

THE DIELECTRIC CONSTANT AND THE MOLECULAR
STRUCTURE OF CS₂

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ABSTRACT

By the radio frequency heterodyne method previously developed measurements have been made of the dielectric constant of CS₂ at various pressures and temperatures. The molecular polarization is shown to be independent of temperature and therefore the electric moment is zero. The previous value published tentatively is shown to be in error. The structure of the CS₂ molecule can now be considered to be rectilinear and symmetrical. The value for the molecular polarization obtained is $P = 22.36$.

Comparisons with other data are given, and some convenient modifications in the experimental method and in the interpretation of dielectric constant data are described.

IN A recent article of this review Dr. J. B. Miles together with the author¹ gave values for the dielectric constant and the electric moment of CO, COS, CS₂, and H₂S. The results then obtained indicated a small electric moment for the CS₂ molecule which seemed to be in contradiction to Williams² results from the study of solutions. The experiments on CS₂ were accompanied by two chief difficulties. First, the apparatus was not adapted to the study of hot vapors, since part of the gas system was always at room temperature and it was therefore possible to work only at pressures below about one-third of an atmosphere. Secondly, the solubility of the CS₂ in the small amount of grease collected around the stopcocks made the results on CS₂ somewhat questionable. For these reasons the values for CS₂ were given only tentatively in the above mentioned article and it was there promised to make more conclusive measurements in the near future. Since then the apparatus has been adapted to work with hot vapors by Dr. J. B. Miles in collaboration with the author, and measurements have been made on CS₂ under excellent experimental conditions.

While this work was in progress there appeared an article by Ghosh, Mahanti, and Mukherjee³ on the dielectric constant and the molecular structure of CS₂ and N₂O, in which the moments of CS₂ and N₂O were found to be zero. The experiments described in the present article verify the conclusion that CS₂ has no appreciable electric moment but the value of the molecular polarization obtained is not in sufficiently close agreement with that of the above mentioned observers. It therefore seems worth while to give a full discussion of the present work.

¹ C. T. Zahn and J. B. Miles, Jr., Phys. Rev. **32**, 497 (1928).

² J. W. Williams, Phys. Zeits. **29**, 177 (1928).

³ P. N. Ghosh, P. C. Mahanti, and B. C. Mukherjee, Zeits. f. Physik **58**, 145 (1929).

EXPERIMENTAL METHOD AND MODIFICATIONS

The radio frequency heterodyne null method was used as previously described and applied to the measurement of a considerable number of gaseous substances.⁴ In the present arrangement of the apparatus there is one stopcock, which is separated from the gas system by liquid CS₂ in the manometer described,⁴ and should therefore not be so likely to introduce impurities even if grease were used in the seal. In order to make perfectly certain of this the grease was replaced by P₂O₅. The CS₂ used was taken from the same purified specimen as used before.¹

Some convenient modifications have been made in the method of interpretation of the dielectric constant data as follows. The dielectric constant should obey Debye's equation:

$$3\left(\frac{\epsilon-1}{\epsilon+2}\right)vT = AT + B$$

where ϵ is the dielectric constant, v is the specific volume referred to the *ideal* volume under S.P.T. conditions, T is the absolute temperature, and A and B are constants.

$$B = \frac{4\pi N_0}{3k} \mu^2 \text{ or } \mu = 1.099_8 \times 10^{-18} B$$

where N_0 is Loschmidt's number, the ideal number of molecules per cc under S.P.T. conditions, $2.705_6 \times 10^{19}$, k is Boltzmann's constant, $1.370_9 \times 10^{-16}$, and μ is the electric moment of the molecule.

In previous experiments it has been customary to determine the difference between the dielectric constants at atmospheric pressure and at approximate vacuum, and to determine the value of v by the van der Waal equation in its approximate form:

$$v = \frac{RT}{p} \left\{ 1 - \frac{(a/vp) - b}{v} \right\}$$

using for v on the right hand side its approximate or ideal value RT/p . This method of calculation is convenient if the dielectric constant is measured at only one pressure. A more satisfactory way to determine $(AT+B)$ is to make measurements of $\Delta\epsilon$ over the whole range of pressure available, and at the same time to test the Clausius-Mossotti relation: $(\epsilon-1)/(\epsilon+2) :: \text{density}$. At a fixed temperature the polarization would be accurately proportional to p only for an ideal gas so that plotting $3(\epsilon-1)/(\epsilon+2)$ against p would not give a straight line. If we plot against p' , the *ideal* pressure which the gas would have at the given temperature and density, we should obtain a straight line of slope $3[(\epsilon-1)/(\epsilon+2)] V/RT$. The value of p' can be

⁴ C. T. Zahn, Phys. Rev. **24**, 400 (1924); C. P. Smyth and C. T. Zahn, Jour. Amer. Chem. Soc. **47**, 2501 (1925); C. T. Zahn, Phys. Rev. **27**, 329 (1926); C. T. Zahn, Phys. Rev. **27**, 455 (1926); C. T. Zahn and J. B. Miles, Jr., Phys. Rev. **32**, 497 (1928); J. B. Miles, Jr., Phys. Rev. **34**, 964 (1929).

calculated as follows. Van der Waal's equation can be rewritten approximately:

$$v = \frac{1}{\frac{p}{RT} \left\{ 1 + \frac{p}{RT} \left(\frac{a}{RT} - b \right) \right\}} \equiv \frac{RT}{p'}$$

which defines:

$$p' = p \left\{ 1 + \frac{p}{RT} \left(\frac{a}{RT} - b \right) \right\}.$$

Hence the effect of the van der Waal constants is to introduce into the actual pressure relation a small quadratic term which can be taken into account by plotting against p' as above mentioned. The final value of $(AT+B)$ is got by multiplying the slope by RT^2 . This is done for a range of temperatures and the values plotted against T . The resulting straight line gives A as the slope and B as the intercept from which the moment is determined. If the molecule studied has no fixed moment then the values of $3(\epsilon-1)/(\epsilon+2)$ v should be constant, and it is not necessary to draw the Debye line in order to determine A . It is only necessary to average the experimental values of $3[(\epsilon-1)/(\epsilon+2)]v$, which are approximately equal for the different temperatures used.

The above method of plotting has another advantage as follows. In a previous paper the author has mentioned the fact that it is impossible to make a reading for the dielectric constant at vacuum because the condenser plates are then so perfectly insulated thermally that a small but very disturbing temperature difference can be set up between them. It is then necessary to extrapolate to vacuum in order to find the actual value of $(\epsilon-1)$. The apparatus can always be so adjusted that the difference values of $(\epsilon-1)$ are approximately the actual values. These values can be divided by the corresponding approximate values of $(\epsilon+2)$ and then $3\{\Delta(\epsilon-1)/\epsilon+2\}$ can be plotted against p' . The linear extrapolation should be very accurate since the correction due to the factor $(\epsilon+2)$ is usually small and, in fact, often negligible. It is easily seen that the factor $\epsilon+2$ has the effect of introducing a small quadratic term in the value of $\epsilon-1$ as a function of the pressure since

$$3 \left\{ \frac{\epsilon-1}{\epsilon+2} \right\} :: p' \text{ or } (\epsilon-1) :: p' \left(1 + \frac{\epsilon-1}{3} \right)$$

and $(\epsilon-1)$ on the right hand side may be set proportional to p' approximately.

For a considerable number of gases there seems to be no question concerning the validity of the Clausius-Mossotti relation. On the other hand there have been performed a number of experiments⁵ in which anomalies

⁵ M. Jona, Phys. Zeits. **20**, 14 (1919); C. T. Zahn, Phys. Rev. **27**, 329 (1926); K. Wolf, Phys. Zeits. **27**, 588, 830 (1926); K. Wolf, Ann. d. Physik **83**, 884 (1927); F. Maske, Phys. Zeits. **28**, 533 (1927); J. B. Miles, Jr., Phys. Rev. **34**, 964 (1929).

have occurred, particularly in the case of vapors near the condensation point. These anomalies have been attributed to two causes, association and actual condensation on the condenser plates. The author has performed experiments to show that both these effects exist; for example, for water vapor. In the case of water vapor condensation on the condenser plates is accompanied by electrical conductivity which can be measured directly. The existence of such effects, whether they be due to association or condensation, or both can be detected by pressure curves such as those described above. If they are found to exist they can usually be eliminated by working at sufficiently low pressures.

TABLE I.

$T^{\circ}\text{K}$	p cm Hg	p' cm Hg	$3\left\{\frac{\Delta(\epsilon-1)}{\epsilon+2}\right\}\times 10^6$	$3\left\{\frac{\epsilon-1}{\epsilon+2}\right\}\frac{10^6}{p'}$	$3\left\{\frac{\epsilon-1}{\epsilon+2}\right\}v\times 10^6$	P
325.1 ₁	14.21	14.25	477	from curve		
	25.33	25.44	835			
	34.42	34.63	1134			
	44.47	44.82	1479			
	53.72	54.23	1779			
	64.49	65.23	2147			
	64.57	65.31	2149			
	53.76	54.27	1782			
	43.82	44.16	1454			
	34.96	35.18	1143			
	24.37	24.48	793			
	15.92	15.96	494	2518	2997	
391.7 ₆	15.21	15.23	305			
	28.93	29.03	697			
	48.81	49.09	1247			
	50.27	50.57	1264			
	30.40	30.51	748			
15.81	15.84	330	2088	2995		
489.2 ₂	14.64	14.66	385			
	22.63	22.67	558			
	33.45	33.53	787			
	43.06	43.19	983			
	52.95	53.15	1199			
	61.71	61.98	1384			
	52.95	53.15	1199			
	43.37	43.50	987			
	33.81	33.89	763			
	24.35	24.39	541			
15.00	15.02	334	1666	2985		
322.3 ₁	13.69	13.72	618			
	24.16	24.26	964			
	33.37	33.57	1284			
	43.26	43.60	1614			
	52.87	53.37	1942			
	62.15	62.85	2264			
	53.13	53.63	1957			
	43.54	43.88	1618			
	33.47	33.67	1286			
	24.10	24.20	958			
	14.15	14.18	633	2538	2995	
					2993, mean	22.36

EXPERIMENTAL RESULTS

In the present measurements on CS_2 complete pressure curves were obtained at four different temperatures in order to insure the absence of such effects. In Table I are shown the experimental values obtained. The fourth column contains the difference readings, $3[\Delta(\epsilon-1)/(\epsilon+2)]$, referred to a fixed point of the experimental condenser system for convenience

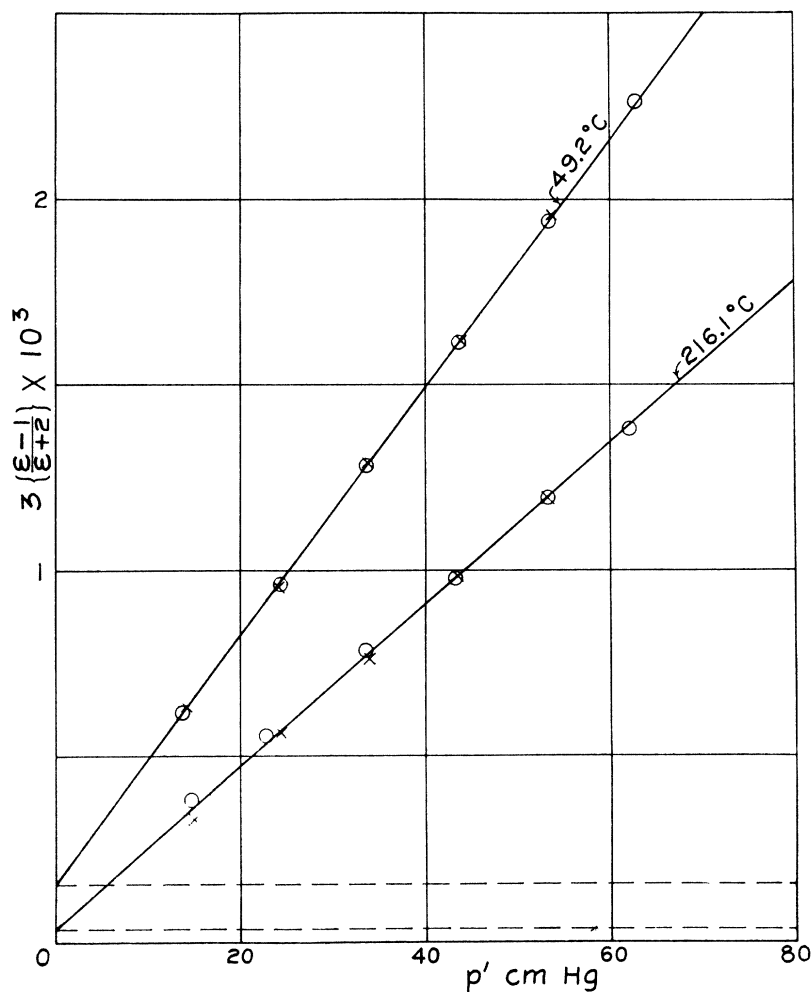


Fig. 1. Variation of polarization with pressure, p' .

in the calculations. The circuits are always adjusted to give the vacuum reading at approximately this fixed point, so that there is no appreciable error introduced in the value of the slope of the pressure curves. A table of calculated values or an accurately drawn chart then serves to facilitate the calculations of ϵ . The true values of $3\{\epsilon-1/\epsilon+2\}$ are measured from the zero values obtained by extrapolation on the curves. In Fig. 1 the values

of $3[\Delta(\epsilon-1)/(\epsilon+2)]$ are plotted against p' and the true values are measured from the horizontal zero lines. For the calculation of p' values of the van der Waal constants were obtained from Kaye and Laby: $a=0.02316$ and $b=0.00343$. Only two of the four sets of data are plotted here for illustration, the best and the worst. The pressure runs were always repeated in the reverse direction in order to eliminate the effect of errors caused by any drifts in the condenser system not due to the CS₂. The part of the readings for increasing pressure is marked by circles; and the part for decreasing pressure, by crosses. The line for the temperature 49.2°C is remarkably well reproduced, while that for 216.1°C shows a slight drift, which is eliminated in the drawing of the line. The strict linearity of these pressure curves indicates that there is no appreciable association or surface condensation throughout the total observed range of pressure.

The last column of Table I contains the value of the molecular polarization. P , or the total induced electric moment per gram-molecule of the substance, calculated from the mean value in the preceding column. $(\epsilon-1)/(\epsilon+2)v$ is the moment or polarization due to N_0 molecules; therefore P can be obtained from the values in the sixth column as indicated by:

$$P = (n/3N_0) \times 3 \{ \epsilon - 1/\epsilon + 2 \} v = 7.4716 \times 10^3 \times 3 \{ \epsilon - 1/\epsilon + 2 \} v$$

where n is Avogadro's number, $6.064_4 \times 10^{23}$. The values of the constants, n , N_0 , L , and k used in these calculations are those given by Birge.⁶

Since the values in the last two columns of Table I are independent of temperature within the limits of experimental error, as mentioned above it is not necessary to draw a Debye line in order to determine the constant A . The results can be summarized by: $A=0.002993$ or $P=22.36$, and $\mu=B=0$.

COMPARISONS WITH OTHER DATA

The result $\mu=0$ is in accord with the observations of Ghosh, Mahanti, and Mukherjee,⁴ but the value of A given by them is 0.002912, about three percent lower than the above value. The discrepancy may be due to a calibration error in either of the two sets of experiments. It is believed by the author that the calibration of the apparatus used for the measurements given here is accurate to a fraction of a percent. Evidence substantiating this has been pointed out by Stuart⁷ and by the author.⁸ Furthermore the value of A for air given by the above mentioned authors is 0.0005797, about one percent higher than that obtained by the author,⁹ 0.000572, and deviates in the opposite direction to that required to explain the discrepancy in the values for CS₂. A part, if not all, of the deviation could be explained by the failure of the above mentioned authors to take into account the departures of the gas from the ideal law. At atmospheric pressure this amounts

⁶ R. T. Birge, Phys. Rev. Supplement, **1**, 1 (1929).

⁷ H. A. Stuart, Zeits. f. Physik **47**, 457 (1928).

⁸ C. T. Zahn and J. B. Miles, Jr., Phys. Rev. **32**, 497 (1928).

⁹ C. T. Zahn, Phys. Rev. **24**, 400 (1924).

to about two percent in such a direction as to increase the values given. Their values of $(\epsilon - 1)$ agree remarkably well for different temperatures, but if they worked at approximately constant density of gas the above mentioned correction would probably not sensibly alter this agreement. In addition there is an unimportant error of a small fraction of a percent introduced by the neglect of the factor $(\epsilon + 2)$. They also give the value of $n_{\infty}^2 = 1.002956$, taken from Graetz's handbook which is *higher* than their value $\epsilon = 1.002912$. Now deviations between n_{∞}^2 and ϵ are usually in the opposite direction¹⁰ because the extrapolation to n_{∞} is usually done from the visible spectrum neglecting the infra-red terms which have been shown to be of importance in the case of CO_2 . In the case of CO_2 the refractivity has been measured over the entire range from the ultra-violet through the infra-red. Fuchs¹¹ has extrapolated for n_{∞}^2 taking into account the infra-red terms and obtains a value differing from the author's value of ϵ by less than one-tenth percent. If the extrapolation had been done without considering the infra-red terms, a value too small would have been obtained. It is therefore difficult to explain experimental observations of ϵ which are smaller than the value of n_{∞}^2 extrapolated from the visible. In the case of CS_2 one would expect ϵ to be larger than such values of n_{∞}^2 all the more because it has been definitely shown to be the case for its structurally similar compound CO_2 . As additional confirmation of the value given here Williams' value of P , as given by Errera,¹⁰ is 22.2 as compared with the value of 22.3₆. The small deviation is in the direction to be expected from data cited by Errera.¹² For the above reasons it is believed that the above mentioned value of $\epsilon = 1.002912$ is about three percent too low.

MOLECULAR STRUCTURE

In the previously cited article¹ the authors discussed values for the electric moment of CO , CO_2 , COS , and CS_2 , with reference to molecular structure. Since in that discussion the moment for CS_2 was tentatively considered to be 0.33×10^{-18} c.g.s. e.s.u., the discussion should be somewhat modified. The moment of COS was found to be 0.65×10^{-18} ; and that of CO , 0.10×10^{-18} . Therefore one would expect the moment of CS to be of the same order as that of COS , and the value of the moment of CS_2 as there found would have to correspond to an approximately linear structure, or to a truly linear structure of the unsymmetrical type suggested by Heisenberg. Since the moment of CS_2 is now definitely proven to be zero the situation is simplified. CO_2 has been shown by Stuart⁷ to have a rectilinear structure since it has no electric moment and for other reasons which he has pointed out. The similar compound CS_2 has now been shown to have no electric moment, and we can therefore consider with a high degree of probability that its structure is rectilinear.

¹⁰ For an excellent discussion of this see: J. Errera, "Polarization Diélectrique."

¹¹ O. Fuchs, *Zeits. f. Physik* **46**, 519 (1928).

¹² Errera, reference 10, p. 68.