Dependence of the Dielectric Coefficient of Air Upon Pressure and Frequency

A. R. JORDAN, JAMES W. BROXON AND FRANK C. WALZ, *University of Colorado*

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A capacity-resistance bridge has been designed to incorporate into an a.c. method of measurement the most desirable features of a previously described electrometer method of determination of the dielectric coefficients of gases. The bridge, which provides for adequate shielding from the effects of solid insulators, has been employed for the measurement of the dielectric coefficient of air at pressures up to 170 atmospheres (18°C) and frequencies up to 70,000 cycles per second. As in the electrometer measurements, the dielectric coefficient at each frequency employed appeared to increase approximately linearly with pressure. The extreme variation among the measured values of the dielectric coefficient, 1.000589 to 1.000593 at N.T.P., was less than one percent, and is considered to lie within the experimental error.

NOT only the early investigations, but to an even greater extent rather recent researches employing highly refined methods, have led to widely discordant values for the dielectric coefficients of air and other gases. The differences among the values obtained by different workers have often greatly exceeded the presumed experimental errors.

There has been some indication that the lack of agreement might to a certain extent be explained in terms of a dependence of the dielectric coefficient upon the frequency of variation of the electric field to which the gas was subjected. Such an explanation is inadequate, however, and it seems the differences must be due largely to unrecognized experimental inaccuracies.

One such source of error has been considered by Cagniard[1] to consist of lack of stability of some of the relatively modern high-frequency arrangements employed. Other plausible causes of disagreement might be varying degrees of impurity among the gases used, unrecognized or improperly corrected mechanical distortion due to variation of gas pressure, and inaccuracies of calibration of variable condensers. Another likely source of error receiving very little consideration from most workers is due to the solid dielectrics introduced for the purpose of maintaining proper spacing of condenser plates and retaining the gas. These solids frequently constitute the dielectric for a considerable fraction of the gas condenser "capacity." Since it is common practice not to eliminate the effects of these solid dielectrics by shielding, and not to take into account the variations[2] in their dielectric coefficients or power losses with variations in pressure, temperature or frequency, it would appear that this might contribute to the discrepancies noted.

In gaseous ionization measurements, it is an essential and common practice to eliminate practically entirely the effects of electrical properties of solid insulators by the employment of properly designed "guard" systems and null methods of measurement. The simple application of this procedure to the "static" measurement of the dielectric coefficients of gases has been described by one of the writers.[3] A further advantage of this method was the elimination of variable condensers and the difficulties of their calibration as well as their mechanical faults. In fact, no absolute capacity measurement was required, the comparatively simple determination of resistances being substituted.

In the present investigation, it has been the purpose of the writers to incorporate the advantages of this method of measurement into an a.c. method. Although the difficulty of securing non-reactive resistances hindered full adaptation to very high frequencies, frequencies up to 70,000 cycles per second have been satisfactorily employed.

EXPERIMENTAL ARRANGEMENT AND PROCEDURE

Detailed description of the equipment and procedure adopted in the case of the "static"

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[1] Cagniard, Ann. de Physique **9**, 460 (1928).

[2] Curtis, MacPherson and Scott, Phys. Rev. **33**, 1080A (1929); Scott, Phys. Rev. **35**, 1429A (1930).

[3] Broxon, Phys. Rev. **37**, 1338 (1931); Phys. Rev. **38**, 2049 (1931).

measurements has been given in an earlier publication.[3] To adapt the significant features to the a.c. measurements, certain modifications were necessary. Instead of the simple capacity-resistance bridge arrangement[3, 4] heretofore employed, a double bridge was designed.

In Fig. 1 the two principal condensers, C_1 and C_2, are shown schematically in longitudinal section, C_1 not being drawn to scale in all respects. C_2 is the same fixed-capacity, air condenser formerly used; its precise construction and details of its insulation and guard system are shown in Fig. 4 of the paper of reference 4. The high-pressure condenser, C_1, was essentially as illustrated by Fig. 3 of the paper of reference 4, the guard system being precisely that shown there but the capacity being increased to practical equality with C_2 by the introduction of two coaxial brass cylinders as illustrated in Fig. 1. The dimensions of the inner cylinder were: I.D., 12/32 in.; O.D., 13/32 in.; O.L., 12.65 cm. Those of the outer cylinder were: I.D., 17/32 in.; O.D., 9/16 in.; O.L., 13.65 cm. Both cylinders were subjected to the same pressure inside and outside. As modified, the capacity or induction coefficient of the inner electrode relative to the outer (the inner being at the potential of the guard) for C_1 at atmospheric pressure was very nearly equal to that of C_2, about 26.3 cm.[4]

That the induction coefficients of the inner conductors of C_1 and C_2 relative to their outer or high-potential conductors could be regarded as "pure" when the inner or central conductor potential was identical with that of the guard system, was assured by the construction of the guards at the critical regions where they served to separate the solid condenser insulation. Here they protected those parts of the solid insulation in contact with the inner conductors from being subjected to any electric field, and prevented the passage of any lines of force to the central conductors from those portions of the solid insulation which were under the influence of electric fields. Under these conditions the charge on an inner conductor corresponding to a given potential of the outer was quite independent of the electrical condition of the insulation, and no conductance current could flow between the inner and outer conductors, apart from that due to the minute natural ionization of the contained gas. The provision of "pure" or non-reactive variable resistances for R_a and R_b, the other two arms of the primary bridge, an equally important requirement, offered some difficulty. At first 500 ohm units were wound by the Ayrton-Perry method in single layers on Pyrex glass tubes 18 in. long and 1 cm O.D. These were mounted at 3-in. intervals in a shielded box. Although these proved to be rather satisfactory at 1000 cycles per sec., the reactances were too great at higher frequencies. They were finally replaced by Leeds and Northrup a.c. resistances, types 4746 and 4745S, of about 10,000 ohms. These were found to be satisfactory for frequencies up to 70,000 cycles per sec.

In the auxiliary bridge arms, c' and c'' consisted of General Radio precision condensers, types 222 and 224, and c_a and c_b, of General Radio type 247E condensers of low power loss. The capacities employed were of the order of a few hundred mmf. r_1 and r_2 consisted of General Radio decade resistances, type 102K, of the order of 10,000 ohms.

A General Radio low-frequency oscillator provided the e.m.f. impressed upon the network. This was directly connected, and was carefully insulated from the guard system which surrounded it. The null indicator, D, consisted of a General Radio type 514A amplifier feeding into a dynatron circuit and producing a beat note which, after amplification, actuated head phones. The D.P.D.T. switch was a highly insulated Leeds and Northrup switch, No. 3298.

As indicated by the dashed lines in Fig. 1, all leads and instruments in the network were individually and thoroughly shielded.

As a preliminary step in balancing the bridge, the switch was thrown into the position grounding (connecting to the guard) the junction point between R_a and R_b and inserting the detector between ground and the central system of the condensers C_1 and C_2. The impedance arms r_1 and c' and r_2 and c'', constituting a "Wagner ground," were then adjusted until the detector did not register, thus indicating that the central system was at the potential of the guard system. Next, the switch was reversed, grounding the

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[4] Broxon, Phys. Rev. **37**, 1320 (1931); see Fig. 2.

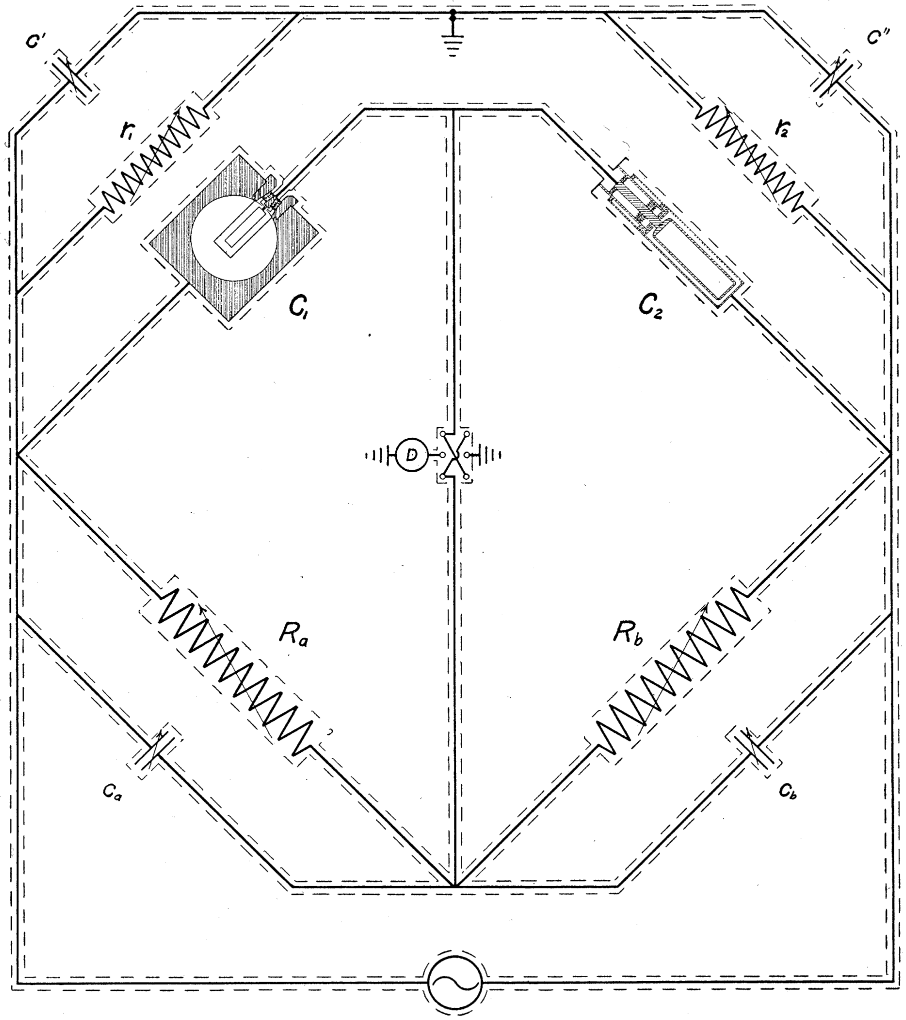

FIG. 1. Wiring diagram.

central system and inserting the detector between ground and the junction point between R_a and R_b. Then R_a and R_b and c_a and c_b were adjusted until a null indication showed that this junction point was at zero potential relative to the earthed guard system. This procedure was repeated until reversal of the switch with no further adjustment resulted in no response from the detector in either position. All "central" points of the network were then at the potential of the surrounding guard system, and the bridge was balanced. It was found that the final conditions at balance were unaltered if the junction point between R_a and R_b was left insulated instead of being grounded during the preliminary adjustment described above. Because the bridge could be balanced a little more rapidly with this arrangement, the cross-member of the switch which served to ground this junction point when the detector was connected to the C_1C_2 central system was omitted during the measurements.

That C_1 and C_2, the induction coefficients of the central conductors of the corresponding principal condensers relative to their respective outer or high-potential conductors, are to be regarded as pure or conductanceless capacitances at balance has been shown above. It has also been pointed out that R_a and R_b consisted of practically non-reactive resistances. Another fact to be borne in mind is that the impedance consisting of the $c'r_1$ combination, and that consisting of the $c''r_2$ combination, might be regarded as including the impedances between the guard system and the high-potential conductors of C_1 and C_2, respectively, with which they were connected in parallel. With these considerations, not neglecting conductances of the auxiliary condensers nor reactances of the auxiliary resistances, the Kirchhoff equations for the network yield at balance the relation

$$\frac{C_1}{C_2}=\frac{R_b}{R_a}\left[\frac{1+R_a/r_a-1/\omega^2 c_a c_b r_a r_b}{1+R_b/r_b-1/\omega^2 c_a c_b r_a r_b}\right],$$

r_a and r_b being the equivalent series resistances of c_a and c_b, respectively, and ω the angular frequency of the impressed sinusoidal e.m.f. With the particular instruments and range of values used in the present investigation, the quantity in brackets varied from unity only slightly more than 10^{-4} under the most extreme conditions at the highest pressure and the highest frequency employed. Therefore, for the purpose of this investigation, the equation

$$C_1/C_2=R_b/R_a$$

served as a very satisfactory approximation, and was used in the calculation of the a.c. values recorded in Table I. Use of the accurate formula gives a value for K at N.T.P. less than that obtained by use of the approximate formula, only by 75×10^{-8} at 70,000 cycles/sec., less than one digit in the last column retained and little more than 0.1 percent of $(K-1)$. The correction would be less at lower frequencies.

The ratio of the induction coefficient of the condenser containing the gas under examination to that of the fixed condenser being equal to the principal resistance ratio, the dielectric coefficient of the gas at any pressure was given by the quotient of the resistance ratio at that pressure by the resistance ratio corresponding to complete evacuation of the gas chamber. This latter value was obtained by a slight extrapolation of the resistance-ratio *vs.* pressure curve as described in earlier work.[3]

The procedure as to preparation of the gas and measurement of pressure and temperature and of resistance was precisely as before[3, 4], except that a more accurate bridge was used for the determination of the d.c. resistances in the present investigation.

OBSERVATIONS

Resistance ratios were determined at about thirteen-atmosphere intervals between atmospheric pressure and 170 atmospheres, for several frequencies extending to 70,000 cycles per sec. The electrometer arrangement[3] was then substituted for the a.c., and the resistance ratios determined by the "static" method with the new capacity arrangement in C_1, for pressures up to about 150 atmospheres. Assuming that after reduction of pressures to a common temperature of 18°C the dielectric coefficient and hence the resistance ratio was a linear function of the pressure, the slope and intercept of the ratio-pressure line upon the resistance ratio axis was determined for each of the frequencies by the method of least squares. The ratio of the slope to the intercept yielded the value of $(K-1)$ for the air at one atmosphere pressure and the average experimental temperature of 18°C. Assuming that at a given pressure $(K-1)$ is inversely proportional to the absolute temperature, the values given in Table I were found for the dielectric coefficient of air at N.T.P. and the designated frequencies.

Some of the data are represented diagrammatically in Fig. 2. In this the open circles represent the 1000 cycle values, and the lower line is the corresponding line determined by least squares. The solid circles represent the 70,000 cycle values, but the upper line is that determined by least squares for the zero fre-

TABLE I. *Dielectric coefficient of air at N.T.P. and various frequencies.*

Frequency cycles/sec.	*K at* N.T.P.	*Frequency* cycles/sec.	*K at* N.T.P.
0	1.000592* 1.000593	30,000	1.000591
1,000	1.000589	50,000	1.000591
16,000	1.000589	70,000	1.000591

* This value was determined in an earlier investigation.[3]

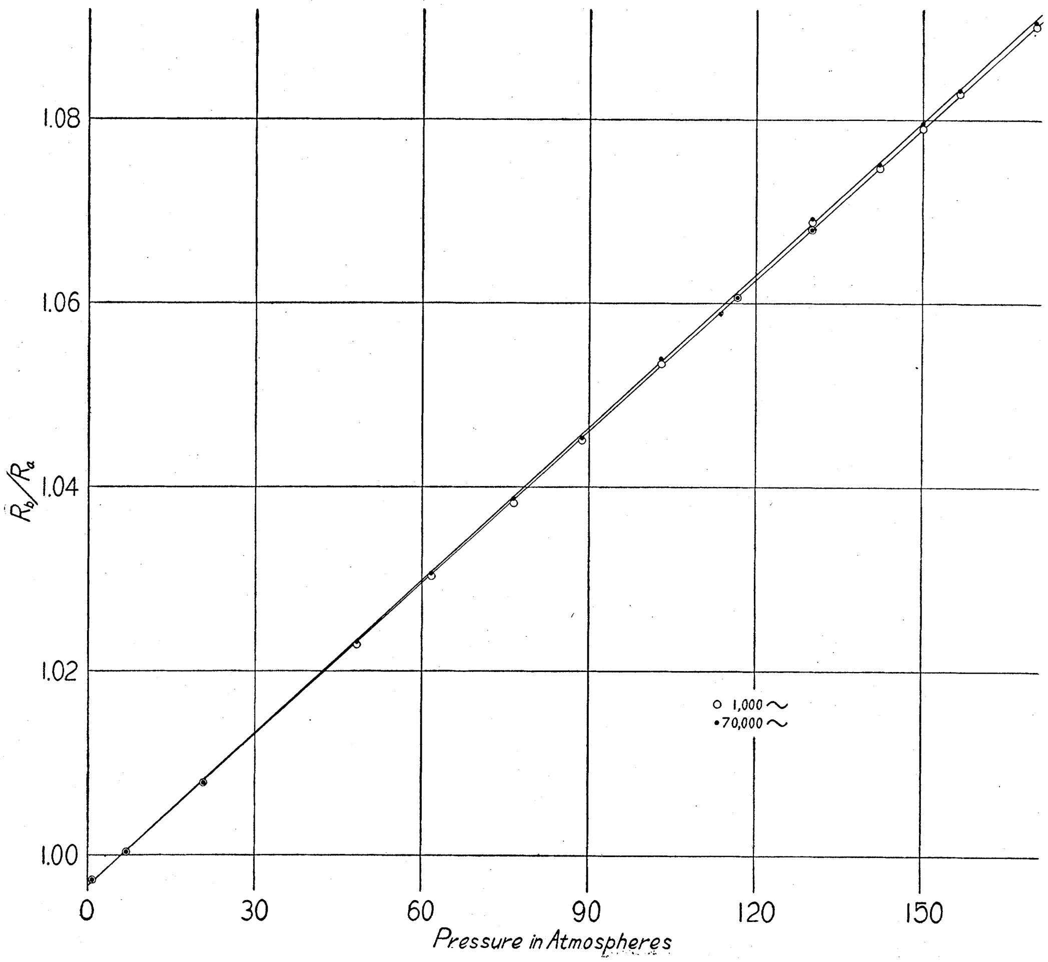

FIG. 2. Variation of resistance-ratio with pressure.

quency values, there being the greatest divergence between this and the 1000 cycle line.

The value formerly[3] obtained from observations by the electrometer method over a pressure range extending to 170 atmospheres was 1.000592. This value was obtained by graphical means. A redetermination from the original data by the least squares method has yielded precisely the same value as did the graphical method for each of the two individual sets of observations on which the graphical determination was based.

DISCUSSION

That an approximately linear relation exists between K and P over the pressure range of the investigation is indicated by Fig. 2, and by Fig. 1 of the first paper of reference 3. In the earlier work it was concluded without detailed statistical analysis that a linear relation between K and P was rather better satisfied by the observations than was the Clausius-Mossotti relation. As a further test, each of the two old sets of data, and the new sets for the frequencies of zero, 1000 and 70,000 cycles per sec. have been investigated in some detail. Employing values of the air density, d, obtained from data by Witkowski[5] and Amagat[6] at 16°C, the only data available, values of $(K-1)/P$, $(K-1)/d$, and $(K-1)/d(K+2)$ were calculated for each

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[5] Witkowski, Phil. Mag. **41**, 288 (1896).

[6] Amagat, Ann. Chim. Phys. (6) **29**, 68 (1893). Taken from Physikalisch-Chemische Tabellen, Vol. I (1923) Landolt-Börnstein, p. 108; values given at 15.7°C.

pressure at which observations were made, for each of these five sets of data. Omitting values corresponding to pressures below 25 atmospheres because of considerable fluctuations in that region, the standard deviation from the mean was calculated for each of the three functions for each set. For each set of data, the fractional deviation for $(K-1)/d$ was greater than that for either of the other functions. For all but the new zero-frequency set, the fractional standard deviation was somewhat less for $(K-1)/P$ than for the Clausius-Mossotti function, but in this one instance the relation was reversed. The fact that the pressure range was less in this case may be of some significance. However, the differences among the deviations were of the order of magnitude of the "probable error" of the $(K-1)/P$ values calculated on the basis of the deviations of the individuals from their average, between 0.3 and 0.4 percent. It is considered, therefore, that the data do not make possible a definite conclusion as to which of the three functions, if any, may be regarded as actually constant over the range of pressures investigated. It is perhaps worth noting that for one of the old sets of data, the constancy not only of the above three functions but also of two others, the Mossotti function, $(K-1)/Kd$, and the Macdonald[7] function, $(K-1)/K^{\frac{1}{2}}d$, were investigated. The constancy of the latter of these was comparable with those of the above three functions, but the fractional deviation of $(K-1)/Kd$ was considerably greater and it displayed a tendency to decrease regularly with increasing pressure.

Various errors in the determinations of pressure, temperature and resistance have been considered before,[3] with the conclusion that the error in $(K-1)$ is probably of the order of 1 percent. Similar considerations would pertain to the present investigation. d.c. resistances could be measured somewhat more accurately, but at 50,000 cycles the principal resistances may have had phase angles amounting to as much as 1.5 degrees according to the manufacturer. This lack of "purity" of the resistances may have accounted for some of the variation of K with frequency with the a.c. arrangement. In any case, however, the extreme variation among all the values obtained was only about 0.7 percent of $(K-1)$. The investigation is considered to indicate, therefore, that the dielectric coefficient of air does not vary with frequency in the range investigated. It is interesting to note that Forró[8] found the dielectric coefficient of air to vary over about the same range as herein given, with variation of frequency at very much higher values. Using a beat frequency method of measurement, Forró found K to increase from 1.000586 at about 6×10^5, to 1.000593 at about 4.3×10^6 cycles per sec.

It is considered that mechanical distortion of the gas chamber resulting from variations in pressure did not produce errors amounting to nearly as much as 1 percent of $(K-1)$. It appears that compression of the material of the cylinder walls without alteration of shape might have introduced an error of about 0.1 percent. Because of the symmetry, not much shape distortion would be expected, but one might anticipate an error due to motion of the central conductor along its axis because of lack of rigidity of the ebonite insulation. Certain considerations lead to the conclusion that appreciable errors were not introduced on this account, however. In the first place, as has been pointed out before,[3] the two former independent sets of observations by the electrometer method yielded precisely the same value for K, indicating that any strains in the insulation must have been of an elastic nature. Then, too, with the two vastly different arrangements of condenser plates in the former and the present investigation (a thin 10-inch rod inside the 1-foot spherical cavity in the one case, and the two cylinders in the present case) errors depending upon deformation of the insulation should have been quite different. Nevertheless, the electrometer measurements in the two cases led to values differing by less than 0.2 percent of $(K-1)$. Even in a third case[9] where the plates consisted of a 0.168 in. diameter tube of 0.011 in. wall thickness inserted into a 3.7 in. diameter sphere of 0.006 in. average thickness within the pressure chamber, the value of K obtained by the electrometer method

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[7] Macdonald, Proc. Roy. Soc. **A113**, 237 (1926).

[8] Forró, Zeits. f. Physik **51**, 374 (1928).

[9] Broxon, Phys. Rev. **42**, 321 (1932).

(1.000587 for 1 atm. at 0°C) differed from the others by just about 1 percent. In this case considerable deformation of the thin sphere was to be expected since its wall thickness was far from uniform.

There may have been some effect due to CO_2, pump oil vapor, and water vapor content of the air. Careful work by Watson[10] and his associates indicates that in the present investigation the air probably was not thoroughly dried.

Variation of the temperature over a range of a few degrees in the neighborhood of 18°C during part of the work may have had some influence upon the measurements. In this connection, it is considered that arrangements for more accurate determination of temperature and of pressure must be provided before the accuracy of the method can be improved materially.

Probably the arrangement herein described is not as sensitive as some others in the detection of minute variations of K. However, the accuracy of determination of the *absolute value* of the dielectric coefficient probably compares very favorably with others in view of the elimination of electrical effects of solid insulators and errors of calibration of condensers, whether fixed or variable.

The writers wish to acknowledge the assistance of Mr. R. V. Cartwright in the construction of the detector system.

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[10] Watson, Rao and Ramaswamy, Proc. Roy. Soc. **A132**, 569 (1931); **A143**, 558 (1934).