THE DIELECTRIC CONSTANT OF AMMONIA AS A FUNCTION OF TEMPERATURE AND DENSITY

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ABSTRACT

The dielectric constant of ammonia has been measured over a wide range of density at several temperatures. The Clausius-Mosotti function $(\epsilon-1)V/(\epsilon+2)$ was found to increase with increasing density. At the lower densities it was adequately represented by the following formula

$$\frac{\epsilon-1}{\epsilon+2}\ V = \frac{4\pi N p_0}{3}\ \frac{1}{1-\lambda\rho}$$

where p_0 is the molecular polarizability, ρ the density, and λ a constant expressible in terms of the equation of state constants, A and b, as

$$\frac{32\pi^2 p_0^2 N^2}{45b}\ \left(1 + \frac{1}{3}\frac{A}{bRT}\right).$$

Previous measurements of the dielectric constant of carbon dioxide are further discussed.

THE correlation of the molecular structure of a substance with its dielectric constant depends upon a knowledge of the average internal field effective in polarizing a molecule. A calculation of the internal field by the cavity method[1] leads to the Clausius-Mosotti equation

$$\frac{\epsilon - 1}{\epsilon + 2}V = \frac{4\pi N}{3}p_0 \tag{1}$$

where ϵ is the dielectric constant, V the molal volume, and N the Loschmidt number.

The molecular polarizability, p_0, for weak fields and moderately high temperatures is given by

$$p_0 = \alpha + \frac{\mu^2}{3kT}. \tag{2}$$

Here α is the sum of the electronic and atomic polarizabilities, μ the per-

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[1] Lorentz, Theory of Electrons, p. 305 (1923). In this method a spherical cavity is excised around a selected molecule in the dielectric. Under the assumption that the remainder of the dielectric is continuously polarized, the field acting at the center of the selected molecule is calculated as arising from an hypothetical surface charge on the interior of the cavity and on the outer boundary of the dielectric. Such an analysis appears highly artificial since in a region of molecular dimensions it is not justifiable to treat the dielectric outside the selected molecule as a continuum of polarized medium. Moreover, the influence of the fluctuations in the internal field, associated with the thermal motion of the surrounding molecules is completely ignored.

manent electric moment of the molecule, k Boltzmann's constant, and T the absolute temperature.

Although the Clausius-Mosotti relation has received adequate empirical confirmation in the case of gases at low pressures, its validity for more dense substances is open to some question. Recent measurements of the dielectric constant of carbon dioxide over a wide range of density[2] lead to the conclusion either that there exists a small deviation from the Clausius-Mosotti relation or that the molecular polarizability of carbon dioxide increases slowly with the density. The fact that the Clausius-Mosotti function shows itself independent of the temperature makes the existence of a dipole form of the carbon dioxide molecule in an appreciable proportion, extremely improbable. In the present article measurements of the dielectric constant of ammonia under similar conditions of temperature and density will be presented. The fact that the ammonia molecule is known to possess a permanent dipole makes these results of particular importance in supplementing the previous investigation on carbon dioxide.

Experimental Results

The apparatus employed in the measurements has been previously described.[2] Except in a few minor details it was identical with that used in the measurement of the dielectric constant of carbon dioxide.

Ammonia from a commercial cylinder was purified by distillation and dried by allowing it to stand over metallic sodium for several months. It was afterwards slowly distilled into a steel reservoir in a pressure line of which the gas condenser was a part. Measurements were made at $100°$ $125°$, $150°$, and $175°C$. The results are listed in the accompanying tables.

The ammonia densities were obtained from the pressure-volume-temperature measurements of Beattie and Lawrence.[3]

The Clausius-Mosotti function, $(\epsilon-1)V/(\epsilon+2)$, has been plotted against density in Fig. 1. It will be observed that the curves for the different temperatures ascend slowly with decreasing slope as the density increases. The form of each of the curves is similar to that of the single curve obtained from the measurements on carbon dioxide at various temperatures, although the deviations from the lines

$$\frac{\epsilon-1}{\epsilon+2}V = f(T) \tag{2a}$$

are relatively much greater.

By extrapolation, the limiting values of the Clausius-Mosotti function at zero density were obtained. According to Eq. (1), undoubtedly valid in this limiting case.

$$\frac{\epsilon-1}{\epsilon+2}VT = \frac{4\pi}{3}N\alpha T + \frac{4\pi\mu^2}{9k} . \tag{3}$$

[2] F. G. Keyes and J. G. Kirkwood, Phys. Rev. **36**, 754 (1930).
[3] J. A. Beattie and C. K. Lawrence, J.A.C.S. **52**, 6 (1930).

TABLE I. *The dielectric constant of ammonia at 100°.*

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (mols/liter)	$\frac{\epsilon-1}{\epsilon+2}V$
20	0.0940	1385	0.72	42.07
25	.1230	1076	0.93	42.37
30	.1538	867	1.15	42.28
35	.1890	718	1.39	42.55
40	.2277	605	1.65	42.68
45	.2723	514	1.95	42.77
50	.3241	441	2.27	43.00
55	.3867	377	2.65	43.05

TABLE II. *The dielectric constant of ammonia at 125°.*

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (Mols/liter)	$\frac{\epsilon-1}{\epsilon+2}V$
20	0.0822	1512	0.66	40.32
30	.1318	966	1.04	40.65
40	.1892	689	1.45	40.88
50	.2568	521	1.92	41.08
60	.3381	406	2.40	41.12
70	.4396	322	3.11	41.15

TABLE III. *The dielectric constant of ammonia at 150°.*

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (mols/liter)	$\frac{\epsilon-1}{\epsilon+2}V$
20	0.0713	1636	0.61	37.98
30	.1125	1055	0.95	38.13
40	.1584	763	1.31	38.28
50	.2101	587	1.70	38.42
60	.2621	479	2.09	38.50
70	.3381	383	2.61	38.81
80	.4203	318	3.14	39.08
90	.5170	266	3.76	39.14
100	.6382	223	4.48	39.12

TABLE IV. *The dielectric constant of ammonia at 175°.*

Pressure (atm.)	$\epsilon - 1$	Molal volume (cc)	Density (mols/liter)	$\frac{\epsilon-1}{\epsilon+2}V$
20	0.0638	1753	0.57	36.49
30	.0998	1138	0.88	36.62
40	.1368	831	1.20	36.24
50	.1818	646	1.55	36.91
59	.2237	533	1.88	36.99
70	.2815	433	2.31	37.14
80	.3402	365	2.74	37.18
90	.4070	313	3.19	37.39
100	.4800	271	3.69	37.38

From the intercept of line obtained by plotting $(\epsilon - 1)VT/(\epsilon + 2)$ against T, the permanent electric moment of the ammonia molecule was calculated to be 1.44×10^{-18} e.s.u. This is in exact agreement with the value reported by Zahn[4] from measurements of the dielectric constant of ammonia at low densities. The part of the molecular polarization independent of temperature, $4\pi N\alpha/3$,, was calculated from the slope of the line to be 7.3 cc. The refractive index in the visible region, of ammonia at low densities yields a value of $(n^2 - 1)V/(n^2 + 2)$ of 5.9 cc. Due to infrared dispersion terms associated with the vibrational states of the molecule, it undoubtedly has a somewhat greater value at the frequency 1010 $k.c.$, of the present dielectric constant measurements.

DISCUSSION

In interpreting the experimental facts which have just been presented, two courses are open. We may assume either that the Clausius-Mosotti equation is valid and that the mean molecular polarizability increases with the density, or that the molecular polarizability, p_0, remains constant and that the Clausius-Mosotti function $(\epsilon - 1)V(\epsilon + 2)$ deviates from the molecular polarization, $(4\pi/3)Np_0$, as the density becomes great.

The first hypothesis may be justified by some very simple considerations. In a gas envisaged as an assembly of molecules in statistical equilibrium there exists a variety of possible molecular types as represented by the rotational and vibrational states of the molecule as well as by complex states arising from molecular association. The distribution among the various molecular states may be of importance in determining the mean molecular polarizability. Thus in the case of a fixed molecular dipole, the distribution among the rotational states of the molecule determines the form of the Debye term, $\mu^2/3kT$. It is possible that to the different vibrational and associational states of a molecule there correspond different atomic polarizabilities and different resultant electric moments.[5] Moreover, if the transition energies of these states were of the order of magnitude of kT, a variation in temperature or density might be capable of producing changes in the distribution among them which would appreciably alter the mean molecular polarizability. It is therefore conceivable that an increase in density should produce an increase in the mean molecular polarizability of carbon dioxide or ammonia through the displacement of an equilibrium between molecular states of different polarizability. However, associated with this effect, a corresponding variation of polarizability with temperature would be expected, which in fact was not observed, at least for CO_2. It is, of course to be remembered that the total observed variation of the Clausius-Mosotti function was small, and that the density range covered in the dielectric constant measurements was relatively much greater than the temperature range. It is accordingly possible that a small abnormal temperature effect associated with the observed density effect might well have escaped detection.

[4] C. T. Zahn, Phys. Rev. **27**, 455 (1926).

[5] C. T. Zahn, Phys. Rev. **35**, 1056 (1930); P. Debye, Handbuch der Radiologie p. 633 (1925).

The band spectra of both carbon dioxide and ammonia give evidence for the existence of frequencies associated with the molecular vibrational states for which $h\nu$ is of the order of magnitude of kT at $300° - 400°K$.[6] However, a quantitative discussion of the effect of the distribution among the various vibrational types on the mean molecular polarizability is impossible without independent information concerning the polarizabilities belonging to each type. Molecular association undoubtedly occurs in all gases to a greater or less extent and becomes increasingly important as the saturation region is approached. However, it is doubtful whether the loose coupling effective in such processes would be sufficient to influence the terms in the polarizability associated with the electrons and with the atoms. It might, however, affect the orientation of the permanent dipoles.

A deviation from the Clausius-Mosotti relation as suggested by the second hypothesis is indeed likely. Recently we have carried out a statistical calculation of the internal field which leads to the following relationship for gases up to moderately high densities

$$\frac{\epsilon - 1}{\epsilon + 2}V = \frac{4\pi}{3}Np_0\frac{1}{1 - \lambda\rho} \tag{4}$$

where ρ is the density in mols per cubic centimeter. If for simplicity, the van der Waal's molecular model is employed, we find

$$\lambda = \frac{32N^2\pi^2p_0^2}{45b}\left(1 + \frac{1}{3}\frac{A}{bRT}\right) \tag{5}$$

where A and b are the constants of the van der Waal's type of equation of state. The constant λ has been computed and Eq. (4) has been plotted for ammonia at the various temperatures of the dielectric constant measurements. From Fig. 1 it may be seen that Eq. (4) conforms closely to the experimental curves until fairly high densities are reached. Thus at $175°$, the deviation does not become appreciable until a pressure of 40 atm. is reached. The divergence of the two curves at higher densities is not surprising, for here the assumptions underlying the deduction of Eq. (4) undoubtedly begin to fail. Eq. (4) assumes that the molecules of the gas are continuously distributed in configuration, but when an appreciable fraction of the molecules are in quantized collision states arising in molecular association, this assumption loses its validity.

The application of Eq. (4) does not meet with similar success in the case of carbon dioxide. The observed deviation from the Clausius-Mosotti relation was found to be many times that predicted by Eq. (4). This may perhaps be explained in the light of the hypothesis which was first discussed. Eq. (4) assumes that the gas may be regarded as an assembly of molecules of identical polarizability. If carbon dioxide is to be regarded as a mixture of several vibrational types of different polarizability, this assumption is not justified. The abnormal behavior of the Clausius-Mosotti function may then be attributed to a variation of the mean molecular polarizability through

[6] Dennison, Phil. Mag. 1, 195 (1926).

a displacement of an equilibrium between several molecular types. In this process only the infrared dispersion terms associated with the atomic oscillators would be affected. This is in accord with the fact that the refractive index of carbon dioxide in the visible region has been found to satisfy the Lorentz-Lorenz relation over a large part of the density range covered by our dielectric constant measurements.[7]

Both in the case of carbon dioxide and of ammonia, our dielectric constant measurements show a deviation from the Clausius-Mosotti relation. For ammonia, they are adequately represented up to moderately high densities by Eq. (4). For carbon dioxide Eq. (4) proves inadequate. In this case it seems necessary to assume the existence of several molecular types with different infrared dispersion terms.

[7] P. Phillips, Proc. Roy. Soc. A47, 225 (1920).