THE DIELECTRIC CONSTANT OF AIR AT HIGH PRESSURES[1]

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Abstract

The dielectric constant of aged, dry, dust-free air was measured at pressures up to 170 atmospheres by an electrometric method. It was found to increase linearly with the pressure.

Frequently quoted values of the dielectric constant of air at high pressures are those obtained by Tangl,[2] in 1908, at pressures up to 100 atmospheres. In 1913, Occhialini and Bodareu[3] made measurements up to 334 atmospheres. In both these investigations, the Clausius-Mossotti relation was found to hold. Both Tangl[4] and Occhialini[5] had announced in earlier papers, however, that the Clausius-Mossotti relation did not hold.

More recent measurements of dielectric constants have been made largely by means of modern high-frequency methods. These have been criticized by Cagniard[6] who has drawn attention to the very large variations among the values of the dielectric constant of air at atmospheric pressure obtained by these methods by various observers, and has contrasted them with the better agreement among values obtained by the older methods.

Very recent investigations by Keyes and Kirkwood[7] of the dielectric constants of carbon dioxide and ammonia have given interesting information concerning their variations over large ranges of density, and the considerable deviations from the Clausius-Mossotti relation.

In the present paper are presented measurements of the dielectric constant of dry air between pressures of 0.821 and 169.4 atmospheres at 18°C, made by a method closely resembling that of Occhialini and Bodareu.[3]

Procedure

In connection with recent measurements of the residual ionization[8] in air at high pressures, the mere addition of a Wheatstone bridge to the equipment otherwise required, and the measurement of two resistances, yielded the values of the dielectric constant of the gas at the various pressures at which observations of the ionization were made. The reader should refer to the

[1] Reported at the Cleveland meeting of the American Physical Society, December, 1930.
[2] Tangl, Ann. d. Physik **26**, 59 (1908).
[3] Occhialini and Bodareu, Ann. d. Physik **42** (1913).
[4] Tangl, Ann. d. Physik **23**, 559 (1907).
[5] Occhialini, Phys. Zeits. **6**, 669 (1905).
[6] Cagniard, Ann. d. Physique **9–10**, 460 (1928).
[7] Keyes and Kirkwood, Phys. Rev. **36**, 754 (1930); Phys. Rev. **36**, 1570 (1930).

preceding paper[8] on the residual ionization for details regarding apparatus, conditions of experimentation and procedure which it is considered unnecessary to repeat here.

The wiring diagram is given in Fig. 2 of the preceding paper. The applied potential difference was impressed across the high resistance system, R, r', r'', and leads run from this to the ionization chamber S (see also Fig. 3 of preceding paper), the guard system, and the exterior cylinder of the auxiliary condenser C (also see Fig. 4 of preceding paper), in order to eliminate effects of fluctuations of the applied P.D. At each pressure, before observations of the ionization current were begun, the apparatus was "balanced" by adjusting the resistance contacts until no deflection of the quadrant electrometer occurred when the large P.D. was suddenly applied or withdrawn from the high resistance system. Due to the rather large residual ionization currents at the high pressures, an accurate balance could be obtained at these pressures only by adjusting the resistances so that sudden removal of the impressed P.D. caused no permanent variation in the small deflection which existed at the instant of removal.

If we designate by V_s and V_c the absolute values of the potential differences between the guard system and the outer conductors of the ionization chamber and the auxiliary condenser, respectively, and by q_{21} and q_{31} the corresponding induction coefficients of these relative to the central system, then we have under the above conditions of balance,

$$q_{21}V_s = q_{31}V_c.$$

This relation is readily established by the following considerations. Let V_1, V_2, V_3, V_4 and V_5 be the respective potentials of the central system, the ionization chamber, the outer cylinder of C, the guard system, and the needle. Let q_{11}, q_{21}, q_{31}, q_{41} and q_{51} be the corresponding induction coefficients of these relative to the central system. Then the charge on the insulated central system may be expressed by

$$Q_1 = q_{11}V_1 + q_{21}V_2 + q_{31}V_3 + q_{41}V_4 + q_{51}V_5.$$

Suppose, for convenience, we consider the potential of the guard system to be the arbitrary zero. Then when the P.D. across R is suddenly removed Q_1, V_4 and V_5 individually remain constant, and in order that V_1 may remain constant while V_2 and V_3 are each reduced to zero, we must have

$$q_{21}V_2 + q_{31}V_3 = 0$$

or

$$q_{21}/q_{31} = -V_3/V_2 = V_c/V_s.$$

Now we may put

$$V_c/V_s = R_c/R_s,$$

where R_c and R_s, respectively, represent the resistances at balance between

[8] Broxon, Phys. Rev. **37,** 1320 (1931). Preceding paper in this issue.

the auxiliary condenser and the guard system and between the ionization chamber and the guard system, across which, in series, the total P.D. of about 1050 volts was applied. Substituting, we have

$$q_{21} = q_{31}(R_c/R_s).$$

The auxiliary condenser, C, being fixed and always at atmospheric pressure, q_{31} remained constant.

If, now, the ratio R_c/R_s be plotted against the total pressure in the ionization chamber, the intercept of this curve upon the ratio axis represents $1/q_{31}$ of the value of q_{21} with the ionization chamber entirely evacuated, while other points on the curve represent $1/q_{31}$ of the values of q_{21} at the corresponding pressures. Hence the value of R_c/R_s at any pressure, when divided by the intercept value, gives the dielectric constant of the gas in the chamber at that pressure, referred to $K=1$ in vacuo.

Observations

The curve of Fig. 1 was obtained in the above manner. The circles represent observations made with the ionization chamber unshielded and the crosses represent values obtained four weeks later with the lead shield in

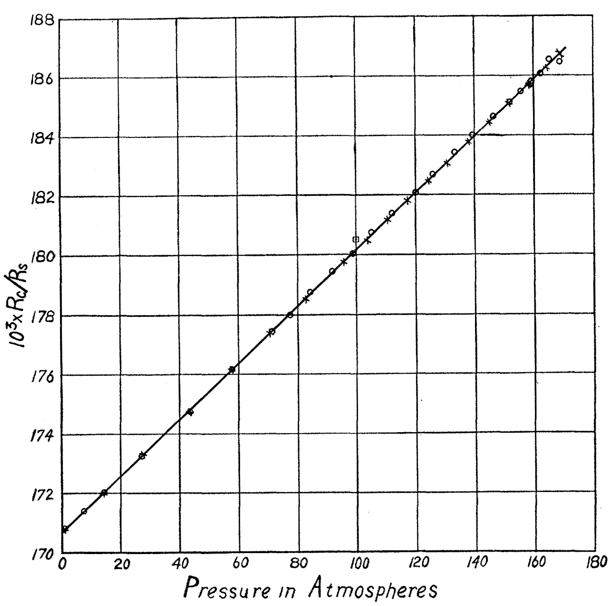

Fig. 1.

position. The two sets of readings give values of R_c/R_s at some 35 distinctly different pressures distributed well over the range. It is seen that both sets of points fall remarkably close to a straight line. Inasmuch as the curve remains straight over a range of nearly 170 atmospheres, and further, since Wolf[9] has

[9] Wolf, Phys. Zeits. **27,** 588 (1926).

found that the dielectric constants of the chief constituent gases of air vary linearly with the pressure to small fractions of an atmosphere, it was considered justifiable to extrapolate by continuing the straight line to zero pressure. Division of the ordinates of the curve by the intercept so obtained, shows that the dielectric constant of air increases uniformly by 555×10^{-6} for each atmosphere increase in pressure at 18°C.

Discussion

If $(K-1)/P=\text{const.}$, then insomuch as σ, the density of the air, varies from proportionality with P, $(K-1)/\sigma$ can not be constant. Also, the Clausius-Mossotti relation

$$(K-1)/\sigma(K+2) = \text{const.}$$

can not be true.

The present investigation, then, confirms the constancy of the first ratio, and denies the constancy of either of the latter ratios, unless the variations in either of these lie within the limits of the experimental error.

This latter possibility deserves careful consideration. According to the Landolt-Börnstein tables (1923), Amagat found the values of PV and hence P/σ for air at 16°C to pass through a minimum in the neighborhood of 80 atmospheres, increasing at higher pressures and reaching atmospheric value at about the upper pressure limit of the present measurements. Using these values and the observed values for K at 18°C, the values of $(K-1)/\sigma$ are found to pass through a corresponding minimum about 2 percent less than the value at atmospheric pressure. $(K-1)/\sigma(K+2)$ is similarly found to pass through a minimum at about 90 atm., which is about 3.7 percent less than the value at atm. pressure.

Accuracy of the measurements

The resistances were measured by means of a Leeds and Northrup portable bridge. Individual resistances of this bridge have a guaranteed accuracy of only 0.1 percent. However, an investigation of the particular coils used in this instance showed the error to be only about 0.01 percent in the resistances measured, apart from inaccuracies in the bridge ratio-resistances, and these latter inaccuracies as well as errors due to temperature variations, cancelled in the ratio R_c/R_s. The error in a particular value of R_c/R_s, then, was probably about 0.02 percent. Since the same coil was used throughout for the first significant figure of R_c, a similar situation holding for R_s, the fractional error in R_c/R_s was in the same direction and of the same order of magnitude throughout, whence the fractional error in $(R_c/R_s)/(R_c/R_s)^0$ may be expected to be of one smaller order of magnitude than the error in a single ratio. Hence the error in K may be estimated to be of the order of 0.002 percent, or an error of less than 1 percent of $(K-1)$ at all pressures above 4 atmospheres. Since the curve was not unduly weighted by the readings at atmospheric pressure, we may therefore expect an error of less than 1 percent in $(K-1)$ throughout the range.

In the above, it is assumed that other conditions were ideal. It was not necessary that the resistivity of the materials constituting the measured resistances remain constant during a series of observations, but it was essential that no change of this type should occur between the time of "balance" and the time when the resistances were measured. No appreciable error could have occurred on this account. R consisted of about 102,000 ohms formed by winding coils of silk-covered high resistance wire of low temperature coefficient, in single layers over thin paraffined paper upon 108 long vertical brass tubes submerged in kerosene. r' and r'' consisted of two large, open tubular slide-wire rheostats, each of about 3000 ohms resistance, shunted across two or three of the thousand-ohm coils of R, one on each side of the earthed point. The maximum current through any of these was of the order of 0.01 ampere. No appreciable heating occurred, and certainly no sudden changes in temperature were possible. The measured values were found in no instance to vary with the time interval between balance and the resistance measurement.

Lead resistances were negligible. The largest ionization currents in parallel with the current in R_s were only of the order of 3×10^{-13} amp. The sensitivity of the electrometer as an indicator of the condition of "balance," with the P.D. employed, was sufficient to detect changes in the resistance ratio which could not be measured with the bridge. Constancy of the applied P.D. was not required.

Errors in the corrected pressure gauge readings were probably of the order of 0.1 percent at the upper end of the scale. The atmospheric pressure could be determined with this accuracy, of course. With the temperature measuring device employed, and with the precautions taken to ensure equilibrium conditions, it is believed that the temperature of the air did not vary by 0.5°C from the recorded temperature in any instance. Moreover, the total variations in temperature were very small. In the first set of readings the temperature varied from 18.3°C to 16.85°C, and in the second set from 18.0°C to 17.0°C over the whole range with the exception of the reading at atmospheric pressure which was made at a temperature of 16.8°C. In view of the small variations in temperature, reductions of pressures to equivalent pressures at 18°C were made on the basis of the proportionality between P and the absolute temperature.

The constancy of q_{31} may be appreciated when it is mentioned that the air in C was always at atmospheric pressure, and that during the second set of observations the atm. pressure did not vary by more than 1 mm of Hg.

From the dimensions, form and material of the ionization chamber and of the central electrode, it appears that no appreciable errors could have resulted from their deformations at the high pressures. Considerations of various conditions, particularly of the agreement between the two independent sets of readings, lead the writer to believe that no appreciable disturbance was caused by deformations of the ebonite insulators.

Perhaps the most outstanding advantage of this method of measurement is that it permits the use of a guard system which, when properly designed, effectively excludes the influence of the solid insulators due to their dielectric properties, surface charges, etc. The necessary presence of solid insulators constitutes a perpetual hazard in other methods of measurement.

In view of the above considerations it would seem that apart from personal errors, an estimated error of 1 percent in the values of $(K-1)$ and their pressure variations would not represent too optimistic an attitude, and that the investigation ought to be capable of testing the accuracy of the Clausius-Mossotti relation. As a further test of this conclusion, it was thought worthwhile to calculate the value of R_c/R_s which would have been required at 100 atm. in association with the intercept value herein used, in order to provide the same value of the Clausius-Mossotti function at that pressure as at atmospheric pressure. This value is designated by the small square in Fig. 1, and is seen to be decidedly farther from the curve than any but the first of the individual readings taken.

Comparison with other investigations

As mentioned above, there is a lack of agreement with the conclusions of Tangl[2] and of Occhialini and Bodareu[3] in that they found the Clausius-Mossotti relation to hold for air at high pressures. In earlier investigations both Tangl[4] and Occhialini[5] had concluded that the $C-M$ function decreased as the pressure increased, in general agreement with the present investigation. In this earlier paper Tangl concluded that $(K-1)$ varied directly with the density. In his 1908 paper, although Tangl concluded that the $C-M$ function was constant, the function actually decreased slightly, according to the tabulated values, with increasing pressure in the case of each of the gases investigated, hydrogen, nitrogen and air.

$(K-1)/\sigma$ and $(K-1)/P$ both decreased with increasing pressure in the case of hydrogen, and increased with increasing pressure in the cases of nitrogen and air. In the case of air, the decrease in $(K-1)/\sigma(K+2)$ between one and 100 atmospheres amounted to nearly 1.5 percent of its value at atmospheric pressure, about 1 percent less than the corresponding increase in $(K-1)/P$.

In the region between 64 and 334 atmospheres, Occhialini and Bodareu found $(K-1)/P$ to decrease about 10 percent, $(K-1)/\sigma$ to increase about 4 percent, and $(K-1)/\sigma(K+2)$ to show no unidirectional tendency, the fluctuations amounting only to about 1 percent.

In connection with the increase in the $C-M$ function observed in the present investigation at pressures above 90 atm., it is interesting to note that Keyes and Kirkwood[7] found the function to increase in the case of carbon dioxide at high densities, approaching a constant value in the liquid state.

The value of K for air at atmospheric pressure is of special interest. Tangl's 1908 value for K at 1 atm. and 19°C is 1.000536. If this be reduced to 1 atm. and 0°C on the basis of the constancy of $(K-1)/P$ and of P/T in this interval, the value obtained is 1.000573. On the same basis, the values obtained in the present investigation are 1.000555 at 18°C and 1.000592 at 0°C. The corresponding value obtained by Occhialini and Bodareu on the basis of the constancy of the $C-M$ function is 1.000585. On the basis of separate investigations some values obtained by other experimenters for air at N. T. P. are: Boltzmann (1875), 1.000590; Klemenčič (1885), 1.000586; Waibel[10] (1923), 1.000584; Carman and Hubbard[11] (1927), 1.000594. Cagniard[6] lists several others.

To explain the differences between the conclusions of the present investigation and others cited does not appear to be a simple matter. It is perhaps significant that Tangl could not have eliminated entirely the effects of solid insulation in the compression condenser. Also, his results depended upon variations in the capacity of a movable plate condenser. In the investigation by Occhialini and Bodareu, extreme constancy of the e.m.f.'s of the batteries they employed was necessary. The relatively low potential differences they used would produce a smaller sensitivity than in the present instance, with the same electrometer sensitivity. In the present investigation, greater accuracy could have been secured by having q_{21} and q_{31} more nearly equal, and by the employment of a more accurate bridge. Some difference between these observations and those of Tangl might be attributed to the fact that he removed both the water vapor and the carbon dioxide, whereas in this investigation only the water vapor was removed, together with possible dust particles.

A feature of some interest consists of the very small residual ionization of the compressed air used in this investigation, probably much less than in any other, and the fact that this ionization was determined at each pressure at which measurements were made.

[10] Waibel, Ann. d. Physik **72,** 161 (1923).
[11] Carman and Hubbard, Phys. Rev. **29,** 299 (1927).