THE ELECTRIC MOMENT OF CO_2, NH_3, AND SO_2

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ABSTRACT

Dielectric constant of N_2, CO_2, NH_3 and SO_2.— By an improved heterodyne null method previously described, measurements were made of the dielectric constant at atmospheric pressure of the carefully purified gases, over a range from 300° to 400° from just above the liquefaction point. These results as well as all others found by the author are represented by the Debye equation $(\epsilon-1)vT = AT+B$, where ϵ is the dielectric constant, T the absolute temperature, and v the specific volume. The values found for A are .000958 (CO_2), .000768 (NH_3), and .001433 (SO_2); and for B are .003 (CO_2), 1.740 (NH_3), and 2.167 (SO_2). The anomaly observed by Jona and attributed to association was not observed except possibly to a slight degree in NH_3. The values of the *electric moment of the molecules* calculated from the constant B differ from Jona's values by 7 percent. It is believed that the explanation of the difference is to be based on the fact that the anomaly is not due to association but to surface effects on the metallic plates of the condenser. The values obtained for the electric moment are, in c.g.s., e.s. units$\times 10^{18}$, .06 (CO_2), 1.44 (NH_3), and 1.611 (SO_2). The small value for CO_2 differs from zero by an amount which is less than the experimental error.

IN an article by Jona[1] on the variation of the dielectric constant of gases with temperature marked deviations from the Debye straight line were recorded in the cases of water vapor, methyl alcohol, and sulfur dioxide near the liquefaction point. These deviations were attributed to association with an accompanying increase in the electric moment of the molecule. In a series of measurements[2] on the halogen hydrides no such deviations from the Debye theory were observed even though the measurements were made near the liquefaction points of the gases studied. For this reason it was thought worth while to make a further investigation of this anomalous effect. To this end measurements were made on several of the gases studied by Jona.

The experimental method used has been described by the author in the above mentioned paper[2] on the electric moments of the halogen hydrides. A heterodyne null method is used in which the beats between the oscillations from two separate electron-tube generators operating at frequencies of about 1,000,000 and 1,001,000 cycles per second are adjusted to the frequency of an electrically driven tuning fork, the small change of capacity due to the introduction of the gas into the measuring

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[1] M. Jona, Phys. Zeits. **20**, 14 (1919).

[2] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

condenser being compensated by a large change in a large capacity in series with this condenser.

According to Debye's theory[3] the dielectric constant of a gas is given by the equation

$$(\epsilon-1)vT = AT+B$$

when ϵ is the dielectric constant, T is the absolute temperature, and v is the specific volume referred to the volume occupied by 1 cc of an ideal gas at 0°C and 760 mm Hg. For an ideal gas $v = T/273$ but for vapours this is corrected by the use of van der Waals' equation. A is a constant which represents the electric polarization due to induced distortion in the molecule and B is a constant which represents the orientation polarization and is proportional to the square of the electric moment of the molecule.

$$(\mu^2 = 1.198 \times 10^{-36} B)$$

If $(\epsilon-1)vT$ is plotted against T there is obtained a straight line of slope A and intercept B which determines μ. For gases of symmetrical structure, i.e., zero electric moment, $B=0$ and the straight line should pass through the origin of coordinates.

Measurements were first made on N_2 as a rough check on the behaviour of the apparatus. Since N_2 is not a polar molecule one should expect zero electric moment for the molecule and the Debye straight line should correspondingly pass through the origin of coordinates. This was found to be the case within the limits of experimental error. It should be noted here that for the measurements on nitrogen the temperature control of the apparatus was not so good as for the other measurements which were made later when an oil bath of large heat capacity was used for the high temperatures. The later measurements are undoubtedly more accurate than those on nitrogen. In the case of nitrogen the maximum deviation from the mean value of $(\epsilon-1)v$ is less than one percent which was the upper limit estimated for the error introduced by the original calibration of the condensers used.[2]

Measurements were also made on CO_2, NH_3, and SO_2. The CO_2 and SO_2 were taken from commercial cylinders and dried and then distilled repeatedly by freezing in liquid air and evaporating, discarding each time small quantities of the gas coming off first and last. NH_3 was obtained by heating concentrated ammonia water and was purified as above.

The measurements are given in Table I and the values of $(\epsilon-1)vT$ are plotted against T in Fig. 1. All these measurements were made by measuring the difference in the capacities of the experimental condenser corresponding to atmospheric pressure and a small pressure of about

[3] P. Debye, Phys. Zeits. 13, 97 (1912).

6 cm of the gas under investigation. (This procedure was adopted because it was found that when the condenser was completely evacuated the heat insulation between the plates was good enough to prevent sufficiently rapid equalization of temperature of the two plates.) The results are reduced to atmospheric pressure by assuming that $(\epsilon-1)$ may be regarded as proportional to the pressure for this small correction. In each case, measurements were made to temperatures within a few degrees of the liquefaction points corresponding to atmospheric pressure. These later points are indicated in the figure by vertical broken lines.

TABLE I

Dielectric constant data

$T°K$	$(\epsilon-1)\times10^6$	$(\epsilon-1)v\times10^6$	$(\epsilon-1)vT$
		Nitrogen	
84.1	1898	572	.0481
197.8	792	572	.1132
273.0	581	581	.1586
562.1	283	583	.3276
		Carbon Dioxide	
199.2	1353	978	.1948
200.6	1345	978	.1962
286.6	926	968	.2774
295.0	909	976	.2878
469.0	561	962	.4512
		Ammonia	
241.7	9280	8142	1.966
274.4	7132	7143	1.962
296.7	6117	6620	1.965
371.4	4018	5452	2.024
456.9	2734	4567	2.086
		Sulfur Dioxide	
265.5	10015	9627	2.547
267.6	9918	9530	2.550
295.5	8176	8770	2.592
297.2	8120	8768	2.606
366.9	5477	7323	2.687
443.8	3911	6336	2.812

The data of particular interest are those for SO_2 and NH_3. For SO_2 Jona obtained at 300°F about a 10% increase of $(\epsilon-1)vT$ over the value corresponding to the limiting slope at higher temperatures; whereas the observations here recorded show no such anomaly, even though the measurements are carried about 35° below Jona's lowest temperature. For NH_3 Jona recorded at room temperature a slight anomaly, whereas Fig. 1 shows no definite deviation for temperatures as low as room temperature, but near the liquefaction point there seems to be a definite increase of about 2%. The obvious inference is that there is some effect that is present only slightly in the present measurements but which was

quite appreciable in Jona's work. It is difficult to imagine how such an
effect could be attributed to association which should reach a definite
equilibrium concentration, unless the time required for association should
be comparable to the time between observations. This latter supposition
seems very unlikely. In fact it is difficult to see how any effect which
is characteristic of the gas itself; i.e., any volume effect could account for
the difference in the two sets of observations, whereas the existence of
surface layers on the metallic plates might reasonably be responsible for
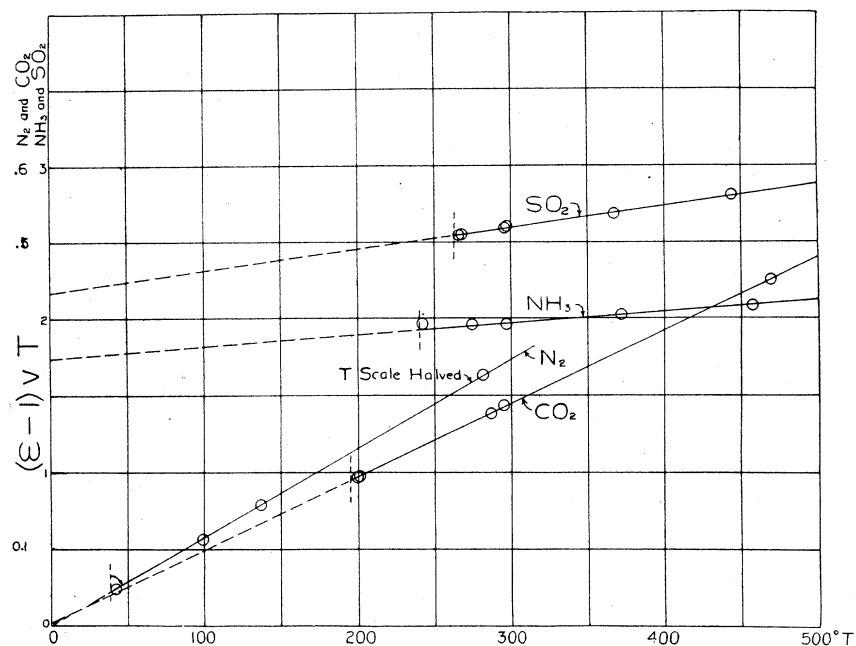the inconsistencies. Such layers might depend upon the nature of the

Fig. 1. Variation of $(\epsilon-1)\nu T$ with temperature.

metal of the condenser and also upon the degree to which the surfaces
had been cleaned by baking and evacuation. For example it is possible
that a surface which had not been properly cleaned might have entirely
different properties as regards adsorption of layers of the gas. In fact
some recent experiments of the author on water vapour suggest that
there is a surface effect in such measurements.[4]

In Table II are given the Debye constants as taken from the data of
Fig. 1 together with the values of electric moment given by Jona, for the
purpose of comparison. From the figure it would appear that CO_2 has a

4 C. T. Zahn, Phys. Rev. **27**, 329 (March, 1926).

slight electric moment but considerably less than that given by Jona. In fact the value is so small as to be within the limit of experimental error, and it cannot be stated definitely that CO_2 has an appreciable electric moment. The difference between Jona's values of μ and those taken from Fig. 1 may be due to an error introduced by his equation

TABLE II
The Debye constants

Gas	$A \times 10^6$	B	$\mu \times 10^{18}$ (c.g.s.,e.s. units)	$\mu \times 10^{18}$(Jona)
CO_2	958	.003	.06	.303
NH_3	768	1.740	1.44	1.53
SO_2	1433	2.167	1.611	1.76

which was developed on the assumption of the existence of associated molecules. This error would present itself in the reduction to standard pressure and would depend on the actual pressures used in the experiments. Since he has not given these pressures, no definite comparison can be made. The difference in the μ values of Table II is about 7% for NH_3 and SO_2 and is well beyond the limit of experimental error for both observers.

In Table III is given a resumé of all the observations taken of the variation of dielectric constant with temperatures with the apparatus

TABLE III
Resumé of dielectric constant data

Gas	$A \times 10^6$	B	$\mu \times 10^{18}$ (c.g.s.,e.s. units)
HCl	1040	.895	1.03
HBr	1212	.52	.79
HI	1856	.12	.38
C_2H_2	1334	0	0
C_2H_4	1444	0	0
C_2H_6	1501	0	0
α–C_4H_8	2694	.115	.37
N_2	580	0	0
CO_2	958	.003	.06
NH_3	768	1.74	1.44
SO_2	1433	2.167	1.61

described previously by the author.[2] There are here included the measurements on the halogen hydrides, those here described, and measurements taken on four hydrocarbons in collaboration with Dr. Charles P. Smyth.[5]

In conclusion the author wishes to acknowledge his indebtedness to Professor K. T. Compton for helpful advice and to Mr. E. W. Cheney for assistance in making some of the measurements.

[5] C. P. Smyth and C. T. Zahn, Jour. Amer. Chem. Soc. **47**, 2501 (1925).