the water-bath through the cell contents and the outer glass tube, and thus involves a mixed dielectric. It should thus be proportional to  $1/(d_1/\epsilon_1)$  $+ d_2/\epsilon_2$ , where  $d_2$  is the thickness of the glass,  $\epsilon_2$  its dielectric constant, and  $d_1$  and  $\epsilon_1$  the corresponding quantities for the fluid in the cell. For cell B,  $d_2 = 1.5$  mm.,  $d_1 = 1.1$  mm., and if  $\epsilon_2$  for glass be taken as 7, the end effect should vary as  $1/(0.21 + 1.1/\epsilon_1)$ . Hence when chlorobenzene ( $\varepsilon = 5.6$ ) is substituted for air ( $\varepsilon = 1$ ) the end effect increases in the ratio of approx. 1:3. This increase was verified experimentally for benzene and chlorobenzene at room temperature. The end effect, or the part of it due to capacity to the water-bath, is therefore not proportional to the dielectric constant of the cell contents, nor is it independent of the cell contents. The latter result can, however, be attained by immersing the cell in a large bath of paraffin, which is itself immersed in the earthed water-This reduces the capacity of the inner layer to the water, and makes the liquid in bath. the cell a small fraction of the total dielectric. With a paraffin-bath 20 cm. in diameter, the capacity of cell B was found to be only 0.15  $\mu\mu$ F higher than when measured remote from conductors. A rough calculation, treating the problem as one of a cylindrical condenser with parallel layers of dielectrics, indicated that the effect should have been  $0.05 \,\mu\mu F$ . The difference is not much larger than the error of measurement and is probably due to the capacity of the inner layer to other earthed conductors, e.g., stands and stirrers. Since the total end effect is now only 0.15% of the air capacity and must be nearly independent of the liquid in the cell, the value found for air can safely be subtracted from the readings found for other dielectrics.

The lead correction was eliminated in the following manner. In Fig. 3, C represents the capacity it is desired to measure,  $c_1$  that of the lead to the inner layer to earth down to the switch, and  $c_2$  that of the inner lead below the switch to earth. If the switch is above the end of the silver film this will not be completely screened and  $c_2$  will be appreciable. With the switch closed, the capacity of this system is  $C + c_1 + c_2$ , and with the switch open the capacity in parallel with the measuring condenser is  $c_1$ ; hence the change in capacity on opening the switch is  $C + c_2$  and is too large. If the switch is in some position within the screen as at B, then the change in capacity on opening the switch is  $C - c_3$ , where  $c_3$  is the capacity of the portion of the lead within the screen to the inner film (since this is in series with the much larger capacity C). The value of  $c_3$  depends chiefly upon the length of lead within the screen and cannot be eliminated by using very fine wire. The problem is that of a cylindrical condenser and  $c_3$  should be given approximately in  $\mu\mu$ F by the expression  $l/(1\cdot8\log_e r_2/r_1)$ , where l is the length of wire within the screen,  $r_1$  its radius, and  $r_2$  the radius of the inner silver film. For cell B and a 5-cm. length of No. 22 S.W.G. wire,  $r_2 = 1\cdot8$  cm.,  $r_1 = 0.036$  cm., and  $c_3 = 0.70 \ \mu\mu$ F. If a 5-cm. length of No. 46 S.W.G. wire is substituted (which is difficult to handle owing to its fragility),  $r_1 = 0.003$  cm. and  $c_3 = 0.43 \ \mu\mu$ F. It is evident that the best position of the switch must be somewhere near the top of the silver films to eliminate this effect. The exact position will depend upon the stray capacities which determine  $c_2$  and was therefore determined experimentally. A series of measurements was made on cell B in position in the thermostat in which the mercury surface of the switch was x cm. below the top of the silver films. The wire was



moved to a point 1 cm. above the mercury surface to open the switch, since it was found that this distance was sufficient to give negligible terminal capacity. With thick and thin wires the following values were found.

|        | x =   | 0     | 1 cm.          | 2 cm.      |
|--------|-------|-------|----------------|------------|
| No. 16 | c = 1 | 02.49 | 102.38         | 102.15 µµГ |
| No. 46 | c = 1 | 02.44 | $102 \cdot 41$ | 102·36 μμF |

With x = ca. 1, the measured capacity is independent of the thickness of the wire; above and below this point, the thick wire gives capacities which are respectively larger and smaller, indicating that  $c_2$  is appreciable in the one position or that the major effect is due to  $c_3$  in the other. In all subsequent measurements the switch was adjusted so that the mercury surface was 1 cm. below the top of the silver films; a lead of No. 40 S.W.G. wire was used as it is rather more easily handled than No. 46.

Other important corrections, which depend upon the resistance of the cell, the inductance of the leads, and the frequency of the alternating current, are

discussed in the appendix (p. 774) and were applied where necessary.

Purification of Liquids.—Benzene. A.R. Reagent was frozen with stirring to produce small crystals, which were separated from mother-liquor on a Buchner funnel. This process was repeated 12 times, and the product then had constant f. p.  $5 \cdot 62^{\circ}$  in the presence of phosphoric oxide;  $D_{4^{\circ}}^{24^{\circ}}$  0.8739. Perkin (J., 1896, 69, 1191) found 0.8741 for benzene from calcium benzoate, and Tyrer (J., 1914, 105, 2534) 0.8735 for coal-tar benzene. The benzene was dried over phosphoric oxide, distilled, and stored over phosphoric oxide or sodium, from which it was decanted for measurement.

Chlorobenzene. This was repeatedly fractionated. The main product boiled within less than  $0.1^{\circ}$ ; it was dried over phosphoric oxide, and distilled immediately before measurement;  $D_{4^{\circ}}^{2^{\circ}}$  1.1011, in good agreement with Perkin (1.1010) and Tyrer (1.1010).

*Ethylene dichloride.* The technical quality was fractionated and gave a main fraction boiling within 0.1°. This was dried over phosphoric oxide and further fractionated;  $D_{4*}^{20}$  1.2445, which is lower than those found by Perkin (1.2458) and Tyrer (1.2468).

Acetophenone. This was frozen out until the ternary f. p. in contact with liquid water was constant to 0.2°. It was dried over calcium chloride and repeatedly distilled at 2 mm. to give a product of low conductivity ( $\kappa = 2 \times 10^{-7}$ );  $D_{4^{\circ}}^{2^{\circ}}$  1.0237 (Perkin, 1.0236).

Benzonitrile. The liquid was repeatedly fractionated at atmospheric pressure in all-glass apparatus; it was thus readily brought to low conductivity ( $\kappa = 1 \times 10^{-7}$ ) and constant b. p.;  $D_{\star}^{2*}$  1.0006 (Perkin, 1.0007).

Nitrobenzene. This was steam-distilled and repeatedly frozen till the f. p. became constant at  $5.72^{\circ}$  in the presence of phosphoric oxide. It was dried over phosphoric oxide and distilled

twice at 2 mm.; it then had low conductivity ( $\kappa = 1 \times 10^{-7}$ );  $D_{4^*}^{\infty}$  1·1982 (Perkin, 1·1985; Tyrer, 1·1984).

Calculation of Dielectric Constants.—To save space, this is given in detail for two cells only  $(E_2 \text{ and } G_2)$ . Air was aspirated through cell  $E_2$  for some hours and the capacity determined with the cell remote from conductors. The mean of several successive measurements was  $C_{\text{air}} = 189.43 \pm 0.05 \ \mu\mu\text{F}$ . If we take  $\varepsilon_{\text{air}} = 1.0006$ , this gives  $C_{\text{vac}} =$ 189.32. The cell was then placed in position in the paraffin-bath and re-measured, giving  $C_{\text{air}} = 189.68$ . Hence the end correction is 0.25. When the cell was filled with benzene at 25°, the capacity was 430.58  $\mu\mu$ F at a frequency of 157 kc./sec. The lead-inductance correction  $[-\delta_2 + \delta_3(2 + c/c_M);$  cf. Appendix, p. 775] is 0.17; deduction of this and the end correction gives  $C_{\text{corr.}} = 430.16$ , whence  $\varepsilon = 2.271$ .

Smaller cells with larger spacing between the silver films had to be used for liquids of higher dielectric constant. The air capacity of these cells was too small to be measured with sufficient accuracy; they were therefore calibrated with benzene and chlorobenzene, for which the dielectric constants were known from measurements on the large cells B and E. The method of calibration may be illustrated by data for the smallest cell  $G_2$ .

In the standard position in the paraffin-bath, this cell had the following capacities in  $\mu\mu F$ : filled benzene 41.47, filled chlorobenzene 101.86. If  $\delta$  is the end correction and  $C_0$  the vacuum capacity, then  $41.47 = \delta + 2.272C_0$ ;  $101.86 = \delta + 5.612C_0$ . Solution of these equations gives  $\delta = 0.40$  and  $C_0 = 18.08$ ; hence for this cell  $\varepsilon = (C - 0.40)/18.08$ . The data found for other liquids in this cell are :

| Liquid.                            | C₂H₄Cl₂. | PhCOCH <sub>3</sub> . | PhCN. | PhNO <sub>2</sub> . |
|------------------------------------|----------|-----------------------|-------|---------------------|
| $C_{\text{corr.}}, \mu\mu\text{F}$ | 188.0    | 315.1                 | 454.9 | 627.0               |
| €25'                               | 10.38    | 17.41                 | 25.14 | 34.66               |

The values deduced in this way for ethylene dichloride and acetophenone agree with those found in the larger cells (see table below).

Discussion of Results.—The results of the measurements on a number of cells are collected below, together with the mean value of the dielectric constant and the mean deviation. All the measurements were made at  $25^{\circ}$  and at frequencies of 200 kc./sec. or less in order to minimise lead induction corrections.

Dielectric Constants at 25°.

| Benzene.  |   | Chlorobenzene.                                    |   | Ethylene dichloride.  |   |  |
|---|---|---|---|---|---|--|
| Cell.<br>B <sub>2</sub><br>E <sub>2</sub><br>,, | $\begin{array}{c}\epsilon_{25}\cdot.\\2\cdot273\\2\cdot271\\2\cdot272\\2\cdot272\\2\cdot272\end{array}$ Mean $2\cdot272\pm0.001.$ | Cell.<br>B <sub>2</sub><br><br>E <sub>2</sub><br> | $\epsilon_{25}$ .<br>5.606<br>5.607<br>5.620<br>5.619<br>5.609<br>5.609 | Cell.<br>$E_2$<br>$A_3$<br>$F_3$<br>$F_3$<br>$F_3$  | $\epsilon_{25}$ .<br>10·34<br>10·35<br>10·33<br>10·36<br>10·37<br>10·39                       |  |
| Acetophenone.                                   |   | Mean 5.612 $\pm$ 0.006.<br>Benzonitrile.          |   | $\begin{array}{c} 0.38\\ \text{Mean } 10.36 \pm 0.02.\\ \text{Nitrobenzene.} \end{array}$ |   |  |
| $B_2 \\ F_2 \\ F_3 \\ G_2$                      | $\begin{array}{c} & 17\cdot 39 \\ & 17\cdot 35 \\ & 17\cdot 41 \\ & 17\cdot 41 \\ \end{array}$ Mean 17\cdot 39 $\pm$ 0.02.        | F <sub>з</sub><br>G <sub>2</sub><br>М             | $25 \cdot 23$<br>25 \cdot 14<br>25 \cdot 19 $\pm$ 0 · 04.               | A3<br>F3<br>F3<br>G2<br>Me  | $\begin{array}{c} 34.87\\ 34.77\\ 34.71\\ 34.66\\ \text{ean} \ 34.75\ \pm\ 0.07. \end{array}$ |  |

The value found for benzene is in very satisfactory agreement with that of Hartshorn (*loc. cit.*), *viz.*,  $2 \cdot 2725$ ; this agreement indicates that the method used for eliminating the end effect is satisfactory. The value for benzonitrile agrees well with Ball's value of  $25 \cdot 20$  (*loc. cit.*); for nitrobenzene, Ball gives  $34 \cdot 89$  which is  $0 \cdot 26\%$  higher than the mean value given above. The difference is not much larger than the mean deviation of the present series of measurements.

Influence of frequency. Since Ball used audio-frequencies and the values in the above table were determined at radio-frequencies, it would seem that the dielectric constant is independent of frequency over a wide range. To test this point, further measurements

were made up to nearly 2000 kc./sec. Small cells were used for the liquids of high dielectric constant to minimise lead inductance corrections. When this correction was applied, no change in dielectric constant was found for any of six liquids examined. To save space the data for one liquid only are given below.

Dielectric Constant of Ethylene Dichloride at Higher Frequencies.

| Frequency, kc./sec        | 1680             | 840            | 500            | 395            | 157              | 67               |
|---------------------------|------------------|----------------|----------------|----------------|------------------|------------------|
| Wave-length, m            | 179              | 357            | 600            | 760            | 1910             | 4477             |
| $\epsilon_{25}$ (uncorr.) | $10.88 \\ 10.42$ | 10·46<br>10·35 | 10·42<br>10·39 | 10·39<br>10·39 | $10.38 \\ 10.38$ | $10.38 \\ 10.38$ |

The dielectric constant is therefore independent of frequency up to frequencies of the order of  $10^3$  kc./sec. (cf. Lunt and Rau, *Proc. Roy. Soc.*, 1930, 126, 213). Higher frequencies were not used since the inductance of the measuring condenser introduced large uncertainties (see Appendix). Definite variations in dielectric constant were found by Colley (*Physikal. Z.*, 1910, 11, 324) at frequencies of the order of  $10^5$  kc./sec.

## SUMMARY.

(1) A simple resonance method of measuring dielectric constants is described, and the errors due to the cell and circuit are discussed and evaluated.

(2) The following values are found for the dielectric constant at  $25^{\circ}$ : benzene 2.272, chlorobenzene 5.612, ethylene dichloride 10.36, acetophenone 17.39, benzonitrile 25.19, nitrobenzene 34.75.

(3) The dielectric constant of these six liquids is found to be independent of frequency up to  $10^3$  kc./sec.

## Appendix. Calculation of Residuals.

The series resonant circuit used can be represented by Fig. 4. Here L and r are the inductance and resistance of the resonance coil which is tuned by the three condensers. C



represents the capacity of the experimental cell, and  $L_1$  the inductance of its leads between the points A and B. It was proved experimentally that the series resistance in this branch was negligible; the shunt resistance due to the conductivity of the liquid is represented by R.  $L_2$  and  $C_M$  represent the inductance and capacity in the branch containing the measuring condenser.  $L_2$  was reduced to a minimum by making the points A and B the terminals of this condenser; the series and shunt resistances in this branch can be neglected.  $C_1$  represents the effective capacity of the loading condenser; there is no need to consider inductance or resistance in this branch since it remains unchanged during an experiment.

When the switch S is closed the coil is tuned to resonance by the effective capacity of the three parallel condensers; the value of this effective capacity and resistance may be calculated by the method of impedance operators or by using the appropriate formulæ for the

shunt capacities of each branch.

If r is the equivalent series resistance,  $C_r$  the capacity of the network between A and B (Fig. 4), and  $\omega = 2\pi \times$  frequency, then

From (1) it is evident that the damping due to R can be diminished by increasing the

total capacity  $C_0$ . This is conveniently done by putting fixed condensers in parallel with the measuring system. In this way liquids with appreciable conductivity could be measured.

Expanding the expression for  $C_r$  in (2), we have

$$C_{\mathbf{r}} = C_{1}(1 - \alpha \delta_{1}) + C_{M}(1 - \alpha \delta_{1} + \delta_{3}) + C\{1 + (1 - \alpha)\delta_{1} + \delta_{2}\}$$

when products of the small quantities  $\delta_1$ ,  $\delta_2$ ,  $\delta_3$  are neglected.

When the switch S is opened and the measuring condenser adjusted to give resonance at a new setting  $C_{\mathbf{M}'}$ ,

$$C_r = C_1 + C_M'(1 + \delta_3')$$
, where  $\delta_3' = \omega^2 L_2 C_M'$ .

The quantity measured experimentally is the difference between the two settings of the measuring condenser, or  $C_{obs.} = C_{M'} - C_{M}$ .

Equating the two expressions for C<sub>r</sub> given above and re-arranging,

$$C_{\text{obs.}} = C\{1 + \delta_1(1 - \alpha) + \delta_2 - (\delta_3'C_M' - \delta_3C_M + \alpha\delta_1C_M + \alpha\delta_1C_1)/C\}.$$

Putting  $\delta_3' = \omega^2 L_2(C_M + C)$ ,  $\alpha = C(C_0 - C)/C_0^2$ , and assuming  $C_0 = C_1 + C_M + C$  in terms involving  $\delta_1$ , this reduces to

$$C_{\text{obs.}} = C\{1 + \delta_1 C/C_0 + \delta_2 - \delta_3 (2 + C/C_M)\}.$$

Hence the true capacity of the experimental cell, C, is given by

$$C = C_{\text{obs.}} \{ 1 - \delta_1 C / C_0 - \delta_2 + \delta_3 (2 + C / C_M) \}$$

The term involving  $\delta_1$  depends chiefly upon the ratio of the dielectric constant  $\varepsilon$  to the conductivity of the liquid, since for any condenser  $RC = 8.84 \times 10^{-13} \varepsilon/\kappa$ , where  $\kappa$  is the specific conductivity in mhos. The smallest value of  $\varepsilon/\kappa$  for the liquids used was found with acetophenone, with  $\varepsilon = 17.4$  and  $\kappa = 2 \times 10^{-7}$ . Hence for cells containing this liquid at a pulsatance  $\omega = 10^6$  (wave-length 1885 m.)

$$\delta_1 = 1/R^2 \omega^2 C^2 = 1.7 imes 10^{-4}.$$

For experiments with this substance the ratio  $C/C_0$  had to be made small (0.2-0.1) to minimise the damping; hence the correction term involving  $\delta_1$  is negligible at this and higher frequencies. From the form of this term, it is evident that at lower frequencies it may have a very large value.

An approximate value of  $L_2$  was obtained by measuring the capacity of a cell at a high frequency ( $\omega = 10^7$ ), large and small values of  $C_M$  being used. From these observations it was found that  $L_2 = 100$  cm. approx. This is chiefly due to the leads inside the case of the condenser, but is partly due to the plates. The latter part of  $L_2$  would vary with the setting of the condenser; the observations indicated that this effect was appreciable, and introduced an uncertainty of the order of 10% in the value of  $L_2$ . For measurements at lower frequencies,  $C_M$  was adjusted to about 300  $\mu\mu$ F; the correction term,  $\delta_3(2 + C/C_M)$ , for a cell of 300  $\mu\mu$ F capacity has the following magnitudes when  $\omega$  varies from 10<sup>6</sup> to 10<sup>7</sup>.

It is evident that this correction becomes appreciable when  $\omega$  is greater than  $3 \times 10^6$ . The uncertainty in the value of  $L_2$  and its variation with the setting of the condenser make it difficult to compute this correction with accuracy; hence a value of  $\omega$  of the order of  $10^6$ was used in most of the measurements. For accurate work at higher frequencies, a measuring condenser with much smaller inductance is evidently necessary.

The value of  $L_1$  was determined from observations on a cell of 500  $\mu\mu$ F capacity over a range of frequencies from  $\omega = 10^6$  to 10<sup>7</sup>. The dielectric used was air, hence the apparent change could be ascribed to lead-inductance corrections. After allowing for the effect of lead inductance in the branch containing the measuring condenser,  $L_1 = 1230$  cm. This agrees approximately with the value calculated from the dimensions and shape of the leads.

Since  $\delta_2 = \omega^2 L_1 C$ , the value of this term increases with the capacity and with the frequency. At  $\omega = 10^6$  and  $C = 100 \ \mu\mu F$ ,  $\delta_2 = 1.2 \times 10^{-4}$ , and is negligible; at higher frequencies and with larger capacities  $\delta_2$  becomes appreciable and the appropriate corrections were made to the observed capacities.

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