THE VARIATION OF DIELECTRIC CONSTANT WITH TEMPERATURE. I. THE ELECTRIC MOMENTS OF THE CARBON BISULPHIDE AND NITROUS OXIDE MOLECULES*

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Abstract

An apparatus has been described which makes it possible to determine dielectric constants of gases and vapors and their dependence on temperature over a range of several hundred degrees. The electric moments of gaseous carbon bisulphide and nitrous oxide have been measured and found to be zero. These results indicate a linear arrangement of the three atoms forming each molecule.

IN RECENT years the study of the constitution of simple polar and non-polar molecules has attracted much attention. There have become available physical methods, among them the dipole theory of Debye,[1] which enable one to determine at least the relative positions of the atoms forming the simpler molecules, and also to say something concerning the symmetry of more complicated ones. In this connection the configuration of the carbon dioxide molecule is of interest. The results of x-ray studies on the solid[2] indicated without any question a linear and symmetrical arrangement of the three atoms which make up the molecule. For a long time, however it was thought that the molecule possessed a finite electric moment, suggesting a triangular arrangement of the atoms for the molecule in the gaseous condition. This conclusion appeared to be substantiated by molecular spectra data, and it was not until Stuart[3] showed its electric moment to be zero that the linear and symmetrical model was accepted for the vapor as well.

There are other triatomic molecules for which electric moment data have been reported in the literature, and in certain cases where rather small values have been reported, the possibility existed that these values were indistinguishable from zero, because of experimental difficulties. Thus an electric moment of magnitude, $\mu = 0.33 \times 10^{-18}$ e.s.u., was reported by Zahn and Miles[4] for the carbon bisulphide molecule, although liquid carbon bisulphide had previously been successfully used as a non-polar solvent for the determination of the electric moment of a number of dissolved molecules.[5] Again,

* This paper is an abstract of a part of the thesis of C. H. Schwingel submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Debye, Handbuch d. Radiologie VI, 597 (1925). Polar Molecules, Chemical Catalog Co., New York, (1929).

[2] Mark, Zeits. f. Elektrochem. **31,** 523 (1925).

[3] Stuart, Phys. Zeits. **47,** 457 (1928).

[4] Zahn and Miles, Phys. Rev. **32,** 497 (1928).

[5] Williams and Ogg, Jr. Amer. Chem. Soc. **50,** 94 (1928).

nitrous oxide shows such a similarity with carbon dioxide in its physical behavior[6] that one might expect it to be non-polar in character as well.

The purpose of this article is to present the results of an experimental study of the temperature variation of the dielectric constant of the vapors of carbon bisulphide and nitrous oxide, and to show that their electric moments do not differ from zero by more than 0.05×10^{-18} in the case of N_2O and by more than 0.02×10^{-18} in the case of CS_2.† The apparatus and method used are briefly described later.

Results

Debye has shown how one may have a dielectric constant, or rather a portion of it that varies with the absolute temperature if it be assumed that there exist permanent electrical dipoles in the molecules. This theory has been amply verified in recent years, so it is only necessary here to give its mathematical result. The total polarization is given by the equation

$$P=\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{d}=\frac{4\pi}{3}N\left[\gamma'+\frac{\mu^2}{3kT}\right] \tag{1}$$

where ϵ is the dielectric constant; M the molecular weight; d the density; N is Avogadro's number; γ' is—a constant; μ the electric moment of the molecule; k the Boltzmann constant; T the absolute temperature; $(4\pi/3)\,N\gamma'$ is the polarization due to deformation of the molecule and $(4\pi/3)\,(N\mu^2/3kT)$ is the polarization due to orientation of the molecule. In the case of gases and vapors this equation may be written with sufficient accuracy in the following form:

$$\frac{\epsilon-1}{4\pi}\cdot\frac{M}{Nd}=\gamma'+\frac{\mu^2}{3kT}=a+\frac{b}{T}$$
$$\text{i.e.}\quad \frac{\epsilon-1}{4\pi}\cdot\frac{m\cdot T}{d}=aT+b=D \tag{2}$$

where m = mass of the molecule in question.

In this equation the function D is a linear function of T. The slope of the line gives the polarization due to deformation, while the "y" intercept $(T=0)$ gives the value of the electric moment squared divided by $3k$, that is, $b=\mu^2/3k$.

The nitrous oxide used was of hospital purity and triple distilled. It was dried thoroughly with P_2O_5 before each determination.

The carbon disulphide, Baker's C.P. analyzed, was allowed to stand over P_2O_5 for several days before use. On distillation high and low-boiling fractions were discarded. It was later distilled directly into the apparatus.

[6] Langmuir, Jr. Amer. Chem. Soc. **41,** 1543 (1919).

† The experimental work reported herein was practically complete when an article by Ghosh, Mahanti and Mukherjee, Zeits. f. Physik **58,** 200 (1929) appeared in which it was found that both nitrous oxide and carbon bisulphide had zero moments. Thus the results of the two investigations are entirely in agreement.

The results of the experimental work are given by Fig. 1 which has, in turn, been constructed from the data given in Tables I and II. All measurements were made at constant pressure. The simple gas law was used to

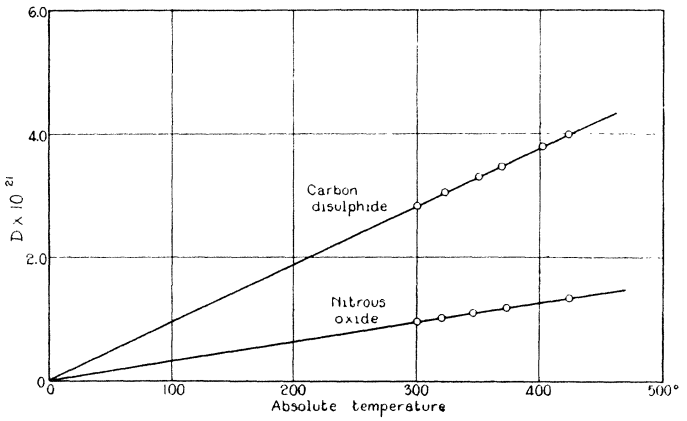

Fig. 1.

calculate the dielectric constant of the gas at 760 mm Hg pressure. The error involved in this method of procedure was proven to be well within the limit of the experimental error of the final result for the electric moments of the molecules.

TABLE I. *Summary of data (Carbon disulphide).*

$T°$	$(\epsilon-1)10^{-5}$ (760 mm)	$D\times10^{21}$	$P=\frac{(\epsilon-1)M}{3d}$
301.6	290	2.84	24.0
322.6	275	3.07	24.2
350.0	250	3.29	23.9
369.8	237	3.45	24.0
400.1	219	3.76	23.9
424.3	206	3.98	23.9

From equation of straight line (Fig. 1), $b=0.001\times10^{-21}=\mu^2/3k$ or $\mu^2=3\times1.37\times0.001\times10^{-37}=0.00041\times10^{-36}$. $\mu=0.020\times10^{-18}$ e.s.u.

TABLE II. *Summary of data (Nitrous oxide).*

$T°$	$(\epsilon-1)10^{-6}$ (760 mm)	$D\times10^{21}$	$P=\frac{(\epsilon-1)M}{3d}$
301.0	993	0.965	8.17
320.5	921	1.02	8.07
347.3	850	1.11	8.10
374.0	780	1.19	8.10
425.6	693	1.35	8.06

From equation of straight line (Fig. 1), $b=0.007\times10^{-21}=\mu^2/3k$ or $\mu^2=3\times1.37\times0.007\times10^{-37}=0.00288\times10^{-36}$. $\mu=0.05\times10^{-18}$ e.s.u.

Experimental Method*

The method used for the determination of the dielectric constants at the various temperatures was similar to that presented by Pungs and Preuner[7] and later improved upon by Zahn,[8] Stuart,[3] Sänger,[9] and others.

Two loosely coupled oscillating circuits, I and II, (Fig. 2) were used to generate constant frequencies, n_1 and n_2. These frequencies, when coupled to a detector, give the frequency $n_d = n_1 - n_2$, which may be detected in the receiver of the detector circuit.

It is evident that a variation of capacity in either circuit will change n_d. If the frequency of circuit II is kept constant, then any change in the frequency of circuit I, due to the change in capacity of C_x, can be detected in

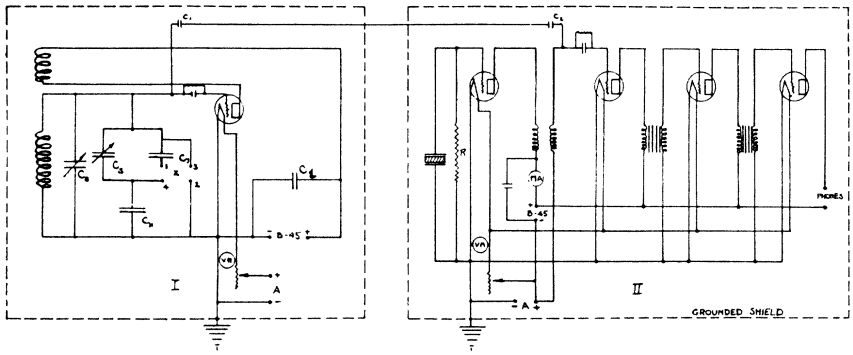

Fig. 2.

the receiver and brought back to the frequency of n_2 by means of a capacity C_s. Circuit I has in series with the gas condenser C_x, a fixed condenser C_y of much greater capacity, and a precision variable condenser C_s. The total capacity is kept constant, determined by the method of counting beats produced in the receivers of the detector circuit. The total capacity of the circuit is changed only by the change in the value of C_x, due to the admission of gases into the previously evacuated condenser; and this is compensated for by means of a change in C_s.

The following equation gives the total series capacity

$$\text{Total capacity} = (1/C_x) + (1/C_y + C_s) \tag{3}$$

If ΔC_x equals the change in capacity due to the admission of gas, and if ΔC_s is the change necessary to bring the circuit to the original frequency of circuit II, then

$$\frac{1}{C_x + \Delta C_x} + \frac{1}{C_y + C_s + \Delta C_s} = \frac{1}{C_x} + \frac{1}{C_y + C_s} \cdot \tag{4}$$

* A diagram of the apparatus without any description was included in an article submitted in June 1929 by one of us (J. W. W.) to the Fortschritte der Chemie, Physik und physikalischen Chemie as part of a discussion of this and related subjects. It is published as Band 20, Heft 5, 1930.

[7] Pungs and Preuner, Phys. Zeits. **20**, 543 (1919).

[8] Zahn, Phys. Rev. **24**, 400 (1924).

[9] Sänger and Steiger, Helv. Phys. Acta. **1**, 369 (1928), et. al.

Solving for ΔC_x, there is obtained

$$\Delta C_x = \frac{C_x^2 \cdot \Delta C_s}{(C_y+C_s)^2+(C_y+C_s+C_x)\Delta C_s} \cdot \tag{5}$$

This can be written with sufficient accuracy

$$\Delta C_x = \frac{C_x^2 \Delta C_s}{(C_y+C_s+\frac{1}{2}\Delta C_s)^2} \cdot$$

If the condenser C_y is very large compared to C_x then a small change ΔC_x will necessitate a large change ΔC_s to bring the circuit to the initial frequency. The frequency of circuit II is kept constant by means of a thermally protected quartz plate.

The electrical connections employed are shown in the figure referred to above. The vacuum tubes were all of the UX 301 type, operated at voltages considerably below rating. It was found that a potential of 4 volts for the oscillating tubes produced the most constant conditions of frequency. The detector tube and amplifiers were operated at full rating. A plate potential of 45 volts was used in all cases. All connections were carefully soldered, and it was found advisable to remove all filament rheostats and voltmeters. The entire apparatus was fastened rigidly in place and thoroughly shielded. Separate shields were used for circuits I and II. Inductances were bakelite tubes wound with silk covered copper wire.

Capacity measurements were made at a frequency of 498.6 kilocycles, corresponding to a wave-length of approximately 600 meters. This frequency was kept constant by means of a quartz crystal, ground and calibrated at the laboratories of the General Radio Company, Cambridge, Mass. For constant conditions of operation, it was found necessary to separate the two circuits by several feet, the only coupling being the single wire as shown in the diagram. Under favorable temperature conditions in the room, the frequency would remain constant to a tenth of a scale division for several minutes, or show a regular increase of several tenths per minute and could be corrected for accordingly. The beats produced in the receiver were amplified by means of two stages of transformer coupled amplification, the zero reading being taken as twenty beats in ten seconds. Capacity C_s was a standard precision condenser of 500$\mu\mu$f capacity, manufactured and calibrated in the laboratories of the General Radio Company. A mica condenser, C_y was calibrated to the latter as standard. All condensers, as well as the entire apparatus, were protected from thermal fluctuations by means of proper insulation.

Gas condenser C_x, was a specially constructed fixed air condenser, made for this particular purpose by the Cardwell Manufacturing Corporation. It is shown diagrammatically in Fig. 3. The construction was of brass and heavily gold plated. The twenty-three plates, each spaced approximately 3 mm, were held in position by means of two strips of Mycalex, the strips being placed as far as possible outside the electrostatic field. The added

capacity correction is negligible, due to their size and position, amounting to not more than 0.2 percent of the total capacity.

This capacity, C_x, was mounted inside a rigidly constructed brass drum (internal diameter, six inches) one terminal of the condenser being grounded to it, and the other leading out through the central glass tube which was used for the entry and removal of gases, and which also contained the thermocouple well. The gas tight drum, containing the condenser, was bolted to the inside of an oil bath, and the capacity when assembled was approximately 444 $\mu\mu$f. The assembly of condenser and thermostat, consisting of (1) thermo-regulator, (2) heater, (3) gas-tight drum, (4) opening for thermocouple, (5) entrance for gas, (6 and 7) condenser terminals, and (8) stirrer, is shown in Fig. 3 and need not be detailed further.

The temperature control bath was a large galvanized iron vessel, insulated completely with "balsam wool," and filled with cotton seed oil. It was kept at constant temperature by means of a heater constructed of nichrome

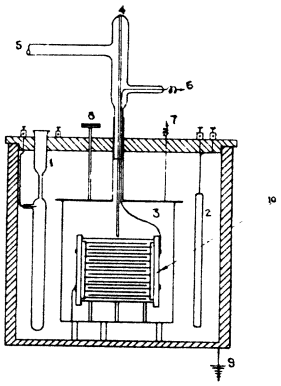

Fig. 3.

wire wound on a grid of "transite." This was immersed directly in the oil. The ordinary make and break type mercury regulator was found satisfactory for keeping the temperature constant to within 0.1° for values up to 100°C, and to within 0.2° for higher temperatures. A calibrated copper-constantan couple placed in close proximity to the condenser served to determine the temperatures. It was found that the temperature became constant after about ten minutes from the time of the gas entry.

In order to evacuate the apparatus, a Hy-Vac oil pump was employed in connection with a water pump. The water pump was used only for the initial clearing out of vapors that might be absorbed by the oil in the pump. In the case of carbon disulphide vapors, and other oil soluble vapors, the system was flushed out thoroughly several times with carbon dioxide, each time evacuating to about 2 cm by means of a water pump. After several of these flushings, the Hy-Vac pump was connected and the system evacuated to 0.01 mm or better. The oil in the pump was changed at frequent intervals. For pressure measurements, a modified U-type manometer was used.

Fig. 4 shows the method used for allowing gases and vapors to enter the condenser chamber. In the case of organic liquids it was necessary to lubricate the stopcocks with a paste made of very finely precipitated silicon dioxide, phosphoric anhydride, and phosphoric acid. This mixture was found to be very satisfactory, having no appreciable vapor pressure, and lasting for the duration of a determination. Outlets g and f were attached to the oil pump and water pump respectively; and d was the connection to the condenser chamber. Stopcock c was used to allow the entrance of gases, while a was the bulb used for holding the liquids which were allowed to evaporate into the system. Liquids were allowed to evaporate into the system until the partial pressure, as read on the manometer, was slightly less than saturation for room temperature; consequently no condensation could take place in the system.

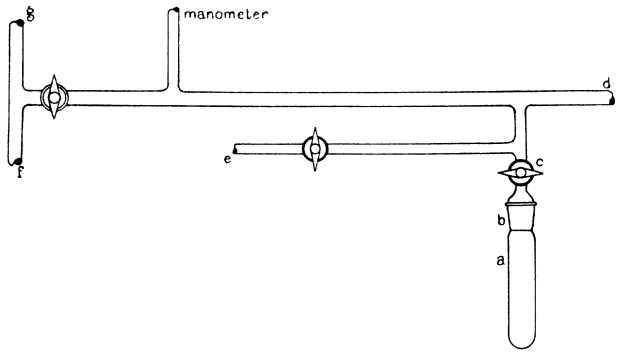

Fig. 4.

To determine the absolute values of the dielectric constants, it was necessary to determine the capacities of all condensers and lead wires.

The capacity of the gas condenser was determined before and after every series of measurements. This was accomplished by means of a mercury switch z, Fig. 2. By connecting 1 and 3, the fixed condenser C_y is short circuited. Then C_x and C_s are connected in series and C_s adjusted to fixed frequency corresponding to capacity C_s'. Then C_x was short circuited by connecting 2 and 4, and C_s adjusted to the original beat frequency, or, in other words, until the original capacity had been reached. Calling the new position C_s'', the equation of the series capacity will be,

$$\frac{1}{C_s''}=\frac{1}{C_x+X}+\frac{1}{C_s'} \tag{6}$$

where X is the capacity of the lead wire from C_x to C_s and to z. Solving

$$C_x+X=\frac{C_s'\cdot C_s''}{C_s'-C_s''}=C. \tag{7}$$

The value for X, calculated from radio formulae was 10.6 $\mu\mu$f, with a maximum variation of 2 $\mu\mu$f. This amounts to not more than 0.5 percent of the total capacity.

The values for the dielectric constants were calculated according to the equation,

$$\epsilon - 1 = \frac{\Delta C_x}{C - X} \tag{8}$$

where C_x is the capacity before the admission of vapor, including X, the lead capacity.

Combining Eqs. (5), (7), and (8)

$$\epsilon - 1 = \frac{C^2}{(C_y + C_s + \frac{1}{2}\Delta C_s)^2} \cdot \frac{\Delta C_s}{C - X} \cdot \tag{9}$$

Errors in the determination of C_x amount to not more than 0.5 percent, in C_y not more than 1.5 percent, and in ΔC_x not more than 1.5 percent. Since errors in the temperature and pressure measurements are small in comparison, the total error in a dielectric constant determination will not be more than 1.5 percent.

For determining values of ΔC_s, the system was flushed out several times and evacuated. After constant temperature conditions were attained, C_s was adjusted to the beat frequency, twenty in ten seconds. Having taken the reading of C_s', the cock was opened to allow the gas or vapor to enter the condenser chamber. When constant temperature conditions had again been attained C_s was adjusted to the capacity corresponding to the original beat frequency, C_s''. The reading C_s' and the difference between C_s' and C_s'' or ΔC_s were substituted in formula (9), along with predetermined values of C, C_y and X. By this means $\epsilon - 1$ is evaluated directly. Any slight drift in C_s must have been predetermined, and taken into consideration.

For each temperature, five to eight readings were taken, evacuation taking place each time. The time for a single temperature measurement amounted usually to approximately eight hours.

In order thoroughly to test our apparatus the electric moment of the ethyl ether molecule was determined. The result, $\mu = 1.12 \times 10^{-18}$ e.s.u., is in perfect agreement with the recent and now commonly accepted results of Sänger[10] and of Stuart.[11] The electric moment of carbon dioxide was also found to be zero.

Conclusions

The results of this article, with those of Ghosh, Mahanti, and Mukherjee, demonstrate that carbon bisulphide and nitrous oxide do not have finite electric moments.

To explain this fact the simplest assumption is to assign a linear and symmetrical arrangement to the three atoms which form the molecule. It is not our intention, however, to conclude that these are necessarily rigid molecules with which we are dealing. A complete knowledge of the vibration-rotation and rotation spectra of a molecule is also of particular importance in such a study, and these data are unfortunately not available at this time.

[10] Sänger, Leipziger Vorträge, 1929.

[11] Stuart, Zeits. f. Physik **51**, 490 (1928).