

THE DIPOLE MOMENT OF
TRIOXANE VAPOR

by

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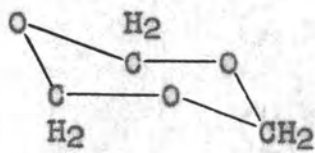
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THE DIPOLE MOMENT OF TRIOXANE VAPOR

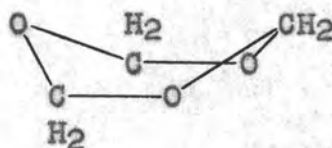
INTRODUCTION

The dipole moment of a molecule is a vector quantity related to its degree of electrical symmetry. If the centers of positive and negative charges in a molecule are not coincident, it possesses a dipole moment equal to the product of the charge and the distance of separation. This quantity is a molecular constant of the order 10^{-18} e.s.u.-centimeters.

Dipole moment studies offer a convenient means of clarifying numerous problems of molecular structure by differentiating between several possible structures. For example, it has been shown (22; 26) that trioxane, the cyclic trimer of formaldehyde (30), can exist in two different configurations. They are usually designated as the "chair" (Z) and the "cradle" (C) forms. The theoretical dipole moments of these two forms were estimated by summing individual bond moments. Values of 2.3 and 0.6 Debyes* respectively were obtained (20).



Z



C

* 1 Debye = 1×10^{-18} e.s.u.-centimeters.

Measurements of the dipole moment of trioxane in benzene solution have been made by Maryott and Acree (20). They found a value of 2.18 Debyes indicating that in benzene solutions trioxane exists principally (if not entirely) in the chair form. A search of the literature revealed no such studies of the vapor phase.

THEORY

If the dielectric constant of a vapor is known as a function of temperature, its dipole moment, μ , can be calculated by application of the well known Clausius-Mosotti equation (6, p.11).

$$P_T = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{D} = \frac{4\pi N}{3} (\alpha_E + \alpha_A + \frac{\mu^2}{3kT}). \quad (1)$$

P_T is generally known as the total molecular polarization. It is equal to the sum of three terms:

$$\frac{4\pi N \alpha}{3} E, \frac{4\pi N \alpha}{3} A, \text{ and } \frac{4\pi N \mu^2}{9kT},$$

which are respectively the electronic, atomic, and orientation polarizations (P_E , P_A , P_O). Since P_E and P_A are not dependent upon temperature, equation (1) can be rewritten as,

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{D} = A + \frac{B}{T} \quad (2)$$

in which A and B are constants. The former is sometimes called the "deformation polarization" and is merely the sum of the electronic and atomic polarizations, the latter being equal to $\frac{4\pi N \mu^2}{9k}$.

Thus if the molecular weight, M, and the density, D, of a substance are known, its total polarization at a temperature, T, can be calculated if its dielectric constant is known at that temperature. If the dielectric

constant is measured at various temperatures and the total polarization calculated and then plotted against the reciprocal of the absolute temperature, a straight line should result having slope B and P_T intercept A. From the value of B thus obtained μ can be readily calculated, since

$$\begin{aligned}\mu &= \sqrt{\frac{9kB}{4\pi N}} \\ &= 0.01273 \sqrt{B} .\end{aligned}\quad (3)$$

In order to avoid the determination of the density of the gas it is usually found satisfactory to assume the validity of the ideal gas law, in which case the molecular polarization is given by,

$$P_T = \frac{(\epsilon - 1) T \times 10^5}{4.810 p}, \quad (4)$$

where p is the pressure in millimeters of mercury and T is the absolute temperature on the Kelvin scale.

Although there are other methods of calculating dipole moments (18, p.42), this method of utilizing the temperature dependence of the polarization is the one which is most generally applicable.

APPARATUS

The measurement of the dielectric constant of a substance involves the measurement of the capacitance of a condenser in which the substance in question is the dielectric and comparing the value thus obtained with the capacitance of the same geometrical arrangement of electrodes with a suitable standard dielectric (e.g., vacuum, air, CO₂, etc.).

For this purpose a condenser cell was designed into which the vapor sample could be introduced and which would withstand the desired range of temperature (which in this case was chosen to be from room temperature to around 200°C.). A cell which had been constructed earlier for use with gases at room temperature could not be employed since polystyrene had been incorporated as the insulating material. This of course would not withstand the high temperatures necessary for the proposed measurements. Thus, the first consideration was of the construction of a suitable cell.

Figure 1 shows the cell which was finally constructed. The electrodes are two sheet nickel cylinders spot-welded to nickel rods which are in turn welded to tungsten supports. The tungsten supports were sealed through a uranium glass press-seal. A graded seal was made to the

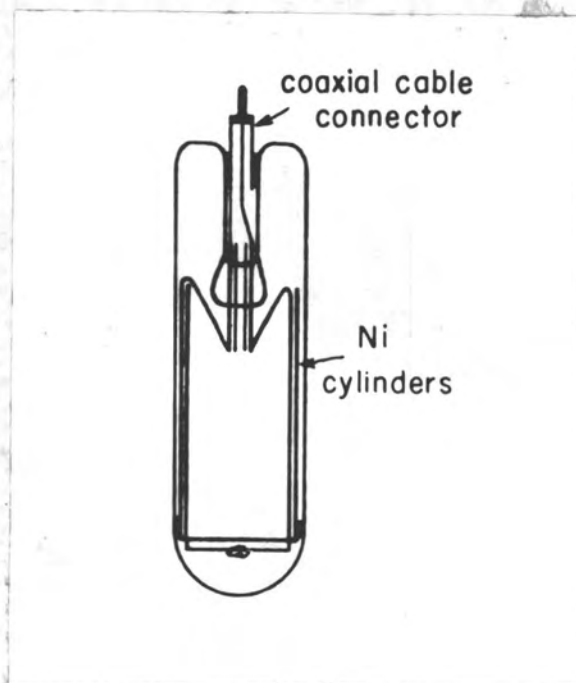


FIGURE 1
CONDENSER CELL

pyrex envelope of the cell through a short section of nonex glass tubing. Spacing of the cylinders was maintained at the bottom end by tungsten wires sealed into uranium glass beads. Small clips were sprung against the inside of the pyrex envelope to add to the mechanical rigidity of the electrodes.

In order to provide for the introduction of samples and standard substances into the cell, the vacuum system shown in Figure 2 was constructed. By closing stopcock A the righthand section can be isolated from the rest of the system. This part was wrapped with asbestos and

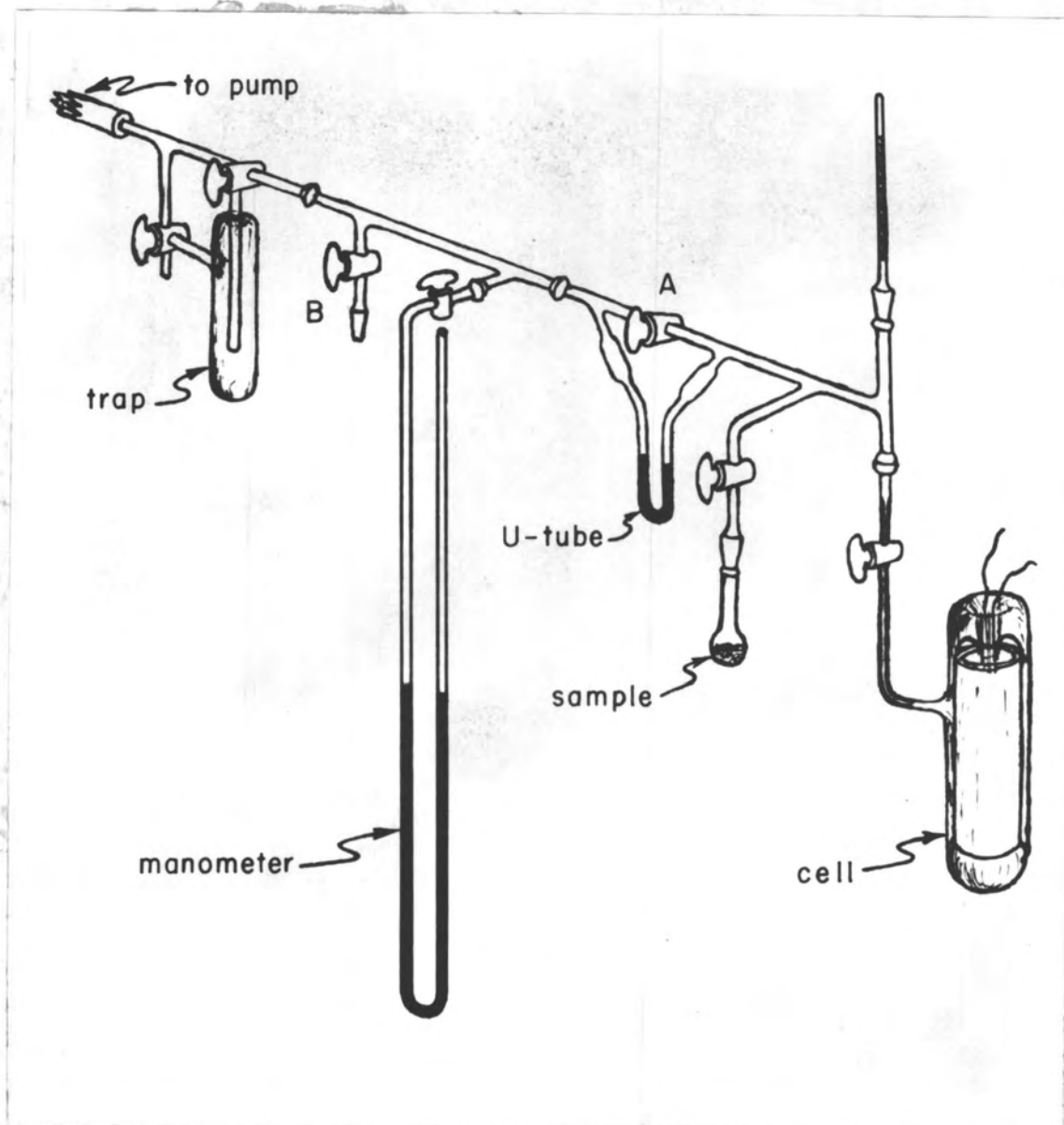


FIGURE 2
VACUUM SYSTEM

electrically heated to prevent the condensation of trioxane. The heating coil was extended down over the mercury in the U-tube to keep the trioxane from condensing on the surface of the mercury. A variable transformer was used to control the heating coil so that the temperature of the system could be adjusted to approximately 120°C.

The next problem was one of adequate thermostating of the cell at any desired temperature over the required wide range. To accomplish this the cell was submerged in a cottonseed oil bath. Cottonseed oil was employed because of its excellent dielectric properties as well as its ability to withstand the maximum of the desired temperature range. The bath used was a cylindrical metal tank with a capacity of about four gallons. This was wrapped with several layers of rock-wool insulation sandwiched between asbestos paper. The bath was heated with three 250 watt knife heaters which were controlled by a thermo-regulator designed and constructed by F. W. Karasek (14).

This thermo-regulator utilizes a Western Electric type 14A thermistor as the temperature sensitive element. The thermistor is included in one arm of a Wheatstone type bridge. After proper amplification the unbalance or "null" signal from the bridge is fed into a discriminator

circuit which serves to control a pulse generating circuit. The generated pulse is applied to the grid of a 6J6 thyratron tube connected in series with the heaters. Thus, its firing is regulated to allow just enough power to the heaters to maintain the desired bath temperature. By employing suitable multiplying resistors, the desired temperature range can be conveniently covered. This principle makes possible continuous variation of the heater current rather than the on or off control of most conventional thermo-regulators. With this device it was found to be quite possible to control the temperature of the bath to within 0.01°C . or better over the desired range.

The next consideration was of the method of indicating small changes in the capacitance of the condenser cell. There are two methods in common use for measuring capacitance with high precision. One method utilizes an impedance bridge of the Wheatstone type, the capacitance cell forming one arm of the bridge. The resistive and reactive components of the cell impedance are cancelled by proper adjustment of circuit components in an adjacent arm of the bridge.

The other method is based on the heterodyne or "beat" principle (5; 11). The condenser cell is incorporated in the resonant circuit of a radio-frequency

oscillator. Thus, any change in cell capacitance results in a change in the frequency of oscillation. The output frequency of the oscillator is compared with some appropriate frequency standard. Usually this system is used as a "null" method, i.e., after a change in cell capacitance the oscillator is retuned to its initial frequency using a standard precision condenser in parallel with the cell. The amount of capacitance by which the standard condenser must be changed to produce the original frequency is then equal to the change in cell capacitance. A device of this latter type has been in use for several years in the physical chemistry laboratory for determining the dielectric constants of solutions (5). This instrument was set up and tested. It was found that it lacked the much higher sensitivity required for vapor phase measurements. The limiting factor appeared to be the precision condenser, which could not be adjusted finely enough to achieve accurate setting. This method was temporarily abandoned while tests were made on the bridge method.

A General Radio 516-C Radio-Frequency Bridge was set up in conjunction with an RCA 167A signal generator and a Halicrafters S-20R communications receiver as shown in Figure 3. A vacuum tube voltmeter was connected to the A.V.C. line of the receiver. The A.V.C. voltage is

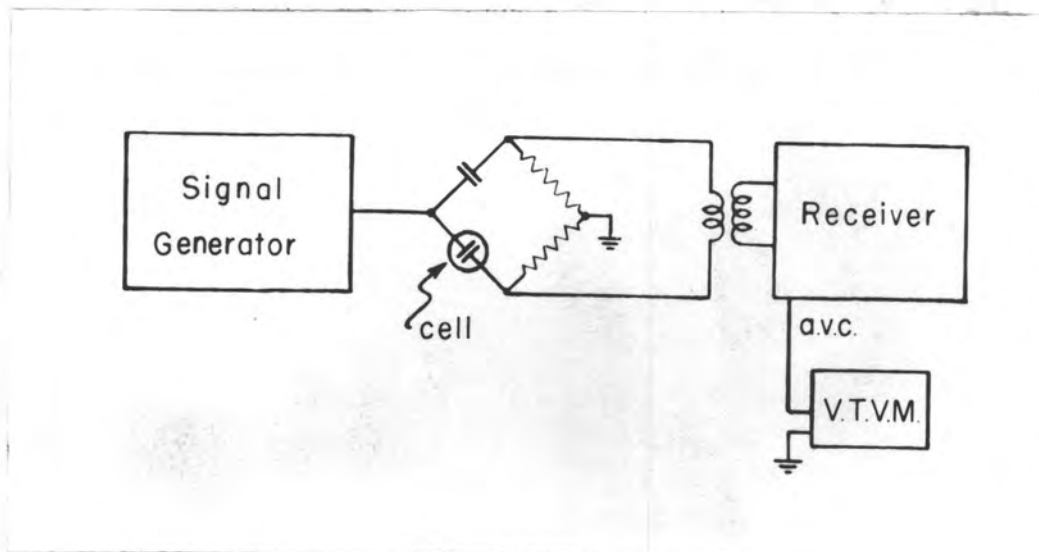


FIGURE 3
BRIDGE APPARATUS

very sensitive to input signal strength provided that the signal is maintained above a certain "threshold" level. The bridge was therefore used in the unbalanced condition making any precision balancing condenser unnecessary.

A comparison of the sensitivities of the two methods revealed that the former, the heterodyne apparatus was apparently slightly superior. For this reason and because it seemed to offer more possibility of further refinement the heterodyne method was chosen for further study.

Before any further work with this apparatus could be attempted, a precision balancing condenser was needed so that precise tuning could be accomplished. Several

low-range precision condensers are described in the literature. Of these the one by Ward and Pratt (31) appeared to be the most likely for the purpose. A greatly modified form of their condenser (Figure 4) was finally constructed.

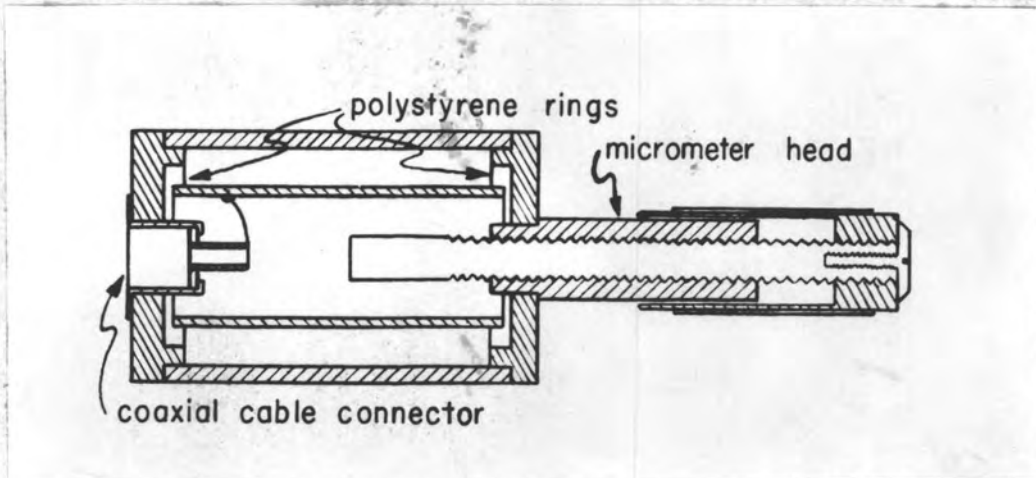


FIGURE 4
MICROMETER CONDENSER

Tuning is accomplished by adjusting the micrometer head, thus moving the inner rod along the axis of the cylinder which acts as the second electrode of the condenser. Over the center portion of the scale where "end effects" are negligible extremely good linearity can be obtained. With this condenser no difficulty was encountered in "zero-beating" the variable frequency oscillator against a crystal controlled fixed oscillator operating at a frequency of about one megacycle per second.

Due to the tendency for the oscillators to "lock" as their frequencies approach each other, the following scheme was adopted (Figure 5). The beat-note from the mixer is applied to the vertical input of an oscilloscope,

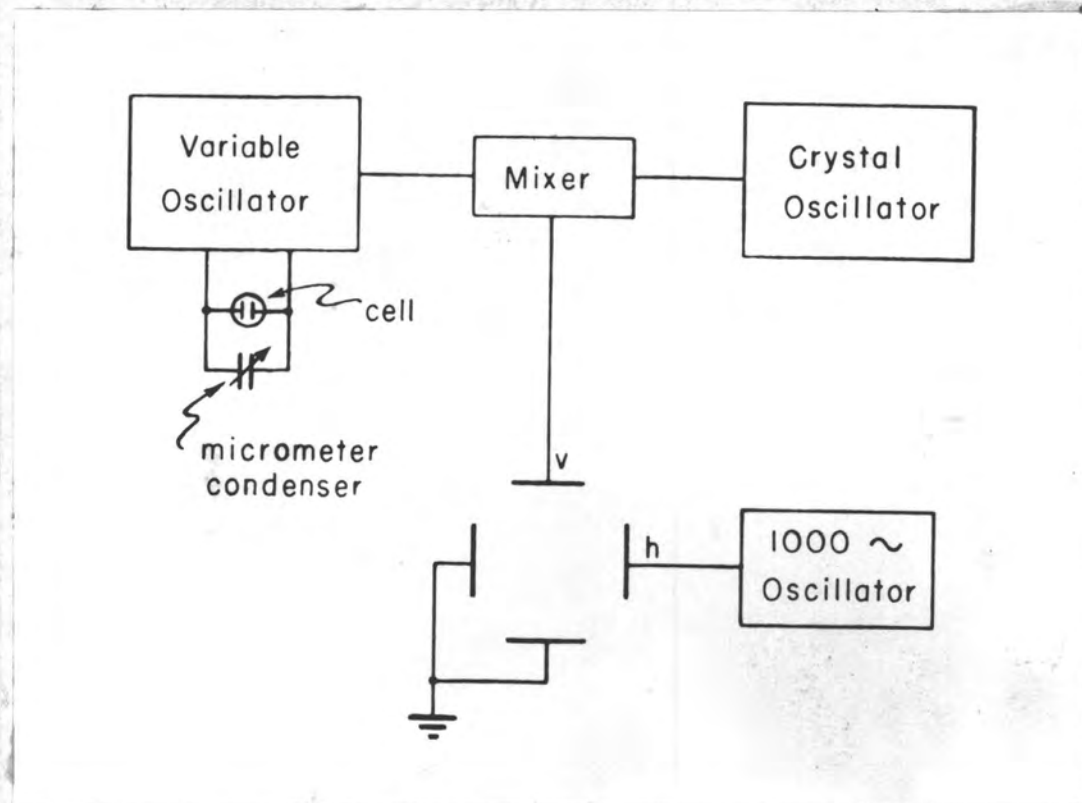


FIGURE 5

HETERODYNE SYSTEM

a 1000 cycle per second tuning fork oscillator is used as the horizontal sweep. When any capacitance change takes place in the tuned circuit of the variable oscillator, a change in the frequency of the beat-note from the mixer stage results. When the frequency of the

beat-note becomes 1000 cycles per second, the Lissajous pattern on the oscilloscope screen will be a stationary ellipse.

The frequency of the fixed oscillator is controlled by a Bliley type BCX crystal at around 999.5 kilocycles per second. From the data supplied by the Bliley Company, the temperature coefficient of the crystal was calculated to be approximately 5 cycles per second per degree centigrade. In an effort to improve oscillator stability the crystal oven shown in Figure 6 was constructed. A Western Electric type 14B thermistor in a Wheatstone bridge is used to control the temperature of the

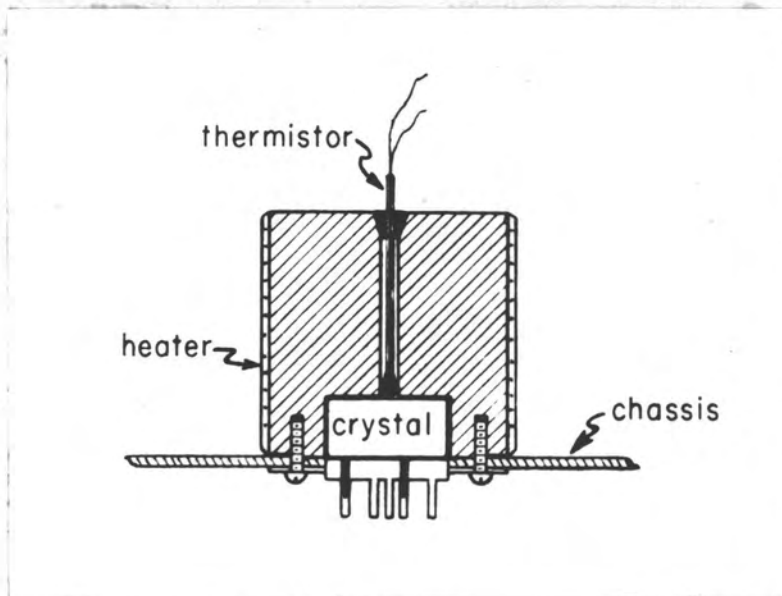


FIGURE 6

CRYSTAL OVEN

oven. The signal from the bridge is amplified to operate a relay as shown in Figure 7.

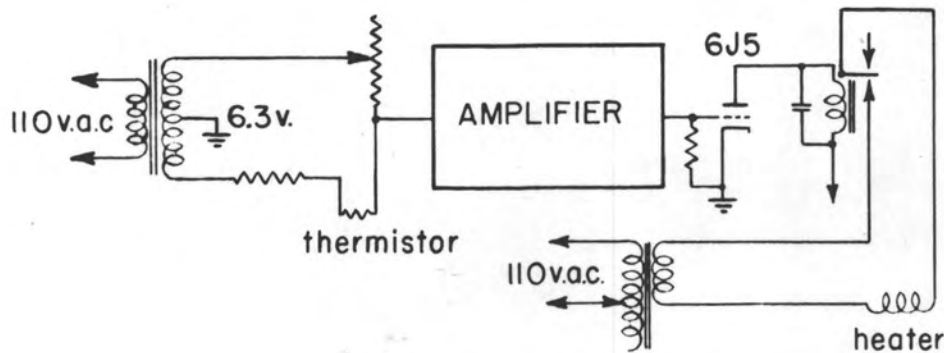


FIGURE 7

CRYSTAL OVEN THERMOSTAT

Thermostating the crystal in the fixed oscillator resulted in but a slight improvement in the stability of the system. The several cycle per second instability is apparently due primarily to other factors, such as mechanical vibrations and variations in the temperature of other circuit components.

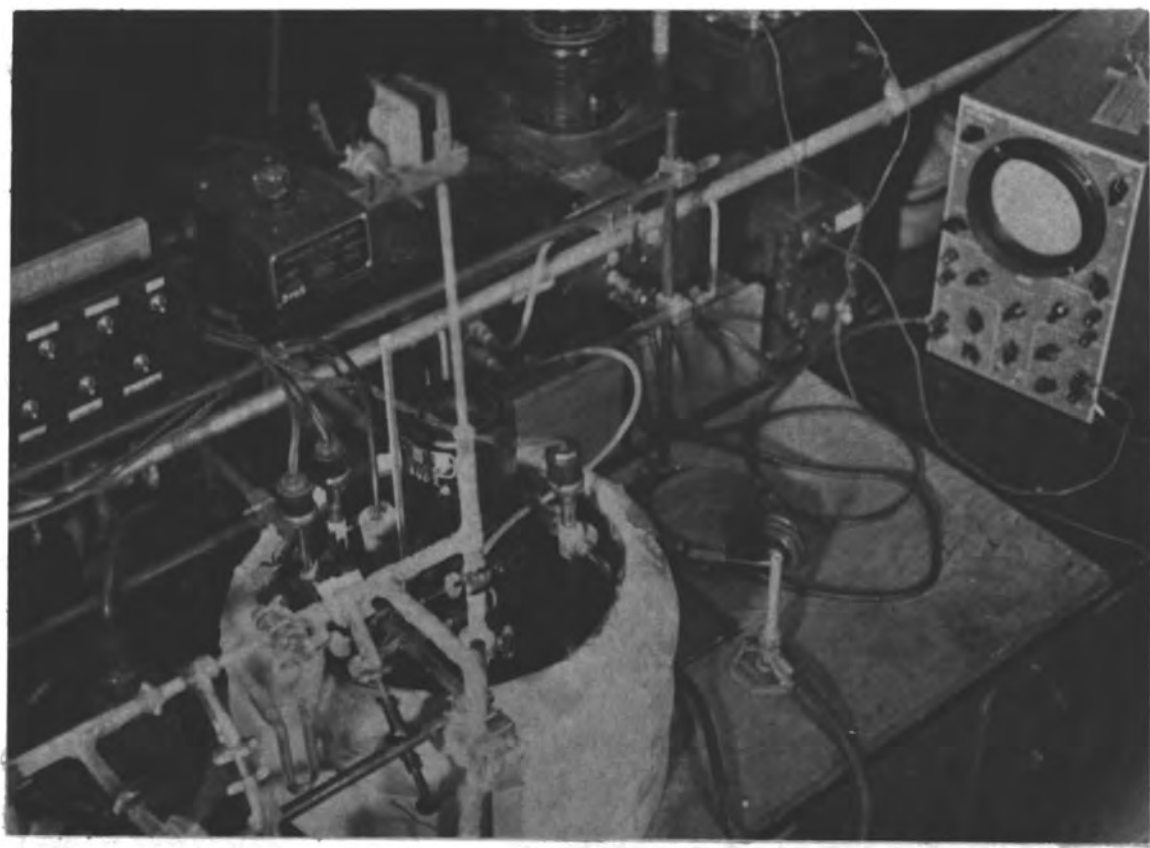


FIGURE 8
COMPLETE APPARATUS

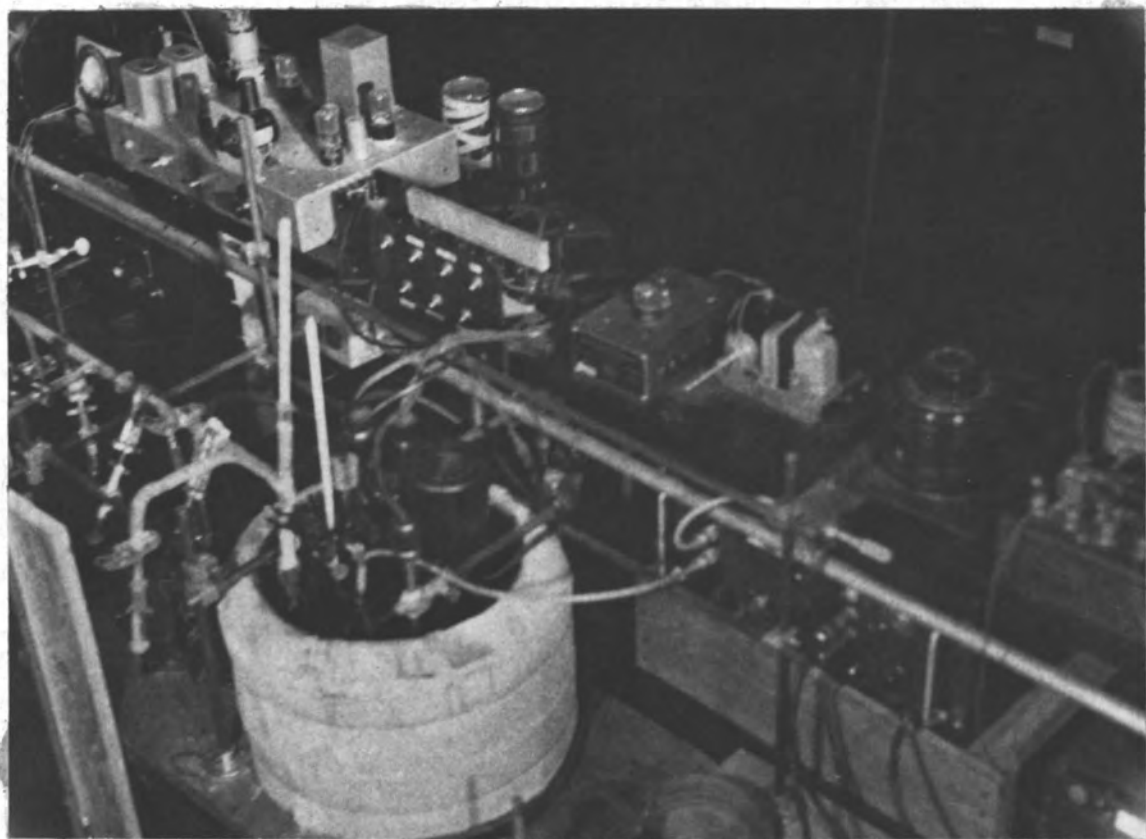


FIGURE 9
COMPLETE APPARATUS

PROCEDURE

Before making any measurements the constant temperature bath is set to the desired temperature and the crystal thermostat and the oscillators and associated circuits allowed to warm up for several hours. The vacuum system is then pumped down to 0.1 millimeters of mercury or less. With stopcock A (Figure 2) closed, the sample is gradually heated. As the pressure in the right hand side of the system increases, stopcock B is carefully "cracked" to keep the pressure difference as indicated by the U-tube to within a few centimeters. When the entire system is up to the desired pressure, the micrometer condenser is adjusted until an ellipse is seen on the oscilloscope screen. It was found advisable to turn off the stirring motor in the oil bath while setting the micrometer condenser in order to reduce interference.

As soon as the condenser is properly adjusted and its setting recorded, stopcock A is opened and the entire system again evacuated. A trap immersed in an ice bath is used to keep trioxane from condensing in the pump. With the system evacuated the micrometer condenser is again set to balance and its reading subtracted from the one found with the trioxane in the system to give Δm .

The relationship between this quantity and the dielectric constant of the vapor was established by passing carbon dioxide into the system through a CaCl_2 drying tower. With the introduction of each carbon dioxide sample, a variable condenser in parallel with the micrometer condenser and the cell was readjusted so that the measurements could be made at various points over the entire range of the micrometer condenser (Figure 10).

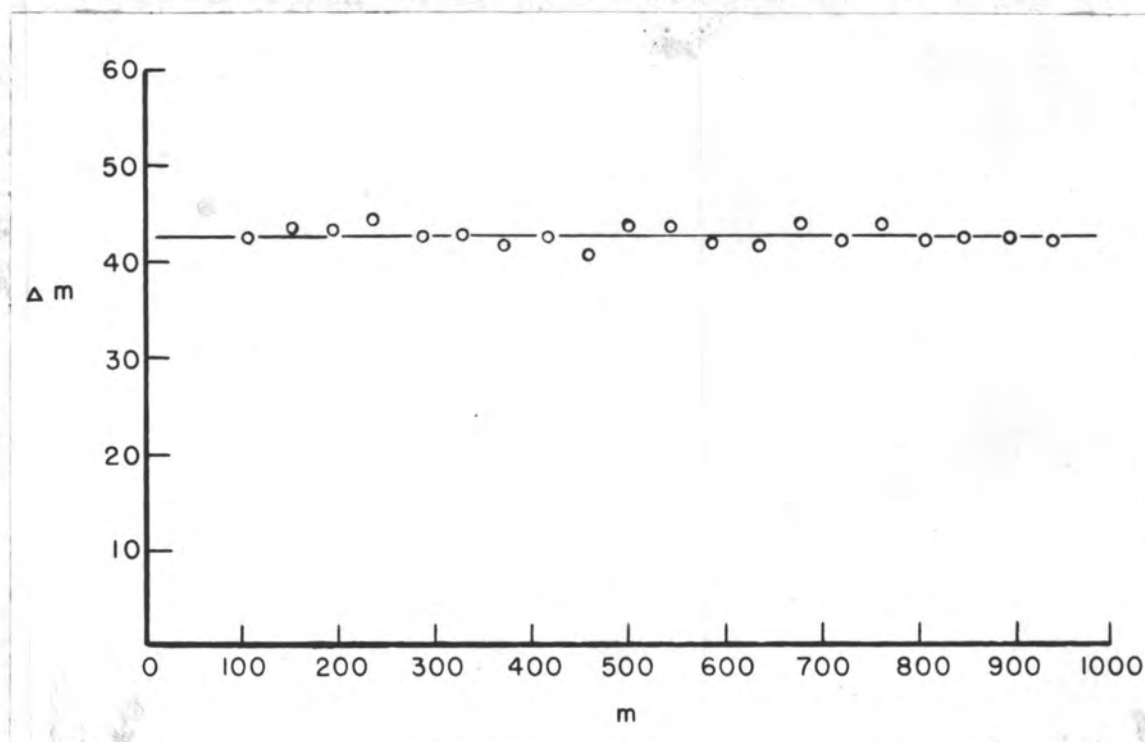


FIGURE 10

LINEARITY OF MICROMETER CONDENSER

This procedure served to effect the calibration of the condenser as well as to check its linearity.

Thirteen absolute determinations of the dielectric constant of carbon dioxide have been made. These are listed in Table I. The various values of $\epsilon - 1$ have been corrected to 25°C. and 760 mm. pressure. Other

TABLE I
THE DIELECTRIC CONSTANT OF CARBON DIOXIDE (19)

$\epsilon - 1 \times 10^4$	Author	Reference
8.67	Boltzmann	1
9.02	Klemencic	16
9.11	Pohrt	23
9.19	Riegger	25
10.13	Jona	13
8.69	Fritts	9
8.91	Zahn	33
9.20	Braunmühl	2
9.04	Stuart	27
8.82	Forro	8
9.06	McAlpine and Smythe	21
9.06	Watson	32
9.05	Kubo	17

determinations at high pressures have been made by Keyes and Kirkwood (15; 28) and John (12). Of the tabulated results, those due to Stuart, McAlpine and Smythe, and Watson are probably the most accurate. Therefore, the value of $\epsilon - 1 = 9.05 \times 10^{-4}$ was chosen as the standard for this work. Since the deviation from the mean value of $\Delta m = 42.6$ appears to be random (Figure 10) the condenser is assumed to be linear. The relation between the change in micrometer condenser setting, Δm , and the

dielectric constant is then:

$$\begin{aligned}\epsilon - 1 &= \frac{9.05 \times 10^{-4}}{42.6} \Delta_m \\ &= 2.11 \times 10^{-5} \Delta_m. \quad (5)\end{aligned}$$

The trioxane used was "High Purity Trioxane" obtained from E. I. du Pont de Nemours & Co. Upon distillation it forms long needle crystals. It is claimed to be better than 99.5% pure.

RESULTS AND CONCLUSIONS

The experimental results are summarized in Table II. The tabulated values of $\epsilon - 1$ were calculated from the observed changes in micrometer setting, Δm , using equation (5). Each value of Δm shown represents the average of three or more determinations. In order to calculate the total molecular polarization at a given temperature, the molar volume, $\bar{V} = \frac{M}{D}$, of the vapor must be known at that temperature. Using the ideal gas law to obtain a value of \bar{V} for the vapor, the values of P_T were calculated and plotted against $1/T$, as shown by the dotted line in Figure 11. The curvature at the low temperature end of the range was attributed to the non-ideal behavior of the trioxane vapor.

At temperatures down near the condensation point the molecules of the vapor are close enough together so that errors resulting from the use of the ideal gas law in calculating the molar volume may become appreciable. Also, at these lower temperatures dipole-dipole interactions may result in further non-linearity in the variation of the polarization with temperature. Since no critical constants or other equation of state data could be found for trioxane it was desirable to obtain some

TABLE II
EXPERIMENTAL RESULTS

p (m.m.)	Δm	$(\epsilon - 1) \cdot 10^3$	$P_T(\text{c.c.})$	$1/T \cdot 10^3$
760	340.0 ± 1.0	7.16	77.0	2.54
760	309.9 ± 2.5	6.52	71.8	2.48
760	289.8 ± 3.5	6.10	68.1	2.45
760	264.1 ± 3.0	5.56	64.4	2.37
760	236.3 ± 0.5	4.97	58.8	2.31
760	208.8 ± 3.5	4.39	54.4	2.21
193	80.1 ± 2.0	1.69	71.4	2.54
368	158.1 ± 2.5	3.34	74.1	2.54
625	273.6 ± 1.5	6.27	76.2	2.54
311	114.2 ± 3.0	2.43	66.3	2.45

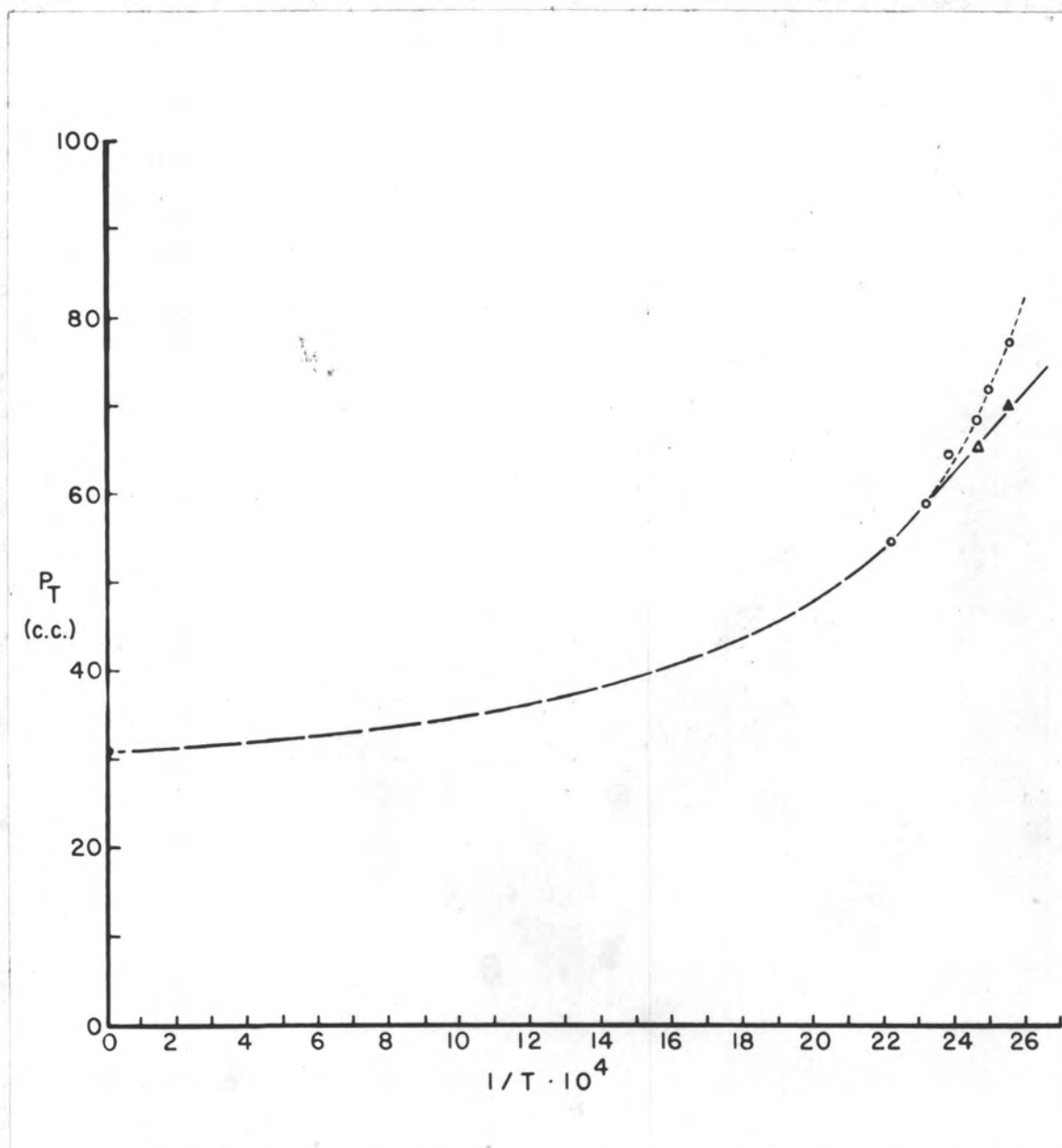


FIGURE 11
VARIATION OF P_T WITH $1/T$

other estimate of the magnitude of the error introduced in P_T as a result of assuming ideal behavior of the vapor.

Such an estimate was made by measuring the dielectric constant of the vapor at various pressures at a fixed temperature. The polarization, P_T , could then be calculated and plotted against pressure. The value of P_T found by extrapolating this curve to zero pressure should represent a more accurate determination of the polarization. The values of P_T obtained by this procedure are also plotted in Figure 11 (solid line).

The slope, B , of this curve is 42,000, giving a value of $\mu = 2.6$ Debyes. This is in fair agreement with the value of 2.3 Debyes estimated for the "chair" configuration of the molecule by Maryott and Acree (20).

In the "chair" model (Figure 12), the symmetry operations are: E , $2C_3$, $3C_2$, constituting the group C_{3v} . All six O-C bonds are equivalent. The C-H bonds fall into two sets of three symmetric members each. The dipole moment necessarily lies along the symmetry axis, C_3 . Thus, the problem of calculating the resultant moment is that of resolving each bond vector along the symmetry axis. Assuming the tetrahedral bond angle of $109^\circ 28'$ for the carbon atoms, one possible configuration of the molecule has three C-H bonds parallel to the symmetry axis and the others set at $109^\circ 28'$. The resultant would then

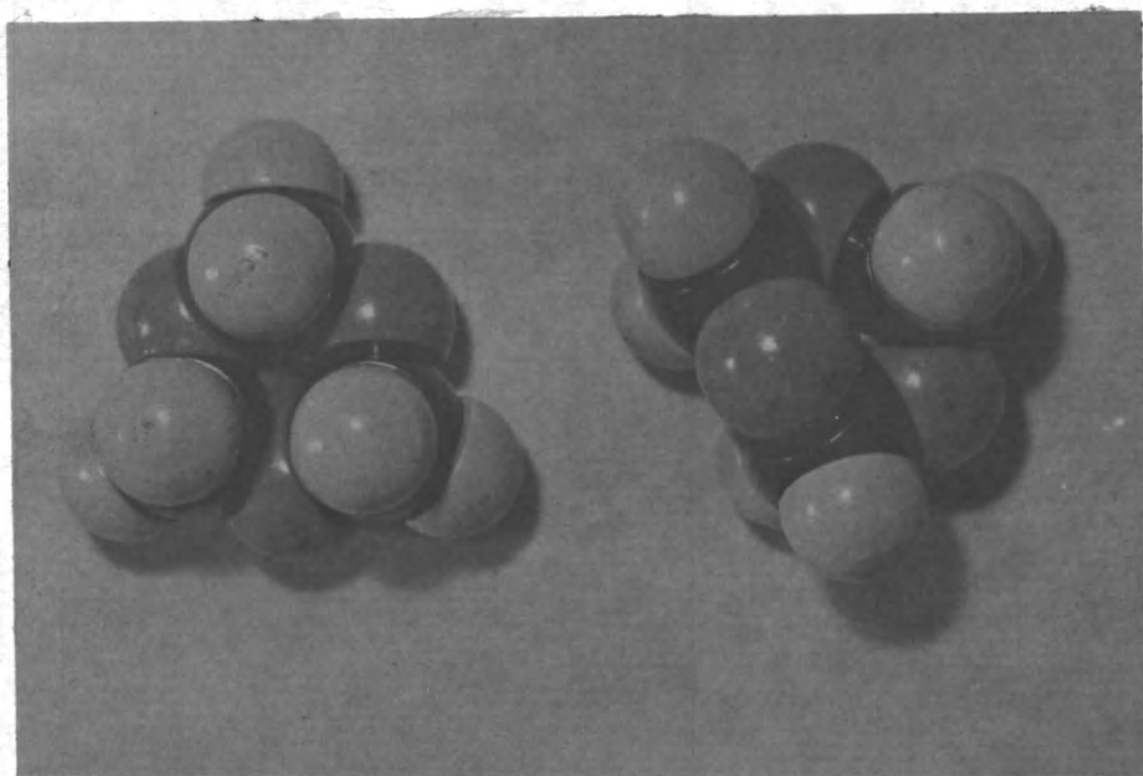


FIGURE 12

"CHAIR" AND "CRADLE" CONFIGURATIONS OF TRIOXANE

be

$$\begin{aligned}\mu &= 3\mu_{\text{CH}} + 3 \cos 109^{\circ}28' \cdot \mu_{\text{CH}} \\ &= 3\mu_{\text{CH}}(1 - 1/3) = 2\mu_{\text{CH}}\end{aligned}$$

for the C-H bonds. To calculate the resultant of the O-C contributions it is necessary to make some assumption about the ring puckering angle. As a rough estimate, one might assume the cosine of the angle between the O-C bond and the symmetry axis to be 1/3. Then the total dipole moment would be given by,

$$\mu = 2\mu_{\text{CH}} + 2\mu_{\text{OC}}.$$

The contributions to the total dipole moment of the C-H and O-C bonds are given by Le Fevre (18, p.64) as 0.4 and 0.7 Debyes respectively. This gives a value of $\mu = 2.2$ Debyes.

Calculations of the dipole moment of the "chair" configuration of trioxane have been made by Calderbank and Le Fevre (4) assuming various bond angles for both the carbon and oxygen atoms. They showed that the estimated value of μ varied from 1.9 to 2.7 Debyes, depending on the particular bond angles chosen. Therefore, the experimentally determined value of 2.6 Debyes is entirely consistent with those estimated by summing individual bond moments.

Some difficulty was encountered when the corrected plot of P_T versus $1/T$ was extrapolated back to infinite temperature in an attempt to obtain an estimate of the polarizability. The intercept of the curve on the P_T axis, and therefore, the polarizability were found to be negative. This, of course, cannot be justified on theoretical grounds. It therefore seemed advisable to attempt a calculation of the induced polarization of the molecule. Two methods of calculating the contribution $\frac{4\pi}{3} N \alpha$ of the induced polarization are suggested by Van Vleck (29, p.60).

By adding the optical refractivities of the atoms in the molecule an approximate value of the induced polarization can be obtained. The contributions of the various atoms are (28, p.34):

$$P_I(C) = 4.86, \quad P_I(H) = 1.29, \quad P_I(O) = 2.90 \text{ c.c.}$$

Thus, P_T for trioxane is approximately 31 cc.

The other method of calculating the induced polarization involves the assumption that the dielectric constant of a compound in the solid state is equal to the square of its refractive index. If the dielectric constant and the density of a solid are known at a temperature well below its melting point, its induced polarization,

$$P_I = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{D},$$

can be calculated. The dielectric constant

of solid trioxane at 20°C. is given by Walker and Carlisle (30) as 3.2 to 3.4. No value could be found for the density of the solid at 20°C. However, its density at 65°C. is 1.17 grams per c.c. (30). The density was therefore taken to be 1.2 grams per c.c., yielding an induced polarization of 32 c.c. This is in excellent agreement with the value obtained by the additivity method.

A value of the induced polarization of around 31 c.c. would seem, therefore, to be a very reliable estimate, although apparently entirely inconsistent with the experimentally determined values of the total polarization. Although the intercept of the curve on the P_T axis is extremely sensitive to small errors in the slope (due to the long distance over which the extrapolation must be made), it is inconceivable that the apparent discrepancy could be due entirely to experimental error.

If the estimated value of the induced polarization is assumed valid, the only reasonable explanation of the apparent anomaly is that the dipole moment is not independent of the temperature. A decrease in the slope of the curve with increasing temperature would correspond to a lower dipole moment at elevated temperatures.

Maryott and Acree (20) estimated a value of 0.6 Debyes for the "cradle" form of trioxane. If it is

assumed that an equilibrium exists between the "chair" and "cradle" forms, the latter being less stable, it would be possible to account qualitatively for the polarization curve.

Estimates of the energy of the reaction "chair" \rightarrow "cradle" for the isoelectronic molecule, cyclohexane, have led to values around 3 kilocalories per mole* (10). At the highest temperature of this investigation (180°C.), the equilibrium mixture should contain roughly a fraction less than $\exp(-3000/RT) = 2.4 \times 10^{-4}$ of the "cradle" form; the dipole moment would thus remain closer to 2.3 than to 0.6 Debyes until temperatures of the order of 1000°K were attained.

Thus, it is concluded that trioxane exists in the "chair" configuration at temperatures below about 200°C. This is in agreement with the infrared spectral data of the compound (7; 24). At elevated temperatures the two forms are in thermal equilibrium. Since thermal decomposition takes place at these higher temperatures (3), experimental verification of this latter conclusion would be somewhat difficult.

*Although this figure is based in part on the well-known barrier to internal rotation in ethane, it may be mentioned that the corresponding barrier for dimethyl ether is of the same order of magnitude.

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