LXXX.—*The Measurement of the Dielectric Constants of Organic Liquids.*

By Alfred Owens Ball.

THE interest aroused within recent years in the measurement of dielectric constants of liquids has been caused not only by the extension of accurate conductivity measurements to non-aqueous solutions and the development of the Debye–Hückel theory of strong electrolytes, but also by the use of the values of this property for determining dipole moments. In both cases a demand has been created for simple and rapid routine methods of proved accuracy and for trustworthy data relating to a few standard liquids for calibration purposes. These requirements can be satisfied in the case of good insulators, for which the heterodyne method is probably the best and simplest (Herweg, *Verh. deut. physikal. Ges.*, 1919, **21**, 272; *Z. Physik*, 1920, **3**, 36; Whiddington, *Proc. Camb. Phil. Soc.*, 1921, **20**, 445; Grützmacher, *Z. Physik*, 1924, **28**, 342) and for which benzene may be used for calibration purposes on the basis of the work of Hartshorn (*Proc. Roy. Soc.*, 1929, *A*, **123**, 664). In the case of liquids which are not good insulators, however, the author is of the opinion that, although the resonance methods (including, as a special type, the heterodyne method) are simpler in operation, they are more likely to be affected by small and unsuspected errors due to conductivity than are the alternating-current bridge methods. Also, there appears to be no liquid possessing any appreciable conductivity for which really concordant results have been recorded, and the discrepancies may be attributable to any of the following causes : (1) experimental errors of the operator; (2) errors inherent in the method employed, these errors being possibly a function of the conductivity and of the frequency at which the determination is made; and (3) a real variation in the dielectric constant with the frequency.

The work described in the present paper was originally commenced in order to determine the dielectric constants of a few organic liquids with a view to correlation with conductivity measurements made in these laboratories (Philip and Oakley, on nitromethane, J., 1924, **125**, 1189; Martin, on benzonitrile, J., 1928, 3270). In view of the considerations outlined above, however, it was decided to attempt to determine the dielectric constants of a few standard liquids over a range of frequency and temperature by means of an alternating-current bridge. This method has the further advantage over the resonance method that it is more convenient for absolute measurements when no calibrating liquid is

available (see p. 582).   It was also intended to use these same liquids
to compare the results afforded by the bridge method and one or
more resonance methods at a constant high frequency.   The results
of using this method at audible frequencies are now recorded.

Alternating-current Bridge Systems.

An alternating-current bridge may be used to determine the
impedance operator of a system in the same manner as a direct-
current bridge is employed to determine resistance.   A theoretically
perfect capacity of magnitude C has an impedance operator $-j/\omega C$,
where $j = \sqrt{-1}$, and if an alternating potential is applied to it,
the current vector will lead the voltage vector by $\pi/2$.   In practice,
however, owing to conductance of current through the medium, or
absorption, or resistance of plates and contacts, the angle of lead is
less, and the impedance operator cannot be represented in this way.

It is very important to emphasise the equivalence of capacity
and resistance circuits to an imperfect condenser.   The condenser
is determined as its impedance operator, that is to say (in theory),
as the quotient of the vector of the current carried by the vector
of the voltage applied.   Let the numerical value so found be
$a + bj$.   Now a capacity C_1 and a resistance R_1 in series have an
impedance operator $R_1 + \dfrac{1}{j\omega C_1}$, and if this be put identically equal
to the value $a + bj$, the two resultant expressions obtained by
equating the real and the imaginary terms can be solved for C_1
and R_1.   Further, a capacity C_2 and a resistance R_2 in parallel
have an impedance operator $\dfrac{1}{1/R_2 + j\omega C_2}$, and again unique
values of C_2 and R_2 can be found which will make this expression
assume the value $a + bj$.   On the other hand, however, the imped-
ance operator of a circuit consisting of a capacity and shunt resist-
ance together with another resistance in series will involve three
constants, and any number of solutions may therefore be obtained
which will give it the value $a + bj$.   That is to say, if a given
imperfect condenser really consists of a capacity with resistances
both in series and in parallel, it is impossible to determine the
capacity simply by measuring the impedance operator of the whole
system.   Such a case as this might be imagined as one in which
there was a conductance leak between the plates of the condenser,
together with a terminal or contact resistance.   The important
point is that, from the impedance operator of a condenser, it is only
possible to calculate values of two capacities, such that either the
one, together with a resistance in parallel, or the other, with a
resistance in series, will have an impedance operator identical with

that of the condenser in question. It is customary to term the resistances in these two cases the " equivalent shunt resistance " and the " equivalent series resistance " respectively, but it must not be forgotten that the corresponding capacity values are also merely " equivalent," and that neither can definitely be said to be the true capacity involved unless information is available regarding the internal physical structure of the system.

It is important, therefore, to consider the type of condenser to be measured, and to ascertain whether it approximates sufficiently closely to one or other of the above systems for the capacity values deduced thereby to be valid. Now, the great majority of organic liquids possess, even when highly purified, an appreciable conductivity, and the most serious imperfection in the condenser is the consequent (relatively) low shunt resistance. If, then, there is any further resistance in series, the equivalent shunt capacity of the system will not be equal to the actual capacity, the error involved being easily calculated in the following manner.

Suppose the condenser consists of a capacity C_1 in parallel with a resistance R_1, both being in series with another resistance R_2. Then its impedance operator will be $Z_1 = R_2 + 1 \Big/ \Big(\dfrac{1}{R_1} + j\omega C_1 \Big)$. This condenser is now to be assumed equivalent to a system consisting of capacity and resistance in parallel. Let this capacity and resistance be C and R respectively, in which case the impedance operator is $Z = 1 \Big/ \Big(\dfrac{1}{R} + \omega C \Big)$. Since the two systems are equivalent, Z and Z_1 must have the same value, and hence after equating the two expressions the following solutions are obtained for the equivalent shunt resistance R and the equivalent shunt capacity C :

$$R = \frac{(R_1 + R_2)^2 + \omega^2 C_1{}^2 R_1{}^2 R_2{}^2}{(R_1 + R_2) + \omega^2 C_1{}^2 R_1{}^2 R_2}$$

$$C = \frac{C_1 R_1{}^2}{(R_1 + R_2)^2 + \omega^2 C_1{}^2 R_1{}^2 R_2{}^2}.$$

Now, the dimensions of the condensers used in this work are such that, with a representative liquid, the capacity and shunt resistance are of the order of 0·001 microfarad and 10^4 ohms respectively. Under these conditions, and for a frequency of 1000, the term $\omega^2 C_1{}^2 R_1{}^2 R_2{}^2$ will be negligible compared with $(R_1 + R_2)^2$ provided that R_2 is small, and in that case

$$C = C_1 \Big(\frac{R_1}{R_1 + R_2} \Big)^2 = C_1 \Big(1 - \frac{2R_2}{R_1} \Big) \text{ (approx.).}$$

From this it appears that it is justifiable to regard the experi-

mental condenser as consisting of a capacity and a resistance in parallel, but only provided that the internal resistance of plates and contacts, together with the resistance effects due to absorption, is sufficiently small. It is shown later (p. 588) that this condition is satisfied by the dielectric containers in use.

Returning now to alternating-current bridge measurements, it is seen that a method is required that will permit of the measurement of a capacity of the order of 0·001 microfarad when shunted by a resistance varying down to less than 10,000 ohms, *i.e.*, a condenser of very large loss angle. The simplest way of determining a pure capacity by an alternating-current bridge is that of De Sautig, adapted for alternating current by Wien (*Ann. Physik*, 1891, **44**, 697), in which two condensers are balanced against two resistances. But in this system no allowance is made for the difference in power factor of the condensers being compared, and, in consequence, the minima obtained are very flat, and indeed in many cases impossible of detection.

Of the methods that have been suggested to correct for this difference in power factor, it is only proposed to consider the parallel resistance method, first elaborated by Nernst (*Z. physikal. Chem.*, 1894, **14**, 622) and Turner (*ibid.*, 1900, **35**, 385), and subsequently used by Philip (*ibid.*, 1897, **24**, 18), Linebarger (*ibid.*, 1896, **20**, 131), Tangl (*Ann. Physik*, 1903, **10**, 748, 1903), Richards and Shipley (*J. Amer. Chem. Soc.*, 1919, **41**, 2002), King and Patrick (*ibid.*, 1921, **43**, 1835), Grimm and Patrick (*ibid.*, 1923, **45**, 2794), and Harris (J., 1925, **127**, 1049). The procedure is usually to introduce the experimental condenser into the first arm of the bridge and then to restore balance by adjustment of a standard condenser and a compensating shunt resistance in the second arm. It must be emphasised, however, that in the case of condensers of very large loss angle this method is subject to certain inaccuracies, because the full bridge system is that shown in Fig. 1. The capacities C_3 and C_4 across the ratio arms III and IV are due (i) to the residual capacity of the component resistances and their connecting leads, and (ii) to the earth capacities from the detector points if the Monasch earth point is used (*Electrician*, 1907, **59**, 416, 460, 504). Now the balance equations for this system are $C_1R_3 = C_2R_4 + R_3R_4(C_3/R_2 - C_4/R_1)$ and $1/R_1R_4 - 1/R_2R_3 = \omega^2 (C_1C_4 - C_2C_3)$; if it is balanced first with R_1 and R_2 large, $C_1R_3 = C_2R_4$; and if the experimental condenser C_x is then introduced across arm I and the new reading of C_1 is C_1', then $(C_1' + C_x)R_3 = C_2R_4 + R_3R_4(C_3/R_2 - C_4/R_1)$, and therefore $C_x = (C_1 - C_1') + R_4(C_3/R_2 - C_4/R_1)$. At balance, R_1 and R_2 are approximately equal, and in the bridge used $R_3 = R_4 = 1000$ ohms.

In the extreme case when R_1 approaches the value 10^4, it is evident that the measured value of C_x will be in error by one-tenth of the difference $C_3 - C_4$, and if the earth capacities from the detector points are involved in this quantity by the use of the Monasch device, the error may be considerable. But even if the Wagner earth point is used, it is impossible to be absolutely certain that the residuals in the ratio arms III and IV are equal, and, moreover, inductance effects constitute an equally likely source of error. It

FIG. 1.
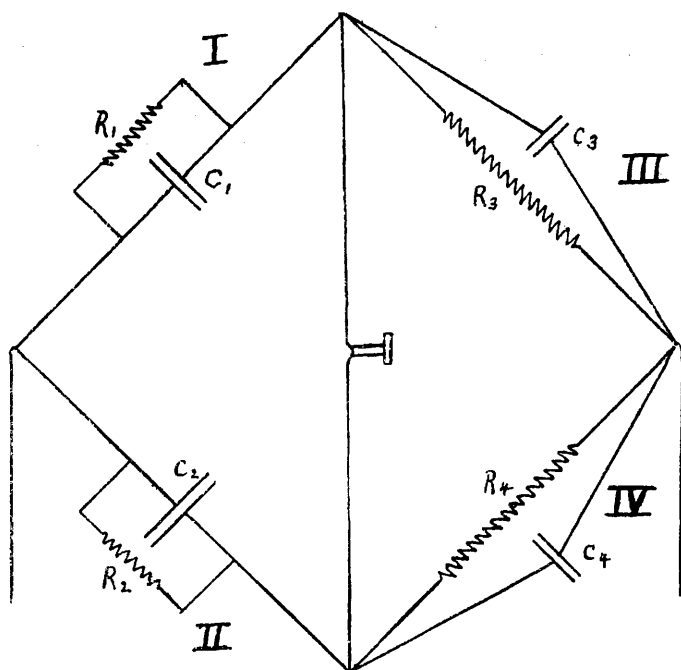
is advisable, therefore, that R_1 and R_2 should be maintained constant during the course of a measurement, and the condenser completely determined by substitution in arm I of the bridge. That is to say, a system is set up such that arm I consists of a capacity and resistance in parallel, the capacity being greater and the resistance less than the equivalent shunt capacity and resistance of the experimental condenser, which is then inserted across this arm, and balance is restored by adjustment of the capacity and resistance in this same arm only.

It should be noted also that the Monasch earth device is quite definitely an approximation, and is valid only when the impedance

of the capacity arms I and II is large compared with that of the ratio arms III and IV. Since this condition does not hold in the present work, the Wagner method of correcting for earth capacities has been used throughout (*Elekt. Z.*, 1911, **32**, 1001; 1912, **33**, 635).

The Compensating Resistances.

The chief requirement of the compensating resistance is that its residual capacity (and inductance) should be constant over the range of operations—which, in the case of the present work, is from a few thousand ohms upwards. Wire resistances of known residuals were not, unfortunately, available, and the Nernst–Turner types of liquid resistance were not entirely satisfactory over the lower part of the range, owing, first, to heating effects of the current, and secondly, to capacity changes which were by no means negligible even when the electrodes were heavily platinised to reduce the polarisation capacity. At first, attempts were made to calibrate for these residuals by means of a platinum-film resistance, but eventually the main substitution was effected by means of a carbon-film resistance, one of the liquid resistances being retained in parallel merely for purposes of fine adjustment. The carbon film used consisted simply of a thick line drawn on a piece of ground glass with an ordinary black-lead pencil, contact being established over any required length of the film by two amalgamated copper wires dipping into small drops of mercury. Provided that the film and mercury contacts are freshly prepared and quite clean, the resistance thus obtained is perfectly definite over a considerable length of time. It is further necessary to provide a distance control for the resistance, and the system used is shown in Fig. 2. A and B are wire electrodes heavily platinised, and C is a solid glass rod controlled from a distance by a cord passing over a pulley. By adjusting the position of A in the narrow tube D the total resistance of the cell can be made large compared with the effective resistance of the whole arm of the bridge with which it is placed in parallel, and thus the movement of the plunger in the wide limb E can be made to afford as fine an adjustment as is required. The electrolyte is the usual solution containing boric acid and mannitol (Magnanini, *Z. physikal. Chem.*, 1890, **6**, 58; Nernst, *ibid.*, 1894, **14**, 631). This resistance is always in circuit, and the electrode A is not moved during the course of a measurement. It is only necessary, therefore, to ascertain whether the movement of the plunger causes any change in the residual capacity of the system. This was done by rebalancing the bridge a number of times, the setting of the auxiliary liquid resistance being altered very slightly each time over a part of its range for which it was known to have no residual error. The position of the

plunger for balance was thus different each time, but even when
the electrode A occupied its minimum position during the test (and
hence carried the maximum current) no change in the capacity
reading of the bridge could be detected.   This determination was
made especially because it was thought probable that polarisation
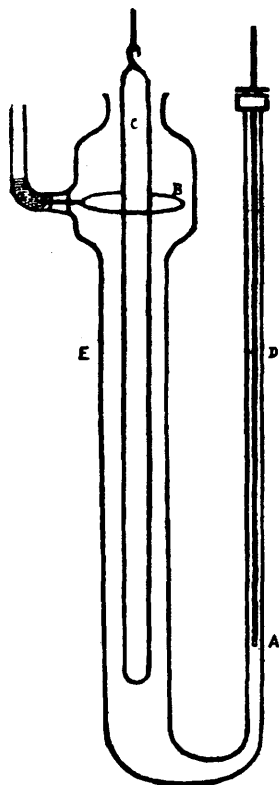
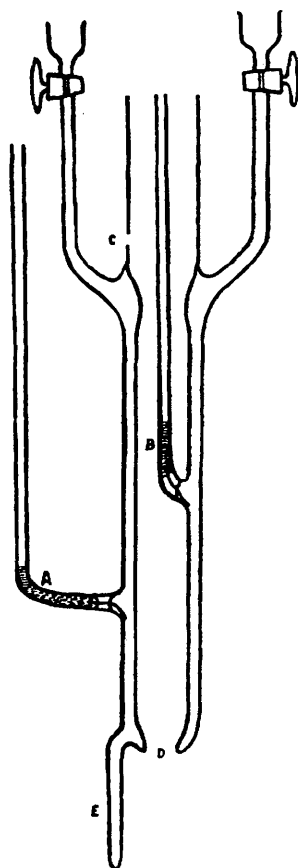FIG. 2.   FIG. 3.

capacities might be set up owing to the small area of the wire
electrodes.

The Standard Condenser and Measuring Systems.

As previously shown, the measurement of the capacity of a con-
denser filled with a liquid of relatively high conductivity is only
possible by means of a substitution method, both the capacity and

the resistance being substituted in the same arm of the bridge. It has also been noted already that, since the dielectric constant is a ratio, it is not necessary to know the capacity of the dielectric container in absolute units, and hence the only requirement of the measuring system is that equal intervals on the scale should correspond to equal capacity changes. Since, however, this is an ideal to which practical systems can only be made to approximate, it is necessary that the appropriate calibration corrections be determined, and applied to every reading.

The standard measuring instrument available for the present work was a Sullivan variable air condenser, having a total range of about 1200 $\mu\mu$ farad. The scale was divided into 180° and was fitted with a vernier reading directly to tenths, and permitting a rough estimate of the second decimal place by means of a lens. It may be noted that, except in the case of liquids of high conductivity, the sharpness of the bridge setting always exceeded the accuracy with which the condenser scale could be read.

Now, a convenient value of the air capacity of a condenser of the Sayce and Briscoe type as used was found to be of the order of 50 $\mu\mu$ farad $\equiv 7°$, and this could therefore be determined with an accuracy of at most 1%, this error being consequently involved in all subsequent dielectric measurements. Since it was desired to reach an ultimate accuracy of at least 0·2%, it was necessary to use either a larger capacity or a more open scale. The former was found to be impracticable with the type of condenser in use, and a measuring system was therefore set up similar to that suggested by Hartshorn (*Proc. Physical Soc.*, 1924, **36**, 399). The standard variable air condenser C_1 was placed in parallel with a fixed mica condenser C_2, both being in series with another fixed mica condenser C_3. C_2 and C_3 were made by Sullivans and had nominal capacity values of 0·002 microfarad and 0·00175 microfarad $\equiv 290°$ and 250° respectively. These condensers were guaranteed constant in capacity and power factor and of very small temperature coefficient, and in use they gave complete satisfaction.

The system constructed in this manner has a much more open scale than the standard condenser alone, but the relation between the capacity of the system and the scale reading of the standard is non-linear. The capacity of the system is $C = (C_1 + C_2)C_3/(C_1 + C_2 + C_3)$, and for a straight-line relationship to hold between C and C_1 it would be necessary that C_1 should be negligibly small in comparison with C_2 and C_3, but in this case not only does the net capacity of the system become inconveniently large, but the degree of constancy required of the fixed condensers will be correspondingly greater. It was therefore decided to use the system as described

x 2

and to perform the calibration in the following manner. A small constant capacity of about 2·5° was measured over successive portions of the scale of C_1, the actual scale differences ranging from about 14° to 20°. Each particular scale reading C_1 was then reduced to the corresponding (approximate) value of C by the formula $C = 250(C_1 + 290)/(C_1 + 290 + 250)$, the nominal values of C_2 and C_3 being used, and since the reduced scale differences so obtained were then found to be constant to a first approximation, it was possible to draw up an ordinary calibration curve showing the correction to be applied at any point on the reduced scale. To demonstrate the order of accuracy attainable in this way, a series of 16 measurements was made on the air capacity of one of the dielectric containers. It was found that, excluding one reading (8·335) which was probably due to an error of observation, the values ranged between 8·299 and 8·323, with a mean of 8·310. It is certainly safe to ascribe an error of less than 0·01° to the arithmetic mean, *i.e.*, an error of about 0·1%.

The measuring system as elaborated in this way gave a total capacity variation of about 25° corresponding to the complete range of C_1. Since the dielectric containers had an air capacity of about 6—8°, it is evident that, for the determination of dielectric constants above 3, the scale had to be extended by the customary device of placing one or more small fixed condensers in parallel with the whole measuring system, so that their capacity could be added to the latter when required. The condensers used each consisted of a small glass tube about 10 cm. long and 1 cm. in diameter sealed off at the lower end and held in position inside a larger tube filled with mercury. Into the inner tube was also placed some mercury (the quantity depending on the magnitude of the capacity required) so that the level was below that in the outer, thus minimising the effect of any slight displacement. A condenser with a glass dielectric in this manner has of course a definite temperature coefficient, and a small power factor : the former was controlled in practice by maintaining the room at a fairly constant temperature and checking the capacity value before and after each series of measurements; the latter was of no importance since it is only the effective shunt capacity of the condenser which enters into consideration.

The method of connexion adopted for these condensers should be noted. The mercury in the outer tube served as a shield, and was kept permanently connected to the screen terminal of the standard condenser, while contact was established between the other terminal and the mercury in the inner tube by a length of quill tubing filled with mercury and having a platinum wire sealed through the lower extremity. The condenser was inserted into

the measuring circuit when required by depressing a copper wire in
the quill tubing, and thus, since the shield was permanently in circuit,
the *change* of capacity on making contact was maintained constant
and independent of any external effects.

The scale of the measuring system as extended in this way was
about 50°, thus enabling liquids to be dealt with up to a dielectric
constant of about 6, and the question then arose as to the advis-
ability of extending it by more fixed condensers so that it covered
the range up to $\varepsilon = 40$. The accuracy of the results obtainable,
however, is governed (see p. 577) by the accuracy with which the
air capacity can be determined, and since this is subject to an error
of about 0·1%, there is no need to determine any other capacity to
a much greater accuracy than this. Now a liquid of dielectric
constant 6 will afford a capacity of about 40°, and since such a
capacity can be determined by direct comparison with the standard
condenser to within $\pm$ 0·05°, it is evident that there will be no loss
of accuracy in determining the liquids of higher dielectric constant
in this way. It is necessary, however, to know the numerical
relation between the two measuring systems, and this was found in
the following manner. If measurements are made on a number
of condensers (all having a capacity of about 40°) with system I, a
series of capacity readings C_1, C_2, C_3, etc., will be obtained which
are all proportional to the absolute magnitude of the capacities
concerned, the constant of proportionality being K. Similarly, if
the same condensers are measured on system II (*i.e.*, by direct
substitution against the standard air condenser) a series of values
C_1', C_2', C_3', etc., will be obtained with a proportionality constant K'.
Then $C_1/C_1' = C_2/C_2' = C_3/C_3' \ldots = K/K'$, K/K' being the
conversion factor between the two systems.

Now the error in determining C' is about 0·1%, and in C about
0·02%, and the following table gives an indication of the accuracy
of the mean value of the ratio K/K'. The actual capacities measured
were the three dielectric containers filled with appropriate liquids
as indicated.

TABLE I.

	Condenser.	Liquid.	C.	C'.	K/K'.
	I	$CHCl_3$	39·200	40·26	1·0271
	II	,,	28·128	28·90	1·0276
	III	,,	37·501	38·56	1·0282
25°	I	$CMe_2Et\cdot OH$	49·273	50·63	1·0276
	II	,,	35·352	36·33	1·0278
	III	,,	47·164	48·44	1·0271
	II	C_6H_5Cl	33·723	34·65	1·0275
	III	,,	44·905	46·15	1·0277
0°	I	$CHCl_3$	43·083	44·25	1·0271
	I	$CMe_2Et\cdot OH$	67·949	69·60	(1·0243)
50°	I	,,	43·304	44·52	1·0280
					Mean 1·0276

The discrepancy observed for condenser I filled with dimethyl-ethyl carbinol at 0° is possibly due to the abnormally large temperature coefficient of the liquid at this point. The dielectric constant is 5·94 at 25° and 8·16 at 0°, so the error in the value 1·0243 could be caused by about 0·1° difference in the temperature of the cell when measured on the two systems.

The relation between these two measuring systems S_1 and S_2 having been obtained, the air capacity of each dielectric container can now be evaluated in terms of S_2 by multiplying the value as determined on S_1 by the conversion factor. For instance, the air capacity of condenser I in terms of S_1 is 8·311 $\pm$ 0·005, and since the conversion factor is 1·0276 $\pm$ 0·0003, the value on the scale of S_2 will be 8·531 $\pm$ 0·008. As measured directly on the scale of S_2, however, it is found to be 8·54 $\pm$ 0·03, and hence the increase in accuracy that has been obtained is obvious.

In conclusion, it must be observed that with an air capacity of 8°, the standard condenser will only cover the range of dielectric constant up to about 20, and therefore the scale was extended by means of auxiliary fixed condensers in just the same manner as was done for the system S_1. In this case, however, two Sullivan mica condensers were used of the same type as those described previously and of nominal value 0·001 and 0·002 microfarad respectively, and this extended scale was capable of dealing with dielectric constants up to 60. The method of connexion of these auxiliary condensers was the same as that noted previously, the screen terminal of each being kept permanently in circuit, and connexion being made as required by means of small mercury cups connected to the other terminals.

The Experimental Condenser.

The satisfactory design of the dielectric container is difficult, and probably most of the discrepancies occurring in the literature are to be attributed to errors in this respect. The essential features of an ideal condenser may be summarised thus (compare Hartshorn, *loc. cit.*) :

1. Its volume capacity should be reasonably small, since many of the organic liquids requiring investigation are expensive and difficult to prepare in bulk.

2. The electrostatic capacity should be as large as possible in order to secure the maximum accuracy of which the measuring system is capable.

3. It must be mechanically rigid, so that it may be handled without fear of any displacement of the conducting system and consequent alteration in capacity.

4. It must be easily cleaned and dried.

5. It must permit of accurate temperature control, and (of somewhat less importance) should be of such shape that it acquires the temperature of the thermostat fairly rapidly.

6. In this work, one other condition has been added that is not always required, *viz.*, that the condenser should be an absolute one, *i.e.*, it should afford direct proportionality between dielectric constant and measured capacity. This point needs explanation. Imagine the ideal case of two conductors placed in a vacuum at an infinite distance from all other conductors. If their capacity could be determined and then the whole of the surrounding space filled with some medium of dielectric constant ε, the capacity would be increased accurately in the ratio $\varepsilon : 1$. The same would hold good of two conductors within a closed conducting shield : the measured capacity would be $C_{12} + C_1 C_2/(C_1 + C_2)$, where C_{12} is the inter-capacity between the conductors, and C_1 and C_2 are the capacities between each conductor and the shield separately, and then, provided the whole of the space within the shield were filled with the medium concerned, not only C_{12} but also C_1 and C_2—and hence the effective measured capacity—would be proportional to the dielectric constant. If, however, the medium does not fill the whole space, this exact proportionality will no longer hold.

In practice this ideal case cannot be realised owing, first, to the leads which have to pass outside the shield to the measuring system, and secondly, to the need of some mechanical support which will fix the two conductors in a rigid position relative to each other and to the screen. It is possible, however, to overcome the difficulty of the leads by arranging that they make and break contact at the surface of the conductor by means of a very small movement, so that if they are of thin wire and pass through correspondingly small apertures in the shield, the change in their own capacity when contact is made becomes vanishingly small compared with the capacity being measured. It is quite a different matter with the second defect. Obviously no system can be devised which shall have no solid dielectric at any part of the field of force, although it is possible to dispose the solid in such a way that it only influences the shield capacities and does not intercept any of the lines of force between the two conductors. If in such a case measurements are made so that C_{12}, C_1, and C_2 can all be found individually (Giebe and Zick-ner, *Arch. Elekt.*, 1922, **11**, 109; Hartshorn, *Proc. Physical Soc.*, 1924, **36**, 399) and the lead correction is eliminated as above, the values of C_{12} thus found will be directly and accurately proportional to the dielectric constant of the medium, just as in the preceding hypothetical cases. It is at this point, however, that one great merit of the bridge method becomes apparent, *viz.*, that by means

of the Wagner or Monasch earth device, these shield capacities can be eliminated, so that one measurement is sufficient to determine C_{12}, as opposed to the three which are required by the other method. This represents not only a certain increase in accuracy, but a considerable saving in time, even in the case of the dual setting necessitated by the Wagner arm.

An alternative way of obtaining direct proportionality between measured capacity and dielectric constant is to determine a virtual capacity. This was the method adopted by Nernst for his absolute dielectric-constant determinations (*Z. physikal. Chem.*, 1894, **14**, 634).

The virtual condenser method is not, however, well suited for routine determinations since, not only has the condenser to be filled and emptied a number of times for each determination, but also the use of four capacity readings instead of two to calculate the dielectric constant increases the probable error. On the other hand, the design of an absolute condenser has usually been achieved only at the expense of using a large volume of liquid. The majority of workers have therefore favoured some kind of relative condenser which can be calibrated in terms of liquids of known dielectric constants.

Consider the system discussed previously of two conductors within a closed conducting shield, and let us suppose this time that some part of the space is filled with a solid dielectric. Then, in general, any elementary tube of force from one conductor to the other will pass partly through a vacuum and partly through the solid, and the total element of capacity between the conductors due to this tube will be the series addition product of these portions. That is, if ΔC_v and ΔC_s represent the capacities due to vacuum elements and solid elements, respectively, the total contribution made to the capacity of the system by this tube of force will be $1\Big/\Big(\Sigma\dfrac{1}{\Delta C_v} + \Sigma\dfrac{1}{\Delta C_s}\Big)$. Let this be written as $1\Big/\Big(\dfrac{1}{c_v} + \dfrac{1}{c_s}\Big)$. The total capacity between the conductors will then be $c_1 = \Sigma 1\Big/\Big(\dfrac{1}{c_v} + \dfrac{1}{c_s}\Big)$, the summation being performed over all the tubes of force. If now a liquid of dielectric constant ε is introduced, it may be assumed as a first approximation that the shape of the field of force remains unaltered, and the new capacity will be $C_1 = \Sigma 1\Big/\Big(\dfrac{1}{\varepsilon c_v} + \dfrac{1}{c_s}\Big)$. The validity of this assumption will be examined later.

For the purposes of measurement it is necessary to express ε as a function of c_1 and C_1, but it is evident that in this general case there is no deducible relationship. There are two cases, however,

in which a simplification is practicable. (1) If the term due to c_s vanishes throughout the summation we have $C_1 = 1/\Sigma \dfrac{1}{\varepsilon c_v}$ or $C_1 = \varepsilon \times$ constant, corresponding to the case of an absolute condenser already discussed. (2) If either c_v or c_s vanishes for each individual term of the summation,

$$C_1 = \Sigma 1 \Big/ \left(\frac{1}{\varepsilon c_v}\right) + \Sigma 1 \Big/ \left(\frac{1}{c_s}\right)$$
$$= \varepsilon \Sigma c_v + \Sigma c_s$$

thus affording a simple linear relation between ε and C_1. This evidently means that such a linear relationship holds if, and only if, each tube of force passes through only one medium. If the lines of force pass at any point from the solid to the liquid, it will not be possible to write $C_1 = A\varepsilon + B$, where A and B are constants depending only on the geometrical configuration of the system and the dielectric constant of the solid medium. The importance of this limitation was definitely recognised by Nernst (*Z. physikal. Chem.*, 1894, **14**, 633), although subsequent workers have sometimes ignored it.

The majority of routine measurements by previous investigators have been made with condensers for which the capacity has been assumed to be a linear function of the dielectric constant, *i.e.*, $C = \varepsilon c_v + c_s$, the calibration constants c_v and c_s being determined from the air capacity and the capacity when filled with some liquid of known dielectric constant. This method suffers from certain drawbacks in our present state of knowledge. First, in view of the limitations under which strict proportionality between measured capacity and dielectric constant has been shown to exist, it does not appear very satisfactory to use only one liquid for calibration purposes over the whole range. Theoretically, the calibration should be performed with a number of liquids such that the range of dielectric constant to be investigated is covered fairly uniformly, and if then it is found that the capacity values so determined are linearly related to the corresponding known dielectric constants it will be permissible to equate the dielectric constant of any other liquid to $(C - c_s)/c_v$. Otherwise, an attempt may be made to represent the results by some empirical expression containing more than two constants, or the capacity may be plotted against the dielectric constant and the value for any unknown liquid read off from the graph. But here the second drawback to this relative condenser method makes itself felt. Not only are there too few liquids of accurately known dielectric constant to show whether strict linear relationship does hold or not, but it is evident that,

even if it does, the accuracy of the results obtained can. never exceed that assumed for the calibrating liquids.

It was pointed out by Hartshorn (*loc. cit.*) in his work on benzene that the obvious criteria to be satisfied by such calibrating liquids are stability, ease and certainty of purification, reasonable cheapness, and (most important) fairly low conductivity, and the number of liquids satisfying these conditions is extremely limited. There are a few from about 2 to 2·5, of which benzene is undoubtedly the best; over the higher ranges, however, apart from chloroform (5), pyridine (12), and nitrobenzene (35), the author has failed to find any which have not some serious drawback to their use as calibrating standards.

Table II gives the results (corrected to 0°, 25°, and 50°) obtained by some of the previous workers for benzene, chloroform, and nitrobenzene.

TABLE II.

Benzene.

	25°.	50°.		25°.	50°.
Nernst	2·22		Graffunder	2·268	2·219
Drude	2·25		Grützmacher	2·277	2·224
Turner	2·274		Meyer	2·234	2·197
Tangl	2·274	2·223	Sayce and Briscoe	2·240	
Errera	2·26		Harris	2·248	
Isnardi	2·268	2·221	Hartshorn	2·273	2·223

Chloroform.

	0°.	25°.	50°.
Nernst		5·08	
Drude		4·80	
Turner		5·05	
Tangl		4·77	4·37
Isnardi	5·25	4·77	4·37
Grützmacher		4·95	4·59
Meyer	5·14	4·63	4·24
Harris		4·64	

Nitrobenzene.

	25°.	50°.
Turner	35·0	
Errera	32·6	
Jezewski	34·3	30·0
Meyer	32·3	28·4
Lange	36·5	
Harris	34·1	

References.—Nernst, *Z. physikal. Chem.*, 1894, **14**, 622; Drude, *ibid.*, 1897, **23**, 269; Turner, *ibid.*, 1900, **35**, 385; Tangl, *Ann. Physik*, 1903, **10**, 748; Errera, *J. Physique*, 1922, **3**, 401; Jezewski, *ibid.*, p. 293; Isnardi, *Z. Physik*, 1922, **9**, 153; Graffunder, *Ann. Physik*, 1923, **70**, 225; Grützmacher, *Z. Physik*, 1924, **28**, 342; Meyer, *Ann. Physik*, 1924, **75**, 801; Sayce and Briscoe, J., 1925, **127**, 315; Lange, *Z. Physik*, 1925, **33**, 169; Harris, J., 1925, **127**, 1049; Hartshorn, *Proc. Roy. Soc.*, 1929, *A*, **123**, 664.

In view of these discordant results it was obviously necessary to use some type of absolute condenser for the present work, and it was found that they fall into two main classes : (1) the virtual capacity type referred to previously ; (2) condensers in which some attempt has been made to ensure that the whole of the lines of force giving rise to the measured capacity pass through the homogeneous medium.   In general it is by no means apparent that

the condensers used by such workers as Grützmacher, Graffunder, Isnardi, or Jezewski were strictly absolute, and although in the absence of detailed dimensions it is difficult to discuss the probable magnitude of the deviation, the author is of the opinion that the greater part of the above discrepancies are to be attributed to this cause, together with the closely allied error introduced by the leads.

For reasons already stated, it was decided to exclude virtual capacity condensers from the scheme of the present work. Some time was spent initially with parallel-plate condensers, but satisfactory results were not obtained. Eventually it was decided to adopt the design first introduced by Sayce and Briscoe (*loc. cit.*) as a basis for further work. Three modifications were constructed, of which the first was uncorrected for the end effect, and the second and third had two completely different devices for eliminating this error.

Condensers.—Condenser I (Fig. 3). This consisted essentially of two concentric glass tubes sealed one within the other, the inner surface of the outer and the outer surface of the inner being silvered over the straight portion of each so that the annular space between them served as the dielectric container. The outer tube was 22 mm. in diameter and the air gap was about 1 mm. Contact with the silver film was made by platinum wires sealed through the walls into side tubes A and B; it should be noted that for good contact these wires must be sealed on to the walls again at some other point besides that at which they pass through into the side tube. Silvering was performed as follows. The lower internal seal was first coated with paraffin wax by drawing up through the tube C a mixture of equal parts of wax and xylene at about 60°. After a few moments, the hot liquid was allowed to drain away leaving a film which, when cold, successfully resists the attack of the silvering solution. The latter was introduced in the same manner, at least three layers were deposited, and the condenser was washed by drawing through it a rapid current of distilled water. It was then dried, and the paraffin wax removed with warm xylene, the tube E being subsequently sealed off.

This cell has the advantage that the water of the thermostat can circulate through the inner cylinder *via* openings C and D, and extremely rapid and efficient temperature control can therefore be maintained.

Lead capacities and method of shielding. In normal use the condenser is sunk in a thermostat so that the water level comes to within about 2 cm. of the taps. Imagine that it is immersed in a silvering bath to this level so that a metallic film is deposited, not only round the body of the cell, but also round the glass tubes down

which the leads pass to the mercury contacts. In these circumstances the following capacities will come into play : (1) the capacity between the two silver films on each side of the annular space; (2) the capacity between each film and the shielding film through the glass wall; (3) the capacity of each platinum mercury contact with the shield; (4) the capacity of each copper lead with the shielding film around the glass side tubes; (5) the capacity between the leads over the length from the shielded tubes to the point at which they are connected to the bridge system. If now the screen is earthed and the bridge balanced by means of the Wagner earth point in the usual manner, capacities 2, 3, and 4 will not be measured, and the only capacity in circuit will be $C_1 + C_5$. Suppose now the leads to be raised in the side tubes so that they just do not make contact with the mercury. The capacity in circuit will then be $C_5' + 1 \Big/ \left(\dfrac{1}{C_a} + \dfrac{1}{C_b} + \dfrac{1}{C_1} \right)$, where C_a and C_b respectively are the small capacities between the leads and the mercury contacts. C_1 is large compared with C_a or C_b, and to a first approximation these may be assumed equal, so that the capacity in circuit may be written $C_5' + C_a/2$. Now this capacity C_a across the broken contact will fall off fairly rapidly as the degree of separation increases, and by making actual measurements on the capacity between a similar lead and the surface of mercury in a small U-tube, it was shown that with a 1-cm. gap the capacity could not be detected. Further the change from C_5 to C_5' due to this 1 cm. increase in the length of the lead between the cell and the bridge is also much less than can be detected—the leads being about 10 cm. apart.

The change that occurs on separating the leads from the mercury contacts by about 1 cm. affords therefore an accurate measure of the capacity.

This result has been arrived at by assuming a metallic shield around the outside of the dielectric cell. It is found in practice, however, that identical results are obtained whether an earthed screen is provided, or whether the cell is merely placed in the water of the thermostat, and the latter earthed. Tap water has a sufficiently high conductivity from this point of view for it to be regarded as a conductor and not as an insulator.

The end effect. It is true that in this cell there is no solid dielectric at any point between the two films which constitute the plates of the condenser (referred to subsequently as the condenser films), but there is sufficient uncertainty regarding the distribution of the field at the extremities to prevent its being regarded *a priori* as a satisfactory form of absolute condenser; it appears possible that

some of the lines of force may bend round so that they pass not only through the dielectric medium but also through the glass walls, although in view of the earthed shield on the other side of each wall, this error is not likely to be large.   Condensers II and III

FIG. 4.   FIG. 5.
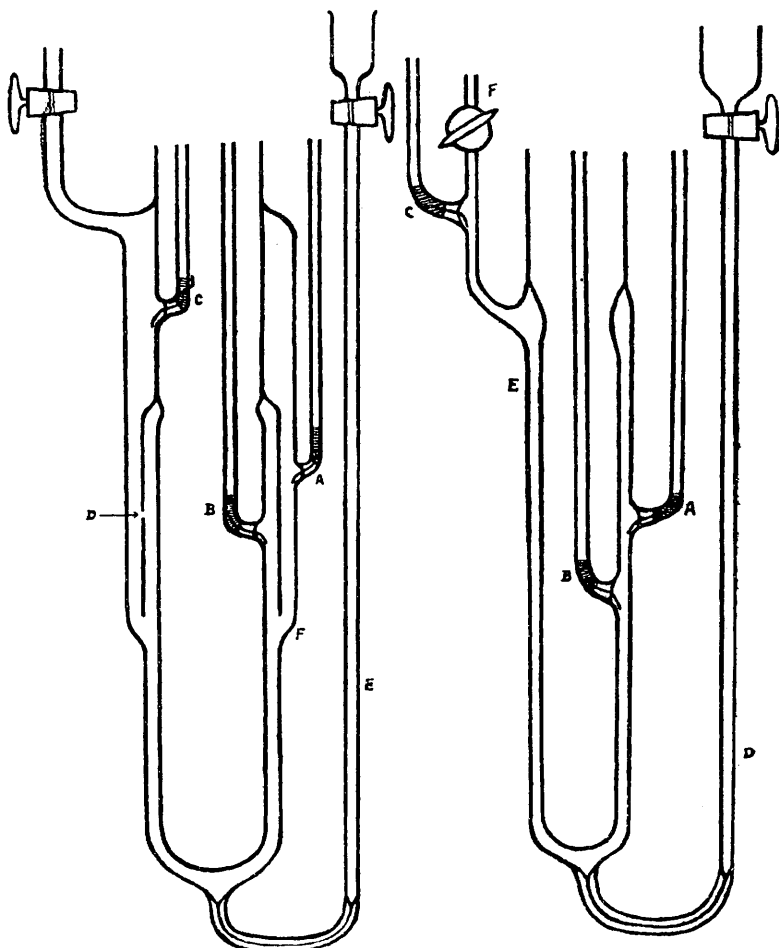
were therefore constructed with a view to eliminating this possibility entirely.

Condenser II (Fig. 4).   In this cell the two glass cylinders corre-sponding to those in condenser I were sealed together at the top only, the outer being drawn off at the bottom to a fairly wide-bore capillary.   About 8 cm. below the seal, another intermediate cylinder

was joined as shown, and this had a small hole indicated at D. The annular space below the point F at which this cylinder terminates was about 10 cm. long with an air gap of 1 mm. Silvering solution was poured into the side tube E until it filled the whole cell to the level of the platinum contact C, a large air bubble, however, being trapped between the inner cylinder and the intermediate one above the hole in the latter. The inside of the inner cylinder was also silvered up to the level of the contact C. The contacts A and B were connected to the bridge in the usual manner, and C was kept permanently earthed.

It is evident that the capacity being measured between the contacts A and B is constituted solely by the field between the condenser films below F, i.e., the end effect in condenser I has here become divided in two between the earthed film and each condenser film respectively, and these earth capacities are, of course, not measured. In other words, the whole of the lines of force giving rise to the capacity between A and B pass through the lower annular space only. This contains an absolutely homogeneous medium and the only points at which distortion of the field can occur due to the dielectric constant of the medium are the extremities of the two condenser films—and these are too remote for there to be any effect on the field at F.

If this view is correct, the measured capacity should be independent of the level of the liquid filling the cell provided it rises at least 1 cm. or so above the point F. This was tested and found to hold even for liquids of high dielectric constant.

Condenser III (Fig. 5). In this cell the end effect is eliminated, not by an earthed cylinder intermediate between the extremities of the two condenser films, but by two earthed cylinders placed above and concentric with them, in such a way that the air gap is as small as possible. In other respects the construction was similar to the two preceding cells. Silvering solution was poured into the side tube D until it rose in the annular space to the point E. After deposition of the silver had been completed, the condenser was inverted and another film was deposited from the side tube F up to the annular space so that there was only about 1 mm. gap between it and the previous film. A and B were the contacts connected to the bridge and C was earthed. For measuring purposes, the level of the liquid in the side tube was adjusted until it had risen at least 1 cm. above the point E.

Two other errors may arise through faulty condenser design, *viz.*, (a) the series resistance error discussed on p. 572, and (b) polarisation capacities.

(a) For the investigation of the first, condenser I was silvered

without a preliminary treatment with paraffin wax, so that the silver film was continuous between the contacts A and B, and the resistance between these points was then measured and found to be about 7 ohms for one deposit of silver, 4 ohms for two, and 2 ohms for three. It was evident that the terminal or contact resistance was small, and that the effective series resistance was that due to the internal resistance of the films.

Measurements were also made on condensers II and III, by pouring in a quantity of saturated potassium chloride solution so that the condenser films were short-circuited at the bottom; in each case the resistance (for three layer deposits) was about 2 ohms.

Now, of the liquids for which accurate results are quoted subsequently, nitrobenzene had the highest conductivity, and the equivalent shunt resistance of the condensers was therefore a minimum when filled with this at 80°, the actual value being about 5000 ohms. Hence (see p. 572), the error caused by a 2-ohm series resistance was less than 0·1%, and at lower temperatures and for other liquids it was, of course, still smaller.

(b) The possibility of an error due to polarisation capacities was investigated in the case of the liquids of higher conductivity by varying the intensity of the oscillator output, and hence the current density through the cell, over at least a five-fold range. No change in the measured capacity was detected.

Apparatus and Procedure.

The Generator.—The triode valve oscillator has now completely supplanted the older types of generator, not only by reason of its ease of manipulation, but by virtue of the purity of wave form obtainable. The actual instrument used was made by Cambridge & Paul. It had a variable capacity unit, by means of which the frequency could be varied between 100 and 5000, and also 3 secondary windings which permitted of the output intensity being varied within fairly wide limits. Satisfactory results were obtained either with an R valve, or a dull emitter valve, or (if more power was required) with a valve of the LS5 type. In general, however, with liquids of any appreciable conductivity, it was found much better to reduce the intensity as far as possible in order to minimise heating effects in the bridge.

The Detector.—A 1000-ohm Brown telephone was used, but since it was found that a low output from the oscillator did not give sufficient sensitivity, a two-valve amplifying circuit was introduced between the bridge and the telephone. The components used were two D.E.L. 410 valves and a Marconi Ideal Transformer of ratio 4 : 1; this amply intensified the effect, but the quality of the note

suffered considerably from the introduction of harmonics. These, however, were almost entirely eliminated by shunting the telephone with a condenser of suitable value to by-pass the notes of higher frequency. Too large a capacity will begin to reduce the intensity of the fundamental, and an optimum value was sought at which the selective reduction of the overtones was a maximum. For a fundamental note of 1000 frequency, a 0·15 microfarad capacity gave satisfactory working.

Bridge Components.—The ratio arms were two Sullivan 1000-ohm non-reactive coils guaranteed equal to each other to within 0·01%. The standard condenser (see p. 577) was fitted with a wooden arm so that it could be controlled from a distance of 8 or 9 feet. The capacity in the second arm of the bridge required to balance that in the measuring arm was made up by a 0·001 microfarad Dubilier variable air condenser, together with two fixed mica condensers of 0·001 and 0·002 microfarad capacity respectively. The compensating resistances were as previously described (p. 575).

The Wagner Earth-point System.—This system (referred to subsequently as the Wagner arms) was constructed in the case of liquids of low conductivity to imitate the main bridge system, *i.e.*, one arm consisted of a 1000-ohm fixed resistance, and the other of a variable capacity shunted by a variable liquid resistance. In the case of liquids of higher conductivity, it was found preferable to make the total impedance of the Wagner arms large compared with that of the bridge, and hence a fixed 0·01 microfarad condenser was used in one arm, while a variable wire resistance (max. 10,000 ohms) in series with a variable condenser (max. 1 microfarad) constituted the second. It is, of course, not necessary that the Wagner arm components should be of the same degree of perfection as those used in the main bridge system.

Bridge Set-up.—The oscillator was placed about 8 feet from the nearest bridge component and was surrounded by an earthed screen, while the amplifier was similarly screened and placed about 6 feet away on the further side of the bridge, the observer being situated just beyond. Connexion between the oscillator, bridge, and amplifier was made by means of armoured flex, the sheath being earthed. All the bridge component shields were connected to one or other of the oscillator points, and were mounted on blocks of paraffin wax.

It was found that the bridge was reasonably free from external influences—in particular the balance point was independent of the observer's position provided he did not approach to within less than 2 feet, and the capacity balance could often be accurately reproduced over a period of hours. Direct action from the oscillator

was negligible, reversal of the connexions to either the bridge or telephone terminals causing no change in the balance point.

Temperature Control.—A gas-heated thermostat was used for temperatures above 18°, and maintained constant to within $\pm$ 0·02°. Temperatures below 18° were suitably controlled by using a bath of large volume insulated with felt, and by working at a temperature within a few degrees of that of the room, the latter also being maintained as constant as possible. Under these conditions, the thermometer reading could be kept within 0·05° over at least $\frac{1}{2}$ hour. The bath at 0° was maintained with tap water and ice (p. 586), the exact temperature being observed on a thermometer. In a number of cases the results quoted have been reduced to even temperatures by using the appropriate temperature coefficient, but such corrections were not used for differences of more than $\frac{1}{2}$°. The thermometer was calibrated against another standardised at the N.P.L.

Method of Measurement.—The following scheme was adopted systematically for all the measurements recorded. The bridge and Wagner arms were first set to approximate balance with the condenser to be determined in circuit, and since, with practice, this could be done fairly accurately, the need for a large number of successive adjustments was avoided. The current was then switched on, each balance corrected to a minimum, and then an accurate bridge balance made from a distance. The standard condenser was set at least twice (once from each direction), and it was usually found (except in the case of liquids of high conductivity) that these readings agreed as closely as could be observed on the vernier. The experimental condenser was removed from circuit, the bridge rebalanced as before, only the measuring system and compensating resistances in the same arm being altered, and finally the condenser was re-connected and the original balance checked to make sure that no shift in the bridge reading had occurred.

It should be noted that a definite displacement of the Wagner arms by an amount considerably greater than the sensitivity of their balance makes no perceptible difference to the bridge reading.

Results.

(1) *Intercomparison of the Dielectric Containers.* — Table III gives the dielectric constants of a number of liquids as determined at 25° in the three cells described previously. The values are quoted only for the purpose of showing the relationship between these condensers, and are not necessarily (except in the case of benzene) to be taken as accurate data for the liquids in question, since no special purification was undertaken beyond that necessary to obtain a reasonably low conductivity, *i.e.*, less than 10^{-7}. The

reproducibility of the results was checked throughout by making two distinct sets of observations on each condenser after emptying and refilling it. As an example, the capacities on the second measuring system for the mixture of toluene and amyl alcohol in condenser III were :

1st Series	86·61	86·60	86·63	⎫ Mean 86·61
2nd Series	86·61	86·62	86·58	⎭

The air capacities of all three condensers on S_1 were :

Condenser.	Number of observations.	Range of observations.	Mean.
I	15	8·299—8·323	8·310
II	16	5·952—5·969	5·956
III	14	7·920—7·945	7·933

Hence the dielectric constant for this mixture relative to air was $86·61/7·933 \times 1·0276 = 10·626$.

TABLE III.

	Air = 1.			Benzene = 1.		
	I.	II.	III.	I.	II.	III.
Hexane	1·910	1·911	1·914	0·8414	0·8409	0·8414
Benzene	2·270	2·273	2·275	—	—	—
Acetal	3·790	3·795	3·800	1·670	1·670	1·670
Chloroform	4·717	4·723	4·728	2·078	2·078	2·078
Dimethylethylcarbinol	5·929	5·936	5·946	2·612	2·612	2·613
Toluene–amyl alcohol						
mixture	10·577	10·615	10·626	4·654	4·670	4·670
isoButyl alcohol	17·88	17·95	17·98	7·874	7·901	7·905
o-Nitrotoluene	26·54	26·69	—	11·69	11·74	—
Nitrobenzene	34·76	34·88	34·92	15·32	15·35	15·35

The dielectric constants relative to air (Table III) show that condensers II and III are in fair agreement, the latter affording results consistently high by about 0·1—0·15%, and that the results given by condenser I are distinctly low—by about 0·5% over the upper range.

For the dielectric constants relative to benzene, the agreement between condensers II and III is extremely good, and hence it appeared probable that the discrepancy between them on the air basis might be due to an error in the air capacity determination of one of them. The benzene measurements were therefore repeated with two samples of specially purified material, and the results obtained were :

Sample.	Condenser.	Capacity.	ϵ.
A	II	13·536	2·273
B	II	13·534	2·273
A	III	18·048	2·275
B	III	18·043	2·275

These values were then taken as standard, and the dielectric constant of benzene at 25° assumed to be 2·273 (Hartshorn, *Proc. Roy.*

Soc., 1929, *A,* **123**, 664); the air capacities calculated on this basis were 5·955 and 7·939.

The agreement between observed and calculated values is exact in the case of condenser II, and for condenser III the difference is less than 0·1%, the calculated value falling well within the range of observations. This discrepancy is too small to justify any conclusions being drawn, and the values calculated from the benzene capacities are therefore taken as standard; on this basis, both condensers II and III afford direct proportionality (within 0·1%) between dielectric constant and measured capacity.

Thus, these two condensers, which have different devices for eliminating the end effect, afford concordant results over the whole scale investigated, within the limits of experimental error. Condenser I, however, which is uncorrected for the end effect, does not agree with them over the whole range either with air or with benzene as unity. Further comment on the discrepancies shown by Condenser I is postponed, but it is claimed that both Condensers II and III are free from errors due to the end effect.

It was also necessary to consider the temperature variation of these condensers. It may be assumed that the silver film expands at the same rate as the glass, and if the coefficient of expansion of glass is taken as 10^{-5}, a change of 100° will only produce 0·1% change in the dimensions of the cell. Further, such change as does occur will increase the area of the plates and also the distance between them, and these two effects will tend to neutralise each other with regard to capacity changes. It is to be expected, therefore, that the change in capacity over 100° range should be too small to be detected, and this is borne out by the following results.

In the first place the air capacities of condensers I and II were measured at 0°, 25°, and 80°, the mean values being :

	0°.	25°.	80°.
Condenser I	8·309	8·311	8·308
Condenser II	5·952	5·956	5·957

Secondly, the benzene capacities for the first condenser were measured at 25° and 50°, and the air capacities calculated on this basis, assuming the dielectric constant of benzene to be 2·273 at 25° and 2·223 at 50° (Hartshorn, *loc. cit.*), are 8·303 and 8·302 respectively.

It is concluded, therefore, that this type of dielectric container has no appreciable temperature coefficient of capacity, and for the purpose of the next section the air capacities have been assumed to be

	II.	III.
Measuring system S_1	5·955	7·939
,, ,, S_2	6·119	8·158

Purification of benzene.   The first of the samples referred to above had been purified by Harris (*J.*, 1925, **127**, 1063) for dielectric-constant determinations.   It had been standing over sodium wire in the meanwhile, and was distilled once before use.   The second sample was purified by the author from A.R. benzene by Richards and Shipley's method (*J. Amer. Chem. Soc.*, 1914, **36**, 1825).

(2) *The Dielectric Constants of Certain Purified Liquids at* 0—80°. —(a) *Standard liquids at* 25°.   *Benzene.*   The results obtained for two samples of specially purified benzene have been summarised on p. 592.   They were subject to a probable error of about 0·1% on the air-capacity determination, and of 0·05% on the benzene, thus affording a mean value of 2·274 $\pm$ 0·004 : the figure 2·2725 $\pm$ 0·0005 which has been accepted from Hartshorn's work (*loc. cit.*) lies well within these limits.

Chloroform.   Three samples of different origin (one from B.D.H. and two from Hopkin and Williams) were purified by the same method.   Each was shaken for 15 minutes with concentrated sulphuric acid, washed twice with dilute sodium hydroxide solution and five times with water, dried over ignited potassium carbonate, and fractionated until a main fraction was obtained boiling within less than 0·1°.   This was kept over calcium chloride in a dark cupboard, and immediately before use was decanted, shaken for a few minutes with a little solid sodium hydroxide, and distilled.

The results obtained are given in Table IV.   The probable error in the air capacity as adjusted by the benzene values is certainly less than 0·1%, and in the chloroform capacities 0·02%, the total error therefore being 1 part in 800 parts ; the mean value accepted for chloroform at 25° is 4·724 $\pm$ 0·006.

Nitrobenzene.   Sample A.   This had been purified by Harris, and distilled completely at practically constant temperature.   It was therefore merely dried over calcium chloride and distilled twice in a vacuum, having then a conductivity of the order 10^{-7} mho. (In the author's experience, the easiest way to obtain good conductivities is to use as high a vacuum as possible for the final distillations : throughout this work 1 mm. or less has been employed for all liquids of high boiling point.)

Sample B.   This was B.D.H. material.   It was fractionated four times in a vacuum, only one-third of the original bulk being retained. It was then dried over calcium chloride and distilled twice in a vacuum ; $\kappa = ca.$ 10^{-7}.

Sample C.   This was synthesised from some of the benzene purified as above, care being taken to prevent the temperature rising above 50° during nitration ; the nitrobenzene layer was separated, shaken once with water and four times with sodium

carbonate solution, steam-distilled in the presence of sodium carbonate, dried over calcium chloride, and then twice distilled in a vacuum ; $\kappa = ca.$ $0\cdot5 \times 10^{-7}$.

The results obtained are given in Table V. The probable error in the nitrobenzene capacity determinations can safely be taken as $0\cdot05\%$, but in this case, as opposed to that of chloroform, there is an additional error of 1 part in 3000 parts due to the conversion factor between the two measuring systems (p. 580). The total probable error will therefore be less than 1 part in 600 parts, and the mean value accepted for nitrobenzene at $25°$ is $34\cdot89 \pm 0\cdot05$. Although two samples were dried over phosphoric oxide for one week and six weeks respectively, no change in the dielectric constant was noticed (see Table V).

Benzonitrile. The material used was kindly provided by Dr. Martin, and had been purified in the same manner as that used for his conductivity work (*loc. cit.*). The results obtained for two different samples are given in Table VIII. These values showed no variation with frequency or current intensity, and the probable error is the same as for the nitrobenzene determinations.

(b) *Temperature variations.* Determinations of the dielectric constant of chloroform at temperatures between $0°$ and $50°$ were made in condensers II and III with each of the three specimens described, and the mean of the six results at each temperature is given in Table VI. Similar determinations were made for nitrobenzene at temperatures between $10°$ and $80°$ (Table VII).

In each case, when these results were plotted against temperature on a very open scale, they lay on a smooth curve within the limits of experimental error quoted.

(c) *Frequency variations.* Determinations of the dielectric constants of both chloroform and nitrobenzene at $25°$ and $50°$ were made at frequencies between 500 and 2500, but in no case was any change detected.

TABLE IV.

Chloroform at $25°$.

Sample.	Condenser.	Measuring system.	Capacity.	ϵ.
A	III	S_1	37·500	4·723
A	II	S_1	28·132	4·724
B	II	S_1	28·125	4·723
C	II	S_1	28·126	4·723
C	III	S_1	37·502	4·724
B	II	S_2	28·90	4·723
B	III	S_2	38·56	4·726
C	II	S_2	28·92	4·726
			Mean	4·724

TABLE V.

Nitrobenzene at 25° (approx.).

Sample.	Drying agent.	Condenser.	Temp.	Capacity.	ϵ.	$\epsilon_{25}°$.
A	$CaCl_2$	II	25·0°	213·55	34·90	34·90
A	,,	III	25·0	284·6	34·89	34·89
A	,,	II (repeat)	25·0	213·4	34·87	34·87
B	,,	II	25·2	213·4	34·87	34·91
B	,,	II	25·2	213·2	34·84	34·88
B	,,	II	25·2	213·3	34·86	34·90
C	,,	II	25·0	213·4	34·87	34·87
C	,,	III	25·0	284·7	34·90	34·90
B	P_2O_5	II	25·0	213·65	34·91	34·91
B	,,	II (repeat)	25·1	213·4	34·87	34·89

Mean 34·89

TABLE VI.

Chloroform.

Temp.	0°	11·2°	18°	25°	30°	40°	50°
ϵ	5·189	4·971	4·848	4·724	4·636	4·473	4·310

TABLE VII.

Nitrobenzene.

Temp.	10°	12·8°	18°	25°	30°	32·9°	40°	54°	60°	80°
ϵ	37·85	37·30	36·23	34·89	33·97	33·48	32·26	29·99	29·08	26·28

TABLE VIII.

Benzonitrile.

Temp.	0°	18°	25°	40°	50·3°	60°	70°
ϵ (sample 1)	27·60	—	25·20	24·01	—	22·67	22·10
ϵ (sample 2)	27·58	25·85	25·21	24·02	23·28	—	—