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THE DIELECTRIC CONSTANT AND THE ELECTRIC MOMENT OF CO, COS, CS_2, AND H_2S

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Abstract

By the heterodyne null method used in previous investigations measurements of the temperature variation of the dielectric constant were made on a further series of gases. The results are very well interpreted by the Debye equation $(\epsilon-1)vT=AT+B$. The values for A are 0.000670 (CO), 0.002798 (CS_2), 0.001970 (COS), and 0.001223 (H_2S); and for B, 0.0078 (CO), 0.089 (CS_2), 0.352 (COS), and 0.722 (H_2S). These values of B give for the electric moment in c.g.s. e.s. units$\times 10^{18}$: 0.10 (CO), 0.326 (CS_2), 0.650 (COS), and 0.931 (H_2S). A comparison of all measurements made on the same apparatus with those of other observers is made, and a discussion of the notable discrepancies in this field is given. As a result of this investigation it seems likely that CS_2 and COS have a rectilinear structure like that of CO_2.

In recent years a number of investigators have made experimental determinations of the variation of the dielectric constant of gases with temperature. A number of these observers have used the heterodyne method of beats between two high frequency electron-tube oscillators. With this method the accuracy of reproducibility is considerably greater than the accuracy of absolute values on account of the difficulty of calibrating the fixed capacities of the high frequency circuits. Therefore one would expect the various observers to differ only by a calibration factor characteristic for each observer (except in the case of v. Braunmühl to be mentioned later). The most notable disagreements are those in the experimental values of the electric moment of carbon dioxide and of carbon monoxide. The values of the electric moment of these molecules are of considerable importance as regards their type of molecular structure. In this connection one of the objects of this investigation was to determine the electric moment of CO, that of CO_2 having been previously found to be zero within the limits of experimental error by the same apparatus[1] used in this investigation. It was also thought of interest to measure the dielectric constant of the related compounds COS and CS_2. Another object of this investigation was to compare the data of various observers and to ascertain whether the discrepancies might be explained on the basis of calibration errors. For this purpose and also for its own sake the value of the electric moment of H_2S was determined. This value together with that of HCl[2] previously determined serves as a basis of comparison with the values recently determined by v. Braunmühl.[3]

The apparatus used in this work is the same as that described in a previous communication[2] on the dielectric constant of air, H_2, O_2, N_2, HCl, HBr, and

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

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

[3] v. Braunmühl, Phys. Zeits. **28**, 141 (1927).

HI. This apparatus has also been used to measure the dielectric constant of C_2H_2, C_2H_4, C_2H_6, and of $\alpha-C_4H_8$;[4] of H_2O at low pressures[5]; and of CO_2, NH_3, and SO_2.[1]

EXPERIMENTAL RESULTS

As before the electric moment is calculated from Debye's equation:

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

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. The electric moment μ is given by

$$\mu^2=1.198\times10^{-36}B$$

where B is determined by the ordinate intercept of the graph of the Debye function $(\epsilon-1)vT$ plotted against T.

It should be noted here that the modifications in Debye's equation, which Pauli's[6] and Pauling's[7] applications of the Sommerfeld-Wilson quantum conditions introduced, are no longer required in the new matrix or wave mechanics. In fact Van Vleck[8] has shown that in general the new quantum mechanics leads to the same equation as that of the classical theory of Debye.

TABLE I. *Experimental data.*

T°K	p (cm Hg)	$(\epsilon-1)\times10^6$	$(\epsilon-1)v\times10^6$	$(\epsilon-1)vT$
		Hydrogen sulfide		
196.7	28.76	2604	4928	0.969
301.0	75.81	3308	3627	1.092
436.6	76.20	1821	2898	1.256
541.9	76.19	1298	2563	1.388
		Carbon monoxide		
89.8	50.69	1557	756	.0678
202.8	50.77	636	706	.1431
295.7	50.66	434	703	.2078
390.9	50.80	320	686	.2680
		Carbon bisulfide		
302.2	29.45	1096	3113	.940
395.4	29.20	805	3025	1.196
490.0	30.00	656	2978	1.458
		Carbon oxysulfide		
201.9	18.20	1216	3748	.7565
273.6	38.34	1647	3263	.8925
294.4	36.19	1398	3159	.9295
364.5	77.55	2255	2942	1.074

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

[5] C. T. Zahn, Phys. Rev. **27**, 329 (1926).

[6] W. Pauli, Jr., Zeits. f. Physik **6**, 319 (1921).

[7] L. Pauling, Phys. Rev. **29**, 145 (1927).

[8] Van Vleck, Phys. Rev. **29**, 727 (1927).

The experimental results are recorded in Table I. The actual observed value of $(\epsilon-1)$ was made between the pressure p (recorded in the second column) and a pressure of about 2 cm Hg rather than vacuum, since complete evacuation insulates the condenser plates thermally and thereby prevents temperature control. Since this lower pressure is relatively small no appreciable error is introduced by assuming that $(\epsilon-1)$ is proportional to the pressure and correcting the observed value accordingly to correspond to the full pressure p. This corrected value of $(\epsilon-1)$ for the pressure p is given in the third column. The value of v is gotten by correcting the ideal value $T/273p$ by the use of the van der Waals' constants obtained from Landolt-Börnstein. The values of $(\epsilon-1)v$ given in the fourth column are really values of $(\epsilon-1)$ referred to the ideal number of molecules per cc under S.P.T. conditions; that is, referred to constant density. For a molecule of zero electric moment these values of $(\epsilon-1)v$ should not vary with the temperature; but for a polar molecule they should increase more and more rapidly with decreasing temperature.

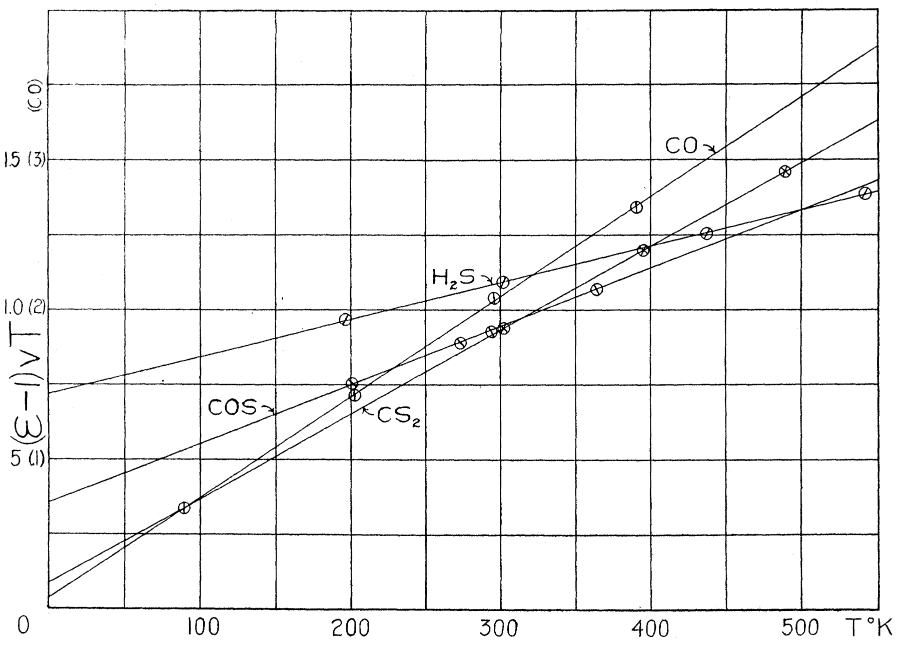

Fig. 1. The Debye function $(\epsilon-1)vT$ as a function of T.

In Fig. 1 is plotted the Debye function $(\epsilon-1)vT$ against the temperature T for the purpose of determining the intercept B and then the electric moment μ. In Table II are given the values of A, B, and μ determined from the Debye lines of Fig. 1.

The H_2S was generated by dropping sulfuric acid onto sodium sulfide; it was then passed through concentrated sulfuric acid and through a P_2O_5

CO was produced by heating sodium formate with concentrated sulfuric acid and freed of CO_2 by passing it through potassium hydroxide. It was dried by passing it through a P_2O_5 tube, and further purified by passing it through a liquid air trap.
tube to absorb water vapor, and later fractionally distilled with the aid of liquid air.

TABLE II. *Debye constants.*

Gas	$A \times 10^6$	B	$\mu \times 10^{18}$ (c.g.s. e.s.u.)
H_2S	1223	0.722	0.93_1
CO	670	0.007_8	0.10
CS_2	2798	0.089	0.32_6
COS	1970	0.352	0.65_0

COS was made by dropping H_2SO_4 (5 volumes acid to 4 volumes H_2O) onto potassium thiocyanate. Then it was passed through potassium hydroxide solution to absorb CO_2, and through a charcoal tube to absorb other impurities, and then through calcium chloride, and finally it was distilled and stored over P_2O_5.

In order to obtain pure gaseous CS_2 first liquid CS_2 was purified by shaking it with mercury and mercuric sulfate until the unpleasant odor disappeared. Then it was evaporated into an evacuated vessel and stored over P_2O_5 until used. Each time either of the gases was used it was redistilled or, in the case of CO, passed through a liquid air trap. Whenever it was possible the gas was frozen and any non-condensible gases present were pumped off.

In the case of CS_2 some difficulty was encountered on account of the solubility of CS_2 in the small amount of grease collected around the stopcocks. The grease itself has no appreciable vapor pressure but there is a possibility that chemical action might occur. Since the results were very accurately reproducible for different specimens of the gas and with varying pressure conditions it is believed that no error was introduced by the presence of the grease. It is proposed, however, in connection with other experiments on vapors to make in the near future measurements on CS_2 at higher pressures and temperatures with an arrangement of apparatus which will obviate the above mentioned difficulty.

COMPARISONS WITH OTHER DATA

(a) *v. Braunmühl's data.* As was previously stated, v. Braunmühl[3] has published values for the electric moment of HCl and H_2S. His values differ widely from the values obtained with the apparatus used here. This difference, as will be seen, cannot be explained on the basis of a calibration error. v. Braunmühl has made no attempt to make an absolute calibration of his apparatus but has standardized the apparatus by taking the value of the dielectric constant of air under S.P.T. conditions from Landolt-Börnstein, 1.000547. This value should be compared with the value 1.000572[2] previously published. If the errors are purely calibration errors one would expect all $(\epsilon-1)$ values to bear the constant ratio $547/572=0.956$; that is v. Braunmühl's values of $(\epsilon-1)$ should be consistently 4.4 percent less than ours, and his values of μ should be 2.2 percent less than ours. Actually his μ values are *greater* than ours in these two cases. The inconsistencies in the ratios of Table III show that there are present errors other than calibration errors. H. A. Stuart[9] has pointed out a possible source of error in v. Braunmühl's work; namely, that he always compared the dielectric constant to be measured with that of oxygen at given pressures and at the same temperature as that of the other gas, assuming that the dielectric constant per molecule of oxygen is independent of temperature. According to Stuart recent accurate measurements seem to indicate that there is a definite small variation of the dielectric constant of oxygen with temperature, independent of the density variation. v. Braunmühl's data could no doubt be corrected on the basis of accurate measurements of oxygen at the various temperatures and pressures he used.

TABLE III.

Gas	*v*. Braunmühl	Zahn Zahn and Miles	Ratio $(\epsilon-1)^{1/2}$ or μ
$(\epsilon-1)$ Air	0.000547	0.000572	0.978
$(\mu\times10^{18})$ HCl	1.118	1.034	1.081
$(\mu\times10^{18}$ H_2S	1.101	.931	1.183

(b) *Watson's data.* Within the last year H. E. Watson[10] has made measurements with apparatus almost identical to ours on NH_3, PH_3, and AsH_3, and air and CO_2 for the purpose of comparison. Table IV gives a comparison of his work with ours. For the two gases considered in this table the differences can be explained fairly satisfactorily by differences in calibration, since Watson's $(\epsilon-1)^{1/2}$ values are about 2.5 to 3 percent higher than ours in both cases.

TABLE IV.

Gas	Watson	Zahn	Ratio $(\epsilon-1)^{1/2}$ or μ
$(\epsilon-1)$ Air S. P. T.	0.000601	0.000572	1.025
$\mu\times10^{18}$ NH_3	1.48_5	1.44	1.031

(c) *Jona's data.* A similar comparison is given in Table V for Jona's[11] data. Since Jona found an anomalous behavior of the dielectric constant near the liquefaction point of these gases and since he also found a moment for CO_2 which almost certainly has none,[9] it is not surprising that the ratio is not constant.

(d) *Stuart's data.* One of the best arguments for at least the consistency of our experiments is shown by Stuart in Table 2 of the above mentioned

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[9] H. A. Stuart, Zeits. f. Physik **47,** 457 (1928).

[10] H. E. Watson, Proc. Roy. Soc. **A117,** 43 (1927).

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

TABLE V.

Gas	Jona	Zahn	Ratio $(\epsilon-1)^{1/2}$ or μ
$(\epsilon-1)$ Air S.P.T.	0.000590	0.000572	1.016
$\mu\times10^{18}$ NH_3	1.53	1.44	1.063
$\mu\times10^{18}$ SO_2	1.76	1.61	1.093

article.[9] Our ratio of the $(\epsilon-1)$ values of CO_2 and air is consistent with that of Stuart and also with that of all the other four observers mentioned excepting Fritts, within the limits of experimental error. Also this very accurate work of Stuart has confirmed the results previously obtained on our apparatus for the electric moment of CO_2; namely, that its moment is zero within the limits of experimental error. A particularly convincing confirmation of this is the excellent agreement of our value of $(\epsilon-1)$ with the value of (n^2-1) recently determined by Fuchs.[12] (In this sense the Maxwellian law should hold only for nonpolar gases.)

(e) *Absolute values.* While the determination of the lead capacities in the high frequency circuits introduces a possible uncertainty in the calibration of our fixed capacities, still there is certain evidence in favor of the absolute values of our apparatus. This has been pointed out by Ebert and Keesom[13] as follows. Our value of ϵ for oxygen, 1.000518, gives for the molecular polarization, $M(\epsilon-1)/\rho(\epsilon+2)$, the value 0.1209. This value is practically coincident; first, with the value 0.1212, which Werner and Keesom[14] have obtained for the greater part of the existence region of liquid oxygen; and also with the value of the molecular *refractivity*, 0.1211, calculated[14] from the data of Levering and Dewar. These measurements of the molecular polarization in the liquid state should be relatively very accurate since the density of the liquid, and hence the measured effect, is about one thousand times as great as that of the gas. The authors claim an accuracy of about 2 per mil. The data of Ebert and Keesom on liquid nitrogen are not used for comparison since they are based on rough preliminary measurements and are not very consistent.

On the other hand one might object to the comparison of the molecular polarization of oxygen in the liquid state with that in the gaseous state. However, this procedure is very probably justified by the fact[13] that the molecular refractivity, 4.395, from data of Gerold,[15] of liquid *nitrogen*, is practically identical to that of gaseous *nitrogen*, 4.396.

ELECTRIC MOMENT OF CO_2 AND CO

Table VI gives a resumé of experimental values of the electric moment of CO_2 and CO determined by Debye's method of temperature variation of dielectric constant. It is interesting to note here that in the case of CO all the values of electric moment given by the various observers agree, well

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[12] O. Fuchs, Zeits. f. Physik **46**, 519 (1928).

[13] L. Ebert and W. H. Keesom, Proc. Roy. Acad. Amsterdam **29**, 1888 (1926). See footnote p. 1192.

[14] W. Werner and W. H. Keesom, Proc. Roy. Acad. Amsterdam **29**, 306 (1926).

[15] E. Gerold, Ann. d. Physique (4) **65**, 93 (1921).

within the limits of experimental error; whereas in the case of CO_2 there is a great divergence between the extreme values given: from zero to 0.303×10^{-18}. It is very difficult to understand why different observers should have such perfect agreement in the case of CO and still such a wide divergence in the case of CO_2. A possible explanation is suggested by the data given in Watson's[10] article on page 58, Table II. He gives two values of $(\epsilon - 1)$ for CO_2 at two different frequencies, 1820 and 1070 kilocycles per second, which differ by about one-half percent. This observed variation with frequency is probably within the limits of experimental error, still one is tempted to suggest that it may be a real variation in the case of CO_2 and that possibly such an effect for CO is negligible. Since the various observations recorded in Table VI are made at probably widely differing frequencies the latter suggestion is not necessarily inconsistent with the facts. Any theory which would explain such a frequency variation would probably involve the temperature and would therefore require a modification of the Debye equation and at the same time explain the discrepancies in the *apparent* value of the electric moment obtained from Debye's equation. Of course, some of these discrepancies may be due to experimental errors such as have been suggested in the case of v. Braunmühl's method; or, indeed, they may all be due to experimental errors.

TABLE VI. *Electric moment of CO_2 and CO.*

Observer	$\mu \times 10^{18}$ (c.g.s.e.s. units)		Observer	$\mu \times 10^{18}$ (c.g.s.e.s. units)	
	CO_2	CO		CO_2	CO
Jona (1919)[11]	0.303		v. Braunmühl (1927)[3]	0.145	0.124
Weight (1921)[16]	0.142	0.118	Forró (1928)[17]	0.208	0.118
Zahn (1926)[1]			Stuart (1928)[9]	0.00	
Zahn and Miles (1928)	<0.06	0.10			

ELECTRIC MOMENT AND MOLECULAR STRUCTURE

H. A. Stuart[9] has recently discussed the question of the molecular structure of CO_2, and has shown that the existing data can in each case be interpreted in favor of a rectilinear, rather than a triangular arrangement of the three nuclei like that of the water molecule. The rectilinear molecule would certainly have a smaller electric moment than the triangular molecule since in the former the induction effects of the two oxygen molecules are opposite and either wholly or partially neutralize each other depending upon the equilibrium conditions of the molecule. For the case of the rectilinear molecule one cannot necessarily assert on the ground of symmetry that the electric moment must be zero.[18] This fallacy becomes evident if one considers the theoretical paper of Heisenberg[19] on the influence of the deformability of ions on the optical and chemical properties of molecules. He has here shown with a plausible model that molecules of the type M_1^+, M_0^{--}, M_1^+

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[16] H. Weight, Phys. Zeits. **22**, 643 (1921).

[17] Magdalena Forró, Zeits. f. Physik **47**, 430 (1928).

[18] cf. J. W. Williams, Phys. Zeits. **29**, 177 (1928).

[19] W. Heisenberg, Zeits. f. Physik, **26**, 196 (1924).

will be built symmetrically around M_0 only if the polarizability of M_0 is below a certain limit which depends on the nature of the binding between M_0 and M_1. If the polarizability exceeds this limit the stable configuration is unsymmetrical. The electric moment resulting from such a dissymmetry would probably be much less than that of the same molecule arranged in a triangle. When the angle of the triangle is not too large the induction effects are almost additive; whereas when the angle is a straight angle, and hence the molecule is rectilinear, the dissymmetry is a differential effect. Heisenberg's theory applies to polar bindings but it is not inconceivable, in fact it seems probable, that such a type of equilibrium might exist in the case of non-polar bindings also.

Referring to Table II it is seen that CS_2 has an electric moment of 0.33×10^{-18} units. In view of the above considerations it is seen that the existence of a moment for CS_2 is not necessarily inconsistent with the absence of a moment in CO_2. Furthermore, it may be only a matter of degree; that is CO_2 may have a very small unmeasurable moment. Also CS_2 is probably a rectilinear molecule. A rough estimate of the moment of CS on the basis of that of COS and of CO would be about 0.75×10^{-18}. A large moment seems consistent with the fact that CS is a solid at ordinary temperatures. Then if CS_2 were a triangular molecule one would expect a moment of at least 0.75×10^{-18}, unless the angle of the triangle were very large and different from 180°, which hardly seems probable. Therefore the actual observed moment of 0.33×10^{-18} might easily be due to the differential dissymmetry associated with peculiar stability conditions introduced by the polarizability of the atoms.

The value of the electric moment of CS_2 here obtained seems to be at variance with the conclusions reached by Williams[18] who finds that CS_2 behaves in the liquid state as a dipole-free solvent. This latter observation may be made consistent with the existence of a moment in the following manner. First of all Williams states that it is very difficult to detect a small electric moment by his method and that the question must finally be decided by taking recourse to investigations on the gaseous molecules. Since the effect of the moment is proportional to its square, the effect for CS_2 is, for example, about one-tenth that for HCl, or about one-sixtieth that for acetone. Furthermore it is quite possible that a large amount of associated molecules of zero electric moment may be formed in the liquid state and thereby reduce the apparent moment to a negligibly small value.

The existence of a moment for CO is quite to be expected owing to the difference between C and O atoms. Finally in the case of COS it seems probable that the molecule is also rectilinear as in the cases of CO_2 and CS_2.

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