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# The Intramolecular Torsional Potential and Dielectric Properties of 2,3-Butanedione

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*Eastern Illinois University*

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THE INTRAMOLECULAR TORSIONAL POTENTIAL AND  
DIELECTRIC PROPERTIES OF 2,3-BUTANEDIONE  
(TITLE)

BY

GEVERT H. MEYER  
B. S., Quincy College, 1973

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
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1975  
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## ABSTRACT

Dipole moment measurements have been carried out on 2,3-butanedione in solution, pure liquid, and the vapor phase. A dipole moment of  $1.03 \pm .01$  Debye was observed for dilute solutions of 2,3-butanedione in carbon tetrachloride. Pure liquid samples exhibit an anomalous dipole of  $1.56 \pm .01$  Debye. The following results were obtained for vapor phase measurements: 1.04, 1.07, 1.08, 1.11, and  $1.17 \pm .01$  Debye at 310.15, 350.15, 370.15, 431.70 and  $472.10 \pm .02^\circ\text{K}$  respectively.

The acetyl torsional potential was characterized from the observed temperature dependence of dipole moment. This torsional mode was described by a two-parameter potential function:  $V(\theta) = \frac{V_1}{2} (1 - \cos\theta) + \frac{V_2}{2} (1 - \cos 2\theta)$  where  $\theta$  is the acetyl torsional angle. The temperature dependence of the dipole moment was analyzed using statistical thermodynamic methods to determine the internal rotation potential parameters  $V_1$  and  $V_2$ . A numerical least squares fit of the data yields  $V_1 = 2890 \pm 30 \text{ cm}^{-1}$  ( $8.26 \pm .09 \text{ Kcal}$  or  $34.6 \pm .3 \text{ KJ}$ ) and  $0.0 < V_2 < 20 \text{ cm}^{-1}$ .

A two parameter potential function has been employed for the first time to characterize the temperature dependence of the dipole moment. The results of this study indicates that in contrast to glyoxal, the cis isomer of 2,3-butanedione is unstable, and accounts for the failure of other experimental methods to observe this isomer.

## ACKNOWLEDGMENTS

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## INTRODUCTION

In general, it should be expected that 1,2-dicarbonyl compounds may exist as both cis and trans isomers. In these compounds, both the cis and trans isomers would be stabilized by p-orbital overlap and pi bonding between the adjacent  $sp^2$  hybridized carbonyl carbon atoms.

The cis isomer of glyoxal,  $H-C(=O)-C(=O)H$ , the simplest 1,2-dicarbonyl compound has recently been experimentally observed. It was first detected in 1970 by Currie and Ramsey<sup>1</sup> with the appearance of a vibrational band at  $4875 \text{ \AA}^0$  in the uv-emission spectra. It was determined from their studies that the cis isomer lies  $1125 \pm 100 \text{ cm}^{-1}$  above the ground vibrational level of the trans isomer. In 1972, further evidence for the cis isomer was obtained from microwave studies made by Durig, Tong, and Li<sup>2</sup> when they observed the  $1\leftarrow 0$  torsional transition frequency of the cis molecule at  $114 \pm 8 \text{ cm}^{-1}$  which compares with a predicted value of  $107 \text{ cm}^{-1}$  for the molecule in the cis form.

The next simplest 1,2-dicarbonyl compound is 2,3-butanedione,  $CH_3-C(=O)-C(=O)CH_3$ . The existence of 2,3-butanedione in two isomeric forms would also be expected but previous experimental work suggests that it exists only in the trans form. Durig, Hannum, and Brown<sup>3</sup> systematically examined the infrared spectrum of

2,3-butanedione in the solid, liquid, and gas phases. They observed an absorption feature at  $52\text{ cm}^{-1}$  which they have assigned to the acetyl torsion mode (Fatuly and co-workers earlier reported a value at  $48\text{ cm}^{-1}$ )<sup>4</sup>, but no evidence was found for the existence of the cis isomer. In 1973, vapor phase electron diffraction studies by Hagen and Hedberg<sup>5</sup> were carried out on 2,3-butanedione. From their studies, they also concluded that 2,3-butanedione exists only in the trans configuration. They calculated the potential barrier to intramolecular rotation to be 11.4 Kcal/mole ( $3989\text{ cm}^{-1}$ ) using the harmonic oscillator approximation. The diffraction data enabled them to estimate the frequency of the torsional mode about the C-C bond to be  $53\text{ cm}^{-1}$ , which is in good agreement with previously reported infrared observations.

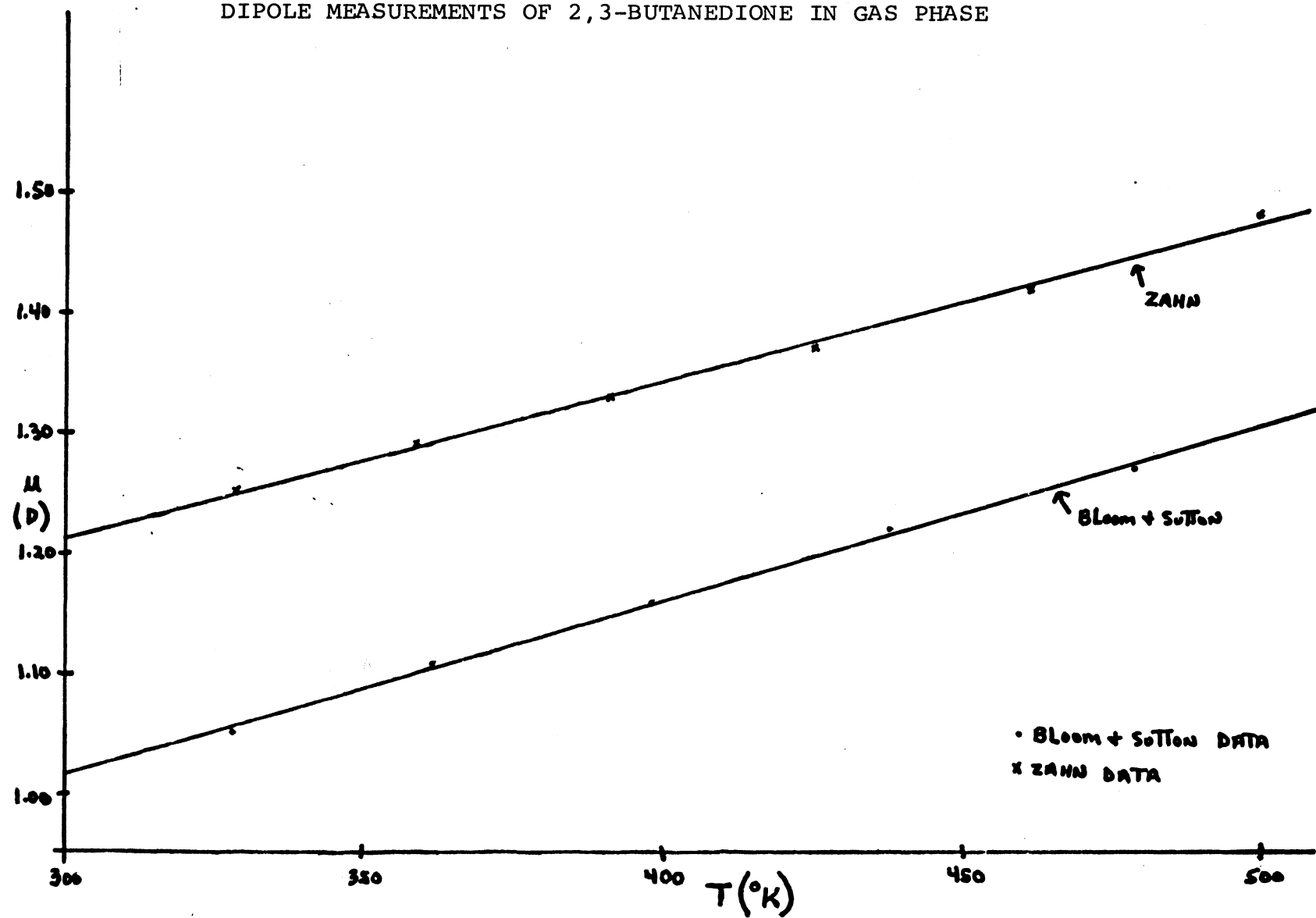
Information about intramolecular rotation about the C-C bond in 1,2-dicarbonyl compounds can also be obtained from the temperature dependence of the dipole moment. In molecules where there are two rotatable dipoles on adjacent carbon atoms, the possibility exists for one dipole to rotate about the C-C bond into the trans position and cancel or nearly cancel the other dipole, or it could rotate into the cis position in which case the resultant of the two dipoles would act in the same direction and give a maximum dipole moment. No temperature dependence of the dipole moment will be observed for cases where free rotation of the dipoles is present and

all positions around the C-C bond are equally probable. In cases where the trans isomer is of lower energy than the cis isomer, i.e. rotation is hindered by a potential barrier, then thermal effects will be observed in the dipole moment measurements. As the temperature of the sample increases, the population of the cis isomer becomes statistically more favored. Therefore an increase in temperature results in a higher boltzman population of polar molecules and an increase in the observed dipole moment.

Dipole moment measurements of 2,3-butanedione have been carried out on two previous occasions; Zahn<sup>6</sup> in 1932, and Bloom and Sutton<sup>7</sup> in 1941. The results of their measurements are shown in Figure (1) and it can be seen that a serious discrepancy exists between their sets of data. It should be pointed out that in both cases the dipole moment measurements showed a temperature dependence. Although Zahn's data appears to be qualitatively correct, no mention was made as to how his measurements were obtained. Furthermore, no attempt was made to fit his data to any type of potential function. Bloom and Sutton did try fitting their data to one parameter linear, cosine, and parabolic potential functions. However, a one parameter potential fails to take into account the possibility of the existence of both cis and trans isomers. A better model would have been a two parameter potential function describing both cis and trans forms. However, without

Figure 1  
A Comparison of Bloom and Sutton's  
Data with Zahn's Data

DIPOLE MEASUREMENTS OF 2,3-BUTANEDIONE IN GAS PHASE



modern day computers, fitting a two parameter potential function to the temperature dependence of the dipole moment was infeasible.

The present dipole moment study of 2,3-butanedione was undertaken to resolve the discrepancy that exists between Bloom and Sutton's dipole moment data and Zahn's data. Moreover, computer techniques will be employed to analyze the dipole moment data to obtain a more accurate description of the torsional potential. The question as to the stability of the cis isomer of 2,3-butanedione can then be answered.

## EXPERIMENTAL

### Materials

For the pure liquid and solution measurements, a series of materials of known dielectric constants were chosen for calibration standards. The physical properties for these standards are given in Table 1.

### Purification of Materials

**2,3-Butanedione:** 2,3-butanedione was fractionally distilled twice with the middle fraction of the second distillate being used for measurements. The purity was confirmed from NMR spectra and vapor phase chromatograms. (See Appendix 1)

**Benzene:**<sup>11</sup> Reagent grade benzene (500ml) was boiled for ten hours with 40g anhydrous aluminum chloride then distilled. The distillate was washed several times with water and finally refluxed for two hours with acetic acid and mercuric oxide. After washing with water and sodium hydroxide it was refluxed over sodium metal for 12 hours and then fractionally distilled over sodium.

**Cyclohexane:**<sup>11</sup> Cyclohexane was passed through an alumina column 3 cm. in diameter and 30 cm. long and fractionally distilled through a 30 cm. fractionating column after refluxing over  $P_{40}10$  for twelve hours. Only the middle fraction was saved.

Table 1  
All Values Given for 25°C

Material	$n_D(\text{Lit})$	$n_D(\text{Exp})$	$\epsilon(\text{Lit})$	VPC (See Appendix)
Cyclohexane	1.4235 <sup>8</sup>	1.4238	2.015 <sup>9</sup>	#1
Carbon Tetrachloride	1.4574 <sup>8</sup>	1.4578	2.228 <sup>9</sup>	#1
Benzene	1.4979 <sup>8</sup>	1.4981	2.275 <sup>8</sup>	#1
Chloroform	1.4429 <sup>8</sup>	1.4429	4.781 <sup>c</sup>	
Chlorobenzene	1.5221 <sup>a</sup>	1.5221	5.621 <sup>9</sup>	
Ethyl Acetate	1.3698 <sup>8</sup>	1.3703	6.02 <sup>9</sup>	
Methyl Benzoate	1.5146 <sup>8</sup>	1.5151	6.57 <sup>d</sup>	
2,3-butanedione	1.3924 <sup>b</sup>	1.3922		#1

<sup>a</sup>Calculated using  $\frac{dn}{dt} = 0.00054^8$   
where  $n_{D,15} = 1.52748^8$   
 $n_{D,20} = 1.52481^8$

<sup>b</sup>Value extrapolated from the following literature  
values  $n_{D,23} = 1.3927^{10}$   
 $n_{D,18} = 1.3933^9$

<sup>c</sup>Calculated using  $\epsilon^{20} = 4.806^9$  and  $\alpha = \frac{-d \log_{10} \epsilon}{dt}$   
where  $\alpha = .0016^9$

<sup>d</sup>Calculated using  $\epsilon^{20} = 6.59^9$  and  $\alpha = .0014^9$

The symbols  $n_D$ ,  $\epsilon$ , and VPC represent index of refraction, dielectric constant, and vapor phase chromatograms respectively. Cyclohexane, carbon tetrachloride, chlorobenzene, 2,3-butanedione, ethyl acetate, and methyl benzoate were obtained from Eastman Kodak Company, Rochester, New York. Chloroform was obtained from J. T. Baker Chemical Co., Phillipsburg, New Jersey.



Carbon Tetrachloride: Carbon tetrachloride was prepared by fractionally distilling twice. The middle portion of the distillation was kept for use.

Chloroform:<sup>11</sup> Chloroform was washed three times with concentrated sulfuric acid, neutralized with  $\text{NaHCO}_3$  and washed with water. After drying over  $\text{MgSO}_4$ , it was fractionally distilled under a nitrogen atmosphere, saving only the middle fraction.

Chlorobenzene: Reagent grade chlorobenzene was used without further purification.

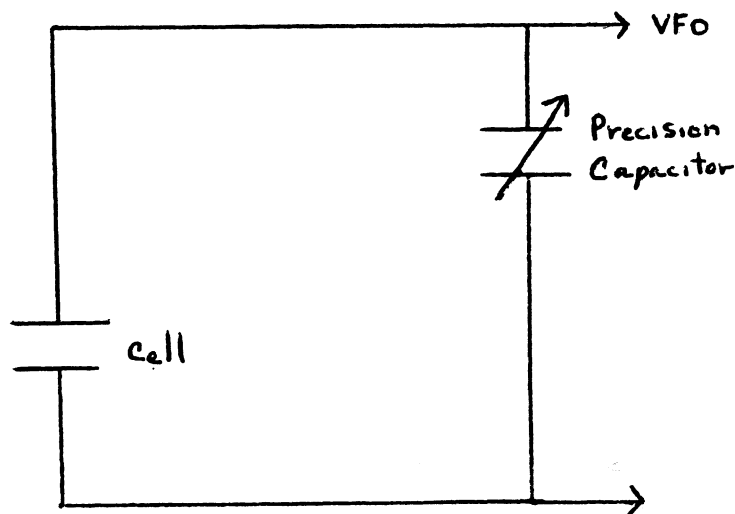
The benzene, cyclohexane, carbon tetrachloride, chloroform, and chlorobenzene were stored in the dark over type 4A molecular sieve, grade 514 that had been freshly prepared by heating at  $320^\circ\text{C}$  for three hours in a thermostated tube furnace.

#### Equipment and Apparatus

The indices of refraction were measured with a Bausch and Lomb Abbe refractometer. The vapor phase chromatograms (VPC) were obtained using a Perkin Elmer Model 154-L, equipped with a thermal conductivity detector, and a 10 ft. column of 15% SE-30 stationary phase, with helium carrier gas at a flow rate of 78 ml/minute. Weight measurements were made using a Sartorius single pan balance. Density measurements for the pure liquid were made using a stopper type pycnometer. Density measurements of solutions were made using 25-ml. volumetric flasks. Infrared (ir) spectra were made using

a Perkin-Elmer 337 Infrared Spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Varian T-60 NMR spectrophotometer system. Mass spectral data was obtained with a Dupont 21-490 Mass Spectrometer. A dielectrometer constructed in this laboratory was used to obtain dielectric measurements by the heterodyne beat method from which dipole moments were calculated.<sup>a</sup>

The dielectric cell (See Figure 2), model 2TN20LV, used for pure liquid and solution measurements was obtained from Balsbaugh Laboratories, Duxbury, Massachusetts and was modified for this experiment.<sup>b</sup> Dielectric measurements of up to  $\epsilon = 3.0$  are permitted by this cell.



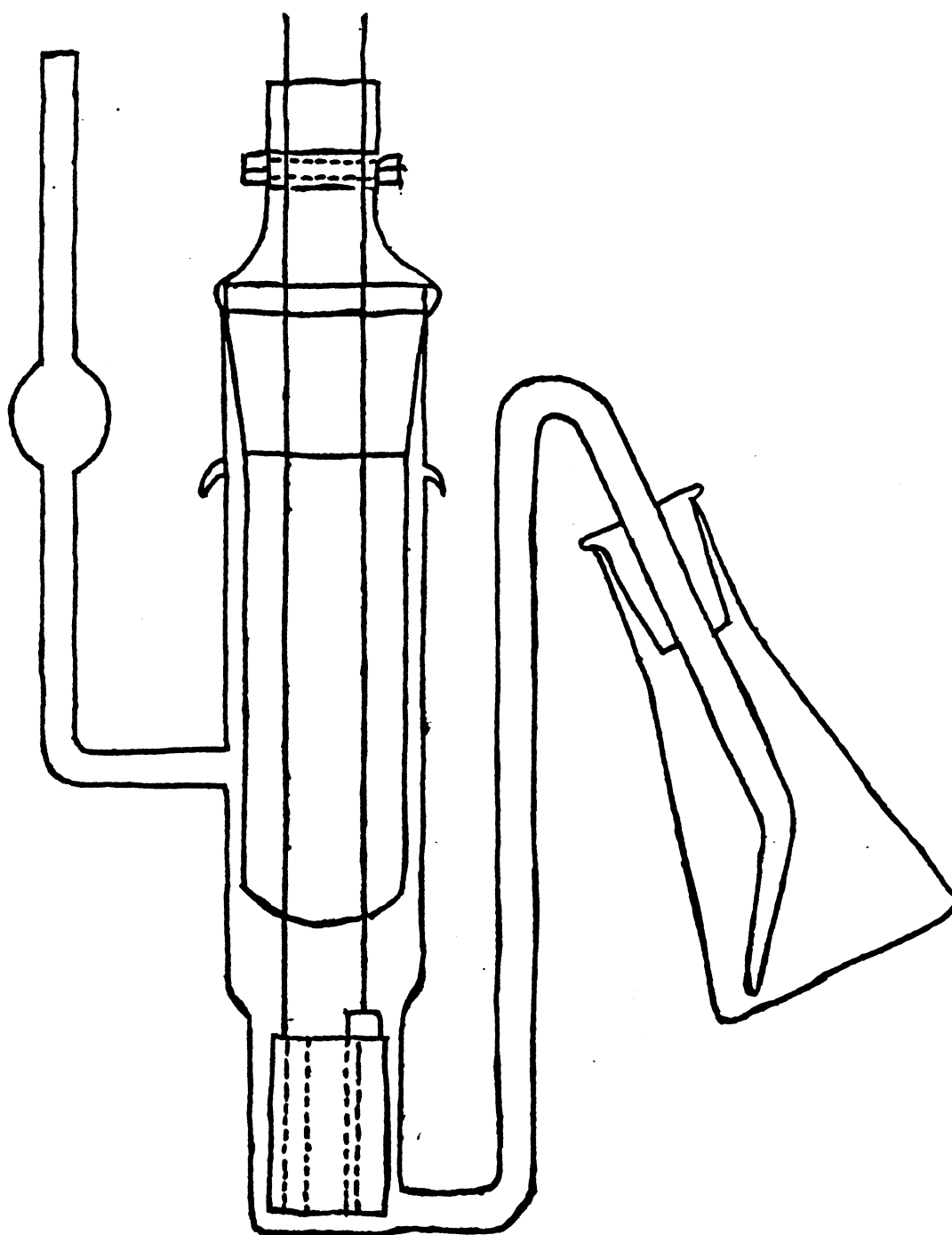
A 110 pf mica capacitor was used in series with the cell to permit measurements of dielectric constants up to  $\epsilon = 15.0$ . This was necessary for pure liquid measurements.

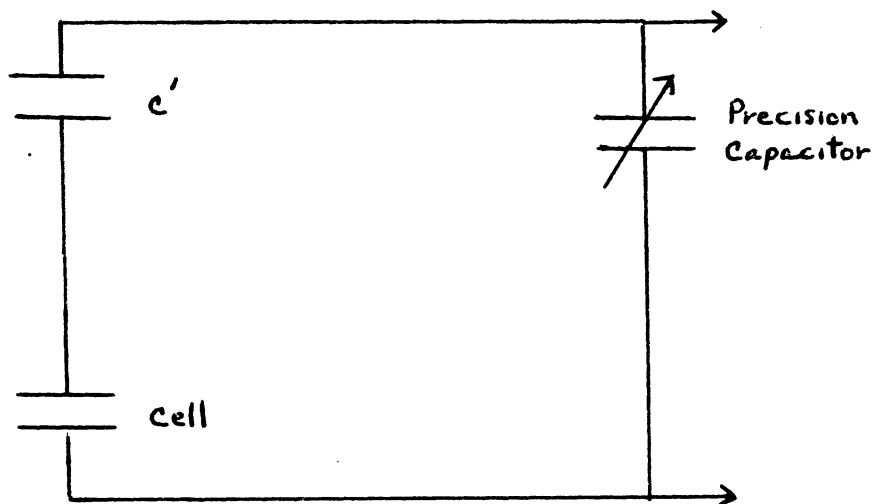
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<sup>a</sup>The instrument was constructed by Mr. James Belcher

<sup>b</sup>Cell modified by Dr. J. W. Ellis

Figure 2  
Dielectric Cell Used for Pure Liquid  
and Solution Measurements





where  $c' = 110 \text{ pf}$

The tuning mechanism of a war surplus frequency meter (Model No. BC221N) was used to measure changes in capacitance. Although the BC221N provides a high precision vernier dial mechanism, an accurate calibration technique is needed since the measured changes in capacitance are nonlinear with respect to dial readings. The samples were introduced into the cell by means of a vacuum and were removed by pressurizing the cell with nitrogen gas. Fifteen to twenty milliliters of liquid are required by the cell for each measurement.

The null points for measurements were obtained under a nitrogen gas atmosphere. Before taking any measurements the instrument was turned on for several days to minimize frequency shifts due to thermal effects. After

introducing each sample into the thermostated cell, five minutes were allowed for temperature equilibrium to be reached. The sample temperature was held constant within  $\pm 0.03^{\circ}\text{C}$ , with a Magni Whirl constant temperature bath.

The calibration of the instrument was achieved by measuring a series of standard materials of known dielectric constant as a function of dial settings. The parameters for a polynomial calibration function were then obtained for this data using a nonlinear least squares fit. (See Appendix 2)

A custom built dielectric cell and vacuum line (See Figure 3 and 4) were used for vapor phase measurements. The cell was placed in an oilbath that was surrounded by vermiculite type insulation. The temperature of the oilbath was controlled by a YSI Model 71A Thermistemp Temperature Controller. A variac voltage regulator was used to maintain the temperature as constant as possible. It was found that each experimental temperature had an optimum voltage at which temperature regulation was best achieved. A Forma Temperature Junior Bath and Circulator was used to regulate the temperature of the 2,3-butanedione sample.

Vapor phase measurements required measuring very small changes in dielectric constants, i.e.  $\Delta\epsilon = 1.0 \times 10^{-4}$ . Therefore, the capacitance of the instrument had to be altered to meet the requirements as shown in the following diagram.

**Figure 3**

**The Dielectric Cell Used for Gas Phase Measurements**

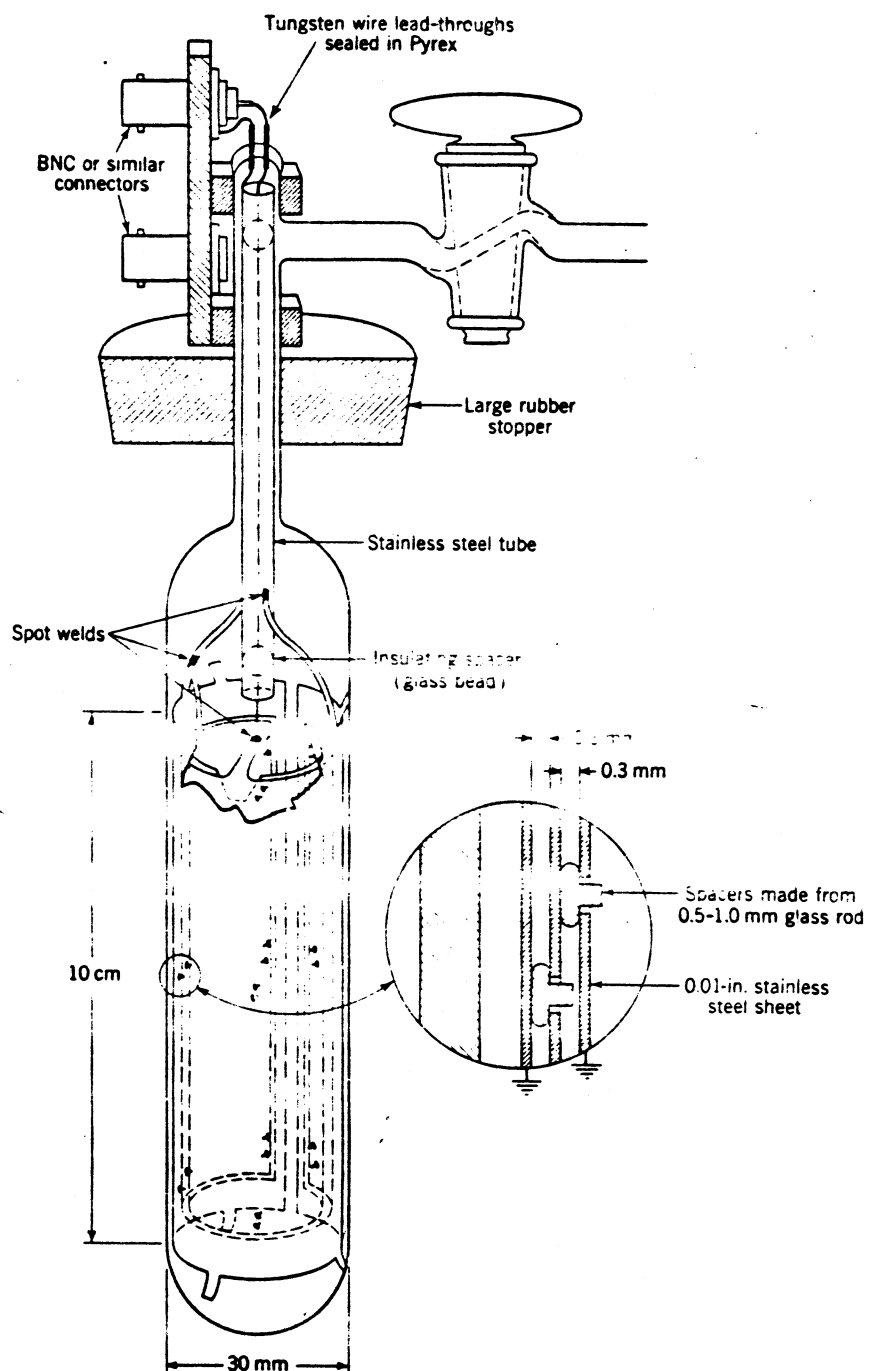
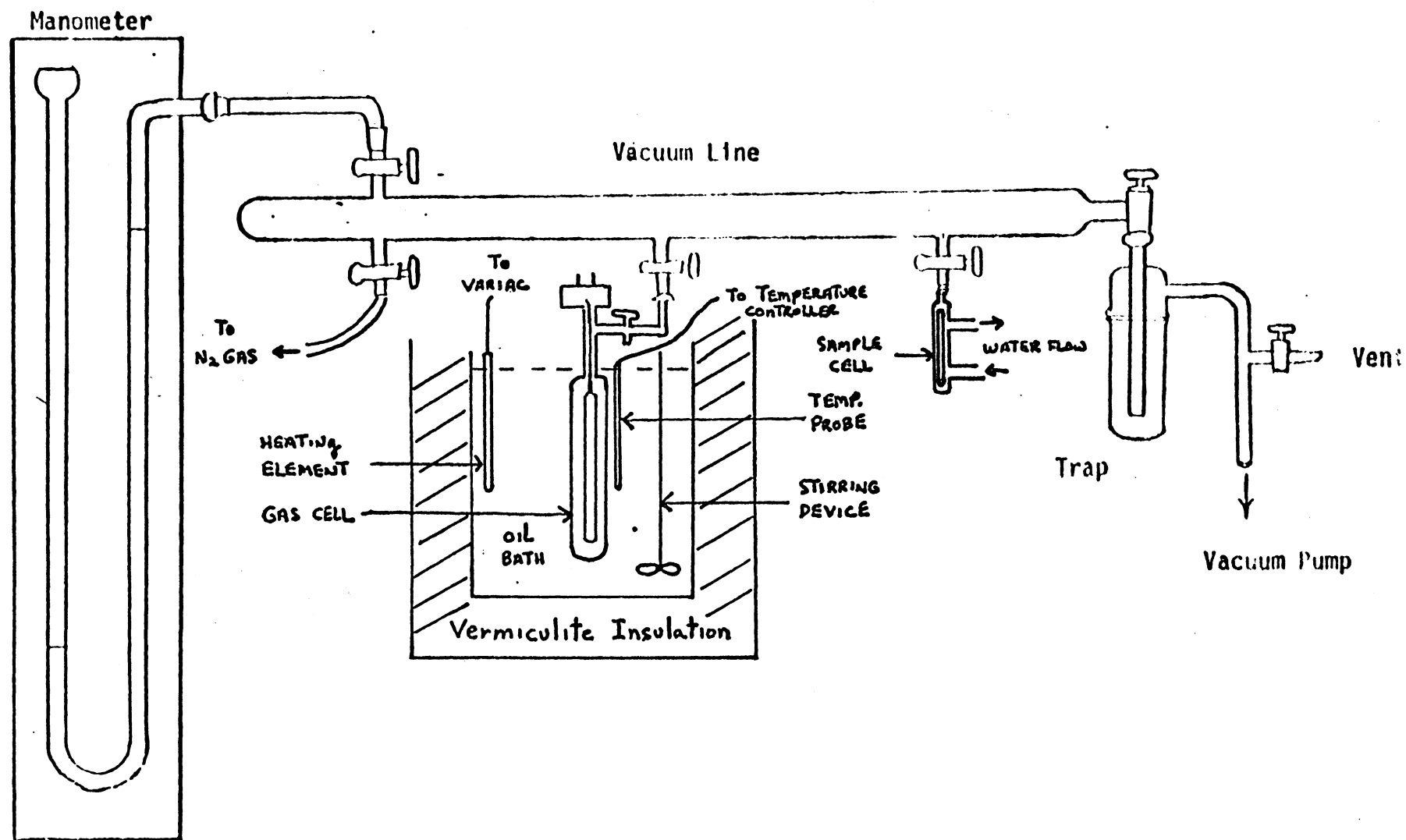
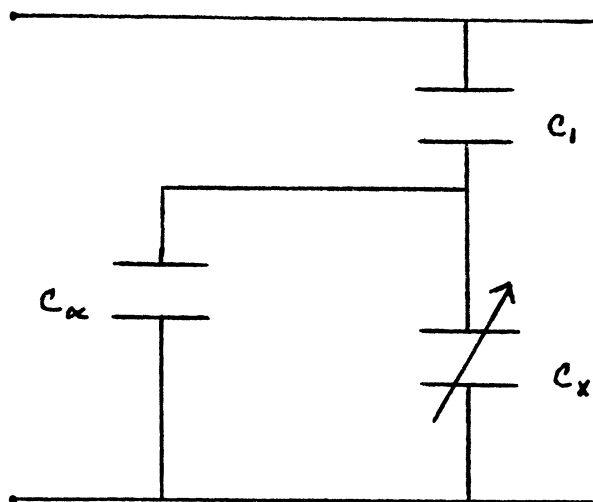




Figure 4  
Vacuum Line Used in Vapor Phase Diagram





where  $c_1 = 200 \text{ pf}$   
 $c_x = 100 \text{ pf}$

The variable frequency oscillator (VFO) was set at 1.30 MHz. The first overtone band was used to zero beat with the fixed crystal oscillator at 2.60 MHz for these measurements.

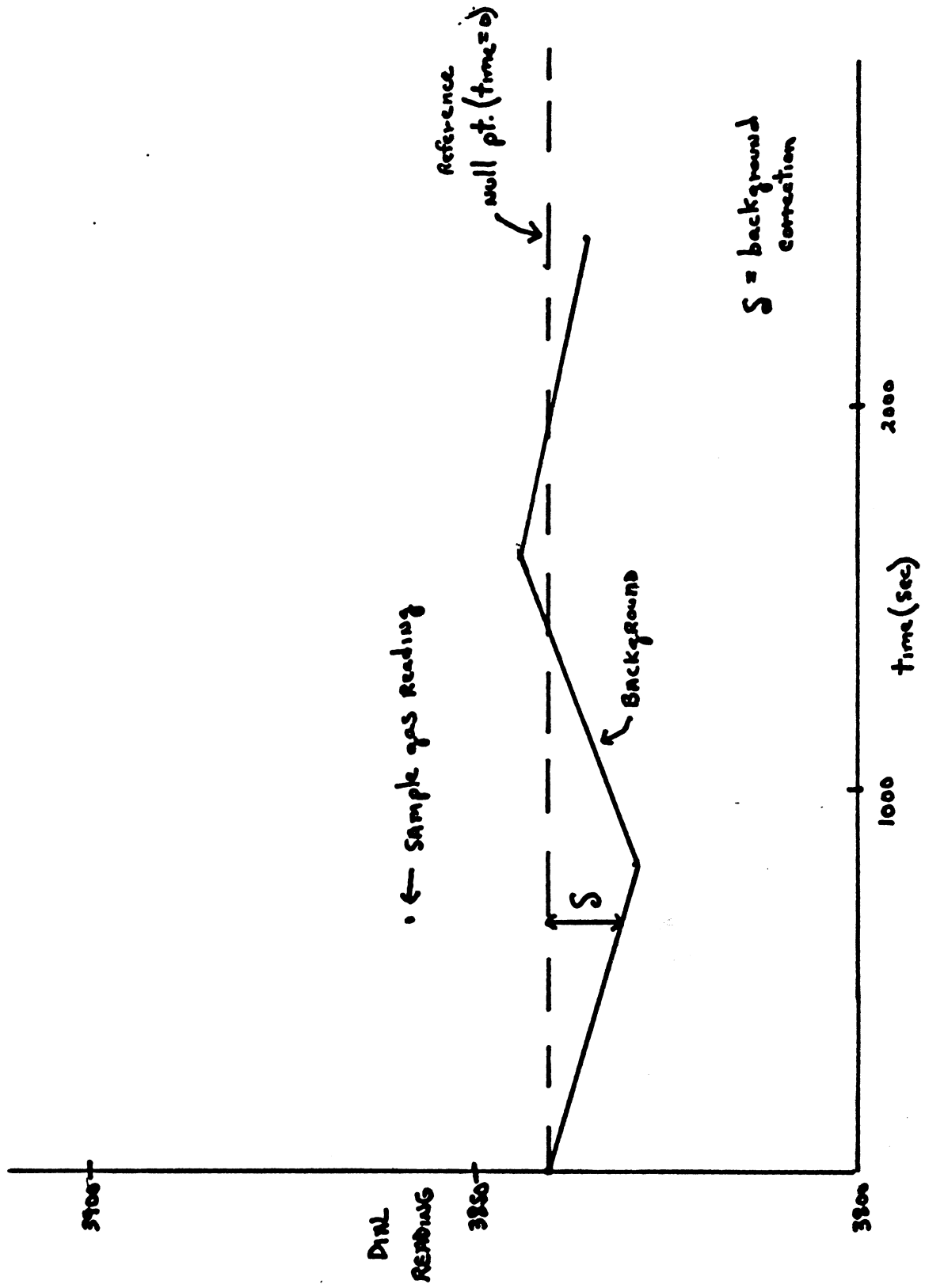
The experimental procedure used for vapor phase measurements was as follows. The dielectric cell, filled with nitrogen gas, was heated to the desired temperature. The heating element power was adjusted until the temperature fluctuation of the oilbath was less than  $\pm 0.02^\circ\text{K}$  for the lower temperatures and  $\pm 0.06^\circ\text{K}$  at the higher temperatures. The nitrogen gas in the cell was then evacuated and a dial reading recorded for the null point of the evacuated cell. A Lab Chron 1400 timer was also started at this point and all readings thereafter were recorded as a function of time.

Background fluctuations were observed by evacuating the cell after each gas measurement and taking a dial reading. Background corrections were then made with respect to the time zero dial setting, i.e. a positive deviation in the background was subtracted from the observed dial setting. (See Figure 5) When taking gas measurements, at least ten minutes were allowed for temperature equilibrium. Dial readings were then taken approximately every forty to fifty seconds for about four minutes. Any change in background could then be observed. An average of all the dial settings was taken and the midpoint of the time readings recorded.

The temperature of the 2,3-butanedione was maintained at  $15.1 \pm 0.1^{\circ}\text{C}$  throughout the course of all gas measurements. Nitrogen gas was used as a dielectric calibration standard having a dielectric constant equal to  $1.0005472^9$  at  $20^{\circ}\text{C}$  and 760 torr pressure. During each set of measurements a calibration curve was obtained by taking nitrogen gas dial readings at pressures of 200, 250, 300, 350, and 400 torr. The parameters for the calibration curve were obtained by using a nonlinear least squares fit. (See Appendix 2)

A determination of the dipole moment at each temperature required some 75 nitrogen calibration null point observations and approximately 45 sample null point observations over a period of approximately six hours. A total of over 2000 vapor phase measurements were made over

Figure 5  
Corrections for Changes in Background Are Shown



the accessible temperature range.

## RESULTS

### Pure Liquid Measurements

The coefficients of the polynomial calibration function were determined from the data in Table II by a non-linear least squares fit. (See Appendix 2)

Table II  
Measurements at 25°C

Material	N	$\bar{\delta}$	$\sigma$	$\epsilon$ (Lit.)
Cyclohexane	4	588.48	.046	2.015 <sup>9</sup>
Carbon Tetrachloride	4	643.98	.538	2.228 <sup>9</sup>
2,3-butanedione	4	1376.2	.524	
Chloroform	4	1406.3	1.304	4.781
Chlorobenzene	4	1719.3	1.055	5.621 <sup>9</sup>
Ethyl Acetate	4	1872.6	2.311	6.02 <sup>9</sup>
Methyl Benzoate	4	2173.1	1.926	6.57

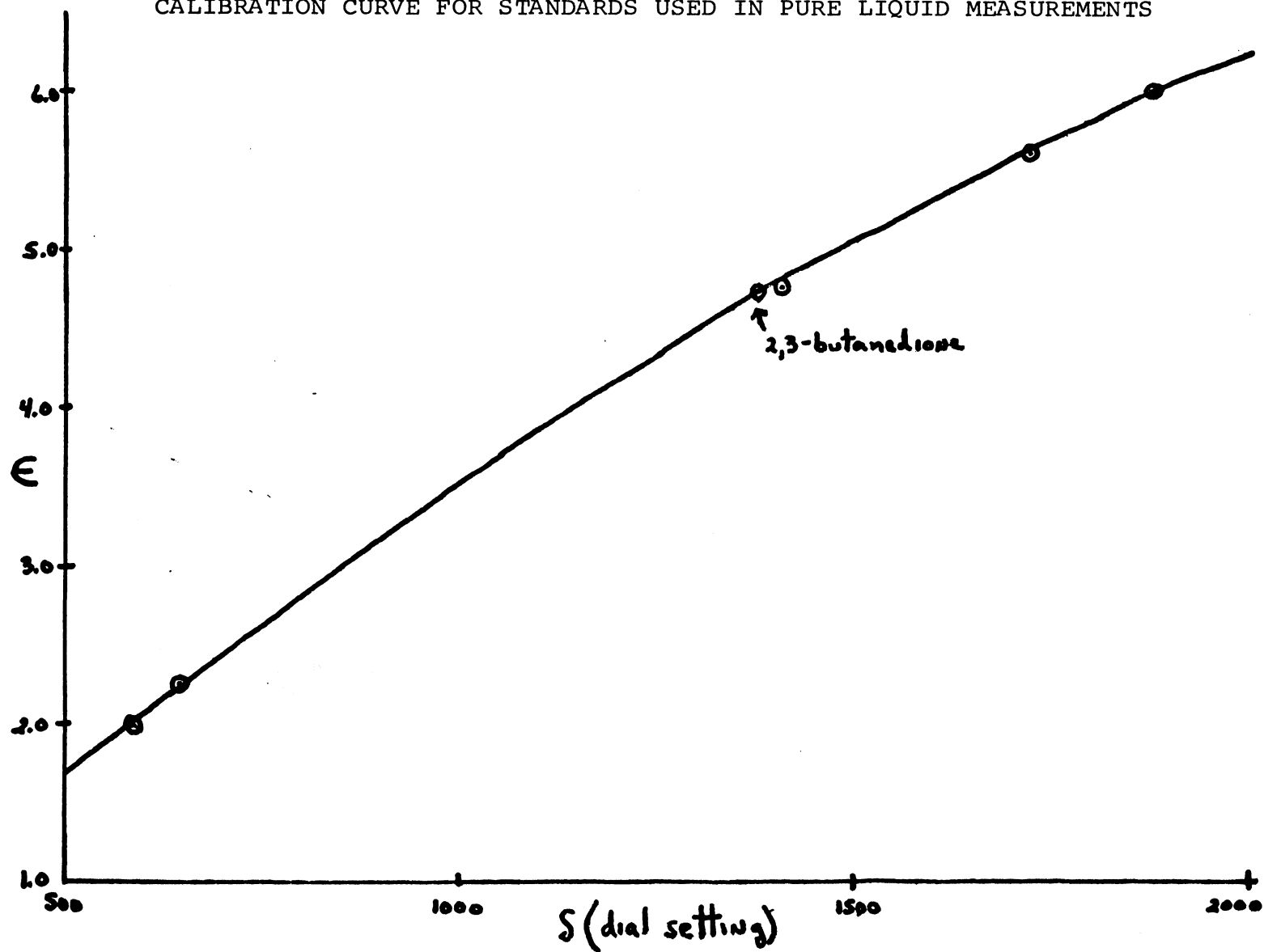
Where N represents number of trials,  $\bar{\delta}$  is the average value for dial setting,  $\sigma$  is the standard deviation for dial setting, and  $\epsilon$  is the dielectric constant.

A second ordered polynomial was found to fit the calibration curve. (See Figure 6) The equation for the



**Figure 6**  
**The Calibration Curve for the Dielectric Standards**  
**Used in the Pure Liquid Measurements**

CALIBRATION CURVE FOR STANDARDS USED IN PURE LIQUID MEASUREMENTS



calibration curve is

$$\epsilon = A_0 + A_1 \delta + A_2 \delta^2$$

$$\text{Where } A_0 = -0.5604519$$

$$A_1 = 0.4770201 \times 10^{-2}$$

$$A_2 = -0.6815654 \times 10^{-6}$$

The dielectric constant of pure 2,3-butanedione was calculated from the observed dial setting and the above calibration equation as  $\epsilon = 4.713 \pm .002$ . The density of 2,3-butanedione was determined as .981 g/ml at 25°C.

The molar polarization ( $P_m$ ), distortion polarization ( $P_d$ ), orientation polarization ( $P_u$ ), and dipole moment were then calculated from the Onsager equation. (See Appendix 3)

$$P_m = \frac{\epsilon - 1}{\epsilon + 2} \left( \frac{M}{\rho} \right)$$

$$R_m = P_E = \frac{n^2 - 1}{n^2 + 2} \left( \frac{M}{\rho} \right) \quad a$$

$$P_u = P_m - P_d = \frac{4 \pi N \mu^2}{9 k T}$$

Where  $\epsilon$  = dielectric constant

$\rho$  = density

---

<sup>a</sup>The distortion polarization,  $P_d = R_E + P_A$ , was taken as 1.1 times the molar refractivity  $R_m$ .

$M$  = molecular weight  
 $n$  = index of refraction  
 $N$  = Avagadro's number  
 $k$  = Boltzmann constant  
 $T$  = temperature  
 $\mu$  = dipole moment

The results for liquid 2,3-butanedione at 25°C:

$$\begin{aligned}
 \epsilon &= 4.713 \pm 0.002 \\
 P_m &= 48.522 \pm 0.038 \\
 P_d &= 22.988 \pm 0.004 \\
 P_u &= 25.534 \pm 0.035 \\
 \mu &= 1.559 \pm 0.001 \text{ D}
 \end{aligned}$$

The dipole moment for 2,3-butanedione in the liquid phase was found to be much higher than expected. (See Figure 1 - Bloom and Zahn Graph) Such deviations have been observed in polar liquids and have been attributed to strong dipole-dipole intermolecular interaction. These interactions can be minimized by measuring dipole moments in dilute solutions rather than in the pure liquid state.

### Solution Measurements

Data for the dielectric standards are given in Table III. The coefficients of the polynomial calibration function were determined from this table by a non-linear least squares fit. (See Appendix 2)

Table III  
Measurements at 25°C

Material	N	$\bar{S}$	$\sigma S$	$\epsilon(\text{Lit.})$
Cyclohexane	3	588.6	0.0	2.015 <sup>9</sup>
Carbon Tetrachloride	3	645.33	.058	2.228 <sup>9</sup>
Benzene	3	655.83	.058	2.275 <sup>8</sup>
Chloroform	4	1409.8	2.56	4.781
Chlorobenzene	4	1725.2	.645	5.621 <sup>9</sup>

N represents the number of trials,  $\bar{S}$  is the average value for dial setting,  $\sigma S$  is the standard deviation for dial setting, and  $\epsilon$  is the dielectric constant.

The coefficients for the calibration function were determined by a non-linear least squares fit. A second ordered polynomial was found to fit the calibration curve. (See Figure 7)

The equation for the calibration curve is

$$\epsilon = A_0 + A_1 S + A_2 S^2$$

$$\text{Where } A_0 = -0.4849983$$

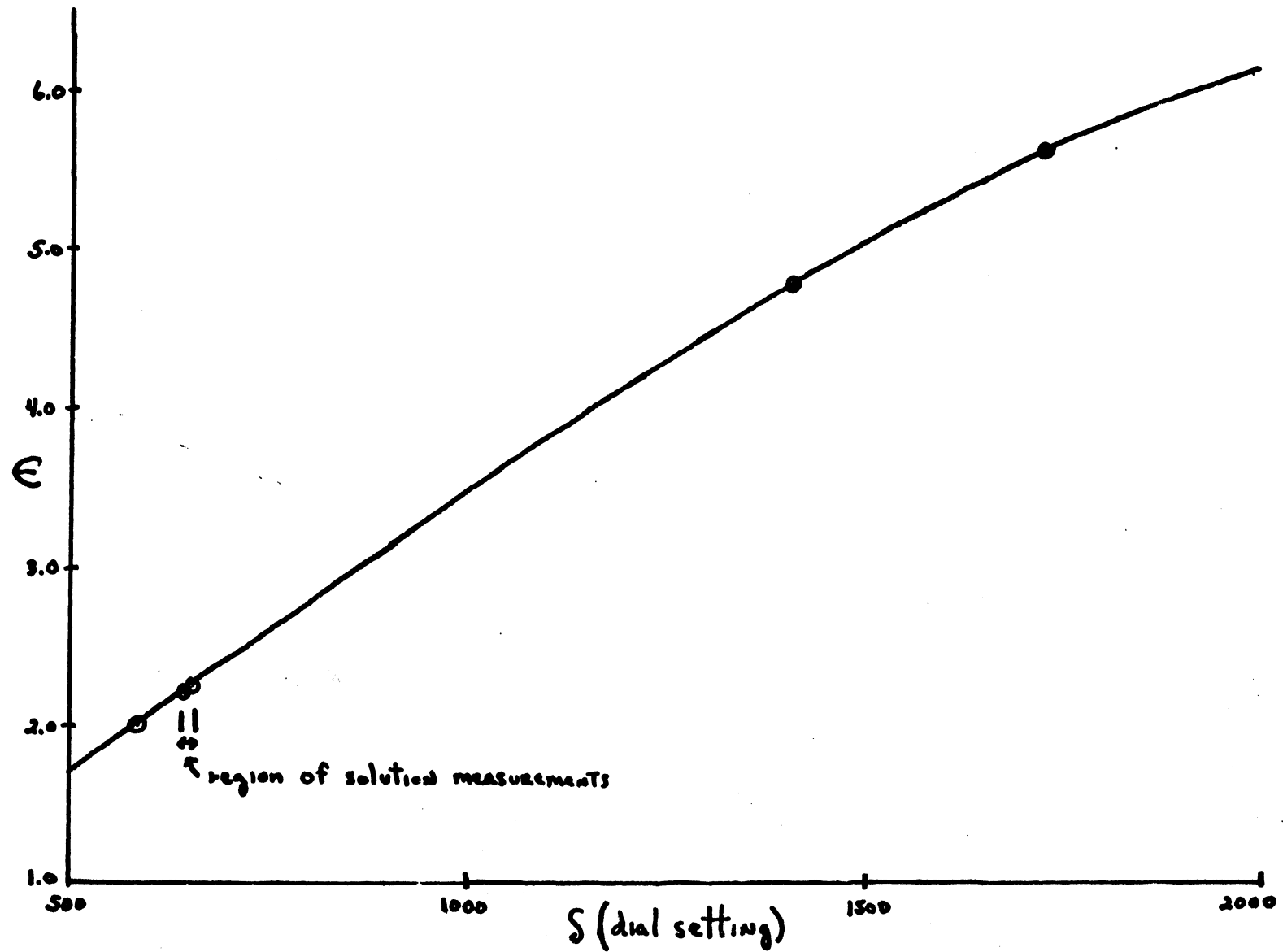
$$A_1 = 0.4610520 \times 10^{-2}$$

$$A_2 = -0.6208537 \times 10^{-6}$$

The parameters for the polynomial calibration function were then used to determine the dielectric

Figure 7  
The Calibration Curve for the Dielectric Standards  
Used in the Solution Measurements

CALIBRATION CURVE OF STANDARDS FOR SOLUTION MEASUREMENTS



constants for dilute solutions of 2,3-butanedione in  $\text{CCl}_4$ . These values are given in Table IV.

Table IV  
Measurements at 25°C

	$\bar{x}_2$	$\bar{\delta}$	$\epsilon$	$\rho$
Pure $\text{CCl}_4$	0.0	645.33	2.232	1.584
Solution #1	0.01564	649.3	2.247	1.580
#2	0.02603	652.0	2.257	1.573
#3	0.03047	655.7	2.271	1.566
#4	0.04569	658.4	2.281	1.558
#5	0.06075	662.9	2.298	1.548

In Table IV,  $\epsilon$  represents dielectric constant,  $\bar{x}_2$  is the mole fraction of solute (2,3-butanedione),  $\rho$  represents density, and  $\bar{\delta}$  is the average value for the dial settings.

Both dielectric constants and densities of the solutions are expected to be linear with respect to mole fractions. (See Figure 8 and 9)

$$\epsilon_{12} = a\bar{x}_2 + \epsilon_1$$

$$\rho_{12} = b\bar{x}_2 + \rho_1$$

Where  $\epsilon_{12}$  and  $\rho_{12}$  represent dielectric constant and densities of solutions respectively,  $\bar{x}_2$  represents



mole fraction of solute, and  $\epsilon_1$  and  $\rho_1$  represent dielectric constant and density of solvent respectively. The Hedestrand parameters (a) and (b), (See Appendix 3), were obtained from the data in Table IV using a least squares fit. (See Appendix 2) These parameters were then used to evaluate the molar polarization and dipole moment of solute.

$$P_{2m} = \frac{3 M_1 a}{(\epsilon_1 - 2)^2 \rho_1} + \frac{\epsilon_1 - 1}{(\epsilon_1 + 2) \rho_1} \left( M_2 - \frac{M_1 b}{\rho_1} \right)$$

$$P_{2d} = \frac{\frac{n_2^2}{n_2^2 + 2} - 1}{\frac{n_2^2}{n_2^2 + 2}} \frac{M_2}{\rho_2}$$

$$P_{2u} = P_{2m} - P_{2d} = \frac{4\pi N_0 \mu^2}{9kT}$$

Where  $M_1$  is the molecular weight of solvent (carbon tetrachloride),  $M_2$  is the molecular weight of solute (2,3-butanedione),  $a$  is the slope of  $\epsilon$  versus  $\bar{x}_2$  graph,  $b$  is the slope of  $\rho$  versus  $\bar{x}_2$  graph,  $n_2$  is the

index of refraction of 2,3-butanedione,  $\rho_2$  is the density of 2,3-butanedione,  $\rho_1$  is the density of carbon tetrachloride,  $\epsilon_1$  is the dielectric constant of 2,3-butanedione,  $P_{2m}$  is the molar polarization of solute,  $P_{2d}$  is distortion polarization of solute, and  $P_{2u}$  is the orientation polarization of solute where 2,3-butanedione is the solute

Values used in calculation are:

$$\begin{aligned} M_1 &= 153.8 \text{ g/mole} \\ M_2 &= 86.09 \text{ g/mole} \\ a &= 1.099137 \\ b &= -0.6269598 \\ n &= 1.3922 \\ \rho_2 &= .9814 \text{ g/ml} \\ \rho_1 &= 1.584 \text{ g/ml} \\ \epsilon_1 &= 2.232 \end{aligned}$$

The summary of results for  $P_{2m}$ ,  $P_{2d}$ ,  $P_{2u}$ , and  $\mu$  are as follows:

$$\begin{aligned} P_{2m} &= 44.86 \text{ cc} \\ P_{2d} &= 22.99 \text{ cc} \\ P_{2u} &= 23.96 \text{ cc} \\ \mu &= 1.03 \text{ D} \end{aligned}$$

Figure 8

Plot of the Dielectric Constant Versus Mole Fraction For  
Solutions of 2,3-butanedione in Carbon Tetrachloride.

⊙ Represent Experimental Values and the Solid  
Line Represents the Least Squares Fit  
of this Data.

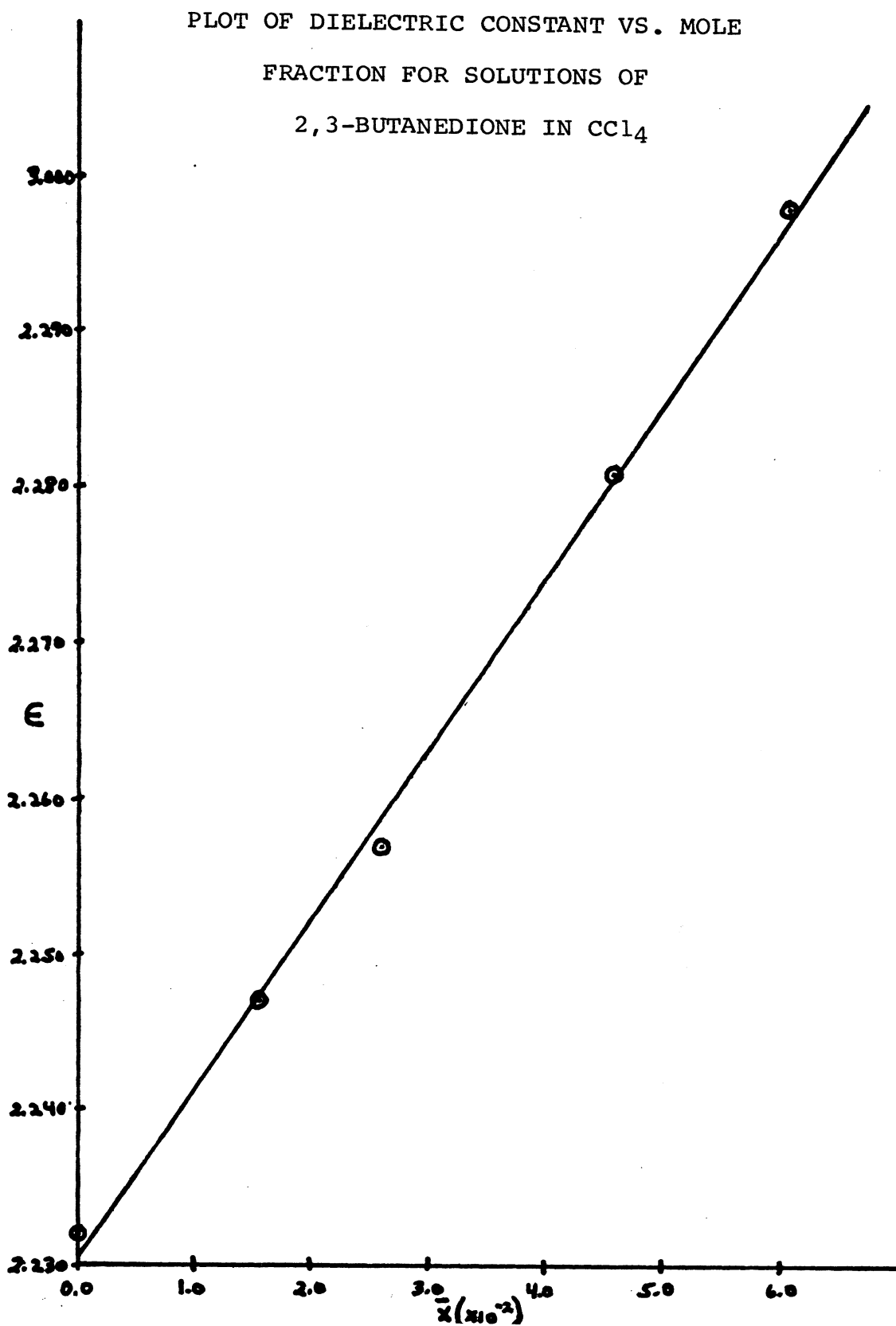
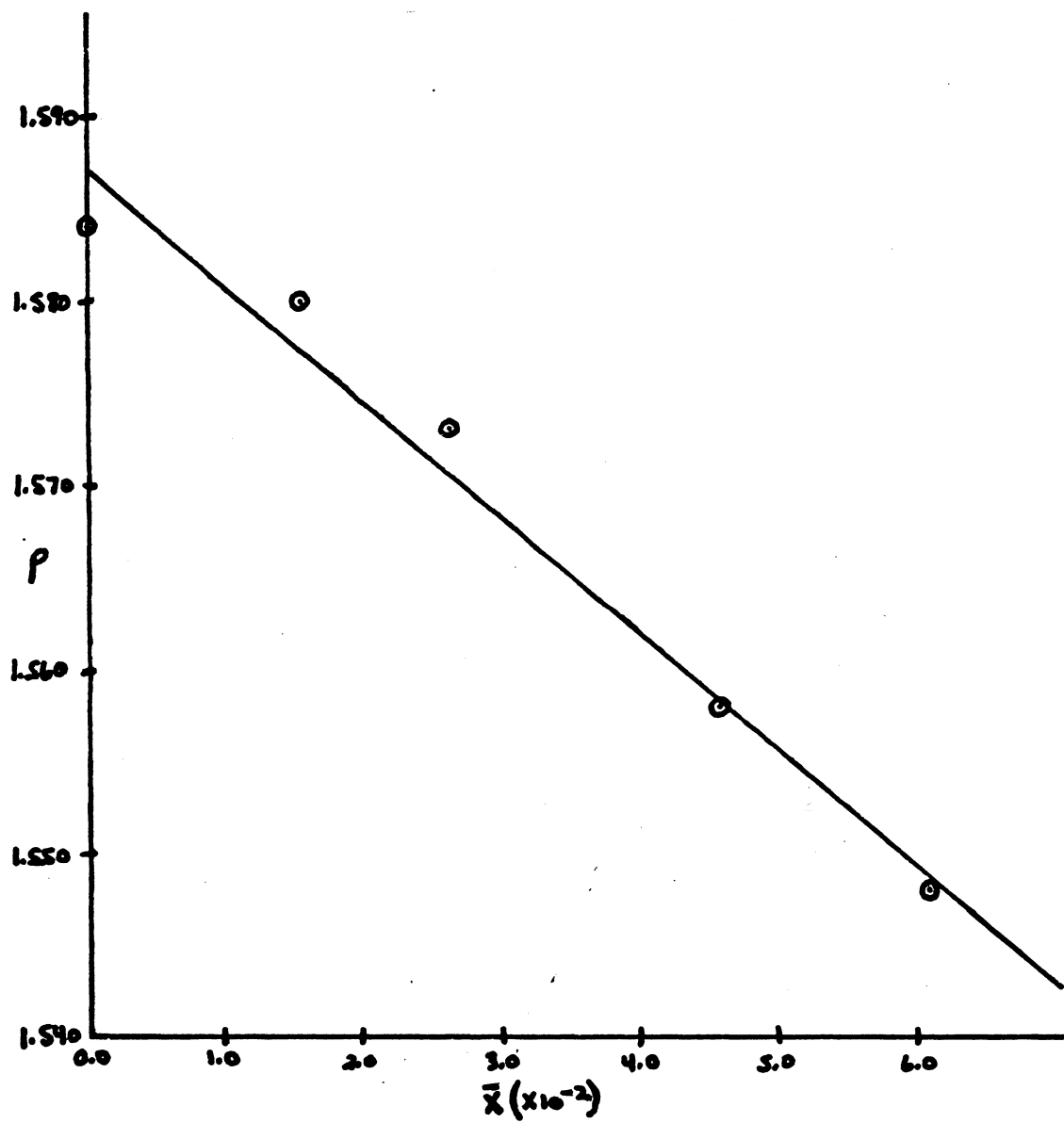


Figure 9

A Plot of the Density Versus Mole Fraction for Solutions of  
2,3-butanedione in Carbon Tetrachloride. The Dots  
Represent Experimental Data Values. The Solid  
Line Represents the Best Least Squares  
Fit for the Data.

PLOT OF DENSITY VS. MOLE FRACTION FOR  
SOLUTIONS OF 2,3-BUTANEDIONE  
IN  $\text{CCl}_4$



### Vapor-Phase Measurements

A nitrogen gas calibration was needed for gas phase measurements at each temperature. Typical calibration data is presented in Table V, which was taken from an experiment at 310.15°K.

Table V

P (atm)	$\bar{S}$	$\epsilon - 1$ ( $\times 10^{-4}$ )
0.5287	3748.4	2.734
0.4632	3728.1	2.395
0.3961	3704.1	2.048
0.3305	3678.2	1.709
0.2645	3661.0	1.368

Symbols used are P represents pressure of nitrogen gas,  $\bar{S}$  represents corrected average dial setting, and  $\epsilon$  represents the dielectric constant. The corresponding calibration curve is presented in Figure 10. In Table V, values for  $\epsilon - 1$  were obtained from the Clausius-Mosotti equation. (See Appendix 3)

$$\epsilon - 1 = 3 P_M \frac{P}{1000 RT}$$

where  $P_M$  = molar polarization of  $N_2$  gas

$$= 4.387 \text{ cc at } 293.15^\circ\text{K}$$

R = gas constant

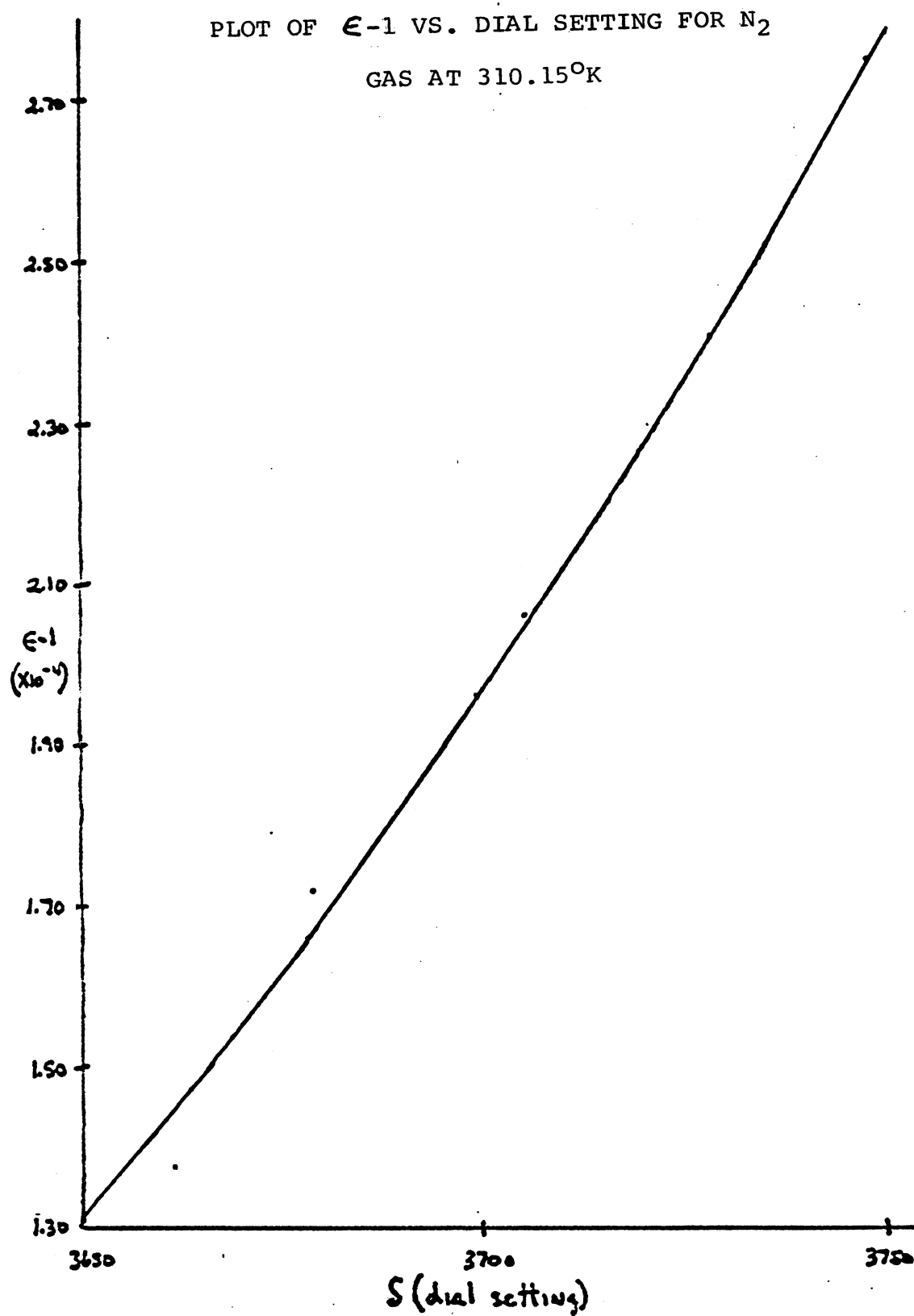
$$= 0.082054 \text{ l-atm/mole-}^\circ\text{K}$$

T = temperature in  $^\circ\text{K}$

P = pressure in atmospheres

Figure 10  
Calibration Curve for Nitrogen Gas at 310.15°K





A second ordered polynomial using a nonlinear least squares fit (See Appendix 2) was found to fit all the calibration curves. The equation for the calibration curve in the preceding table is

$$\epsilon - 1 = A_0 + A_1 S + A_2 S^2$$

$$\text{where } A_0 = 0.3608931 \times 10^{-1}$$

$$A_1 = -0.2089099 \times 10^{-4}$$

$$A_2 = 0.3024361 \times 10^{-8}$$

The dielectric constant for 2,3-butanedione is then calculated from its dial setting, its pressure, and the above calibration equation. The molar polarization for 2,3-butanedione was then calculated from the data presented in Table VI.

Table VI

$S$	$\epsilon - 1 \text{ (} \times 10^{-4} \text{)}$	P (atm)
3709.9	2.141	.04105
3720.1	2.296	.04105
3705.9	2.050	.04079

Symbols used are  $S$  represents dial setting,  $\epsilon$  represents dielectric constant, and P represents pressure in atmospheres.

$$P_m = \frac{(\epsilon - 1)(RT) 1000}{3P}$$

where  $P_m$  = molar polarization

$\epsilon$  = dielectric constant

R = gas constant

T = temperature in °K

P = pressure in atm.

The dipole moment was then calculated using the Debye Equation. (See Appendix 3)

$$P_m = P_d + \frac{4 \pi N_o \mu^2}{9 k T}$$

where  $P_m$  = molar polarization

$P_d$  = distortion polarization

= 22.99

$N_o$  = Avagadro's number

=  $6.0229 \times 10^{23}$

k = Boltzmann constant

=  $1.38044 \times 10^{-23}$

T = temperature in °K

$\mu$  = dipole moment

All results made in the vapor phase for 2,3-butanedione are summarized in Table VII.

Table VII

T ( $^{\circ}$ K)	$\epsilon-1$ ( $\times 10^{-4}$ )	P (atm)	$P_m$	$\mu$
310.15	2.296	.04105 $\pm$ .00013	46.97	1.11 $\pm$ .05
310.15	2.238	.04289	44.26	1.04
310.15	2.141	.04105	43.64	1.02
310.15	2.050	.04079	42.63	1.00
330.15	2.050	.04158	44.52	1.08
330.15	1.955	.04237	41.67	1.01
350.15	1.959	.04211	44.56	1.11
350.15	1.793	.04158	41.30	1.03
370.15	1.807	.04237	43.18	1.11
370.15	1.681	.04158	40.93	1.04
390.15	1.673	.04421	40.37	1.05
390.15	1.672	.04211	42.38	1.11
390.15	1.618	.04211	41.01	1.07
390.15	1.606	.04263	40.19	1.05
390.15	1.591	.04053	41.89	1.10
390.15	1.586	.04211	40.20	1.05
431.35	1.409	.04000	41.56	1.15
431.35	1.348	.04105	38.74	1.06
431.35	1.274	.03921	38.33	1.04
432.04	1.537	.04000	45.41	1.26
432.04	1.326	.04079	38.41	1.05
472.10	1.349	.04026	43.26	1.25
472.10	1.251	.04026	40.12	1.15
472.10	1.248	.04158	38.76	1.11

Symbols used are T represents temperature,  $\epsilon$  is dielectric constant, P is pressure,  $P_m$  is molar polarization, and  $\mu$  is dipole moment.

## DISCUSSION

### Comparison of Results with other Dipole Studies

Dipole measurements have been carried out on 2,3-butanedione on two occasions prior to this experimental work (Zahn in 1932<sup>6</sup> and Bloom and Sutton in 1941<sup>7</sup>). These results are compared in Figure 11. It can be seen that a serious discrepancy existed between Zahn's data and Bloom and Sutton's. The results of our vapor phase measurements are in best agreement with Bloom and Sutton's data. Moreover, both Le Fevre<sup>12</sup> and these solution dipole measurements of 2,3-butanedione are in good agreement with Bloom and Sutton's vapor phase measurement extrapolated to 298 °K: Bloom and Sutton's extrapolated dipole equals 1.01 D; Le Fevre's solution dipole equals 1.02 D<sup>a</sup>; these solution measurements equals 1.03 D. Since Zahn gives no experimental details, it can only be speculation as to why his results are inaccurate. Sample impurities are the most likely cause for inaccuracies in dipole measurements. Contamination of either the 2,3-butanedione or the dielectric calibration gas could result in the anomalously high dipole reported by Zahn. Since the error seems to be of a systematic nature throughout the entire experiment,

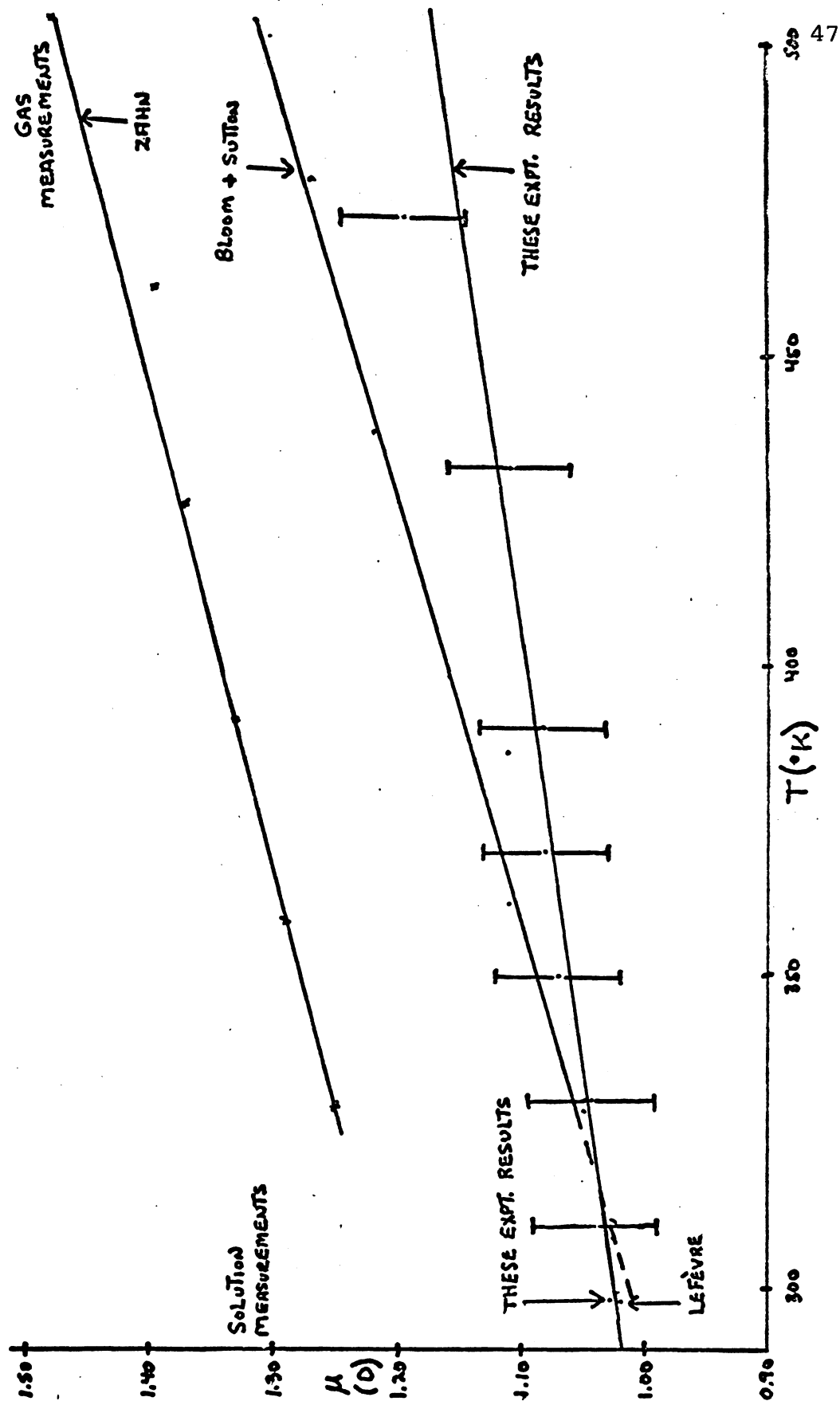
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<sup>a</sup>Atomic Polarization was neglected in Le Fevre's dipole calculation ( $\vec{\mu} = 1.04$  D). This value was obtained from the approximation  $P_d = 1.1 R_m = P_E + P_A$  where

$$R_m = \frac{n^2 - 1}{n^2 + 2} \left( \frac{M}{\rho} \right) = 20.7 \text{ cc}$$

Figure 11  
Comparison of Results with other Dipole Studies

# DIPOLE MOMENT MEASUREMENTS OF 2,3-BUTANEDIONE



it would seem that the problem was one of dielectric standardization.

At low temperatures, there is good correlation between Bloom and Sutton's and these vapor phase studies. As higher temperatures are attained, Bloom and Sutton's dipole measurements increase at a more rapid rate. When comparing the two sets of data, it appears that Bloom and Sutton's data has much better precision. However, the accuracy of their measurements is questionable, since they reported difficulty in the synthesis and purification of their 2,3-butanedione.

The sample used in these measurements was already of high purity when purchased from the Eastman Kodak Company. Further purification was obtained by twice fractionally distilling the sample. Since the sample used in these measurements was of very high purity, it is believed that the results obtained in our measurements are accurate.

#### Dipole Moment and Intramolecular Rotation

For molecules which contain a single fixed dipole, the dipole moment is calculated by

$$\vec{\mu} = q \cdot \vec{r}$$

where  $q$  = charge

$r$  = distance of charge separation

$\vec{\mu}$  = dipole moment

In molecules containing several fixed dipoles, the



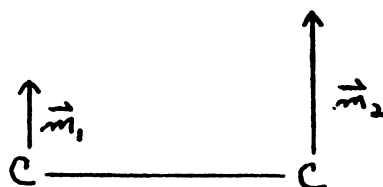
dipole moment calculation becomes more complicated.<sup>13</sup> For this case a set of reference axes in the molecule must be chosen and the dipole component along each axis calculated. The resultant dipole moment is then obtained by summing the squares of the component sums  $m_x$ ,  $m_y$ , and  $m_z$  along each axis and taking the square root, that is

$$\vec{\mu} = (m_x^2 + m_y^2 + m_z^2)^{1/2} \quad (1)$$

Equation (1) is also a good approximation for molecules that contain dipoles that are free to rotate and all positions of rotation are equally probable. However, in molecules where there are two rotatable dipoles on adjacent carbon atoms such as found in 1,2-dicarbonyls, then equation (1) generally cannot be employed. In these cases, the dipole moment depends on the shape of the torsional potential function. Molecules of high potential energy are statistically unfavored and make smaller contributions to the observed dipole. The observed moment is then lower than the value calculated by equation (1) and tends to increase with temperature. The temperature dependence of the dipole moment is good evidence that rotation about the chemical bond is hindered. No temperature dependence of the dipole moment will be observed for cases where free rotation of the dipoles is present and all positions around the C-C are equally probable. In cases where the trans isomer is of lower energy than the cis isomer i.e. rotation is hindered by a potential barrier, then thermal effects will be observed in

the dipole measurements. As the temperature of the sample increases, the population of the cis isomer becomes statistically more favored. Therefore an increase in temperature results in a higher Boltzmann population of polar molecules and an increase in the observed dipole moment.

At this point, a more in depth look at the calculation of the dipole moment for 1,2-dicarbonyl compounds must be undertaken. For the more general case where there are two dipoles on adjacent carbons as shown below



where  $m_1$  and  $m_2$  represent the components of the resultant dipole moment for each carbonyl group, perpendicular to the C-C bond axis. The total dipole moment is found by vectorially summing up the two dipoles.

$$\vec{\mu} = (\vec{m}_1 + \vec{m}_2) \quad (2)$$

Dipole moments cannot be measured directly in the laboratory but instead must be obtained from dielectric measurements. However, the measured dielectric constant is sensitive to the square of the dipole moment rather than the dipole as shown by equation (3). (See Appendix 3)

$$\frac{\epsilon - 1}{\epsilon + 2} \left( \frac{n}{\rho} \right) = \frac{4\pi}{3} N_0 \left( \alpha_0 + \frac{\vec{\mu}^2}{3kT} \right) \quad (3)$$

The square of the dipole moment is equal to the dot product of the sum of the dipoles.

$$\vec{\mu}^2 = (\vec{m}_1 + \vec{m}_2) \cdot (\vec{m}_1 + \vec{m}_2) \quad (4)$$

Upon solving, equation (4) becomes

$$\vec{\mu}^2 = m_1^2 + m_2^2 + 2 m_1 m_2 \cos \phi \quad (5)$$

where  $\phi$  is defined in the diagram below. Note that the direction associated with the dipole moments has been lost when taking the dot product.



Introducing A and B, where  $A = m_1^2 + m_2^2$  and  $B = 2m_1m_2$ , yields for the molecular dipole (See Appendix 4)

$$\vec{\mu}^2 = A + B \cos \phi \quad (6)$$

This equation gives the dipole moment for only one torsional angle about the C-C bond. Classically there should be no constraint put on the torsional angle and the square of the observed dipole moment can be calculated by allowing  $\cos \phi$  to be averaged over all possible orientations, that is

$$\langle \vec{\mu}^2 \rangle = A + B \langle \cos \phi \rangle \quad (7)$$

When solving the  $\langle \cos \phi \rangle$  term, each possible

configuration of the molecule must be accounted for by taking a Boltzmann distribution of the molecules as a function of the torsional potential angle such that

$$N(\phi) = e^{-\frac{v(\phi)}{kT}}$$

where  $N(\phi)$  = number of molecules with angle  $\phi$

$k$  = Boltzmann constant

and averaging over all possible configurations resulting in

$$\langle \cos \phi \rangle = \frac{\int_0^\pi \cos \phi e^{-\frac{v(\phi)}{kT}} d\phi}{\int_0^\pi e^{-\frac{v(\phi)}{kT}} d\phi} \quad (8)$$

Equation (7) then becomes

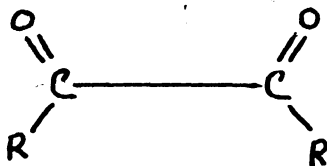
$$\langle \vec{\mu}^2 \rangle = A + B \frac{\int_0^\pi \cos \phi e^{-\frac{v(\phi)}{kT}} d\phi}{\int_0^\pi e^{-\frac{v(\phi)}{kT}} d\phi} \quad (9)$$

where  $v(\phi)$  represent the torsional potential function.

The nature of this function will be discussed in the following section.

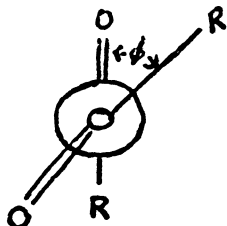
#### Torsional Potential Model

For 1,2-dicarbonyl compounds of the general form



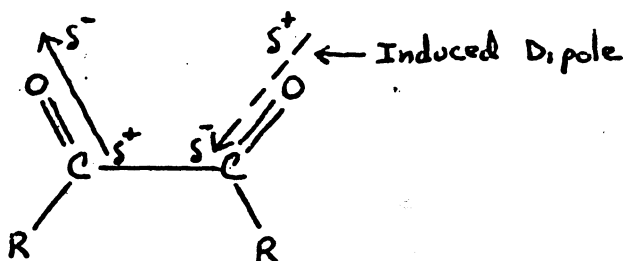
at least five different types of intramolecular forces

contribute to the torsional potential. The following coordinate system below will be used to describe the angular dependence of these interactions in the following discussion.



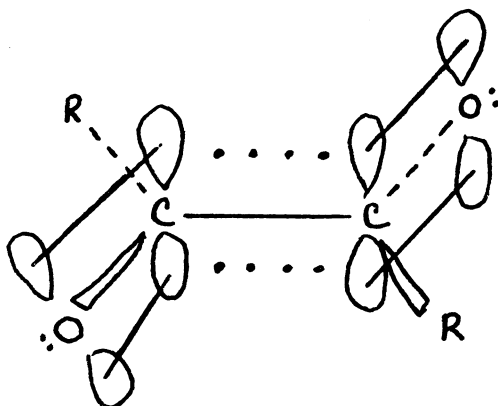
Note that the torsional angle  $\phi$  is zero for the trans configuration.

Both attractive and repulsive intramolecular forces contribute to the total torsional potential. Dipole-induced dipole, van der Waals, and pi-bonding are all attractive forces. The dipole-induced dipole force occurs when the permanent dipole associated with a carbonyl group induces an oppositely oriented dipole in the adjacent carbonyl group resulting in an attractive force. (See diagram below)



Attractive van der Waals forces result from interactions between dipoles in one carbonyl group induced by a temporary dipole in the adjacent carbonyl group. These small temporary instantaneous dipoles arise from rapid motion of the charge density along the highly polarizable carbonyl functional group. Van der Waals forces and dipole-induced dipole forces will both give a potential

energy curve that is qualitatively the same and is shown in Figure 12.1. A single parameter potential function expressed in the form  $\frac{V_1}{2} (1 - \cos \phi)$  can be used to represent these interactions where  $V_1$  represents the height of the potential curve. The third type of attractive force found is due to p-orbital overlap. In forming the  $sp^2$  hybridized carbonyl carbon atoms, one p-orbital containing a single electron remains unused. This p-orbital consists of two equal lobes of charge density oriented perpendicular to the plane of the three  $sp^2$  orbitals. A molecular orbital description of these molecules shows partial pi-bonding between these carbonyl atoms due to p-orbital overlap.



A plot of the potential energy curve for the p-orbital overlap (See Figure 12.3) is found to be quite different than for the other attractive forces. This difference is due to the fact that the attractive forces associated with the p-orbital overlap are periodic in every  $180^\circ$ . This potential curve exhibits a  $\cos 2\phi$  angular dependence. Thus the potential of the form  $\frac{V_2}{2} (1 - \cos 2\phi)$  provides an

Figure 12  
Angular Dependence of Three One-Parameter  
Potential Functions

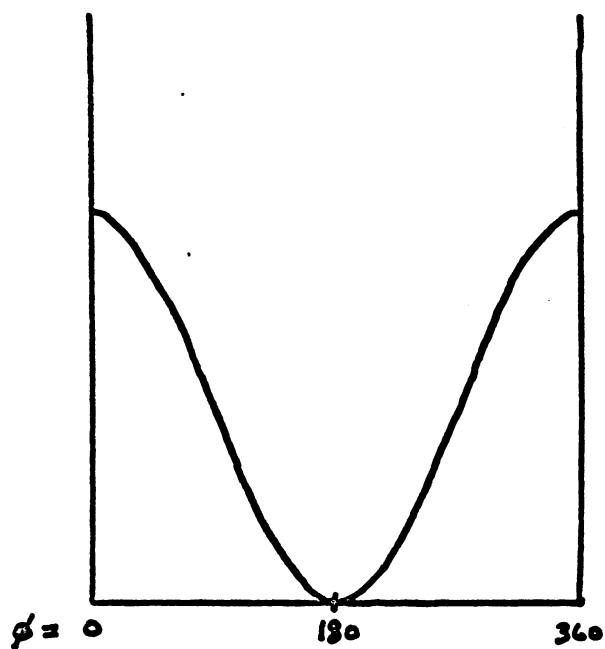


FIG. 12.1

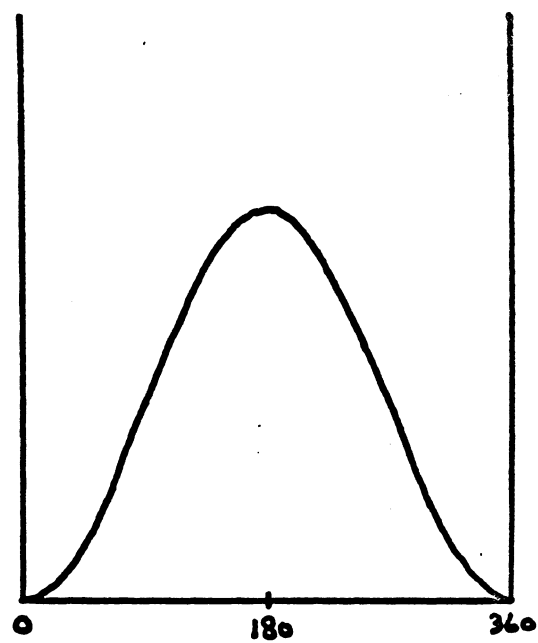


FIG. 12.2

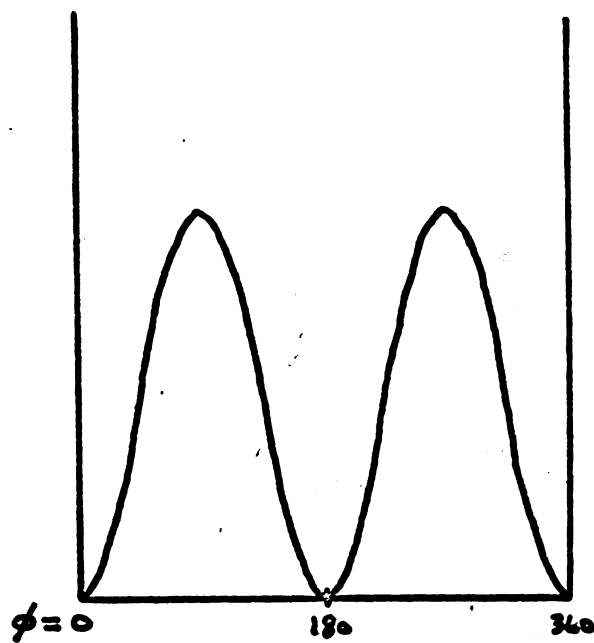
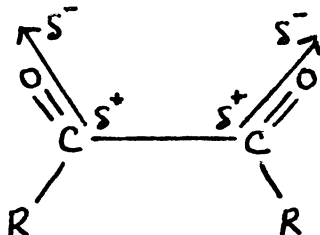


FIG 12.3



approximate description of the interaction due to p-orbital overlap.

In contrast to the attractive forces previously mentioned, dipole-dipole and steric forces are repulsive. The nature of the dipole-dipole interaction can be seen from the diagram below.



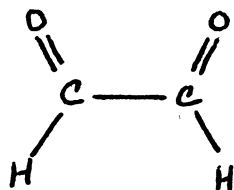
The permanent dipoles of the adjacent carbonyl groups prefer an orientation with the carbonyl oxygens as far away as possible on the basis that like charges will repel each other. Steric forces will also be of a repulsive nature in 1,2-dicarbonyl compounds. As the R groups become more bulky and crowding results, then the repulsive forces associated with the steric strain increases causing the groups to want to be as far away from each other as possible. For very bulky groups the trans configuration would relieve this strain and be most favored.



Both dipole-dipole and steric forces can be qualitatively represented by the potential curve in Figure 12.2. It should be pointed out that differences between the curves in Figure 12.1 and Figure 12.2 are due to the nature of the forces involved. With attractive forces the sign of  $V_1$  in  $\frac{V_1}{2}(1-\cos\phi)$  will be positive, whereas repulsive forces result in a negative  $V_1$ .

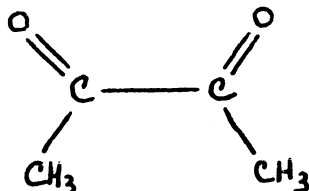
After analyzing all of the intramolecular forces associated with 1,2-dicarbonyl compounds, it is now apparent that a two parameter potential must be used for the potential energy function. A potential model may best be expressed as  $v(\phi) = \frac{V_1}{2}(1-\cos\phi) + \frac{V_2}{2}(1-\cos 2\phi)$ . The  $\frac{V_1}{2}(1-\cos\phi)$  term is associated with van der Waals, dipole-induced dipole, dipole-dipole, and steric forces. The second term  $\frac{V_2}{2}(1-\cos 2\phi)$  is associated with forces due to p-orbital overlap.

The cis isomer of glyoxal, the simplest 1,2-dicarbonyl compound, has been experimentally observed on two different occasions (Currie and Ramsey in 1970<sup>1</sup> and Durig, Tong, and Li in 1972<sup>2</sup>). Upon considering the structure of glyoxal it is evident that



steric factors between the hydrogen atoms will be

negligible. This lack of steric forces which in turn allows for greater contributions of the  $V_2$  term associated with p-orbital overlap may account for the existence of the cis isomer of glyoxal. In contrast, the cis isomer of 2,3-butanedione, the next simplest 1,2-dicarbonyl compound, has not been experimentally observed. All existing experimental evidence (ir, uv, and electron diffraction) indicates that



2,3-butanedione exists only in the trans form. It will be shown that this dipole study supports these findings.

#### Determination of Potential Parameters

Since an expression for the potential function,  $V(\phi)$ , has been obtained, equation (9) can be written in the form

$$\langle \mu^2 \rangle = A + B \frac{\int_0^\pi \cos \phi e^{-\frac{[V_1(1-\cos \phi) + \frac{V_2}{2}(1-\cos 2\phi)]}{kT}} d\phi}{\int_0^\pi e^{-\frac{[V_1(1-\cos \phi) + \frac{V_2}{2}(1-\cos 2\phi)]}{kT}} d\phi} \quad (10)$$

The potential parameters  $V_1$  and  $V_2$  that best fit the experimental dipole moment measurements can be found from the above equation. This is accomplished by calculating dipole moments as a function of temperature for

specific values of  $V_1$  and  $V_2$ , which were systematically varied.

The integrals in equation (10) were evaluated by numerical methods on an IBM-360 computer using Simpson's rule. (See Appendix 2) A search grid of  $1500 \text{ cm}^{-1} < V_1 < 3500 \text{ cm}^{-1}$  and  $0 \text{ cm}^{-1} < V_2 < 600 \text{ cm}^{-1}$ , using increments of  $\Delta V_1 = 10 \text{ cm}^{-1}$  and  $\Delta V_2 = 10 \text{ cm}^{-1}$ , requires the evaluation of more than a million integral areas.

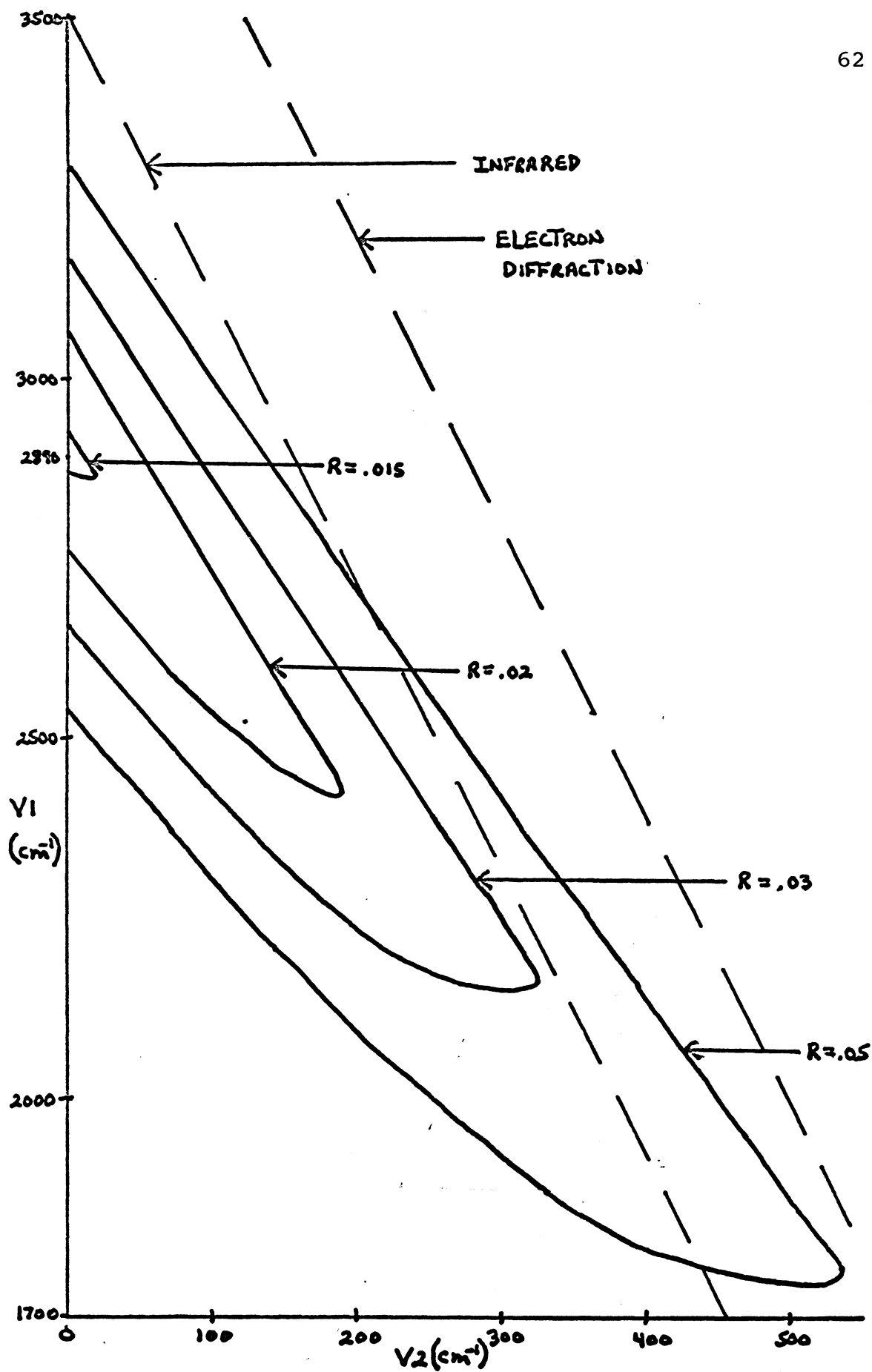
The calculated dipoles are compared to the experimental values to assess the quality of the potential parameters. The results of each comparison can be expressed by a regression value (R)

$$R = \sum_{i=1}^n S_i^2$$

where  $S$  = the difference between the calculated dipoles and observed dipoles.

The regression (R) will equal zero when the experimental and calculated dipoles are equal. Hence, the best potential parameters correspond to a minimum regression. A regression contour map best illustrates the results of this parameter search. (See Figure 13) The precision of these dipole measurements allows the best values for the  $V_1$  and  $V_2$  potentials to lie anywhere within the regression equal to 0.015. The best regression fit corresponds to  $V_1 = 2890 \text{ cm}^{-1}$  and  $V_2 = 0.0 \text{ cm}^{-1}$ .

Figure 13  
Regression Contours for  $R = 0.05, 0.03, 0.02,$  and  $0.015$ .  
Also Included Are Electron Diffraction and Infrared  
Constraints for  $V_1$  and  $V_2$  (See "Potential  
Parameters from other Methods"  
in Discussion)



### Potential Parameters from other Methods

Values for the potential parameters  $V_1$  and  $V_2$  have been estimated from infrared<sup>3,4</sup> and electron diffraction<sup>5</sup> data. In both cases, these values were calculated from the harmonic oscillator model. This model assumes that the torsional vibrational spacings are governed by a parabolic potential function. Indeed a cosine function can be approximated by a parabola near its minimum value. If a cosine function is expanded in a power series, then it becomes

$$\cos \phi = 1 - \frac{\phi^2}{2!} + \frac{\phi^4}{4!} - \frac{\phi^6}{6!} + \dots \quad (11)$$

For cases where the angle  $\phi$  is small, then the higher order terms can be neglected and the series truncated at the second order term.

In earlier discussion, the potential function for 1,2-dicarbonyl compounds was found to be described by

$$V(\phi) = \frac{V_1}{2} (1 - \cos \phi) + \frac{V_2}{2} (1 - \cos 2\phi) \quad (12)$$

This equation can then be rewritten in the following manner

$$V(\phi) = \frac{V_1}{4} \phi^2 + V_2 \phi^2 \quad (13)$$

after substituting the expression given in equation (11) for the  $\cos \phi$  term. Upon simplification, equation (13)

can be rewritten

$$V(\phi) = \frac{1}{4} (V_1 + 4V_2) \phi^2 \quad (14)$$

If  $V^*$  is introduced to represent the quantity  $V_1 + 4V_2$ :

$$V^* = V_1 + 4V_2 \quad (15)$$

This allows equation (14) to now be written

$$V(\phi) = \frac{1}{4} (V^*) \phi^2 \quad (16)$$

which is the expression given for the harmonic oscillator having the force constant

$$k = \frac{V^*}{2} \quad (17)$$

i.e.

$$V(\phi)_{\text{ho}} = \frac{1}{2} k \phi^2 = \frac{1}{2} \left( \frac{V^*}{2} \right) \phi^2$$

In addition, the frequency of oscillation can also be related to the force constant and reduced moment of inertia in the following manner:<sup>15</sup>

$$\bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu_r}} \quad (18)$$

where  $\mu_r$  = reduced moment of inertia

$k$  = force constant

$\bar{\nu}$  = frequency of oscillation



Substituting  $V^*/2$  for  $k$ , equation (18) becomes

$$\bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{V^*/2}{k_2}} \quad (19)$$

From equation (19), the value for  $V^*$  can then be obtained by measuring the torsional transition frequency,  $\bar{\nu}$ , associated with the torsional mode about the C-C bond. Using infrared data,<sup>4a</sup>  $V^*$  has been reported as  $3520 \text{ cm}^{-1}$ , whereas electron diffraction<sup>5</sup> analysis found it to be equal to  $3989 \text{ cm}^{-1}$ . Values of  $V_1$  and  $V_2$  that satisfy the infrared and electron diffraction for  $V^*$  are shown as straight lines in Figure 13.

From dipole moment data, the best regression fit of the potential parameters gave values of  $V_1 = 2890 \text{ cm}^{-1}$  and  $V_2 = 0.0 \text{ cm}^{-1}$ .<sup>a</sup> When comparing these values with other experimental results, it can be seen that a wide variation exists in the three values for  $V_1$  when  $V_2$  equals zero.

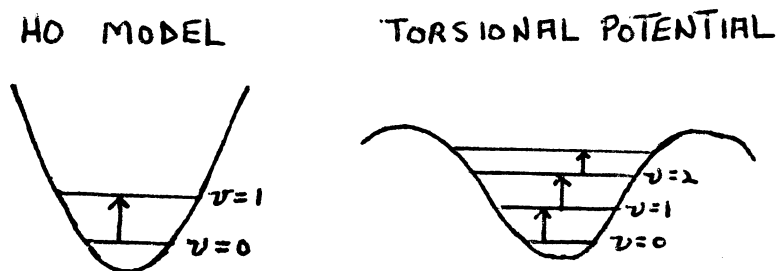
	<u><math>V_1(\text{cm}^{-1})</math></u>	<u><math>V_2(\text{cm}^{-1})</math></u>
Dipole Moment	2890.0	0.0
Electron Diffraction <sup>5</sup>	3989.0	0.0
Infrared <sup>4</sup>	3520.0	0.0

This discrepancy may be attributed to approximations that are made in obtaining the values for  $V_1$  and  $V_2$  using

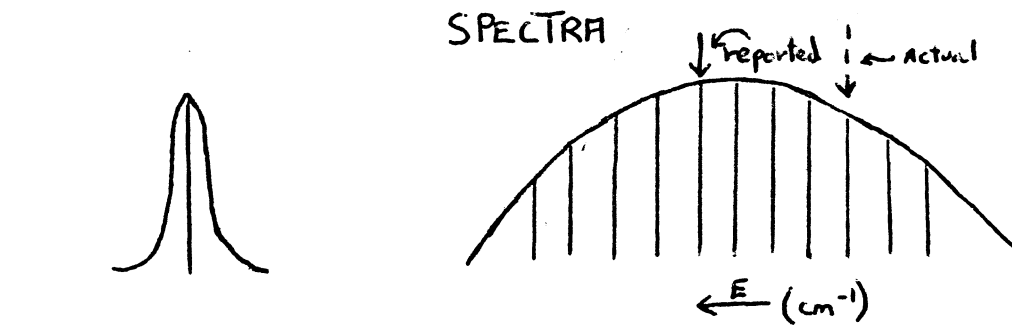
---

<sup>a</sup>The best fit of Bloom and Sutton's data gave  $V_1 = 2630 \text{ cm}^{-1}$  and  $V_2 = 0.0 \text{ cm}^{-1}$ .

infrared and electron diffraction. Treating the torsional potential curve like a true harmonic oscillator is a poor approximation, at best, since any anharmonicity present in the potential has been neglected. Moreover, the absorption maximum has been interpreted as a single transition ( $\nu=1 \leftarrow \nu=0$ ) as shown below.



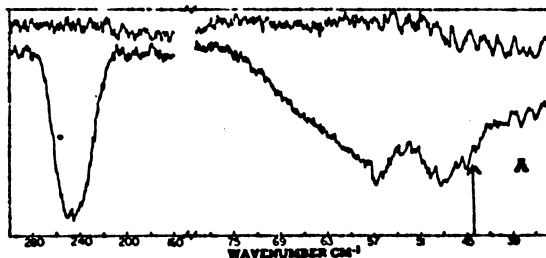
This would be true if only the lower torsional vibrational level was populated. Since the vibrational spacings, ( $\Delta E \cong 50 \text{ cm}^{-1}$ ),<sup>a</sup> is much smaller than  $kT$ , all of the vibrational levels are significantly populated in accordance with a Boltzmann distribution. This results in the torsional absorption spectrum made up of several closely spaced transitions. Therefore, the  $1 \leftarrow 0$  torsional transition of interest should lie at a lower value than reported. (See Diagram Below) Since this torsional



<sup>a</sup>Durig et al<sup>3</sup> report  $\bar{\nu} = 52 \text{ cm}^{-1}$ , Fately et al<sup>4a</sup> and Harris et al<sup>4b</sup> report  $\bar{\nu} = 48 \text{ cm}^{-1}$ .

transition is at a very low energy (approximately  $50 \text{ cm}^{-1}$ ), a small uncertainty in the reported transition frequency can have large effects on the value for  $V^*$  and likewise on the potentials  $V_1$  and  $V_2$ .

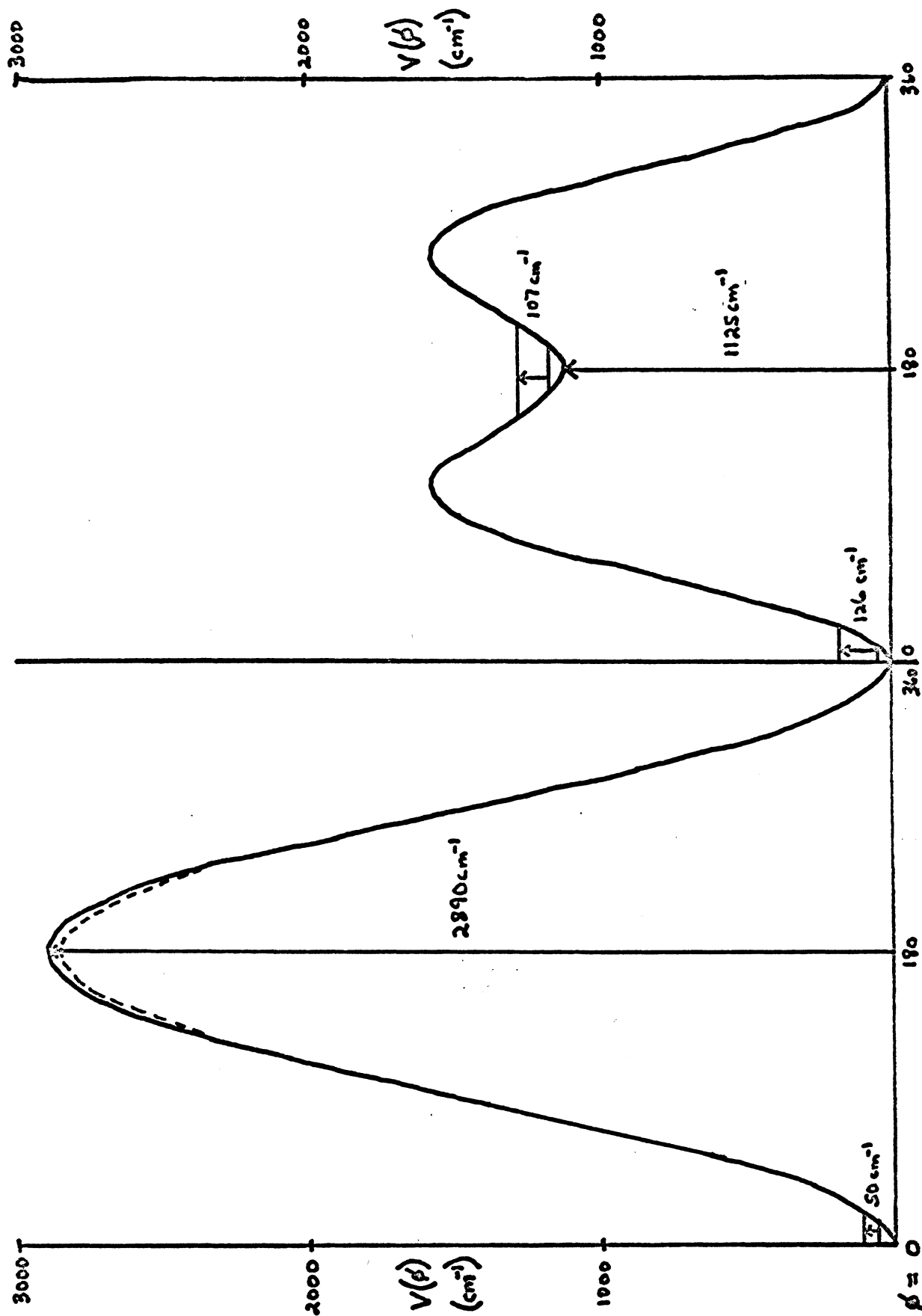
Using the optimum potential parameters determined from the temperature dependence of the dipole moment,  $V_1 = 2890 \text{ cm}^{-1}$  and  $V_2 = 0.0 \text{ cm}^{-1}$ , the harmonic oscillator torsional frequency can be calculated from equation (15) and (19) as  $\bar{\nu} = 44 \text{ cm}^{-1}$ . This frequency is indeed compatible with the observed far infrared absorption.



The Far IR spectrum of 2,3-butanedione, reproduced from Durig, Hannum and Brown, Journal of Physical Chemistry, LXXV (1971), 1953. The arrow at  $44 \text{ cm}^{-1}$  corresponds to the  $1 \leftarrow 0$  harmonic transition frequency calculated from this dipole moment study.

This dipole study provides convincing theoretical evidence that the cis isomer of 2,3-butanedione is unstable. The regression contours derived from these measurements indicates that the intramolecular forces that are periodic in  $2\pi$  are very small. Hence, spectroscopic detection of the cis isomer would seem highly improbable. The limiting potentials derived from this study are depicted in the Figure 14.1. It is of interest to compare the

Figure 14  
Limiting Potential Energy Curves for Internal Rotation  
in 2,3-Butanedione Compared with Glyoxal



intramolecular torsional potential of 2,3-butanedione with glyoxal as shown in Figure 14.2.

Just as steric arguments were used to explain the existence of the cis isomer for glyoxal, steric arguments may also be used to account for 2,3-butanedione existing only in the trans form. As the hydrogen atoms in glyoxal are replaced by the more bulky methyl groups, steric forces would increase between the two methyl groups which results in the trans isomer becoming more stable and sterically favored over the cis form.

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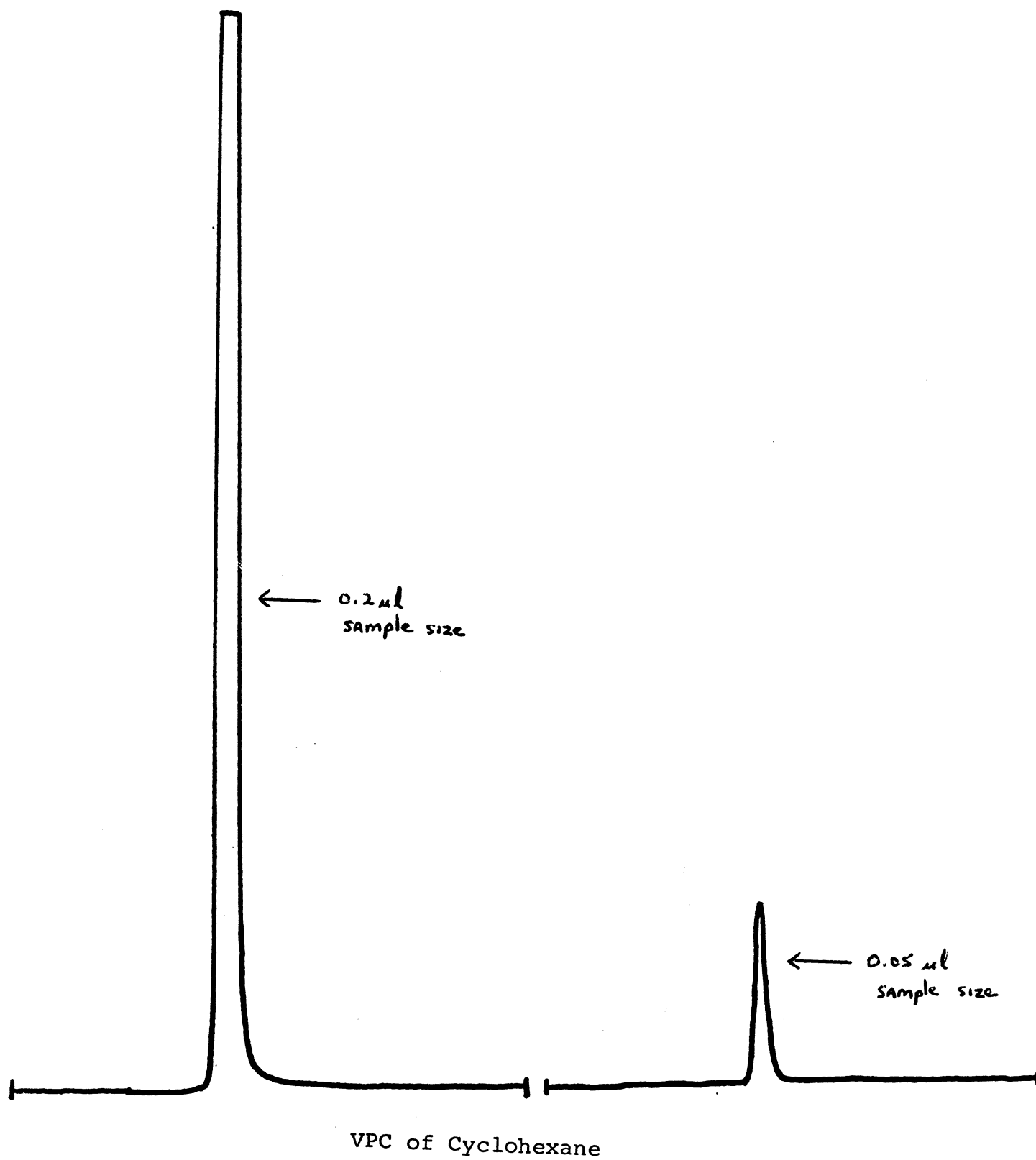
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Appendix 1  
Spectral Data and Vapor Phase Chromatographs

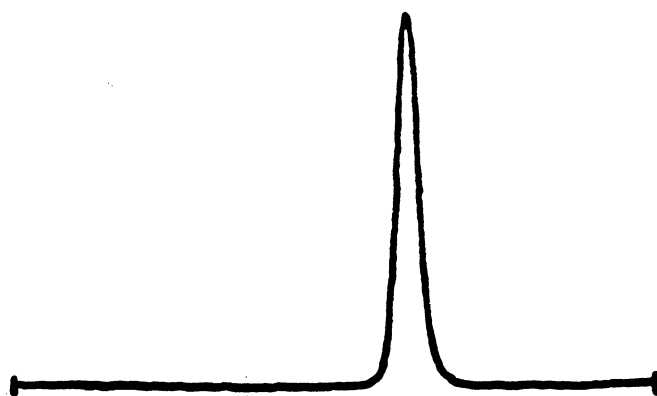
## VPC OF CYCLOHEXANE

INSTRUMENT: P.E. 154-L  
COLUMN LENGTH: 10 ft.  
SUPPORT: Solid  
CARRIER GAS: Helium  
FLOW RATE: 72 ml/min.  
CHART SPEED: 1 inch/min.  
DETECTOR: 15% SE-30  
PRESSURE: 10 psig  
TEMPERATURES: Column 128°C  
Detector 128°C  
SENSITIVITY: 2  
SAMPLE SIZE: 0.2  $\mu$ l, 0.05  $\mu$ l



## VPC OF CARBON TETRACHLORIDE

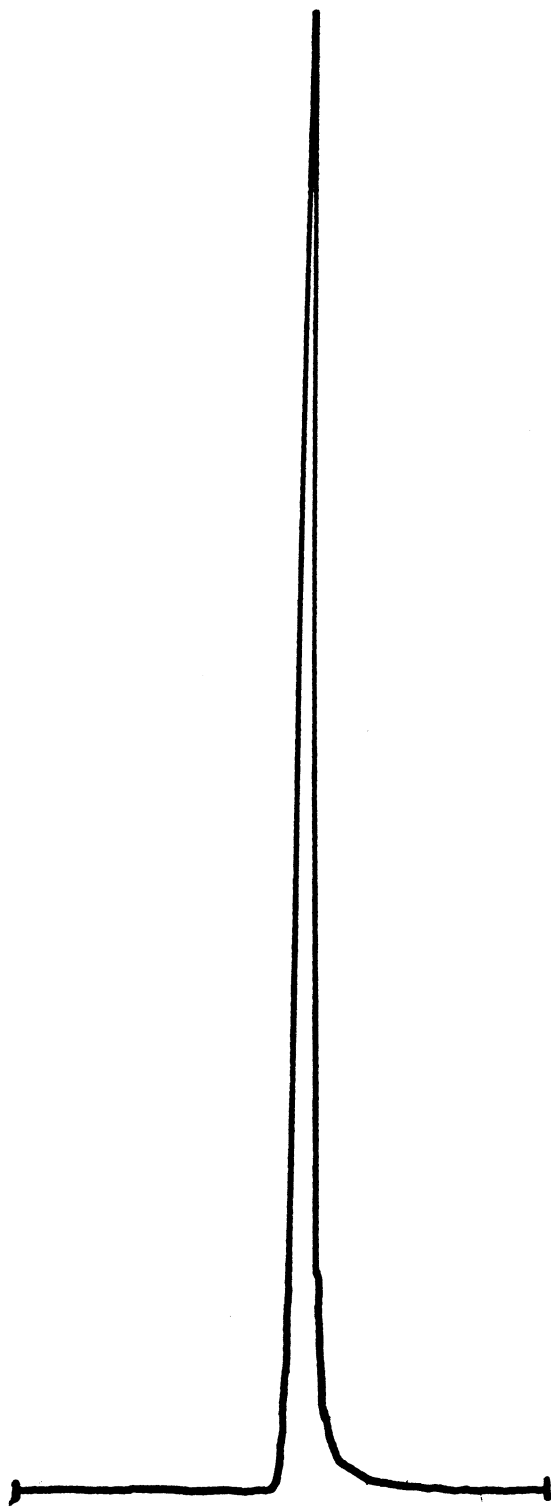
INSTRUMENT:	P.E. 154-L
COLUMN LENGTH:	10 ft.
SUPPORT:	Solid
CARRIER GAS:	Helium
FLOW RATE:	72 ml/min.
CHART SPEED:	1 inch/min.
DETECTOR:	15% SE-30
PRESSURE:	10 psig
TEMPERATURES:	Column 96°C Detector 96°C
SENSITIVITY:	2
SAMPLE SIZE:	0.2 <i>ul</i>



VPC of Carbon Tetrachloride

## VPC of BENZENE

INSTRUMENT:	P.E. 154-L
COLUMN LENGTH:	10 ft.
SUPPORT:	Solid
CARRIER GAS:	Helium
FLOW RATE:	72 ml/min.
CHART SPEED:	1 inch/min.
DETECTOR:	15% SE-30
PRESSURE:	10 psig
TEMPERATURES:	Column 128°C Detector 128°C
SENSITIVITY:	2
SAMPLE SIZE:	0.2 $\mu$ l

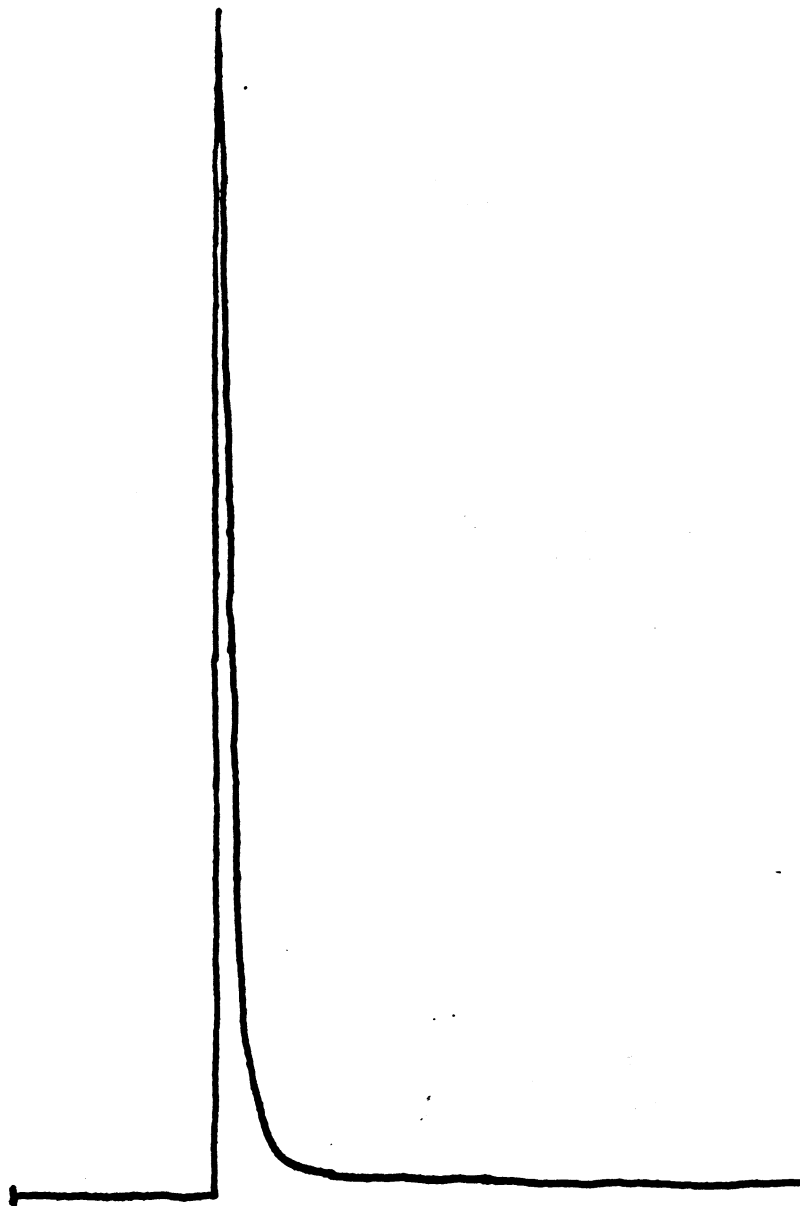


VPC of Benzene

## VPC OF 2,3-BUTANEDIONE

INSTRUMENT:	P.E. 154-L
COLUMN LENGTH:	10 ft.
SUPPORT:	Solid
CARRIER GAS:	Helium
FLOW RATE:	78 ml/min.
CHART SPEED:	1 inch/min.
DETECTOR:	15% SE-30
PRESSURE:	10 psig
TEMPERATURES:	Column 114°C Detector 114°C
SENSITIVITY:	8
SAMPLE SIZE:	0.2 <i>ul</i>

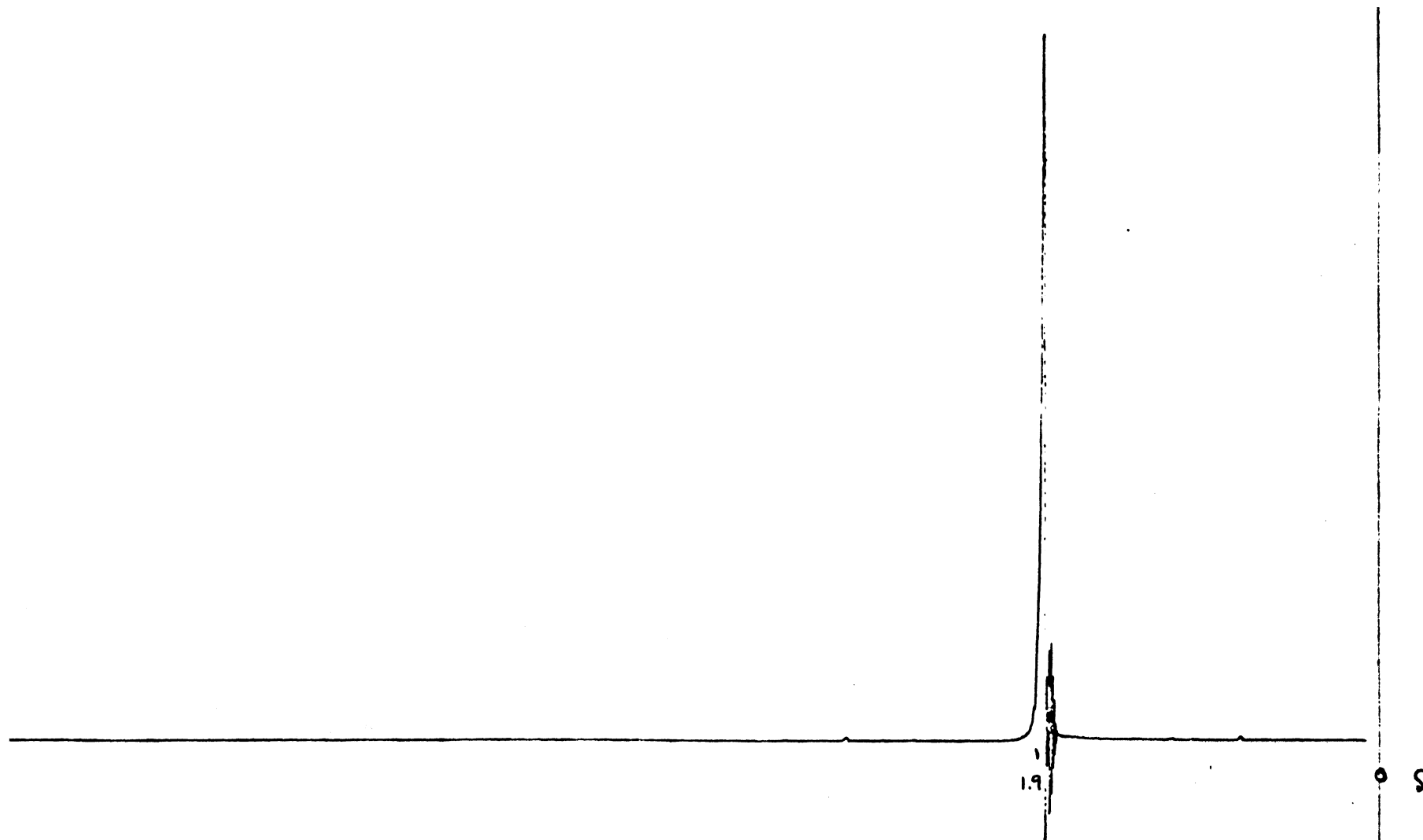




VPC of 2,3-butanedione

## 60 MHz NMR of 2,3-BUTANEDIONE

SWEEP OFFSET:	0Hz
SPECTRUM AMPLITUDE:	0.25
SPINNING RATE:	42 rps
SWEEP TIME:	250 Sec
SWEEP WIDTH:	500 Hz
FILTER:	1.0
RF POWER:	0.05



NMR spectra of 2,3-butanedione

Appendix 2  
FORTRAN Computer Programs

Computer Program Used in Calculating Dipole Moment,  
Dielectric Constant, Molar Polarization,  
Distortion Polarization and Orientation  
Polarization for Pure Liquid  
Measurements.

```

$JOB      105GEVERT MEYER  CHEMISTRY  WATFIV
          DIMENSION DC(2),XA(2),U(2),PD(2),PU(2)
          WRITE(6,10)
10        FORMAT(1H1,25X,25HDIPOLE MOMENT CALCULATION)
C        VALUES FOR CONSTANTS
11        XN=6.0248E23
12        XK=1.38046E-16
13        PI=3.14159265
C        INTRODUCE DATA VALUES
14        READ(5,20) T,DT
20        FORMAT(2F10.0)
21        READ(5,30) RI,DI
30        FORMAT(2F10.0)
31        READ(5,40) C,DD
40        FORMAT(2F10.0)
41        READ(5,50) S,DS
50        FORMAT(2F10.0)
51        READ(5,60) RM
60        FORMAT(1F10.0)
61        READ(5,70) CA,CB,CC
70        FORMAT(2F10.0,F20.0)
71        READ(5,80) N
80        FORMAT(I3)
81        READ(5,90) XM
90        FORMAT(F10.0)
          READ(5,100) R
100       FORMAT(F10.0)
          WRITE(6,110)
110      FORMAT(1H0,20X,12HDIAL SETTING,20X,19HDIELECTRIC CONSTANT)
C        INITIATE DC LOOP FOR DIAL SETTING VERSUSDIELECTRIC CONSTANT TABLE
          DO 200 I=1,N
            XI=I
            XS=(XM*XI)+R
            XD=CA+(CB*XS)+(CC*(XS*XS))
C          PRINT TABLE
            WRITE(6,111) XS,XD
111      FORMAT(1H0,25X,F7.2,25X,F6.3)
200      CONTINUE
C        INITIATE LOOP FOR DIPOLE CALCULATION
          DO 300 I=1,2
C          DC(I) IS DIELECTRIC CONSTANT
205      DC(I)=CA+(CB*S)+(CC*(S*S))
206      EI=RI*RI
207      YA=RM/D
208      XF=(DC(I)-1.0)/(DC(I)+2.0)
C          XA(I) IS MOLAR POLARIZATION
209      XA(I)=XF*YA
210      XB=(EI-1.0)/(DC(I)+2.0)
211      XB=XB*YA
212      XC=XA(I)-XB
213      XD=(3.0*DC(I))*(EI+2.0)
214      XE=((2.0*DC(I))+EI)*(DC(I)+2.0)
215      XF=XD/XE
216      XH=XC/XF
217      YR=0.0*XK*T
218      YC=4.0*PI*XN
219      YD=YR/YC
220      UV=XH*YD
221      U(I)=SORT(UV)
C          U(I) IS DIPOLE MOMENT

```

```

      U(I)=U(I)/1.0E-18
222    FA=(EI-1.0)/(EI+2.0)
      Z=FA*YA
      ZA=Z*0.1
C      PD(I) IS DISTORTION POLARIZATION
      PD(I)=Z+ZA
C      PU(I) IS ORIENTATION POLARIZATION
      PU(I)=XA(I)-PD(I)
C      CHANGE INCREMENTS
225    D=D-DD
226    S=S+DS
227    RI=RI-DI
228    T=T+DT
300    CONTINUE
301    DCS=DC(2)-DC(1)
302    XAS=XA(2)-XA(1)
303    US=U(2)-U(1)
304    PDS=PD(2)-PD(1)
305    PUS=PU(2)-PU(1)
306    WRITE(6,310)U(1),US
310    FORMAT(1H0,20X,15HDIPOLE MOMENT =,F6.3,1X,6HDERIVES,10X,11HPRECISION
      IN =,F6.3)
311    WRITE(6,320)DC(1),DCS
320    FORMAT(1H0,20X,21HDIELECTRIC CONSTANT =,F6.3,11X,11HPRECISION =,F6.
      2,3)
321    WRITE(6,330)XA(1),XAS
330    FORMAT(1H0,20X,20HMOLAR POLARIZATION =,F7.3,12X,11HPRECISION =,F6.
      23)
331    WRITE(6,340)PD(1),PDS
340    FORMAT(1H0,20X,25HDISTORTION POLARIZATION =,F7.3,6X,11HPRECISION :
      3,F6.3)
341    WRITE(6,350)PU(1),PUS
350    FORMAT(1H0,20X,26HORIENTATION POLARIZATION =,F7.3,5X,11HPRECISION:
      4,F6.3)
      RETURN
      END

```

CONT DV

Least Squares Program for Nonlinear Function



```

$JOB      105GEVERTMEYER    WATFIV CHEMISTRY
C      LEAST SQUARES CURVE FITTING BY ORTHOGONAL POLYNOMIALS
      DIMENSION P(15,14),A(15),X(100),Y(100),W(100)
      WRITE(6,10)
10     FORMAT(1H1,18X,53HLEAST SQUARES CURVE FITTING BY ORTHOGONAL POLYNOMIALS)
20     READ(5,1000)NX,N,M,K
30     IF(M-N)40,40,50
40     N=M-1
50     NX=NX+1
60     IF(K)110,70,110
70     DO 90 I=1,M
80     READ(5,1001)X(I),Y(I),W(I)
90     CONTINUE
100    GO TO 150
110    DO 140 I=1,M
120    READ(5,1001)X(I),Y(I)
130    W(I)=1.0
140    CONTINUE
150    DO 180 I=1,15
160    DO 180 J=1,14
170    P(I,J)=0.0
180    CONTINUE
190    P(1,1)=1.0
200    XSUM=0.0
210    YSUM=0.0
220    DO 250 J=1,M
230    XSUM=XSUM+X(J)*W(J)
240    YSUM=YSUM+W(J)
250    CONTINUE
260    P(2,2)=1.0
270    P(2,1)=-XSUM/YSUM
280    NN=N+1
290    DO 540 I=3,NN
300    II=I-1
310    IX=I-2
320    XSUM=0.0
330    YSUM=0.0
340    USUM=0.0
350    ZSUM=0.0
360    DO 470 K=1,M
370    SUMY=0.0
380    SUMX=0.0
390    DO 420 L=1,I
395    IF(L-1)400,395,400
400    SUMY=SUMY+P(II,L)*X(K)**(L-1)
410    SUMX=SUMX+P(IX,L)*X(K)**(L-1)
420    CONTINUE
430    XSUM=XSUM+X(K)*SUMY**2*W(K)
440    YSUM=YSUM+SUMY**2*W(K)
450    USUM=USUM+X(K)*SUMY*SUMX*W(K)
460    ZSUM=ZSUM+SUMX**2*W(K)
470    CONTINUE
480    B=XSUM/YSUM
490    G=-USUM/ZSUM
500    P(I,1)=-B*P(II,1)+G*P(IX,1)
510    DO 540 J=2,I

```

```

520 JJ=J-1
530 P(I,J)=P(II,JJ)-B*P(II,J)+G*P(IX,J)
540 CONTINUE
550 DO 670 I=1,NN
560 XSUM=0.0
570 YSUM=0.0
580 DO 650 K=1,M
590 SUMZ=0.0
600 DO 620 L=1,I
610 IF(L-1)610,605,610
605 SUMZ=SUMZ+P(I,L)
620 GO TO 620
610 SUMZ=SUMZ+P(I,L)*X(K)**(L-1)
620 CONTINUE
630 XSUM=XSUM+Y(K)*SUMZ*W(K)
640 YSUM=YSUM+SUMZ**2*W(K)
650 CONTINUE
660 A(I)=XSUM/YSUM
670 CONTINUE
680 DO 790 I=1,NN
690 DO 710 J=1,I
700 P(15,J)=P(15,J)+P(I,J)*A(I)
710 CONTINUE
720 IF(I-NX)790,730,730
730 L=I-1
740 WRITE(6,1003)L
750 DO 780 K=1,I
760 KK=K-1
770 WRITE(6,1004)KK,P(15,K)
780 CONTINUE
790 CONTINUE
1000 FORMAT(4I5)
1001 FORMAT(3F10.8)
1003 FORMAT(///12X24HTHE POLYNOMIAL OF ORDER 14,28H THAT BFST FITS THE
1004 1CURVE IS //26X10HPOWER OF X,12X11HCOEFFICIENT)
1004 FORMAT(29X14,10XE14.7)
1005 RETURN
END

```

\$FENTRY

Least Squares Program for Linear Function

```

$JOB      105GEVERT-MEYER  WATFIV  CHEMISTRY
C      PRINT HEADINGS
10      WRITE(6,10)
      FORMAT(1H1,7X,5HLEAST,1X,7HSQUARES,1X,3HFIT,1X,3HFOR,1X,6HLINEAR,
      21X,8HFUNCTION)
20      WRITE(6,20)
      FORMAT(1H0,28X,4HDATA)
30      WRITE(6,30)
      FORMAT(1H0,19X,1HX,21X,1HY)
C      ASSIGN VALUES TO VARIABLES
      XSUM=0.0
      YSUM=0.0
      XYSUM=0.0
      XSUMSQ=0.0
C      DETERMINING THE NUMBER OF DATA CARDS
40      READ(5,40)N
      FORMAT(I3)
      DO 100 I=1,N
C      READ AND WRITE DATA
      READ(5,50)X,Y
50      FORMAT(2F10.0)
      WRITE(6,60)X,Y
60      FORMAT(1H0,10X,F10.3,12X,F10.3)
C      INCREASE SUMS
      XSUM=XSUM+X
      YSUM=YSUM+Y
      XYSUM=XYSUM+X*Y
      XSUMSQ=XSUMSQ+X*X
100     CONTINUE
C      CALCULATIONS
      XSUMXZ=XSUM**2.
      XM=N
      D=((XN*XSUMSQ)-(XSUMXZ))
      A=((XN*XYSUM)-(XSUM*YSUM))/D
      R=((XSUMSQ*YSUM)-(XSUM*XYSUM))/D
      WRITE(6,70)A
70      FORMAT(1H0,10X,7HSLOPE =,F14.7)
      WRITE(6,80)R
80      FORMAT(1H0,10X,11HINTERCEPT =,F14.7)
      RETURN
      END
$ENTRY

```

Computer Program Used for Evaluating the  
Torsional Potential Parameters

```

$JNR      105GEVERTMEYER,TIME=30,PAGES=9999 WATFIV  CHEMISTRY
C      T IS USED TO REPRESENT TEMPERATURE VALUES
C      UEXP IS USED TO REPRESENT EXPERIMENTAL DIPOLE MOMENT VALUES
C      U IS USED TO REPRESENT THEORETICAL DIPOLE MOMENT VALUES
C      DIMENSION T(10),UEXP(10),U(10)
C      ND IS THE NUMBER OF DATA POINTS
      READ(5,10)ND
10      FORMAT(I2)
      DO 25 K=1,ND
      READ(5,20)T(K),UEXP(K)
20      FORMAT(2F10.0)
25      CONTINUE
C      PRINT HEADINGS AND DATA
      WRITE(6,30)T(1),T(2),T(3),T(4),T(5),T(6)
30      FORMAT(1H1,30X,11HTEMPERATURE,5X,F6.2,5X,F6.2,5X,F6.2,5X,F6.2,5X,F
26.2,5X,F6.2)
      WRITE(6,40)UEXP(1),UEXP(2),UEXP(3),UEXP(4),UEXP(5),UEXP(6)
40      FORMAT(1H0,15X,26HEXPERIMENTAL DIPOLE MOMENT,5X,F6.2,5X,F6.2,5X,F6
1.2,5X,F6.2,5X,F6.2,5X,F6.2)
      WRITE(6,50)
50      FORMAT(1H0,6X,4HV(1),10X,4HV(2),12X,1HR,20X,24HCALCULATED DIPOLE M
2CMENT)
C      ASSIGN VALUES TO CONSTANTS
      PI=3.14159265
      R=1.9872/2.858
      A=11.91
      R=11.91
      XI=0.0
      XF=180.0
C      CHANGE ANGLE FROM DEGREES TO RADIANS
C      XI REPRESENTS THE ANGLE IN THE TRANS POSITION
C      XF REPRESENTS THE ANGLE IN THE CIS POSITION
      XI=XI*(2.*PI/360.)
      XF=XF*(2.*PI/360.)
C      J IS USED TO INDEX THE V2 LOOP
C      L IS USED TO INDEX THE V1 LOOP
C      K IS USED TO INDEX THE LOOP FOR EACH SET OF DATA VALUES
      V2=0.0
      DO 500 J=1,9
      V1=800.0
      DO 300 L=1,17
      V1=V1+200.0
      DO 100 K=1,ND
C      RHON IS USED FOR NUMERATOR INTEGRAL
C      RHOD IS USED FOR DENOMINATOR INTEGRAL
C      N IS THE NUMBER OF INCREMENTS
C      X REPRESENTS INTEGRATOR COORDINATE
C      XM EQUALS NUMBER OF INCREMENTS
C      DX EQUALS HORIZONTAL DISTANCE BETWEEN F(0) AND F(1)
C      DX2 EQUALS TWO TIMES THE HORIZONTAL DISTANCE F(0) AND F(1)
      RHON=0.0
      RHOD=0.0
      X=XI
      N=50
      XM=N
      DX=(XF-XI)/XM
      DX2=2.*DX
C      SET UP LOOP TO DO CALCULATIONS
C      I IS USED TO INDEX THE CALCULATION LOOP
      DO 60 I=2,N,2

```

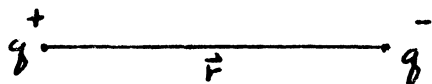


Appendix 3  
Theoretical Relationships of Dielectric Constant,  
Polarization, and Dipole Moments



### APPENDIX 3

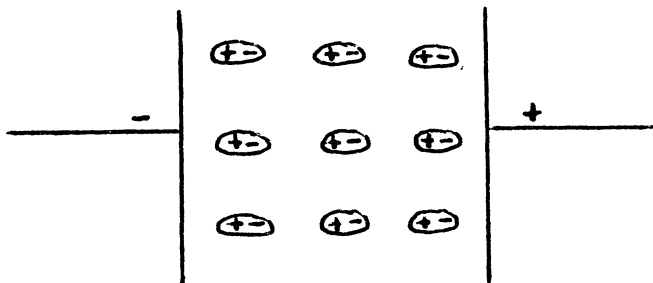
A molecule will possess an electric dipole when the centers of positive and negative charge do not coincide. This case is represented in the diagram



where  $q^+$  and  $q^-$  are point charges separated by a vector  $r$ . The electric dipole moment is then defined

$$\vec{\mu} = q \cdot \vec{r}$$

All molecules placed in an electric field, i.e. between the plates of a charged capacitor, will have an induced dipole moment due to distortion polarization. This type of polarization results when the molecule becomes slightly deformed as the electrons tend to shift their average position closer to the positive plate, leaving the nuclei closer to the negative plate as shown below.



Since the magnitude of this induced dipole depends upon the polarizability of the molecule then the total distortion polarization,  $P_d$ , can be given by<sup>14</sup>

$$P_d = \frac{4\pi}{3} N_o \alpha \quad (1)$$

where  $N_o$  = Avagadro's number

$\alpha$  = polarizability of the molecule

In addition to the distortion polarization, polar molecules also have orientation polarization,  $P_u$ , due to the presence of a permanent dipole moment.<sup>14</sup>

$$P_u = \frac{4\pi}{3} N_o \frac{\mu^2}{3kT} \quad (2)$$

where  $k$  = Boltzmann constant

$T$  = temperature in  $^{\circ}\text{K}$

$N_o$  = Avagadro's number

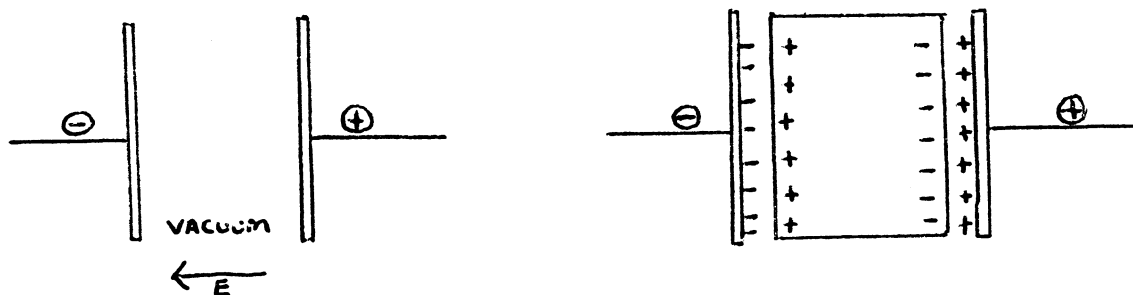
$P_u$  = orientational polarization

In an electric field, polar molecules tend to align with the applied field in so far as allowed by thermal motion. The total molar polarization,  $P_m$ , for polar molecules in an applied electric field is then the sum of the distortion polarization and the orientation polarization.

$$P_m = P_d + P_u \quad (3)$$

The measurement of the orientation polarization,  $P_u$ ,

is of primary importance since the calculation of the dipole moment is dependent upon its solution. However,  $P_u$  cannot be measured directly in the laboratory, but rather must be obtained by taking measurements of the dielectric constant,  $\epsilon$ .



$C_0$  = Capacitance in vacuum

$C$  = Capacitance with dielectric media present

As shown above, when a dielectric media is placed between the plates of a charged capacitor, the dielectric media induces an opposite charge on the plates causing the capacitor to have an additional charge. The dielectric constant is then related to these changes in capacitance where

$$\epsilon = \frac{C}{C_0} > 1$$

Once the dielectric constant has been obtained, then the total molar polarization can be calculated from the Clausius-Mosotti equation.<sup>14</sup>

$$P_m = \frac{\epsilon - 1}{\epsilon + 2} \left( \frac{m}{\rho} \right) \quad (4)$$

where  $P_m$  = molar polarization

$\epsilon$  = dielectric constant

M = molecular weight

$\rho$  = density

The final quantity needed to solve equation (3) for the orientation polarization is the distortion polarization,  $P_d$ . This can be determined by placing the sample in an electric field that alternates very rapidly and the molecules cannot turn fast enough to keep up with the changing field. As a result, the electrons move much more rapidly and the distortion polarization alone is observed. Thus at optical frequencies the dielectric constant,  $\epsilon$ , is equal to the index of refraction squared. In the laboratory, distortion polarization is measured by finding the index of refraction. This is given by the relationship presented by Lorentz-Lorenz.<sup>14</sup>

$$P_d = \frac{n^2 - 1}{n^2 + 2} \left( \frac{M}{\rho} \right) \quad (5)$$

where  $P_d$  = distortion polarization

n = index of refraction

M = molecular weight

$\rho$  = density

Once solution for the molar polarization,  $P_m$ , and distortion polarization,  $P_d$ , have been obtained, then the dipole moment,  $\mu$ , can be calculated. Upon rearrangement and the substitution of equation (2) for  $P_u$ , equation (3) then becomes

$$P_m - P_d = \frac{4 \pi N_e \mu^2}{9 k T} \quad (6)$$

Another form for equation (6) is

$$\frac{\epsilon-1}{\epsilon+2} \left( \frac{m}{\rho} \right) - \frac{n^2-1}{n^2+2} \left( \frac{m}{\rho} \right) = \frac{4 \pi N \mu^2}{9 k T} \quad (7)$$

where  $\epsilon$  = dielectric constant

$M$  = molecular weight

$\rho$  = density

$n$  = index of refraction

$N$  = Avagadro's number

$k$  = Boltzmann constant

$T$  = temperature in  $^{\circ}K$

$\mu$  = dipole moment

which is known as the Debye equation.<sup>13</sup> The Debye equation is used to calculate dipole moment for gases at or below atmospheric pressure. When dipole moment measurements are carried out on pure polar liquids, the Debye equation is modified in the following manner.<sup>13</sup>

$$\frac{\epsilon-1}{\epsilon+2} \left( \frac{m}{\rho} \right) - \frac{n^2-1}{n^2+2} \left( \frac{m}{\rho} \right) = \frac{3 \epsilon (n+2)}{(2 \epsilon + n)(\epsilon+2)} \frac{4 \pi N \mu^2}{9 k T} \quad (8)$$

which is known as the Onsager equation. The Onsager equation differs from the Debye equation by the factor

$$\frac{3 \epsilon (n+2)}{(2 \epsilon + n)(\epsilon+2)}$$

This is due in part to the dipole moment in pure liquids being affected by the interaction of adjacent molecules.

In solutions, a polar solute molecule is surrounded by non-polar solvent thereby eliminating dipole-dipole (solute-solute) interactions which occur in pure liquids. The subscripts (1), (2), and (1,2) used in the upcoming equations have the meaning given below

- (1) = non polar solvent
- (2) = polar solute
- (1,2) = solution properties

In dilute solutions where a polar solute is surrounded by non-polar solvent molecules, the total molar polarization can be written<sup>14</sup>

$$P_m = \bar{X}_1 P_{1m} + \bar{X}_2 P_{2m} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \frac{(\bar{X}_1 M_1 + \bar{X}_2 M_2)}{\rho} \quad (9)$$

Since the solvent is non-polar and has only distortion polarization, the molar polarization for the solvent is the same as found in the pure solvent, that is

$$P_{1m} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \left( \frac{M_1}{\rho_1} \right) \quad (10)$$

The  $P_{2m}$  term, which contains the dipole moment, can be solved upon rearrangement of equation (9)

$$P_{2m} = \frac{1}{\bar{X}_2} \left( P_m - P_{1m} \bar{X}_1 \right) \quad (11)$$

In the laboratory, this quantity can be obtained by a method known as the Hedestrand method.<sup>14</sup> For this case,

the assumption is made that a linear dependence exists between  $\epsilon$  and  $\rho$  on mole fraction  $\bar{x}_2$ .

$$\epsilon = \epsilon_1 + a \bar{x}_2 \quad (12)$$

$$\rho = \rho_1 + b \bar{x}_2 \quad (13)$$

Equations (9), (10), (11), and (12) all can be combined and rearranged to form the Hedestrand equation, which solves for the molar polarization of the pure solute.

$$P_{2m}^{\circ} = \frac{3M_1 a}{(\epsilon_1 + 2)^2 \rho_1} + \frac{\epsilon_1 - 1}{(\epsilon_1 + 2) \rho_1} \left( M_2 - \frac{M_1 b}{\rho_1} \right) \quad (14)$$

After making the assumption that the molar distortion polarization, at infinite dilution, is equal to the molar refractivity of pure solute,<sup>a</sup> the following equation can be written.

$$P_{2d}^{\circ} = R_{2m} = \frac{n_2^2 - 1}{n_2^2 + 2} \left( \frac{M_2}{\rho_2} \right) \quad (15)$$

The orientational polarization of the pure solute can now be solved for in terms of the total molar polarization and distortion polarization.

$$P_{2u}^{\circ} = R_{2m} - P_{2d}^{\circ} = \frac{4\pi N_0 \mu^2}{9kT} \quad (16)$$

Equation (16) allows for the dipole moment of the pure solute in solution to be solved for.

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<sup>a</sup> $P_{2d}^{\circ} = R_{2m} \times 1.1$

## Appendix 4

### Bond Moments and Molecular Dipole Moment



#### APPENDIX 4

The values for A and B in equation (6) were calculated as follows: The dipole moment for the carbonyl group was averaged from three different sources.

- (1) Acetone<sup>1</sup>

$$\vec{\mu}_{\text{co}} = 2.86 \text{ D}$$

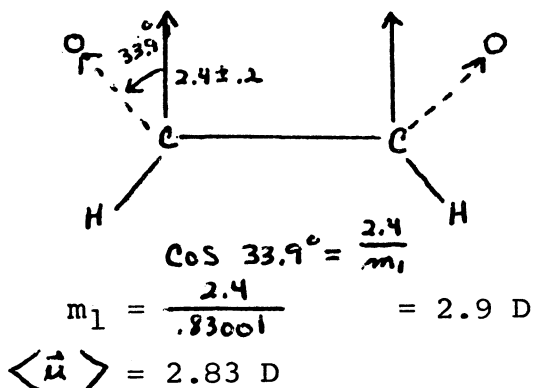
- (2) Camphorquinone<sup>2</sup>

$$\vec{\mu}_{\text{co}} = 2.72 \text{ D}$$

- (3) Cis-glyoxal<sup>3</sup>

$$\vec{\mu} = 4.8 \pm .2 \text{ D}$$

$$\angle \text{CCO} = 123.9^\circ$$



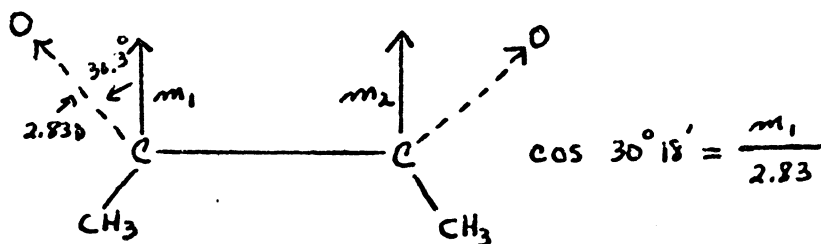
<sup>1</sup>A. L. McClellan, Table of Experimental Dipole Moments (San Francisco: W. H. Freeman and Co., 1963).

<sup>2</sup>P. H. Cureton, C. G. Le Fevre, and R. J. W. Le Fevre, "Molecular Polarisability: The Conformations of Biacetyl, Benzil, and Furil as Solutes in Benzene or Carbon Tetrachloride," Journal of Chemical Society, (1961), 4447-4451.

<sup>3</sup>J. R. Durig, C. C. Tong, and Y. S. Li, "Microwave Spectrum of cis-Glyoxal," The Journal of Chemical Physics, LVII (1972), 4425-4427.

The average dipole moment for the carbonyl functional group was then used in conjunction with the structure of gaseous 2,3-butanedione as determined by electron diffraction.<sup>4</sup>

$$\angle \text{CCO} = 120.3^\circ$$



$$m_1 = 2.44$$

The values for A and B can then be calculated

where

$$A = m_1^2 + m_2^2$$

$$B = 2m_1m_2$$

For 2,3-butanedione

$$A = B = 2m_1m_2$$

$$= 2 (2.44) (2.44)$$

$$A = B = 11.91 \text{ D}^2$$

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<sup>4</sup>K. Hagen and K. Hedberg, "Conformational Analysis, IV. Molecular Structure and Composition of Gaseous 2,3-Butanedione as Determined by Electron Diffraction," Journal American Chemical Society, VC (1973), 8266-8269.