

THE DIELECTRIC CONSTANT OF CARBON DIOXIDE AS
A FUNCTION OF TEMPERATURE AND DENSITY¹

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ABSTRACT

The dielectric constant of carbon dioxide has been measured over a wide range of temperature and density. It has been found that the Clausius-Mosotti function $(\epsilon-1)V/(\epsilon+2)$, although independent of temperature increases slowly with increasing density.

THE polarization of molecules by an homogeneous electric field has received adequate theoretical treatment. Both classical mechanics² and quantum mechanics³ lead to the following expression for the mean electric moment, m , of a molecule in weak fields at moderately high temperatures:

$$m = \left(\alpha + \frac{\mu^2}{3kT} \right) F$$

where F is the field strength, α the sum of the electronic and atomic polarizabilities, μ the permanent electric moment of the molecule, k Boltzmann's constant, and T the absolute temperature. The applicability of the above expression is further limited by the requirements that the frequency of the applied field be lower than any of the characteristic frequencies of the molecule, and that no transitions in internal atomic and electronic energy states occur with changing temperature.

The theory has been used with a large measure of success in the study of the molecular structure of gases of low density and of substances in dilute solution. In these cases the internal polarizing field may be calculated with very little ambiguity, and it is possible to obtain a relation between the dielectric constant of the substance and the constants α and μ of its constituent molecules.

The application of the theory to gases at high densities as well as to liquids and solids, has, however, been attended by great uncertainty because of the difficulty in calculating the average internal field effective in polar-

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¹ Preliminary work on air at low densities was carried out by Miss Charlotte T. Perry who constructed the first gas cell and measuring circuits.

² P. Debye, *Handbuch der Radiologie* **6**, 600 (1925).

³ J. H. Van Vleck, *Phys. Rev.* **29**, 727 (1927).

izing a molecule. The only guide in this matter has been the Clausius-Mosotti relation, which gives the molecular polarization as

$$\frac{\epsilon - 1}{\epsilon + 2}V = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3kT}\right)$$

where N is the Loschmidt number, ϵ the dielectric constant, and V the molal volume. Several attempts have been made to verify the Clausius-Mosotti law experimentally. Measurements of Tangl⁴ indicate that it is valid up to a hundred atmospheres for air, nitrogen, and hydrogen at 20°C. It is to be noted, however, that the largest of his values of $\epsilon - 1$ are still so small that it is evident that the contribution of the polarization of the dielectric to the internal field is very small relative to the contribution of the external applied field. Measurements of Phillips⁵ on the refractive index of

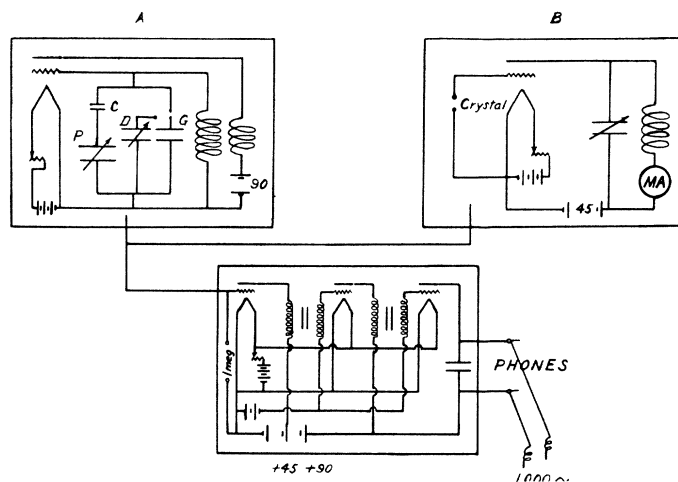


Fig. 1. Diagram of oscillator circuits.

carbon dioxide indicate that the corresponding Lorentz-Lorenz relation is valid even as far as the critical density for this substance. But the great experimental difficulties involved in the measurement of the refractive indices of compressed gases would make a verification of the values desirable.

In the present paper measurements of the dielectric constant of carbon dioxide over a wide range of temperature and density will be presented. We believe that they throw an important light on the limitations of the Clausius-Mosotti law, which the customary deduction, depending upon the cavity method for calculating the internal field, does more than suggest.

METHODS AND APPARATUS

Measurements of the dielectric constant were carried out by a resonance method which depended upon counting the beats between two heterodyne

⁴ K. Tangl, *Ann. d. Physik* **29**, 59 (1908).

⁵ P. Phillips, *Proc. Roy. Soc.* **A47**, 225 (1920).

oscillators. Since this method has been widely used in recent years, a detailed description will not be undertaken. The oscillator circuits (Fig. 1) were similar to those of Zahn.⁶ Oscillator *A* contained a condenser circuit consisting of the precision condenser *P*, the fixed mica condenser *C*, the gas condenser *G*, and the counterpoise condenser *D*. The precision condenser was a General Radio Variable Air Condenser, type 220, calibrated at the

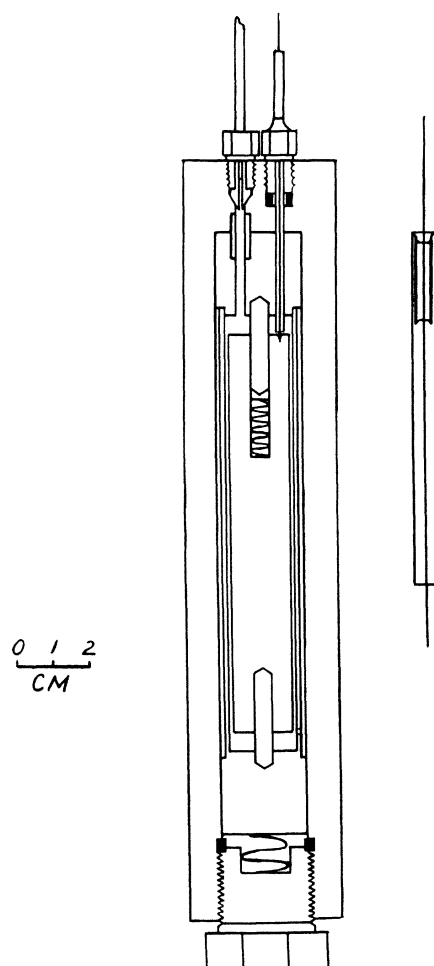


Fig. 2. Diagram of gas condenser.

Bureau of Standards. Sangamo fixed mica condensers of capacity appropriate to the magnitude of the dielectric constant to be measured occupied the position of *C*. All auxiliary capacities were calibrated in terms of the precision condenser at the working frequency. Oscillator *B* was maintained at a constant frequency of 1010 k.c. by means of a General Radio quartz crystal. The heterodyne note was amplified and then compared with the

⁶ C. T. Zahn, Phys. Rev. **23**, 781 (1924).

1000 cycle note of a mechanical oscillator. The resulting beats were counted in telephone receivers.

The gas condenser, Fig. 2, was constructed of chrome vanadium steel. The high potential side consisted of a solid cylinder held in position by two quartz supports, conically ground at both ends and fitting accurately into the end members of the cell. The low potential side of the condenser consisted of a shell, one millimeter in thickness. The separation of the cylinder and shell was 0.3 mm. The length of the condenser was 16 cm. The entire cell was surrounded by a steel jacket which bore the stress of the pressure, reducing the elastic deformation of the condenser itself to a minimum. The correction for deformation due to compression of the walls never amounted to more than one percent of $\epsilon - 1$. The outer jacket was closed at the lower end and made pressure tight by means of an aluminum washer. The insulating joint, inset Fig. 2, which carried a lead from the oscillator to the inner cylinder of the condenser was constructed in the following manner. A two centimeter length of two millimeter steel tubing was welded into a seven centimeter length of three millimeter steel tubing. This was silver soldered into a fitting which was later made tight in the head of the gas cell by means of an aluminum washer. A section of lead glass capillary coated with a flux of the same coefficient of expansion as the steel was fused to the inner tube and around the platinum wire leading from the inner cylinder of the condenser. Below the seal, the lead was protected by a length of quartz capillary extending down to the point where it was made fast in the cylinder.

The free capacity of the gas cell was found to be $167.4\mu\mu f$. It was roughly calculated to be $165\mu\mu f$ from the dimensions of the cell.

The temperature of the gas cell was controlled in an oil bath of large heat capacity by means of a mercury regulator. Temperatures were measured with a platinum resistance thermometer.

The pressure line was constructed of Shelby steel tubing with double cone connections. Connection with the pressure gauge, of the floating piston type,⁷ was made through a mercury-in-steel U.

At the beginning of a series of measurements the oil bath was brought to the desired temperature and the variable condenser D was adjusted to the same capacity as the evacuated gas cell. They could be alternately inserted into the oscillator circuit by a switch of small capacity. Gas was then admitted from a steel reservoir in the pressure line, and the pressure brought approximately to the desired value by heating or cooling the reservoir. It was finally adjusted to the proper value by means of a mercury piston compressor. From the two readings of the precision condenser with G and D alternately in the circuit, the dielectric constant could be calculated. After completing a measurement, the pressure was increased by means of the mercury piston and measurements made at regular pressure intervals. The use of the counterpoise condenser D made it possible to compensate

⁷ F. G. Keyes and Brownlee, *Thermodynamic Properties of Ammonia*, Wiley and Sons 1916. F. G. Keyes and J. Dewey, *J.O.S.A.* **14**, 491 (1927).

for drift in the oscillator between measurements. The dielectric constant was calculated by the following formula, evident from the condenser circuit:

$$\epsilon - 1 = \frac{C^2(P_2 - P_1)}{(P_1 + C)(P_2 + C)G_0}$$

Here P_1 and P_2 are the two readings of the precision condenser, C the capacity of the fixed condenser, and G_0 the free capacity of the gas condenser.

For each series of measurements, the function $(\epsilon - 1)/(\epsilon + 2)$ was plotted against the density. The point at which the extrapolated line intercepted the axis of $(\epsilon - 1)/(\epsilon + 2)$ was taken as the zero point to which all of the values of $\epsilon - 1$ were referred. The intercept was in every series of measurements small and sometimes negligible. It was evidently the result of an initial extraneous capacity change attending the introduction of the gas, caused by incomplete temperature equilibrium in the evacuated gas cell.

EXPERIMENTAL RESULTS

Measurements of the dielectric constant of carbon dioxide were made upon the gas at 35°, 70°, 100°; and upon the liquid at 0°. The results are listed in the following tables.

TABLE I. *Measurements on gaseous carbon dioxide at 100°.*

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (mols/liter)	$\frac{\epsilon - 1}{\epsilon + 2} V$
10	0.00753	2991	0.33	7.485
20	.01549	1461	.68	7.505
30	.02404	947	1.06	7.528
40	.03333	691	1.45	7.593
50	.04306	535	1.87	7.570
60	.05269	434	2.30	7.491
70	.06447	361	2.77	7.595
80	.07707	306	3.27	7.664
90	.09005	263	3.80	7.664
100	.1041	229	4.37	7.687
126	.1456	167	5.99	7.730
151	.1912	129	7.75	7.729

TABLE II. *Measurements on gaseous carbon dioxide at 70°.*

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (mols/liter)	$\frac{\epsilon - 1}{\epsilon + 2} V$
10	0.00831	2728	0.37	7.536
20	.01717	1321	.76	7.517
30	.02693	842	1.19	7.491
40	.03748	606	1.65	7.478
50	.04950	464	2.16	7.532
60	.06305	369	2.71	7.596
70	.07810	300	3.33	7.612
80	.09616	248	4.03	7.702
90	.1159	207	4.83	7.699
100	.1396	173	5.78	7.693
126	.2165	115	8.70	7.739
151	.3072	84.7	11.81	7.868

TABLE III. Measurements on gaseous carbon dioxide at 35°.

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (mols/liter)	$\frac{\epsilon - 1}{\epsilon + 2} V$
10	0.00971	2352	0.43	7.588
20	.02021	1135	.88	7.595
30	.03228	713	1.40	7.590
40	.04649	497	2.07	7.584
50	.06461	363	2.75	7.653
60	.08838	269	3.72	7.698
70	.1309	191	5.24	7.986
80	.3146	88.5	11.23	7.986
90	.4206	65.6	15.24	8.066
100	.4559	58.3	17.15	7.691

TABLE IV. Measurements on liquid carbon dioxide at 0°C.

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (mols/liter)	$\frac{\epsilon - 1}{\epsilon + 2} V$
50	0.6016	46.75	21.39	7.809
75	.6187	45.56	21.95	7.790
100	.6321	44.97	22.24	7.826
125	.6425	44.34	22.55	7.821
150	.6526	43.78	22.84	7.822
175	.6603	43.31	23.09	7.813
200	.6674	42.85	23.34	7.798

The molal volumes were obtained from Amagat's pressure volume temperature measurements, the best at present available for carbon dioxide. The Clausius-Mosotti function, $(\epsilon - 1)/(\epsilon + 2)V$, is expressed in cubic centimeters

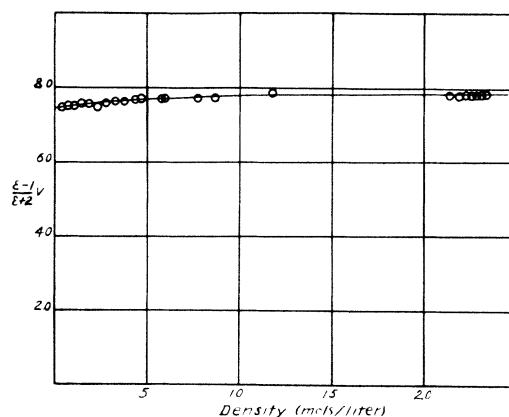


Fig. 3. The points above the density 20 are for the liquid at 0°; the others are for the gas at 100°.

per mol. At 35° above 60 atmospheres, the Clausius-Mosotti function, when plotted against the density, shows very great irregularity. We believe this to be due to error in Amagat's data, extremely probable in view of the very large value of $-(dV/dP)$ in this region. Except in this region, the

maximum error in measurements of Amagat which have been used is probably about 0.25%.

Extrapolation of $(\epsilon-1)V/(\epsilon+2)$ calculated from our measurements yields a value of about 7.4 cc in the low density region covered by other investigators. This is in satisfactory agreement with the value 7.3 cc calculated from the measurements of Zahn.⁸ We estimate the maximum random experimental error in $\epsilon-1$ to be $\pm 0.5\%$. With increasing density, it becomes progressively smaller. Absolute error originating in the calibration of the apparatus, we believe to be not more than one percent.

DISCUSSION

Within the limit of our experimental error, the Clausius-Mosotti function $(\epsilon-1)V/(\epsilon+2)$ is found to be independent of temperature. It is not, however, independent of density. To illustrate its behavior, $(\epsilon-1)V/(\epsilon+2)$, for the gas at 100°, as well as for the liquid at 0°, has been plotted against density in Fig. 3. The curve rises slowly with increasing density, but there is a gradual decrease in slope so that when the liquid densities are reached, it has become, within the limit of observation, parallel to the density axis. It is to be remembered however, that the deviation from the line

$$\frac{\epsilon-1}{\epsilon+2}V = \text{constant}$$

required by the Clausius-Mosotti law in its usual form, is small. Indeed the total increment in $(\epsilon-1)V/(\epsilon+2)$ in passing from the gas at the lowest density of the measurement to the liquid is only four percent.

A few brief speculations relative to the cause of the observed deviation from the Clausius-Mosotti law may be of value. The calculation of the average internal polarizing field F by the familiar cavity method yields

$$F = E + \frac{4\pi}{3}P \quad (1)$$

where E is the mean electric intensity in the dielectric and P the polarization per unit volume. The following formal generalization of the above expression has been suggested:

$$F = E + \nu P. \quad (1a)$$

Let us write

$$\nu = \frac{4\pi}{3} + \beta.$$

We also have at our disposal the familiar relations involving the displacement, D .

$$D = \epsilon E \quad (2)$$

$$D = E + 4\pi P \quad (3)$$

⁸ C. T. Zahn, Phys. Rev. **27**, 455 (1926).

Moreover

$$P = \frac{N}{V} p_0 F$$

where N is the Loschmidt number, V the molal volume, and p_0 the molecular polarizability, $\alpha + \mu^2/3kT$. Elimination of D , E , and F from (1a), (2) and (3) gives

$$\frac{\epsilon - 1}{\epsilon + 2} V = \frac{4\pi N}{3} p_0 \frac{1}{1 - \beta N p_0 \rho} \quad (4)$$

where ρ is the density in mols per cubic centimeter. Eq. (4) may be made to conform to the curve of Fig. 3, if the polarizability p_0 is assumed to be a function of density of appropriate form. Change in the polarizability of a molecule with density could be attributed only to a change in the internal structure of the molecule or to molecular association. Such an hypothesis does not seem desirable without independent confirmatory evidence and in any case is of a purely qualitative nature. The fact that the carbon dioxide molecule gives no evidence of possessing a permanent electric moment is unfavorable to this type of explanation. Indeed, the polarizability, α , associated with the perturbation of the electronic orbits is not greatly affected even by interaction involving actual valence forces.

We are inclined to believe the cavity method of calculating the internal field is inexact and that the formal generalization (1a) is valid only if β is a function of density. If this view is accepted, we must conclude that the Clausius-Mosotti function, while furnishing a good approximation, is not an exact representation of the molecular polarization, $4\pi N p_0/3$, except in the limiting case of infinitely low density.

In conclusion, we wish to express our cordial appreciation to Professor H. B. Phillips for continued advice regarding the electrical circuits employed in these measurements.