# THE ELECTRIC MOMENTS OF SOME ALIPHATIC HYDROCARBONS AND THE ELECTRIC MOMENTS AND CONFORMATIONAL ANALYSIS OF SOME DIHALOGENO-AND DIKETO-CYCLOHEXANES

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
James Marquess Canon
1961

**This is to certify that the**

**thesis entitled**

The Electric Moments of Some Aliphatic Hydrocarbons
and the Electric Moments and Conformational
Analysis of Some Dihalogeno- and Kiketo-Cyclohexanes

**presented by**

James Marquess Canon

**has been accepted towards fulfillment**
**of the requirements for**

Ph.D. **degree in** Chemistry

Max T Rogers
**Major professor**

**Date** May 15, 1961

**O-169**

# ABSTRACT

## THE ELECTRIC MOMENTS OF SOME ALIPHATIC HYDROCARBONS AND THE ELECTRIC MOMENTS AND CONFORMATIONAL ANALYSIS OF SOME DIHALOGENO- AND DIKETO-CYCLOHEXANES

by James Marquess Canon

The electric moments of 2-methylpropane, 2-methylbutane, *cis*-2-butene, *trans*-2-butene, 3-methyl-1-butyne, 3, 3-dimethyl-1-butyne, *trans*-1, 2-dibromocyclohexane, *trans*-1-bromo-2-chlorocyclohexane, *trans*-1, 2-dichlorocyclohexane, and 1, 4-cyclohexanedione have been measured in the vapor phase. Small moments were found for both 2-methylpropane and 2-methylbutane. A value of the electric moment of *cis*-2-butene somewhat smaller than expected may be explained by consideration of the resonance structures. The variation of electric moment with structure in the aliphatic mono-acetylenes may be attributed to dipole-induced-dipole interaction and calculated from polarizability data. Energy differences between conformational isomers of the halogen compounds were calculated from the data. For 1, 4-cyclohexanedione the experimental data permitted qualitative limits to be set for the difference in energy between conformational isomers.

# THE ELECTRIC MOMENTS OF SOME ALIPHATIC HYDROCARBONS AND THE ELECTRIC MOMENTS AND CONFORMATIONAL ANALYSIS OF SOME DIHALOGENO- AND DIKETO-CYCLOHEXANES

By

James Marquess Canon

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1961

# ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor M. T. Rogers for his guidance and encouragement throughout the course of his graduate studies.

He wishes further to acknowledge gratefully the assistance of Mr. Forest E. Hood and Mr. Frank Betts in the construction of the experimental apparatus.

Gratitude is also extended to the National Science Foundation and to The Upjohn Company for grants of financial assistance which have in part supported this research.

***********

# VITA

James Marquess Canon
Candidate for the degree of
Doctor of Philosophy

Major Field of Study: Physical Chemistry

Minor Fields of Study: Organic Chemistry and Physics

Biographical:

Born, March 13, 1924 in Waco, Texas

Bachelor of Arts in Economics, University of Michigan, Ann Arbor, Michigan, 1950

Bachelor of Science in Chemistry, Western Michigan University, Kalamazoo, Michigan, 1955

Graduate Studies in Physical Chemistry and Allied Sciences, Michigan State University, East Lansing, Michigan, 1955-1960

# TABLE OF CONTENTS

# LIST OF TABLES

LIST OF TABLES - Continued

# LIST OF FIGURES

# INTRODUCTION

In 1912 P. Debye (1) showed that when the dielectric constant of a substance is not a constant, but varies with temperature, the explanation is to be found in consideration of the distribution of positive and negative electrical charges in molecules of the substance. This concept, the electric dipole moment, was subsequently developed by Smyth (3), Errara (4), and others (2, 5) in terms of individual bond moments which combined to yield the molecular moment. As a further development of this point of view moment values were empirically assigned (6, 7) to a large number of specific inter-atomic bonds, the vector addition of which could be used to predict with considerable accuracy the electric moments of many molecules. Finally, and perhaps more important than a basis for the prediction of the property itself, a series of conventions came into being by means of which variance between predicted and measured values could be explained. These conventions, which ranged from the somewhat qualitative inductive effects, through steric electrostatic repulsions and attractions, to the quantum mechanical concept of resonance were, until the 1950's, virtually the only experimentally supported insight into the electronic configurations of molecules.

The electric moments of thousands of polar molecules have been determined over the years, but of these only a few--less than 400--have been determined in the vapor phase, the only state in which, in theory, the Debye equation strictly applies. In some instances experimental results have been rendered ambiguous by reason of the unknown interferences of the solvent in solution measurements while in other instances vapor phase measurements have failed to yield satisfactory values of small moments because of experimental error.

The aim of the present work has been to employ vapor phase investigation to determine the moments of an assortment of hydrocarbons which would be expected to have small moments but have either not been reported or have been reported to be zero, and to re-examine the moments of 1, 4-cyclohexanedione and of a group of trans-1, 2-dihalogenocyclohexanes previously measured in solution and employed in the calculation of isomeric energy differences.

The moments of a number of hydrocarbons previously investigated in the vapor phase are listed in Table I and the previously determined moments and isomeric energy differences (16, 17, 18) of the substituted cyclohexanes in Table II.

Table I--Vapor Phase Electric Moments of Hydrocarbons

| Compound | μ Debye | Reference |
|---|---|---|
| Methane | 0 | 11 |
| Ethane | 0 | 8 |
| | 0 | 11 |
| | 0 | 10 |
| Propane | 0 | 11 |
| | 0 | 11 |
| | 0.083 | 47 |
| n-Butane | 0 | 14 |
| 2-Methylpropane | 0 | 14 |
| | 0.132 | 46 |
| n-Pentane | 0 | 12 |
| n-Hexane | 0 | 9 |
| | 0 | 12 |
| n-Heptane | 0 | 9 |
| | 0 | 12 |
| Ethylene | 0 | 8 |
| Propene | 0.34 | 11 |
| | 0.35 | 10 |
| 1-Butene | 0.30 | 14 |
| | 0.38 | 8 |
| trans-2-Butene | 0 | 14 |
| 2-Methylpropene | 0.49 | 14 |
| Acetylene | 0 | 11 |
| Propyne | 0.72 | 14 |
| | 0.78 | 15 |
| | 0.75 | 21 |
| 1-Butyne | 0.80 | 15 |
| 1-Pentyne | 0.86 | 15 |
| 1-Hexyne | 0.89 | 15 |
| 1-Heptyne | 0.87 | 15 |

Table II--Solution Electric Moments and Isomeric Energy Differences in Substituted Cyclohexanes

| Compound | $\mu$ Debye | T °C | ΔE* Cal/Mole Benzene | ΔE* Cal/Mole $CCl_4$ | Reference |
|---|---|---|---|---|---|
| trans-1, 2-Dibromo-cyclohexane | 2.14 | 10 | -80 | -500 | 18 |
| | 2.13 | 30 | | | |
| | 2.14 | 50 | | | |
| | 2.11 | 25 | -70 | -400 | 19 |
| | | | -70 | -700 | 17 |
| trans-1-Bromo-2-chlorocyclohexane | 2.49 | 25 | 370 | | 19 |
| | | | 560 | -220 | 17 |
| trans-1, 2-Dichlorocyclohexane | 2.52 | 30 | 400 | -50 | 18 |
| | 2.50 | 50 | | | |
| | 2.66 | 40 | 300 | | 16 |
| | 2.67 | 25 | 650 | | 19 |
| | | | 820 | 140 | 17 |
| cis-1, 2-Dibromo-cyclohexane | 3.06 | 25 | | | 19 |
| cis-1-bromo-2-chlorocyclohexane | 3.16 | 25 | | | 19 |
| cis-1, 2-Dichloro-cyclohexane | 3.13 | 25 | | | 19 |
| | 3.1 | 30 | | | 18 |
| | 3.13 | 25 | | | 16 |
| 1, 4-Cyclohexanedione | 1.3 | 25 | 1900 | | 20 |

*$\Delta E = E_{axial} - E_{equatorial}$

# THEORY

All the material media may be roughly classified, with respect to their electrical properties, as either conductors or dielectrics. The former characteristically contain charges, electrons or ions depending upon the conductor, which are free to move through the conductor under the influence of an electric field, while the latter generally respond to an electric field only through polarization mechanisms.

The electrons and nuclei of all molecules are sufficiently mobile that when a molecule is placed in an electric field a small displacement occurs between these negative and positive electrical centers creating an electric dipole. This polarization which is a function of the strength of the electric field from which it derives may be expressed in vector notation as;

$$\underline{P} = \chi \underline{E} \qquad (1)$$

in which $\underline{P}$, the polarization, is the induced dipole moment per unit volume, $\underline{E}$ is the intensity of the applied field and $\chi$ is the electric susceptibility.

The charge per unit volume of a dielectric due to polarization may be shown to be $-\nabla \cdot \underline{P}$. If one takes the total charge enclosed in the surface of the dielectric to be the sum of the charge, q, on the charged bodies present, and the polarization charge, then, by Gauss law;

$$\int \underline{E} \cdot \underline{ds} = 4\pi \left[q - \int \nabla \cdot \underline{P}\, d\tau\right] \qquad (2)$$

in which $\underline{ds}$ is an element of surface and $d\tau$ is an element of volume. By Gauss' theorem this becomes

$$\int \underline{E} \cdot \underline{ds} = 4\pi \left[q - \int \underline{P} \cdot \underline{ds}\right]$$

from which

$$\int (\underline{E} + 4\pi \underline{P}) \cdot \underline{ds} = 4\pi q$$

The quantity in parenthesis is a vector called the displacement which depends upon the charge, q, only.

$$\int \underline{D} \cdot \underline{ds} = 4\pi q$$

$$\underline{D} = \underline{E} + 4\pi \underline{P} \qquad (3)$$

The ratio of the displacement to the applied field is constant for static and low frequency alternating fields for dielectrics at constant temperature and is called the dielectric constant, $\epsilon$ .

$$\frac{D}{E} = \epsilon \qquad (4)$$

Combining this relation with equations (1) and (3) gives:

$$\underline{D} = (1 + 4\pi \chi)\ \underline{E} \qquad (5)$$

and

$$\epsilon = 1 + 4\pi \chi \qquad (6)$$

The electric intensity inside the region occupied by a single atom in a dielectric in an electric field may be separated into three parts. The first part is that due to the applied field, which, if the charge from which the field derives is immediately adjacent to the surface of the dielectric or separated from the surface by vacuum only, is equal to the displacement D.

$$\underline{E_1} = \underline{D}$$

The second part is that due to the surface charge of polarization of the dielectric which may be shown to be:

$$\underline{E_2} = -4\pi \underline{P}$$

The third part is that due to the surface charge of polarization inside the hypothetical spherical cavity occupied by the atom which is;

$$\underline{E}_3 = \frac{4\pi \underline{P}}{3}$$

The effective field in the region occupied by the atom is then;

$$\underline{E}_{eff} = \underline{E}_1 + \underline{E}_2 + \underline{E}_3$$

$$\underline{E}_{eff} = \underline{E}_1 + \frac{4\pi \underline{P}}{3} \qquad (7)$$

The polarization, as was stated above is proportional to the field from which it derives. This relation, in the case of the effective field, $E_{eff}$, requires a new constant of proportionality, $\alpha$, called the polarizability.

$$\underline{P} = \alpha \, \underline{E}_{eff} \qquad (8)$$

Combining equation (8) with equations (1) and (7) gives

$$\chi \underline{E} = \alpha \underline{E} \left(1 + \frac{4\pi \chi}{3}\right) \qquad (9)$$

Combining equation (9) with equation (6) gives;

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi \alpha \qquad (10)$$

The polarization, $\underline{P}$, which was used in the derivation of this relation was the total induced dipole moment per unit volume. If there are n individual induced dipoles $\underline{p}$ per unit volume then

$$\underline{P} = n\underline{p} \qquad (11)$$

and equation (10) becomes

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi \, n \, \alpha \qquad (12)$$

which is the Clausius-Mosotti (22, 23) equation for the induced electronic and atomic polarization of a dielectric in an electric field.

If the negative electrical center of a molecule does not coincide with the positive electrical center in the absence of an applied field, the molecule is said to possess a permanent electric moment. In the presence of an electric field these permanent electric dipoles are influenced away from the completely random orientation due to thermal agitation and toward alignment in the direction of the field, giving rise to an orientation polarization.

Denoting the permanent electric moment of the individual molecular dipole by $\underline{\mu}$, the potential energy of the dipole in the external field is given by:

$$U = -\mu E_{eff} \cos \theta \tag{13}$$

in which $\theta$ is the angle between the dipole and the field. The average value of U over the entire sample is given by;

$$\overline{U} = \frac{\int U \exp. \frac{-U}{kT} \, dU}{\int \exp. \frac{-U}{kT} \, dU} \tag{14}$$

from which

$$\overline{\mu} = \mu \frac{\int \cos \theta \exp. x \cos \theta \, d\cos \theta}{\int \exp. x \cos \theta \, d\cos \theta}$$

in which

$$x = \frac{\mu E_{eff}}{kT}$$

The solution to this equation is known as the "Langevin function" (24), and is given by;

$$\overline{\mu} = \mu(\coth x - \frac{1}{x})$$

which for most ordinary electric fields reduces to

$$\overline{\mu} = \mu \coth x$$

$$= \frac{\mu x}{3}$$

$$\overline{\mu} = \frac{\mu^2 E_{eff}}{3kT} \tag{15}$$

As in Equation 11

$$\underline{P} = n\,\underline{\mu}$$

Substituting this relation into Equation 15 gives

$$\underline{P} = \frac{n\mu^2\,\underline{E}\mathrm{eff}}{3kT}$$

which, as in equations (8), (9) and (10) gives

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\, n\mu^2}{9kT} \qquad (16)$$

For a dielectric the polarization of which is due to both permanent and induced dipoles, equations (12) and (16) are combined to give;

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi n\,(\alpha + \frac{\mu^2}{3kT}) \qquad (17)$$

which is known as the Debye equation (1).

The number of particles per unit volume of a gas at one atmosphere is given by;

$$n = \frac{N}{\widetilde{V}} \qquad (18)$$

in which N is Avogadro's number and $\widetilde{V}$ is the volume of a gram molecular weight of the gas at the temperature in question. Combining equations (17) and (18) gives;

$$\frac{\epsilon - 1}{\epsilon + 2}\quad \widetilde{V} = \frac{4\,\pi\,\alpha}{3} + \frac{4\,\pi\,\mu^2}{9R}\cdot\frac{1}{T} = P_M \qquad (19)$$

If experimental values of the left hand side of equation (19), which is the total molar polarization, $P_M$, are plotted against the reciprocal of the absolute temperature the resulting line is straight except in certain special cases to be treated below

$$P_M = P_o + \frac{B}{T} \qquad (20)$$

The intercept of this line is $P_O$, the sum of induced atomic and electronic polarizations,

$$P_o = P_A + P_E$$

while the slope B is the coefficient of the second term on the right and may be used to calculate the permanent dipole moment, $\mu$.

$$B = \frac{4\pi}{9R} \quad \mu^2$$

$$\mu = 0.0128 \times 10^{-18} \sqrt{B} \quad \text{esu. cm.} \tag{21}$$

An approximate value of the quantity $\frac{4}{3}\pi a$ may be obtained by substituting the Maxwell relation;

$$\epsilon = \eta_\infty^{\ 2} \tag{22}$$

where $\eta_\infty$ is the refractive index of the dielectric at infinite wave length, into Equation 12 (25).

$$P_E = \frac{\eta_\infty^{\ 2} - 1}{\eta_\infty^{\ 2} + 2} \quad \tilde{V} \approx \frac{4\pi a}{3} \quad \approx P_o \tag{23}$$

The value of $P_o$ calculated in this way using refractive indices measured with visible light is in error by the amount of the atomic polarization. The positions of nuclei are unaffected by light of these wave lengths with the result that only the electronic polarization, $P_E$, occurs.

It has been shown (2, 3, 4, 5) that the net permanent electric moment of a molecule can, in most cases, be considered to be the vector sum of all of the individual bond dipoles in the molecule, the angles of addition being simply the appropriate bonding angles. However, when a molecule is so constructed that bond dipoles may change their directions relative to one another by rotation about bonds in the molecule, the resultant net moment may not be so simply treated. In those instances in which the rotation is perfectly free and all relative orientations equally probable the resultant molecular moment has been shown to be a mean square sum of the individual bond moments (13). In other instances, when differences in energy exist between various conformations of the molecule, some orientations are more probable than others and no uniform relation exists between the individual bond moments and the net dipole moment, because the latter changes as temperature variations give rise to redistributions of the probability between the various conformations of different energy.

The study of the polarization of molecules of the latter type does not yield a linear relation of that quantity with reciprocal temperature as predicted by the discussion leading to equation (19), but rather a line which is slightly curved, and which, consequently, will not yield a unique value for the dipole moment. Such a study is, however, anything but useless, for, since the variation of the moment with temperature is related to the energy difference between conformational isomers, it may be used to study this energy difference, a quantity which, for many compounds, may not be obtained by any other means.

The net electric moment measured for a material composed of two species having different moments may be expressed, as a first approximation, by the following expression:

$$\mu^2 = \frac{n_1 m_2^2 + n_2 m_2^2}{n_1 + n_2} .$$

$$\mu^2 = \frac{m_1^2 + \frac{n_2}{n_1} m_2^2}{1 + \frac{n_2}{n_1}} \qquad (24)$$

in which the $n_i$ are the numbers of molecules having the moments $m_i$. The distribution between the two energy levels represented by the $m_i$ may be expressed as the ratio of the Boltzman distribution factors;

$$\frac{n_i}{\sum_i n_i} = g_i e^{-(E_i/RT)} \qquad (25)$$

$$\frac{n_2}{n_1} = \frac{g_2 e^{-(E_2 - E_1)/RT}}{g_1} \qquad (26)$$

in which the $g_i$ are the products of the partition functions and the degeneracies or statistical weights of the levels, and the $E_i$ are the total molar energies of the levels. R is the molar Boltzmann constant and T is the absolute temperature.

Combining these relations yields

$$\mu^2 = \frac{m_1^2 + ae^{-\Delta E/RT} m_2^2}{1 + ae^{-\Delta E/RT}} \tag{27}$$

$$a = \frac{g_2}{g_1}$$

which may be rearranged to give

$$-\Delta E = RT \ln \frac{m_1^2 - \mu^2}{a(\mu^2 - m_2^2)} \tag{28}$$

from which $\Delta E$ may be calculated from moments measured at specific temperatures.

# EXPERIMENTAL METHODS

## Materials

Instrument grade (99.9 mole per cent) 2-methylpropane was obtained from The Matheson Co. Inc., Joliet, Illinois. Research grade cis-2-butene (99.3 mole per cent) and trans-2-butene (99.8 mole per cent) were obtained from Phillips Petroleum Company. 2-Methylbutane, obtained from K & K Laboratories, Long Island City, New York, was distilled through a fractionating column of approximately six theoretical plates, dried over metallic sodium and redistilled. A fresh sample of each material was introduced into the vacuum system described below, where it was purified to the extent of removing uncondensable materials by freezing with dry ice and pumping on the thawing solid.

3-Methyl-1-butyne and 3,3-dimethyl-1-butyne were synthesized by a procedure similar to that described by Ivitsky (26) and purified by distillation. These materials were stored in the vacuum system over sodium sulfate and fractionated there immediately before each run by distillation between traps.

trans-1,2-Dichlorocyclohexane and trans-1,2-dibromocyclohexane were synthesized by addition of the respective halogen to cyclohexene (27). trans-1-Bromo-2-chlorocyclohexane was synthesized by bubbling HCl into a slurry of N-bromosuccinimide, chloroform and cyclohexene (19). All three materials were purified by vacuum distillation. 1,4-Cyclohexanedione was obtained from K & K Laboratories, Long Island City, New York, and purified by recrystallization from water and benzene.

Ammonia was obtained from Ohio Chemical and Surgical Company. It was condensed in the system on metallic sodium and further purified by repeated distillation between traps and by degassing as described above.

The physical constants of the experimental materials are given in Table III.

## Dielectric Constant Determination

The method employed for the determination of the dielectric constant depended upon the measurement of the difference in the capacitance of a condenser alternately filled with a vapor and evacuated. The total capacitance of the condenser and its leads corresponding to each of these conditions is given respectively by;

$$C_T = C_O + C_f$$

$$C_T = C_X + C_f$$

in which $C_T$ is the total capacitance, $C_f$ is the fixed capacitance of the leads, $C_O$ is the capacitance of the condenser only, evacuated, and $C_X$ is the capacitance of the condenser only, filled with vapor. The difference in capacitance for these conditions is;

$$\Delta C = C_X - C_O.$$

Substituting the dielectric constant, $\epsilon$, as defined by the expression;

$$\epsilon_X = \frac{C_X}{C_O}$$

the change in capacitance is given by;

$$\Delta C = C_O (\epsilon_X - 1)$$

which may be rearranged to give;

$$\epsilon_X - 1 = \frac{\Delta C}{C_O} \qquad (29)$$

The quantity $\Delta C$ was measured using ammonia to obtain $C_O$ by equation (29), and again measured using the material under investigation to obtain $\epsilon_X$ by equation (29).

Table III--Physical Constants of Subject Materials

| Compound | m.p. °C | b.p. °C | d. g./ml. | $\eta$ |
|---|---|---|---|---|
| 3-Methyl-1-butyne |  | 29.0 | 0.6727$^{20}$ | 1.3756$^{20}_{D}$ |
| 3, 3-Dimethyl-1-butyne | -78.21 | 37.7 | 0.6678$^{20}$ | 1.3736$^{20}_{D}$ |
| *cis*-2-Butene | -138.9 | 3.72 | 0.635$^{0}$ | ----- |
| *trans*-2-Butene | -105.6 | 0.94 | 0.635$^{0}$ | ----- |
| 2-Methylpropane | -145.0 | -12.2 | 0.6108$^{-25}$ | 1.3514$^{-25}_{D}$ |
| 2-Methylbutane | -159.6 | 27.95 | 0.6197$^{20}$ | 1.3598$^{20}_{D}$ |
| *trans*-1, 2-dibromo-cyclohexane | -2.5 | 92.3 | 1.784$^{25}$ | 1.5507$^{25}_{D}$ |
| *trans*-2-dichloro-cyclohexane | -6.3 | 71.1 | 1.1839$^{20}$ | 1.490$^{20}_{D}$ |
| *trans*-1-bromo-2-chlorocyclohexane | -18. | 77. | 1.479$^{25}$ | 1.5173$^{25}_{D}$ |
| 1, 4-cyclohexanedione | 78. | ---- | ----- | ----- |

## The Capacitance Cell

The condenser for which $\Delta C$ was measured consisted of five nickel plated copper cylinders pressed together coaxially using small rectangular Teflon spacers (32). It was enclosed in a Pyrex glass cell schematically represented in Figure 1. The cell was provided with access to a vapor handling system and a pressure switch and fitted axially with a deep well into which a bundle of copper wires was inserted to assist in temperature equilibration of the enclosed space.

The innermost, middle and outermost cylinders of the condenser were connected together by a platinum wire lead silver soldered into the cylinders. This lead was led to ground by means of a tungsten electrode sealed through the cell wall. A lead from the two intermediate cylinders was led through the cell wall in the same way, and connected by means of a rigid coaxial cable to the measuring circuit.

## Capacitance Measurement

Since only the values of changes in the capacitance of the cell corresponding to changes in its condition were required for the calculation, the method of measurement involved only a means of detecting such changes and a calibrated means of reversing the effect.

The circuit employed, called a heterodyne-beat circuit, a block diagram of which is shown in Figure 2, consisted of a balancing or measuring network and a type of beat-note null-point detector.

The balancing network (32), diagramed in Figure 3, consisted of an arrangement of variable condensers connnected in parallel with the cell. The capacitance of the network was the sum of the capacitance of the cell and the total capacitance of the variable branch, so that for a change, $\Delta C$, in the capacitance of the cell the capacitance of the network changed by an equal amount and by an equal and opposite change in the capacitance of the variable branch, the capacitance of the network was restored to its original value.

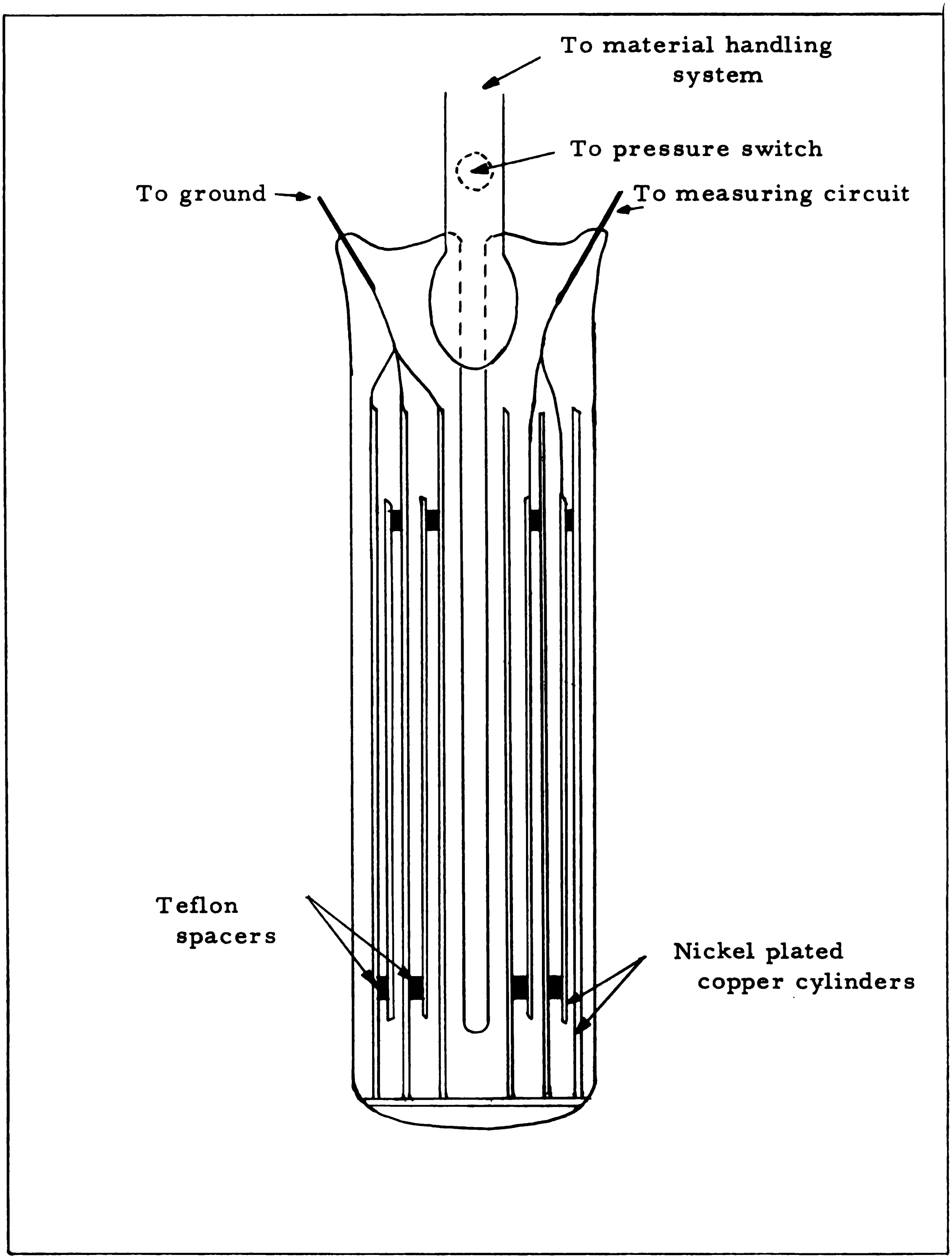


Figure 1. The Capacitance Cell

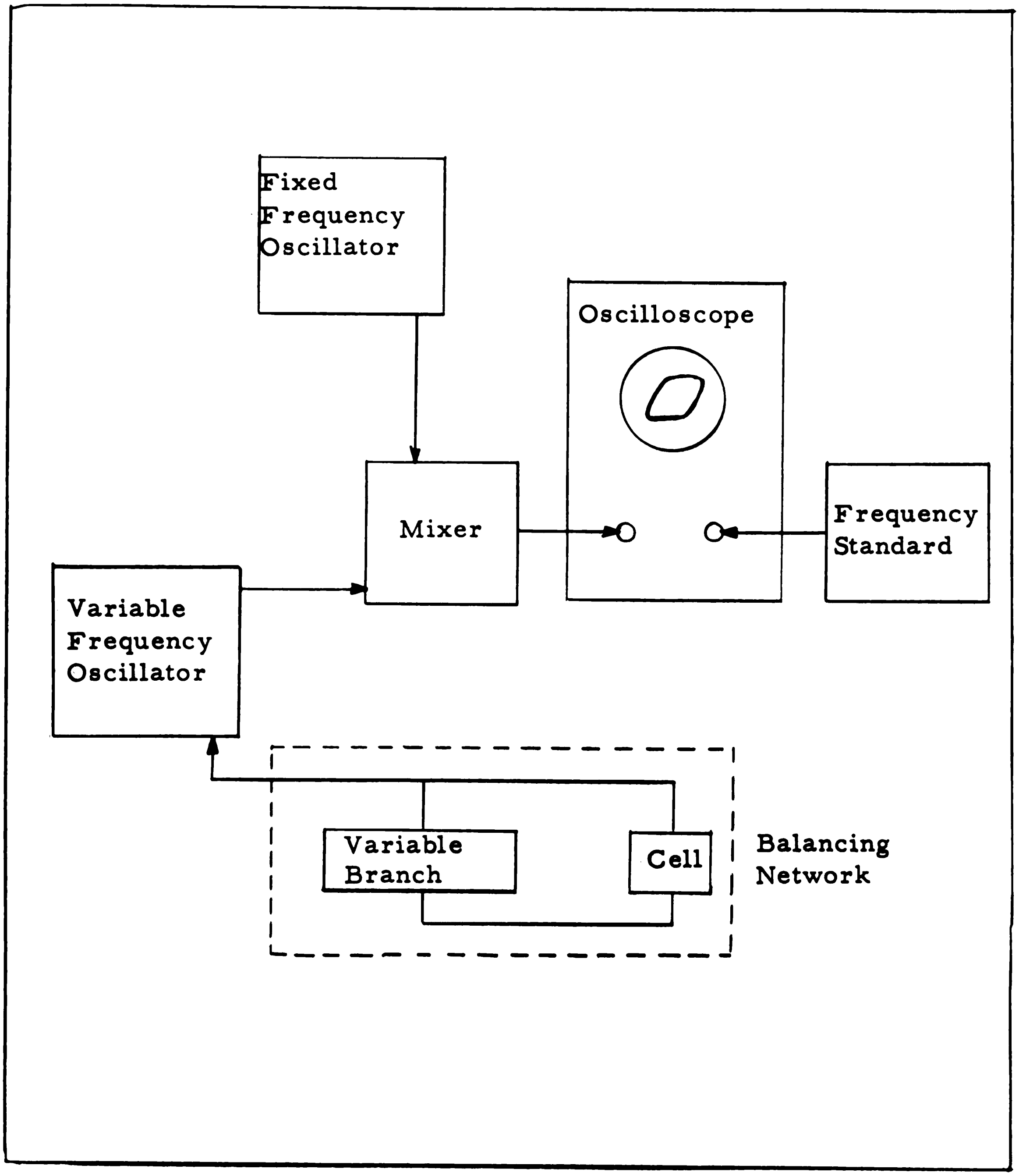


Figure 2. Block diagram of heterodyne-beat apparatus.

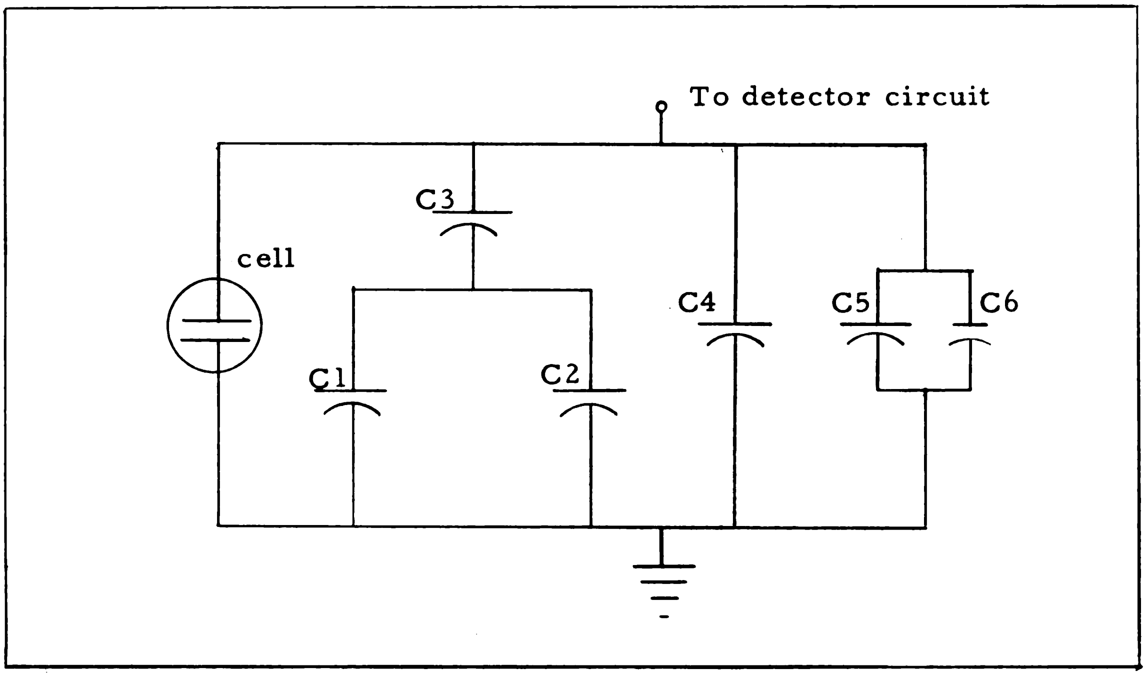


Figure 3. The balancing network.

| | |
|---|---|
| C1 | General Radio 100-1100μμf precision variable condenser Type 722N. |
| C2 | General Radio $10^4$-$10^5$μμf decade condenser. |
| C3 | 175μμf variable air condenser. |
| C4 | Primary standard condenser. |
| C5 | 335μμf variable air condenser. |
| C6 | 10μμf ceramic trimmer. |

The null-point detector (32, 33), shown in Figure 4, consisted of five elements, a crystal controlled 500 kc oscillator, a variable frequency oscillator having the measuring network in its tuning circuit, a mixing circuit in which the signals from the two oscillators were subtracted, a cathode ray oscilloscope, and a reference frequency oscillator employing an American Time Products Inc. type R2003 thermally compensated bimetallic fork frequency standard.

The tuning circuit of the variable frequency oscillator was an inductance-capacitance (L-C) resonant loop. The frequency of oscillation of the resonant loop determined the frequency of the oscillator and was itself determined by the value of its elements according to the expression;

$$f = \frac{1}{2\pi\sqrt{LC}} \qquad (30)$$

in which f is the frequency, L is the inductance and C is the capacitance. Since the inductance, L, was fixed in value, the frequency of the variable oscillator depended upon the value of C, which consisted of the measuring network. A change in the capacitance of the cell was, therefore, detectable as a change in the frequency of the oscillator, and restoration of the original value of the capacitance of the balance network by adjustment of the variable branch resulted in restoration of the original signal frequency.

The signal from the variable oscillator was combined with that from the fixed oscillator in the mixing circuit, resulting in a new signal having a frequency equal to the difference between these two. This signal, which was subject to some synchronization near the zero beat (equal frequency setting) was led to the horizontal deflection plates of a cathode ray oscilloscope while a 400 cycle signal generated by the reference oscillator was led to the vertical deflection plates. The resulting figure on the face of the tube was a Lissajous figure which was circular or elliptical when the mixer signal frequency was 400 cycles.

## Figure 4. Legend

### Capacitors (μμf)

| | | |
|---|---|---|
| C7, C8, C10, C17 | $10^7$ | 400 volt electrolytic |
| C23 | $10^7$ | 25 volt electrolytic |
| C22 | $2.5 \times 10^5$ | 600 volt paper |
| C16, C20, C21, C24 | $10^5$ | 600 volt paper |
| C12 | $10^4$ | 600 volt paper |
| C9, C13, C15 | $5 \times 10^3$ | 500 volt paper |
| C11 | $2.5 \times 10^3$ | mica |
| C18 | 25 | mica |
| C17 | 335 | variable air |
| C14, C19 | 50 | ceramic trimmer |

### Resistors (kohm)

| | | | |
|---|---|---|---|
| R1, R7 | 20 | R12 | 7 |
| R2, R3, R26 | 500 | R13 | 0.7 |
| R4, R6, R11, R22 | 15 | R14, R16, R18, R23 | 100 |
| R5 | 25 | R15 | 22 |
| R8 | 27 | R17 | 33 |
| R9 | 50 | R20 | 0.2 |
| R10, R18, R19, R25 | 47 | R21 | 82 |
| | | R24 | |

### Miscellaneous

| | |
|---|---|
| X | 500 kilocycle crystal |
| L | 200 μh. |
| RFC | Radio-frequency choke |

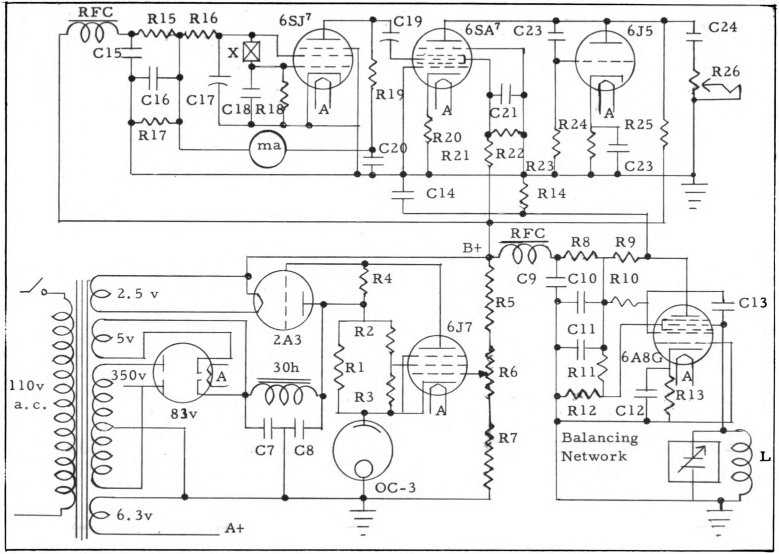


Figure 4. The heterodyne beat apparatus.

It was thus possible, by adjusting the variable branch of the balance network to obtain a circular Lissajous figure on the oscilloscope, changing the condition of the cell, and restoring the original figure by making a calibrated adjustment of the variable branch, to measure the change in capacitance corresponding to the change in condition of the cell.

The components of the variable branch of the balance network, which are listed in the legend of Figure 2, were chosen to give a calibrated range of variability of about 1.5μμf with a maximum of linearity. The derivative of the balancing network with respect to the calibrated precision variable condenser C1, is:

$$\frac{dC_T}{dC1} = \frac{C3^2}{(C1 + C2 + C3)^2} \tag{31}$$

It is apparent from this equation that for large values of C2 the curve is substantially linear and that the range of variability is to a large extent a matter of choice since it may be altered significantly by altering either C2 or C3 or both.

The scale of the precision variable condenser, C1, which had ten thousand divisions, was calibrated against the primary standard capacitor, C4. With C3 set for its maximum value and C2 set for 30,000μμf this calibration was;

$$\frac{dC_T}{dC1} \simeq 0.00015 \ \frac{\mu\mu f}{\text{scale div.}}$$

The primary standard employed for the calibration (34) had 2600 scale divisions of which only the central 200 were used. The capacitance change per scale division of this condenser was 0.001057μμf per scale division.

All of the circuit elements except the primary standard condenser, C4, the oscilloscope and the reference frequency oscillator, which are temperature compensated, were inclosed in a wooden box lined with grounded copper screen as an electrostatic shield. The temperature of the box was controlled at about 40°C by a sealed mercury thermoregulator and thyratron relay. The heating element was a 50 watt incandescent light bulb. Power for all units except the oscilloscope was regulated by means of a Stabiline Type 1E5 1002 A.C. voltage regulator manufactured by The Superior Electric Company, Beverly, Massachusetts.

## Temperature Control and Measurement

The capacitance cell was suspended by means of a copper frame in a constant temperature bath which is shown in Figure 5. The bath consisted of a massive cast aluminum cylinder seven inches in diameter with a hole in its center only slightly larger than necessary to allow insertion of the cell and its frame. Two spirals of No. 18 Nichrome resistance wire, separated from the block and from each other by asbestos paper, were wound around the bath and terminated in ceramic terminals. The outermost coil was connected directly to a power transformer to be used as ballast heat at higher temperatures. The innermost coil was connected to a temperature control circuit.

Temperature regulation was accomplished through a saturable reactor, the current in which was controlled by the phase sensitive detector circuit (35) diagramed in Figure 6. The temperature sensing element was a 100 kohm, 2% thermistor inserted in a small hole drilled vertically into the wall of the aluminum bath.

The top of the bath was closed by mounting the pressure switch, described below, in the ring which served to anchor in place the frame in which the cell was suspended.

Temperature was measured by means of a copper-constantan thermocouple, and a Leeds & Northrop Model K-2 potentiometer using National Bureau of Standards conversion data. The reference junction was a slurry made from solid distilled water in a Waring blender.

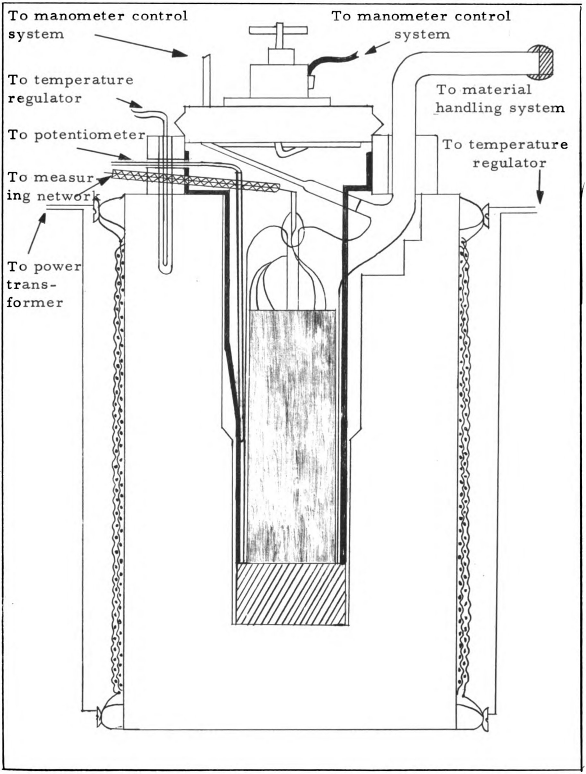


Figure 5. Constant temperature bath.

## Figure 6. Legend

### Capacitors (μf)

| | |
|---|---|
| C25, C26, C31, C34 | 0.05 |
| C27, C29 | 0.25 |
| C28, C32, C33, C35 | 10.0 |
| C30 | 0.5 |

### Resistors (kohm)

| | |
|---|---|
| R27, R30, R34 | 2000 |
| R28, R32, R36, R41 | 5 |
| R29 | 50 |
| R34, R35, R39, R40 | 1000 |
| R33 | 500 |
| R38 | 10 |

| | |
|---|---|
| T | Thermistor |
| B | Balance resistor |
| | Ratio arm |
| SR | Saturable reactor |

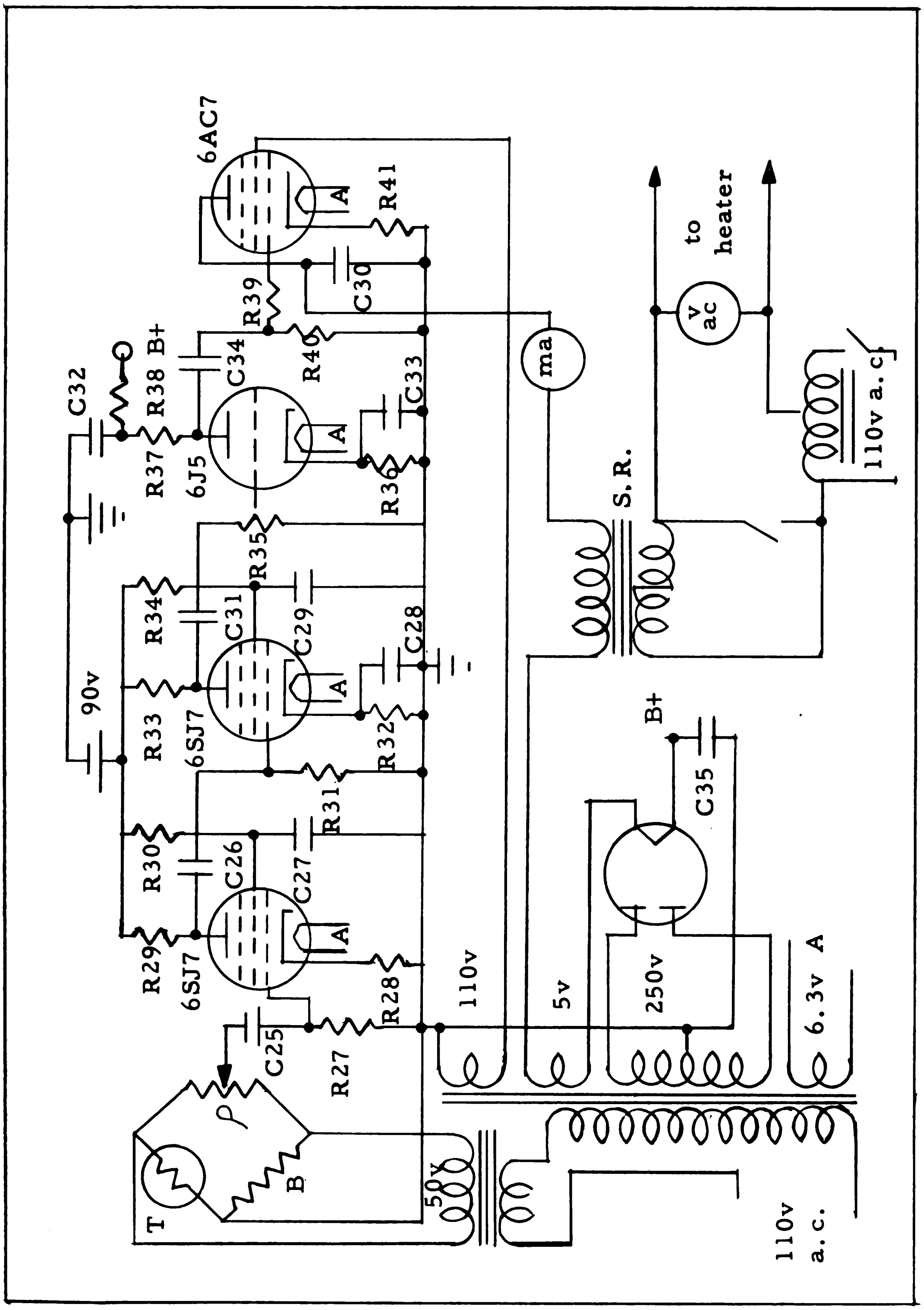


Figure 6. Temperature control circuit.

The hot junction of the thermocouple, supported by a double-barrel ceramic tube was tightly wedged between the wall of the cell and the cell support frame in such a way that the junction hung in the space between. Although this arrangement allowed measurement of the temperature of the bath rather than that of the cell it was found preferable to one in which the thermocouple was placed in the tube in the center of the cell, because the heat conducted out of that region by the thermocouple wires tended to disrupt temperature equilibrium between the plates and produce drift in the capacitance of the cell.

The entire bath was enclosed in a wooden box 24 inches on each edge and surrounded by expanded mica insulation.

With this arrangement temperatures at the junction location varied less than $0.2^{\circ}C/hr$ above $400^{\circ}C$ with short range variations of $0.1^{\circ}C$ or less. At lower temperatures control was slightly better.

## Pressure Measurement

All vapor pressures were measured using an absolute mercury manometer and cathetometer. The manometer, which was constructed from 16 mm diameter Pyrex tube, was surrounded by a 5 inch Pyrex tube closed at both ends by wooden blocks. A thermometer was hung in the dead air space thus created.

All pressures were reduced to $0^{\circ}C$ mercury temperature and corrected for the thermal expansion of the stainless steel scale of the cathetometer according to the following equation;

$$P_O = P - P \left[\frac{\alpha t - \beta(t - 20)}{1 \alpha t}\right] \qquad (32)$$

in which

$P_O$ = pressure reduced to $0^{\circ}C$ mercury temperature
$P$ = observed pressure
$t$ = ambient pressure in $^{\circ}C$

$\alpha$ = $1.818 \times 10^{-4} cm^3/^{o}C$ cubical coefficient of expansion of mercury

$\beta$ = $10 \times 10^{-6} cm/^{o}C$ linear coefficient of expansion of stainless steel scale

Pressure measurements involving the hydrocarbon series were made with the manometer open to the system and the vapors in direct contact with the mercury column. The substituted cyclohexanes, however, were rather involatile and required constant application of heat to create sufficient vapor pressure for the measurement.
In handling the latter materials the cell and vapor handling unit were isolated from the rest of the system to prevent condensation of the vapors, and pressures were transmitted by the pressure switch and manometer control system to the manometer where they were measured in the usual way.

The pressure switch, which is shown schematically in Figure 7 (36), consisted of a circular nickel diaphragm welded at its periphery between two circular half-shells of nickel clad steel, and surmounted at its center with a silver plated copper contact. The upper half-shell was fitted at its center with another silver plated contact well insulated electrically from the half-shell, and adjustable in height. Copper tubes issued from the enclosed spaces formed by the two half-shells, the lower one being sealed into the cell using a Kovar glass to metal seal and the upper one leading to the manometer control system.

The manometer control system which is shown in Figure 8 consisted of a vacuum pump separated from the manometer and pressure switch by a needle valve, a venting system for the manometer and pressure switch consisting of a hypodermic needle with its point ground off butted against the rubber faced armature bar of a relay, and circuitry for actuating the relay upon the closing of the two contacts of the pressure switch.

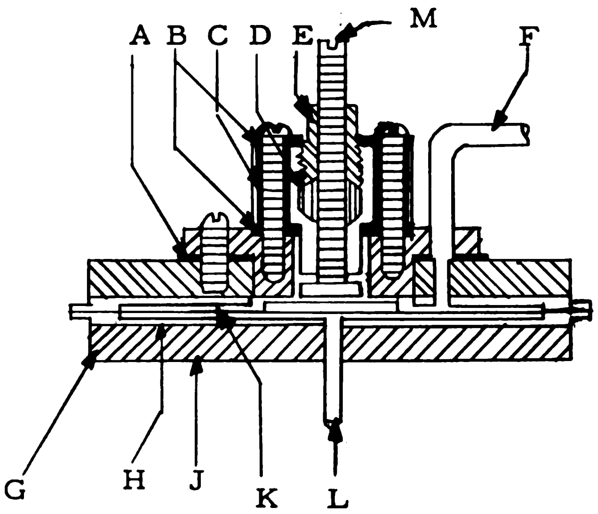


Figure 7. The pressure switch.

| | |
|---|---|
| A | Teflon gasket |
| B | Bakelite insulators |
| C | Fiber insulation |
| D | Teflon packing |
| E | Gland |
| F | Air balancing connection |
| G | Diaphragm case made from nickel clad steel |
| H | Nickel |
| J | Steel |
| K | .003 inch Nickel diaphragm |
| L | Process gas connection |
| M | Adjustable contact |

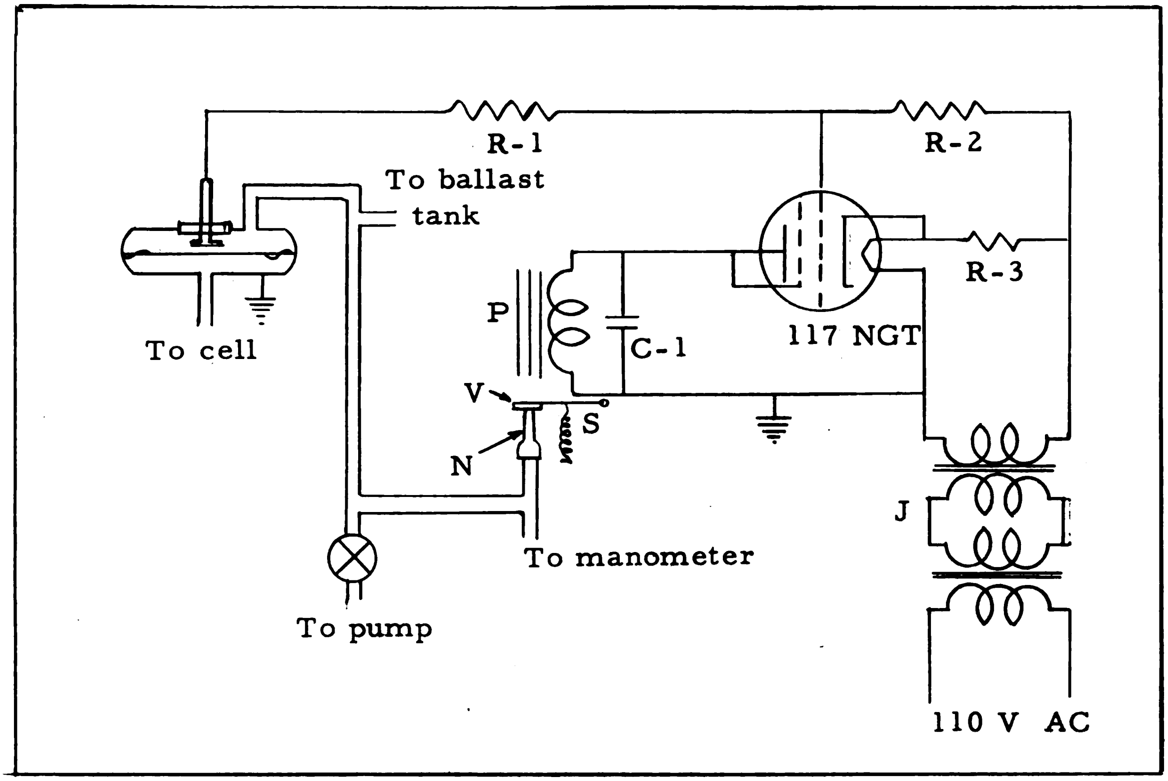


Figure 8. The manometer control system.

| | |
|---|---|
| P | Plate relay |
| N | Blunt hypodermic needle |
| V | Rubber faced armature bar of P |
| S | $\frac{1}{4}$-inch coil spring |
| J | Two filament transformers wired in series |
| R-1 | 1 megohm $\frac{1}{2}$ watt |
| R-2 | 15 kilohms $\frac{1}{2}$ watt |
| R-3 | 250 ohms 10 watt |
| C-1 | 0.008 μf |

In operation the vacuum pump, working through the needle valve, reduced the pressure in the control system until it was slightly less than that in the cell. The pressure switch contacts then closed, actuating the relay, drawing the armature bar away from the vent and allowing the pressure in the system to increase until it was equal to or slightly greater than that in the cell. The pressure differential then opened the contacts allowing the vent to close. This cycle repeated itself at small intervals during operation of the apparatus, holding the mercury level in the manometer practically constant.

The pressure indicated by the manometer when the transmitter was in use was subject to some variation over a wide range of pressures, the variation being greater or less depending upon the adjustment of the movable contact in the pressure switch. These variations were charted at each temperature at which the transmitter was used and appropriate corrections made to experimental readings.

## The Materials Handling System

A vacuum system constructed from Pyrex tube, schematically diagramed in Figure 9, was used for purification, handling and storage of materials. The upper half of the system was used with subject materials and the lower half was used with ammonia. The system was provided with access to a Kontes Glass Company Type-A McLeod-Lippincott gauge having a range of 0.001 to 1.0 mm Hg and to a series of four drying tubes containing, variously, $Na_2O$, $CaSO_4$ and $Mg(ClO_4)_2$.

Two interchangeable parts were made for the link which connected the cell to the system. One of these, shown attached to the system, was used with the hydrocarbons and the other, shown in the box, was used with the substituted cyclohexanes.

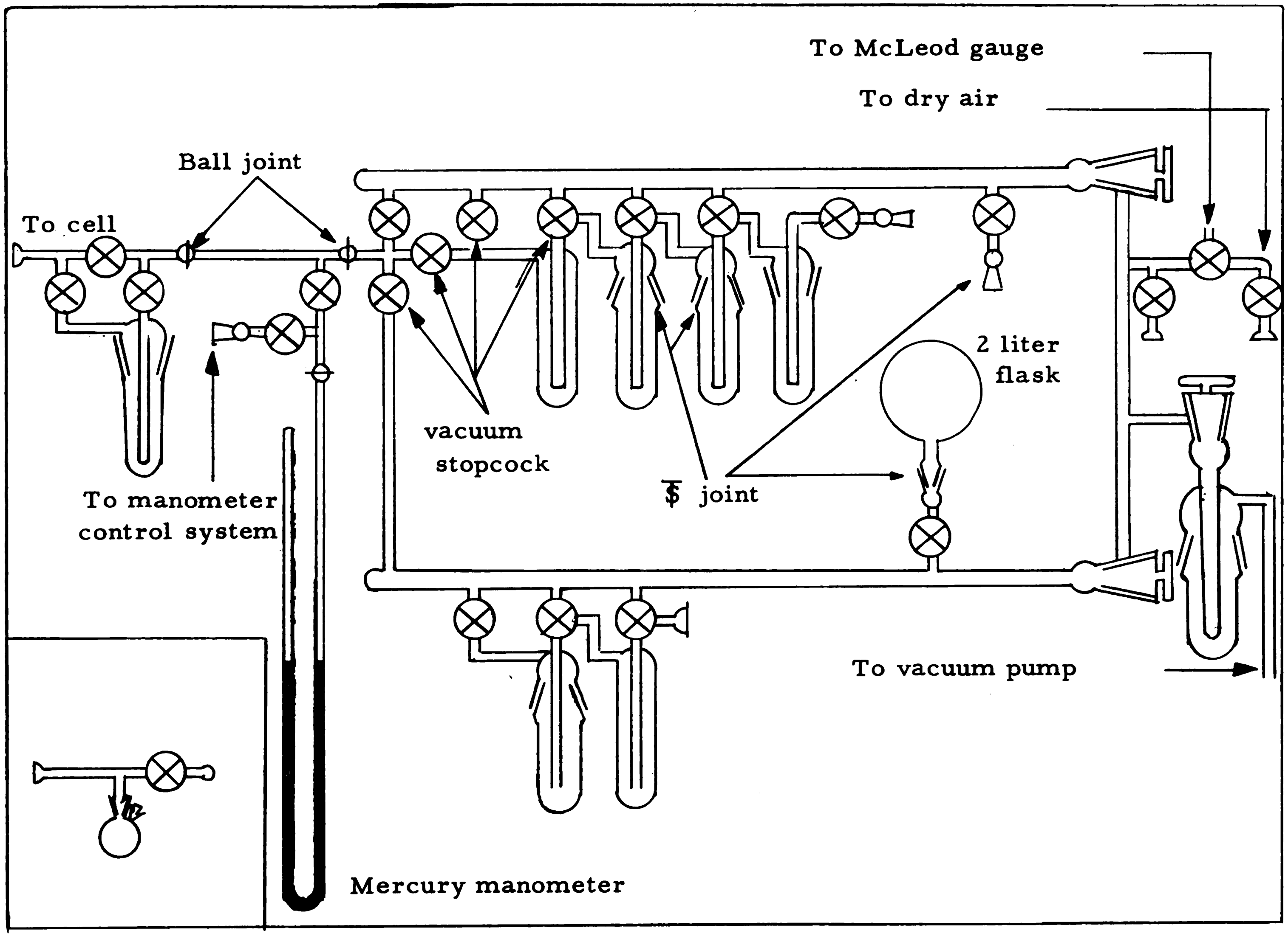


Figure 9. The materials handling system.

# PROCEDURES

Preliminary to making a series of measurements it was frequently found necessary to remove all T-bore stopcocks in the system, clean both the plug and the barrel with a mixture of petroleum ether and chloroform and regrease them. The grease used for this purpose was Dow Chemical Company High Vacuum Stopcock Grease. Twice during the period in which the system was in use it was cleaned throughout using a mixture of 20 ml. of 50% aqueous KOH and 80 ml. of ethyl alcohol.

## Constant Temperature Bath

Adjustment of the bath temperature was always carried out at least eight hours in advance of its anticipated use to allow complete temperature equilibration of the components of the cell. Adjustment was made, with the detector in place, by setting the ratio and the balance controls of the Wheatstone bridge of which the detector is the unknown arm. Balance of the thermistor resistance at its temperature was detected by a gradual increase in the milliammeter reading as the ratio potentiometer was advanced from zero, terminated by a sharp drop in this reading when the balance point was reached. Further advance of the ratio potentiometer resulted in another more gradual increase in the milliammeter reading usually terminated by the destruction of the thermistor, the symptom of which was the complete absence of a drop in the reading as the ratio potentiometer was advanced from zero through the scale. At this point it might be well to note that condenser C30 may be destroyed by too great an instantaneous unbalance in the bridge. The symptom for this difficulty was maximum current through the milliammeter regardless of control settings.

The procedure for the temperature adjustment was as follows:

1. With saturable reactor set for manual control, and its powerstat set at some relatively high value, and the booster powerstat on and set at about 75 volts, the bath was allowed to heat and its progress followed using the thermocouple.
2. When the thermocouple registered a temperature about 15° less than that desired both powerstats were turned off.
3. When thermocouple readings leveled off the balance point of the controller was located, starting with the largest balance resistor, by advancing the ratio potentiometer from zero. Progressively smaller values of the balance resistance were then substituted to bring the balance point near the center of the ratio potentiometer scale.
4. A setting of the saturable reactor powerstat was chosen which would require that about 2 milliamperes of current flow to maintain the balance temperature.
5. If sufficient power could not be taken from the saturable reactor a small amount of power was added from the booster. This amount never exceeded 25 volts, however, even at temperatures above 200°C.
6. If the temperature established in this way was not satisfactory, the ratio was adjusted in the appropriate direction to provide more or less power at balance.

It was found that the temperature could be changed by about 35°C by changing the balance resistance one scale unit with no change in ratio.

## Measurements

The procedure for finding the Lissajous figure consisted of evacuating the cell, setting the precision variable condenser to a value about 100 divisions below its upper limit and tuning using C4 until the circular figure was located and its rotation almost stopped. The figure was then stopped with either C5 or C6. In routine practice it was not necessary to readjust C5 although the figure had frequently to be adjusted using C4 or C6 to compensate for drift in oscillator frequencies, which was almost always present to a greater or less degree.

The drift mentioned here derived from two sources; changes in ambient conditions resulting in changes in the values of the many air condensers in the circuits, and changes taking place in the cell as a result of the cooling of the plates by the subject gases. In order to cancel the effects of these changes upon the measurement a procedure was adopted which consisted of making sets of eight or more capacitance-pressure measurements with alternate measurements corresponding to reverse changes in condition. Thus, a measurement of $\Delta C$ and $\Delta P$ for a pressure reduction was followed after a fixed equilibration period by a measurement of $\Delta C$ and $\Delta P$ for a similar pressure increase. This was followed after the same equilibration period by a repetition of the first measurement and so forth.

The procedure for making the measurement consisted of allowing the vapor to evaporate from the trap in which it was condensed, usually the one nearest the cell, until a pressure of about $\frac{3}{4}$ atmosphere was attained. After the equilibration period capacitance and pressure were recorded and vapor was withdrawn by condensing in one of the traps until the pressure was reduced to about 100 mm. The equilibration period was again observed and readings made, following which the pressure was increased again to about $\frac{3}{4}$ atmosphere. Temperature was recorded about every half hour or when a significant change took place. It was usually checked during every equilibration period.

The pressure range used was chosen to avoid the adsorbtive effects which were shown to occur at low pressures and minimize the effects of non-idealities of the gases at higher pressures.

## Low Boiling Materials

The procedures described below are typical of those employed in measurements involving ammonia, which was used for obtaining the cell constant, as well as those involving the subject materials.

The usual procedure for handling the hydrocarbon materials was to introduce them into the system by condensing them in the trap fitted for this purpose and degassing them as described in the section on materials. The lighter materials were introduced into the system studied and discarded while the acetylenes were stored in the system permanently. The material being studied was condensed in the trap nearest the cell in sufficient quantity to last the experiment and evaporated into the cell as occasion demanded. Withdrawals were made by condensing the vapor in the appropriate trap on the manifold.

At the end of a run with one of the materials the parts of the system which had been used were completely evacuated and washed several times with dry air. Before the next compound was studied the system was washed with its vapors.

## High Boiling Materials

The procedures practiced in making the measurements on substituted cyclohexanes differed primarily in the handling of the materials.

Small quantities of the materials were introduced into the heating flask which was substituted for the trap nearest the cell. The sample was degassed and the flask and cell isolated from the vacuum system, and pressure and capacitance were recorded. The entry tube to the cell was heated to 170°C with a heating tape and the flask was heated by a sand bath held at 165°C. Heating was continued until pressure equilibrium was attained, and pressure and capacitance were read immediately. The sand bath was then removed and a dry ice bath substituted to condense the vapors. An equilibration time was allowed which corresponded to the time necessary for the pressure build up, and pressure and capacitance were again measured. This procedure was repeated several times with fresh samples of each material.

Pressures of these vapors were measured by means of the pressure transmitter. The necessary plot of variation between transmitted pressure and true pressure was made before the measurements at each temperature by introducing dry air into the system and measuring its pressure directly and by transmission. If the variations determined in this way were large, the height of the movable contact of the pressure switch was adjusted and variations again plotted.

# DATA AND CALCULATIONS

The following pages contain tabulated capacitance, pressure, and temperature data for the ten compounds studied and calculations leading to the molar polarization, $P_M$, at each temperature. Plots of $P_M$ as a function of the reciprocal temperature are also presented although the slopes and intercepts of these lines were determined by the method of least squares for the purpose of calculating the results.

As was mentioned above, pressure-capacitance data was taken in sets of eight or more measurements in alternate directions of change at each temperature. The ratio of the average capacitance change in μμf to the average corrected pressure change in mm, dC/dP, was converted to ΔC, the capacitance change per atmosphere. ΔC was then used with the cell constant to calculate the quantity $(\epsilon-1)$ by Equation 29.

## The Cell Constant and the Dielectric Constant of Ammonia

Capacitance-pressure data was taken for ammonia at each temperature and converted to ΔC as above. This value was then used with the appropriate dielectric constant to calculate $C_O$ by Equation 29. The dielectric constants of ammonia were calculated at several temperatures by the Debye equation using published dipole moment and $P_o$ values (28, 29, 30), and molar volumes calculated from the following equation of state (31).

$$V = \frac{RT}{P} + B + \frac{\gamma}{RT}$$

$$B = 2.36 \times 10^{-3} - \frac{625}{T^2} - \frac{0.494 \times 10^8}{T^4} \qquad (33)$$

$$\gamma = -259.1 \times .10^{-6} + \frac{50.48}{T^2} - \frac{3.035 \times 10^6}{T^4}$$

The calculated dielectric constants were plotted as a function of temperature on a large graph from which the value corresponding to any temperature could be taken. The data for this plot as well as corresponding values of the molar volume are tabulated in Table IV.

## Molar Volumes and Molar Polarization

The total molar polarization in the form of the Debye equation expressed by Equation 19;

$$P_M = \frac{\epsilon - 1}{\epsilon + 2} \tilde{V}$$

requires the molar volume at one atmosphere of pressure at each temperature at which the calculation is to be made. These were calculated using Van derWaals' equation

$$\tilde{V}^3 - (b + RT)\tilde{V}^2 + a\tilde{V} - ab = 0$$

The parameters, a and b, which are listed in Table V, were estimated from critical constants using the following expressions

$$a = \frac{27R^2T_c^2}{64P_c} \tag{34}$$

$$b = \frac{RT_c}{8P_c} \tag{35}$$

When critical data were unavailable the parameters were estimated by structural analogy with compounds for which critical data were available (37).

## Molar Refractions

Since the dipole moments of the substituted cyclohexanes were expected to vary, they were determined for each molar polarization value by calculating $P_E$ by equation 23, and using the equation

Table IV--Calculated Dielectric Constants of Ammonia*

| T, °C | $\tilde{V}$ l. | $(\epsilon-1) \times 10^6$ |
|---|---|---|
| 300 | 24.60 | 6000 |
| 310 | 25.43 | 5639 |
| 320 | 26.25 | 5311 |
| 330 | 27.07 | 5013 |
| 340 | 27.89 | 4735 |
| 350 | 28.71 | 4489 |
| 360 | 29.53 | 4257 |
| 370 | 30.36 | 4043 |
| 380 | 31.18 | 3845 |
| 390 | 32.00 | 3664 |
| 400 | 32.82 | 3496 |
| 410 | 33.64 | 3337 |
| 420 | 34.46 | 3192 |
| 430 | 35.28 | 3054 |
| 440 | 36.10 | 2928 |
| 460 | 37.74 | 2694 |
| 480 | 39.39 | 2495 |
| 500 | 41.03 | 2312 |

*At one atmosphere pressure.

Table V--Van der Waals' Constants

| Compound | a $l^2$ atm. mole$^{-2}$ | b l. mole$^{-1}$ | Reference |
|---|---|---|---|
| 2-Methylpropane | 12.9 | 0.11 | 37 |
| 2-Methylbutane | 18.1 | 0.14 | 37 |
| cis-2-Butene | 12.8 | 0.11 | 38 |
| trans-2-Butene | 12.9 | 0.11 | 38 |
| 3-Methyl-1-butyne | 13.4 | 0.11 | |
| 3, 3-Dimethyl-1-butyne | 16.5 | 0.12 | |
| trans-1, 2-Dibromo-cyclohexane | 30.87 | 0.17 | |
| trans-1-Bromo-2-chlorocyclohexane | 31.88 | 0.18 | |
| trans-1, 2-Dichloro cyclohexane | 33.33 | 0.19 | |
| 1, 4-Cyclohexanedione | 32.32 | 0.16 | |

$$\mu = 0.0128\sqrt{(P_M - P_E)T} \qquad (36)$$

The quantity $\frac{\eta_\infty^2 - 1}{\eta_\infty + 2}\tilde{V}$, which is referred to as the molar refraction was calculated by summation of refraction equivalents for the sodium D line of the various atoms in the molecule (13).

## Dipole Moments and Distortion Polarizations

The slopes and intercepts of the $P_M$ vs $1/T$ plots for hydrocarbon vapors were calculated by the method of least squares which provides parameters for the line yielding the minimum squared deviation of the points from the line. The parameters were calculated using the following relations;

$$P_M = y \qquad 1/T = x$$

$$y = a + bx$$

$$a = \frac{N_a}{D} \qquad b = \frac{N_b}{D}$$

$$N_a = \sum_i y_i \sum_i x_i^2 - \sum_i x_i \sum_i x_i y_i$$

$$N_b = n \sum_i x_i y_i - \sum_i y_i \sum_i x_i$$

$$D = n \sum_i x_i^2 - (\sum_i x_i)^2$$

Dipole moments of the hydrocarbons were calculated by Equation 20 using slopes obtained in this way while those of the substituted cyclohexanes were calculated by the same equation using slopes derived from single experimental points and the molar refraction.

Energy differences between conformational isomers of the various substituted cyclohexanes were calculated using Equation 27.

Table VI--Capacitance-Pressure Data for 2-Methylpropane

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 451.38°K | | T = 425.08°K (cont.) | | T = 385.13°K (cont.) | |
| 0.076 | 106.03 | 0.082 | 101.48 | 0.301 | 352.43 |
| 0.080 | 108.07 | 0.076 | 98.30 | 0.319 | 371.46 |
| 0.082 | 108.81 | 0.079 | 97.70 | 0.331 | 375.64 |
| 0.080 | 108.07 | 0.085 | 102.98 | 0.346 | 392.82 |
| 0.078 | 110.95 | 0.083 | 106.11 | 0.321 | 382.86 |
| 0.118 | 160.36 | 1.517 | 1934.26 | 0.319 | 363.67 |
| 0.078 | 107.52 | | | 3.829 | 4409.14 |
| 0.070 | 107.32 | dC/dP = 0.784 x $10^{-3}$ | | | |
| 0.083 | 107.27 | | | dC/dP = 0.868 x $10^{-3}$ | |
| 0.072 | 99.90 | | | | |
| 0.070 | 103.39 | | | | |
| 0.118 | 157.42 | T = 405.72°K | | | |
| 0.072 | 97.66 | | | T = 367.39°K | |
| 0.076 | 105.43 | 0.271 | 327.75 | | |
| 0.081 | 104.83 | 0.284 | 340.45 | 0.340 | 365.92 |
| 0.077 | 102.69 | 0.272 | 344.83 | 0.339 | 368.01 |
| 0.087 | 117.63 | 0.277 | 327.35 | 0.352 | 380.76 |
| 0.084 | 116.78 | 0.257 | 318.74 | 0.351 | 381.60 |
| 1.482 | 2030.13 | 0.268 | 327.25 | 0.353 | 378.86 |
| | | 0.273 | 332.56 | 0.332 | 375.68 |
| dC/dP = 0.730 x $10^{-3}$ | | 0.258 | 312.45 | 0.352 | 381.95 |
| | | 0.257 | 312.15 | 0.353 | 381.15 |
| | | 0.230 | 267.52 | 0.345 | 372.99 |
| | | 0.219 | 267.87 | 0.334 | 370.70 |
| T = 425.08°K | | 0.290 | 352.04 | 0.361 | 376.37 |
| | | 3.156 | 3829.96 | 3.812 | 4133.99 |
| 0.069 | 96.13 | | | | |
| 0.074 | 91.40 | dC/dP = 0.824 x $10^{-3}$ | | dC/dP = 0.922 x $10^{-3}$ | |
| 0.084 | 106.13 | | | | |
| 0.084 | 105.63 | | | | |
| 0.079 | 102.20 | | | | |
| 0.088 | 108.32 | T = 385.13°K | | T = 350.56°K | |
| 0.110 | 159.74 | | | | |
| 0.079 | 102.43 | 0.318 | 364.40 | 0.358 | 386.38 |
| 0.077 | 98.84 | 0.314 | 358.77 | 0.358 | 378.47 |
| 0.079 | 100.34 | 0.303 | 358.37 | 0.358 | 366.82 |
| 0.078 | 98.54 | 0.319 | 366.64 | 0.361 | 377.92 |
| 0.080 | 100.44 | 0.330 | 371.32 | 0.373 | 379.96 |
| 0.131 | 157.55 | 0.308 | 350.76 | 0.357 | 365.27 |

Table VI - Continued

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 350.56°K (cont.) | | T = 335.67°K (cont.) | | T = 320.06°K | |
| 0.360 | 372.49 | 0.371 | 367.01 | 0.384 | 352.83 |
| 0.371 | 382.00 | 0.366 | 362.98 | 0.352 | 342.32 |
| 0.351 | 359.10 | 0.369 | 362.43 | 0.377 | 348.64 |
| 0.350 | 361.64 | 0.366 | 362.23 | 0.371 | 350.29 |
| 0.350 | 364.97 | 0.383 | 378.27 | 0.371 | 354.22 |
| 3.947 | 4095.02 | 0.390 | 375.43 | 0.398 | 365.22 |
| | | 0.393 | 390.11 | 0.378 | 357.81 |
| dC/dP = 0.964 x $10^{-3}$ | | 0.399 | 392.21 | 0.381 | 354.96 |
| | | 0.372 | 361.93 | 0.382 | 354.06 |
| | | 0.359 | 355.61 | 0.369 | 349.24 |
| | | 4.469 | 4418.78 | 0.396 | 364.63 |
| T = 335.67°K | | | | 0.394 | 372.94 |
| | | dC/dP = 1.011 x $10^{-3}$ | | 4.553 | 4267.16 |
| 0.353 | 347.99 | | | | |
| 0.348 | 362.58 | | | dC/dP = 1.067 x $10^{-3}$ | |

Table VII--Molar Polarization Data for 2-Methylpropane.

| T °K | ΔC μμf/atm | $10^6$x (ε-1) | $10^6$x $\frac{(\epsilon-1)}{(\epsilon+2)}$ | $\tilde{V}$ cc/mole | $P_m$ cc/mole | $10^3$x 1/T $(^\circ K)^{-1}$ |
|---|---|---|---|---|---|---|
| 451.38 | 0.5548 | 1643 | 547.4 | 36770 | 20.13 | 2.215 |
| 425.08 | 0.5958 | 1746 | 581.9 | 34600 | 20.13 | 2.353 |
| 405.72 | 0.6262 | 1852 | 617.0 | 33000 | 20.36 | 2.465 |
| 385.13 | 0.6597 | 1952 | 650.2 | 31280 | 20.34 | 2.597 |
| 367.39 | 0.7007 | 2048 | 682.2 | 29820 | 20.34 | 2.722 |
| 350.56 | 0.7326 | 2142 | 713.5 | 28420 | 20.28 | 2.853 |
| 335.67 | 0.7684 | 2246 | 748.1 | 27180 | 20.33 | 2.979 |
| 320.06 | 0.8033 | 2348 | 782.1 | 25870 | 20.23 | 3.124 |

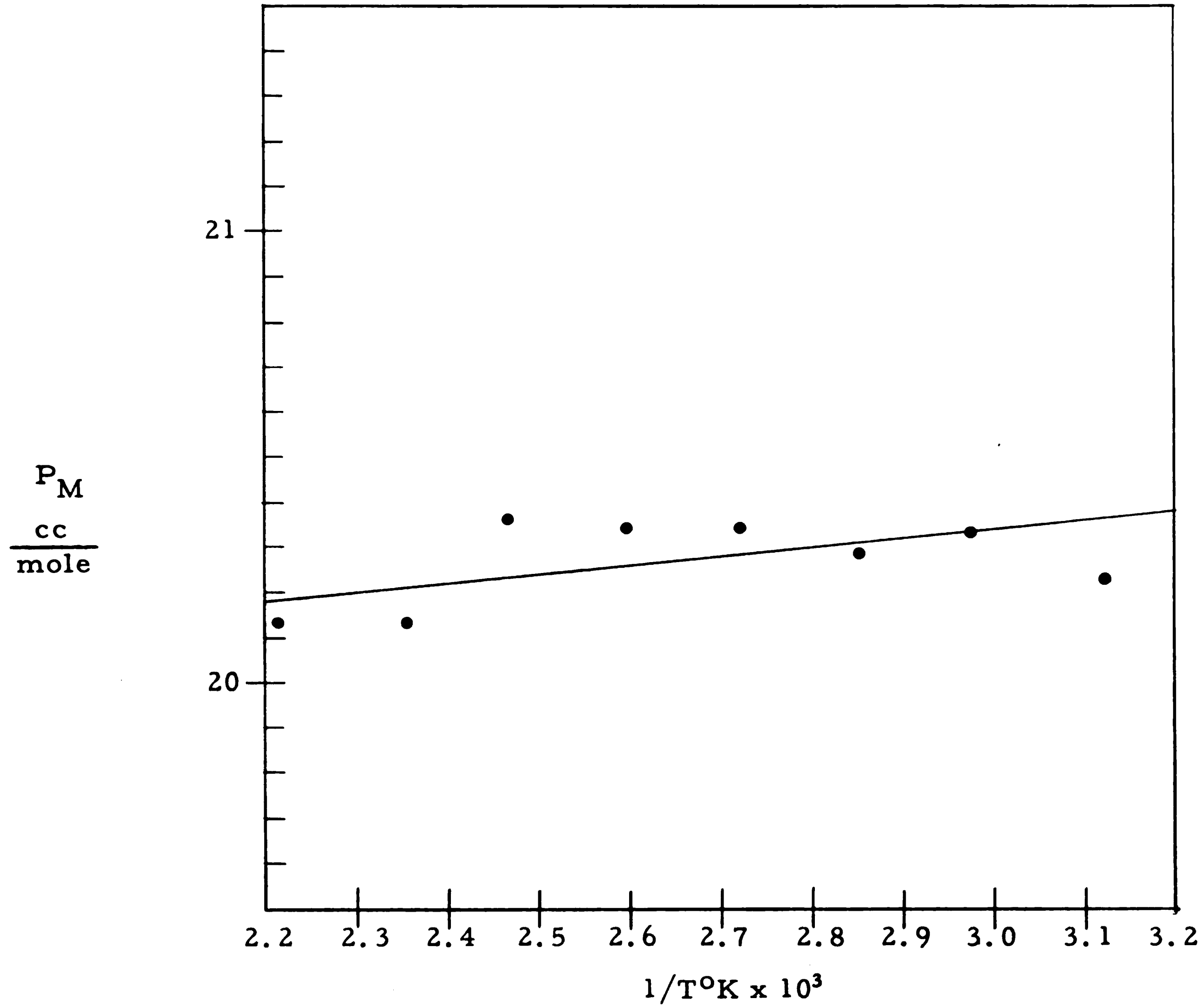


Figure 10. Molar polarization versus the reciprocal of the absolute temperature for 2-methylpropane.

Table VIII--Capacitance-Pressure Data for 2-Methylbutane

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 452.69°K | | T = 425.34°K | | T = 385.09°K | |
| | | (cont.) | | (cont.) | |
| 0.096 | 105.23 | 0.102 | 105.57 | 0.423 | 388.54 |
| 0.092 | 114.69 | 0.150 | 149.34 | 0.398 | 374.40 |
| 0.110 | 112.65 | 0.095 | 93.66 | 0.401 | 369.57 |
| 0.107 | 109.71 | 0.095 | 94.26 | 0.387 | 360.80 |
| 0.088 | 107.52 | 0.095 | 96.75 | 0.357 | 337.79 |
| 0.178 | 104.33 | 0.098 | 99.64 | 0.366 | 346.76 |
| 0.085 | 199.15 | 0.104 | 103.67 | 0.254 | 237.79 |
| 0.104 | 100.45 | 1.686 | 1723.00 | 0.281 | 267.12 |
| 0.100 | 107.22 | | | 0.369 | 343.97 |
| 0.088 | 105.28 | dC/dP = 0.973 x $10^{-3}$ | | 0.360 | 333.51 |
| 0.100 | 98.70 | | | 0.324 | 299.50 |
| 0.096 | 105.23 | | | 4.251 | 3976.93 |
| 0.089 | 101.09 | | | | |
| 0.091 | 100.84 | T = 405.68°K | | dC/dP = 1.069 x $10^{-3}$ | |
| 0.087 | 104.98 | | | | |
| 0.087 | 88.89 | 0.331 | 325.92 | | |
| 1.598 | 1765.96 | 0.334 | 324.13 | | |
| | | 0.317 | 319.90 | T = 367.36°K | |
| dC/dP = 0.905 x $10^{-3}$ | | 0.323 | 314.22 | | |
| | | 0.320 | 316.33 | 0.356 | 317.64 |
| | | 0.316 | 312.30 | 0.395 | 346.27 |
| | | 0.307 | 303.24 | 0.385 | 339.10 |
| T = 425.34°K | | 0.310 | 311.55 | 0.388 | 340.20 |
| | | 0.364 | 351.63 | 0.389 | 340.70 |
| 0.104 | 100.29 | 0.339 | 336.84 | 0.386 | 337.36 |
| 0.097 | 98.49 | 3.261 | 3216.06 | 0.386 | 339.50 |
| 0.096 | 105.76 | | | 0.386 | 343.74 |
| 0.104 | 104.32 | dC/dP = 1.014 x $10^{-3}$ | | 0.398 | 342.69 |
| 0.098 | 95.11 | | | 0.384 | 342.69 |
| 0.095 | 95.01 | | | 0.396 | 340.55 |
| 0.047 | 47.80 | | | 4.249 | 3730.39 |
| 0.099 | 110.00 | T = 385.09°K | | | |
| 0.099 | 109.35 | | | dC/dP = 1.139 x $10^{-3}$ | |
| 0.108 | 113.98 | 0.331 | 317.18 | | |

Table VIII - Continued

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 350.53°K | | T = 335.73°K | | T = 320.03°K | |
| 0.432 | 361.41 | 0.413 | 330.82 | 0.452 | 343.42 |
| 0.417 | 336.86 | 0.408 | 328.18 | 0.443 | 335.25 |
| 0.454 | 384.32 | 0.412 | 331.77 | 0.430 | 327.53 |
| 0.472 | 392.13 | 0.402 | 323.95 | 0.434 | 335.70 |
| 0.434 | 382.78 | 0.411 | 329.78 | 0.443 | 333.91 |
| 0.462 | 372.32 | 0.414 | 331.12 | 0.423 | 325.29 |
| 0.407 | 352.41 | 0.408 | 326.54 | 0.546 | 422.62 |
| 0.446 | 370.98 | 0.415 | 334.90 | 0.544 | 407.24 |
| 0.381 | 318.46 | 0.425 | 338.98 | 0.402 | 311.70 |
| 0.386 | 326.42 | 0.414 | 332.26 | 0.433 | 330.07 |
| 0.490 | 407.08 | 0.412 | 334.06 | 0.541 | 408.04 |
| 0.497 | 395.23 | 0.418 | 335.25 | 0.519 | 398.13 |
| 5.278 | 4400.40 | 4.952 | 3977.61 | 5.610 | 4278.90 |
| dC/dP = $1.199 \times 10^{-3}$ | | dC/dP = $1.245 \times 10^{-3}$ | | dC/dP = $1.131 \times 10^{-3}$ | |

Table IX--Molar Polarization Data for 2-Methylbutane

| T°K | ΔC μμf/atm | $10^6 x(\epsilon-1)$ | $10^6 x \frac{(\epsilon-1)}{(\epsilon+2)}$ | $\tilde{V}$ cc/mole | $P_M$ cc/mole | $10^3 \times 1/T$ $(°K)^{-1}$ |
|---|---|---|---|---|---|---|
| 425.69 | 0.6878 | 2037 | 678.5 | 36780 | 24.96 | 2.209 |
| 425.34 | 0.7395 | 2167 | 721.8 | 34410 | 24.84 | 2.351 |
| 405.68 | 0.7706 | 2279 | 759.1 | 32860 | 24.94 | 2.465 |
| 385.09 | 0.8124 | 2404 | 800.8 | 31140 | 24.94 | 2.597 |
| 367.36 | 0.8656 | 2530 | 842.6 | 29670 | 25.00 | 2.722 |
| 350.53 | 0.9112 | 2664 | 887.2 | 28260 | 25.07 | 2.852 |
| 335.72 | 0.9462 | 2766 | 921.2 | 27020 | 24.89 | 2.979 |
| 320.03 | 0.9964 | 2913 | 970.1 | 25700 | 24.93 | 3.125 |

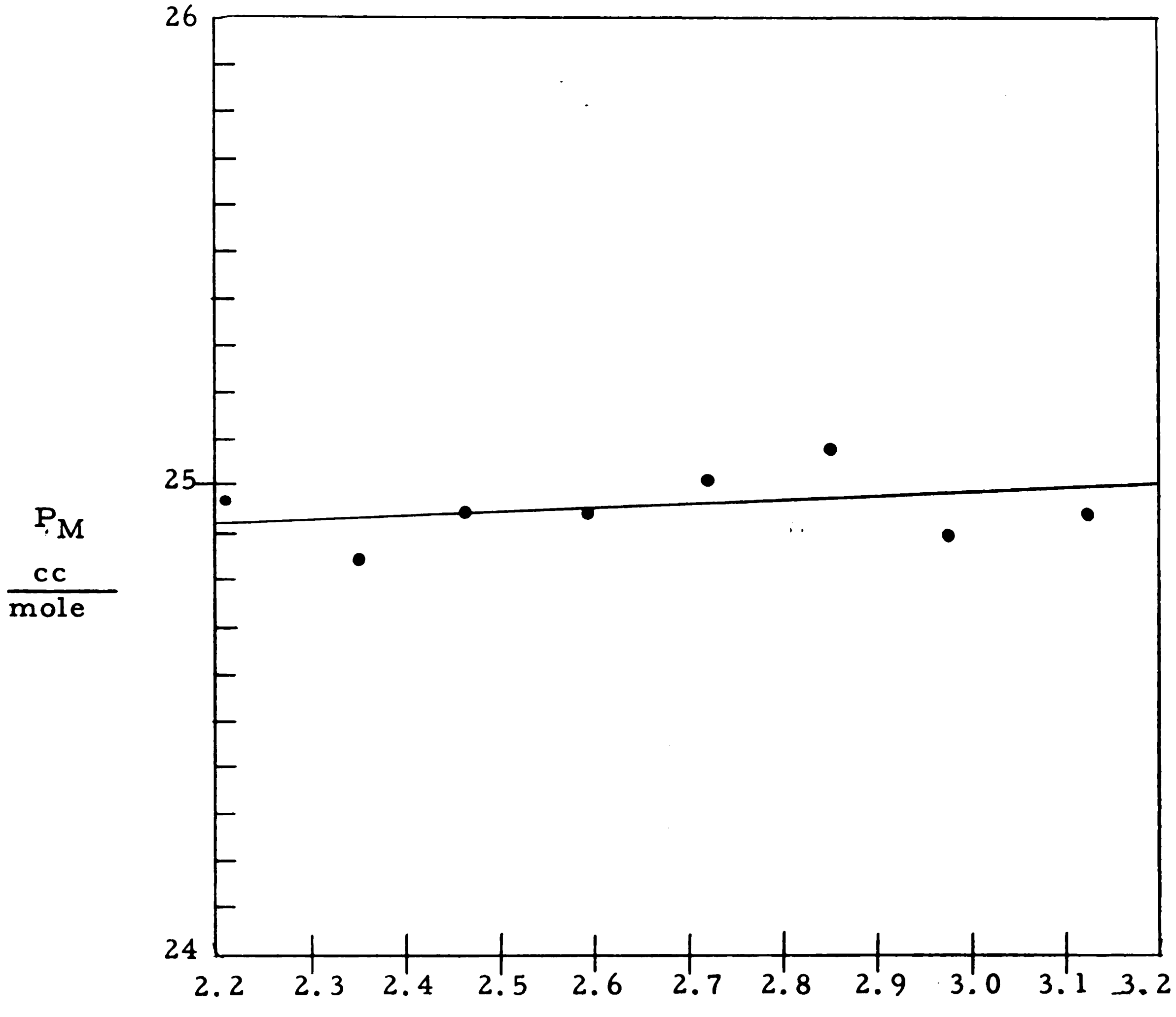


Figure 11. Molar polarization versus the reciprocal of the absolute temperature for 2-methylbutane.

Table X--Capacitance-Pressure Data for *cis*-2-Butene

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 451.66$^\circ$K | | T = 425.26$^\circ$K (cont.) | | T = 384.13$^\circ$ K | |
| 0.072 | 98.21 | 0.081 | 97.20 | 0.320 | 357.18 |
| 0.071 | 102.89 | 0.082 | 98.35 | 0.322 | 353.44 |
| 0.079 | 105.62 | 0.084 | 100.98 | 0.342 | 365.59 |
| 0.078 | 102.39 | 0.087 | 103.08 | 0.319 | 353.79 |
| 0.073 | 101.49 | 0.090 | 107.86 | 0.319 | 352.20 |
| 0.068 | 99.10 | 0.084 | 102.03 | 0.342 | 376.35 |
| 0.101 | 143.71 | 0.079 | 99.34 | 0.339 | 371.47 |
| 0.080 | 104.79 | 0.086 | 105.27 | 0.335 | 370.97 |
| 0.081 | 108.30 | 0.083 | 102.58 | 0.345 | 379.89 |
| 0.078 | 99.69 | 0.079 | 96.30 | 0.347 | 383.14 |
| 0.074 | 100.64 | 0.079 | 99.29 | 0.334 | 378.29 |
| 0.073 | 101.58 | 1.579 | 1889.63 | 0.321 | 342.89 |
| 0.115 | 151.13 | | | 3.985 | 4385.20 |
| 0.088 | 113.28 | dC/dP = 0.836 x $10^{-3}$ | | | |
| 0.090 | 115.28 | | | dC/dP = 0.909 x $10^{-3}$ | |
| 0.076 | 96.85 | | | | |
| 0.071 | 92.62 | | | | |
| 0.073 | 95.06 | T = 405.76$^\circ$K | | | |
| 1.441 | 1932.63 | | | T = 367.75$^\circ$K | |
| | | 0.303 | 348.98 | | |
| dC/dP = 0.746 x $10^{-3}$ | | 0.284 | 330.37 | 0.349 | 359.45 |
| | | 0.310 | 361.10 | 0.338 | 352.33 |
| | | 0.320 | 367.10 | 0.323 | 339.13 |
| | | 0.313 | 362.25 | 0.322 | 338.13 |
| T = 425.26$^\circ$K | | 0.305 | 356.72 | 0.331 | 340.66 |
| | | 0.299 | 347.80 | 0.324 | 350.27 |
| 0.091 | 104.47 | 0.313 | 367.73 | 0.339 | 334.79 |
| 0.088 | 106.56 | 0.316 | 365.53 | 0.319 | 356.70 |
| 0.092 | 104.32 | 0.303 | 352.88 | 0.356 | 366.75 |
| 0.089 | 104.47 | 0.302 | 352.13 | 0.366 | 357.64 |
| 0.092 | 105.57 | 0.306 | 358.41 | 0.329 | 357.44 |
| 0.085 | 101.13 | 3.674 | 4280.04 | 0.338 | 358.49 |
| 0.128 | 150.83 | | | 4.034 | 4211.78 |
| | | dC/dP = 0.858 x $10^{-3}$ | | | |
| | | | | dC/dP = 0.958 x $10^{-3}$ | |

Table X - Continued

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 350.57°K | | T = 335.69°K | | T = 319.99°K | |
| 0.367 | 364.80 | 0.361 | 357.26 | 0.401 | 352.62 |
| 0.352 | 354.74 | 0.392 | 366.82 | 0.383 | 346.60 |
| 0.363 | 349.56 | 0.391 | 365.57 | 0.400 | 354.91 |
| 0.380 | 368.63 | 0.374 | 349.99 | 0.392 | 352.23 |
| 0.404 | 384.57 | 0.389 | 353.02 | 0.386 | 342.12 |
| 0.373 | 372.32 | 0.391 | 363.33 | 0.380 | 340.73 |
| 0.352 | 344.33 | 0.386 | 357.36 | 0.379 | 335.80 |
| 0.347 | 351.05 | 0.371 | 352.73 | 0.380 | 340.88 |
| 0.365 | 368.53 | 0.387 | 359.05 | 0.387 | 345.76 |
| 0.373 | 364.90 | 0.382 | 359.50 | 0.397 | 355.61 |
| 0.369 | 358.77 | 0.375 | 351.38 | 0.403 | 357.90 |
| 0.361 | 365.74 | 0.374 | 345.71 | 0.394 | 354.12 |
| 4.406 | 4347.94 | 4.573 | 4281.72 | 4.682 | 4179.29 |
| $dC/dP = 1.013 \times 10^{-3}$ | | $dC/dP = 1.068 \times 10^{-3}$ | | $dC/dP = 1.120 \times 10^{-3}$ | |

Table XI--Molar Polarization Data for <u>cis</u>-2-Butene.

| $T^{\circ}K$ | $\Delta C$ μμf/atm | $10^6 x (\epsilon - 1)$ | $10^6 x \frac{(\epsilon-1)}{(\epsilon+2)}$ | $\tilde{V}$ cc/mole | $P_M$ cc/mole | $10^3 x 1/T$ $(^{\circ}K)^{-1}$ |
|---|---|---|---|---|---|---|
| 451.66 | 0.5670 | 1679 | 559.4 | 37810 | 21.15 | 2.214 |
| 405.76 | 0.6521 | 1929 | 642.6 | 33000 | 21.21 | 2.465 |
| 385.13 | 0.6908 | 2044 | 680.9 | 31300 | 21.31 | 2.597 |
| 367.75 | 0.7281 | 2128 | 708.8 | 29850 | 21.16 | 2.719 |
| 350.57 | 0.7699 | 2251 | 749.8 | 28420 | 21.31 | 2.853 |
| 335.69 | 0.8117 | 2373 | 790.4 | 27180 | 21.48 | 2.979 |
| 319.99 | 0.8512 | 2488 | 828.7 | 25870 | 21.44 | 3.125 |

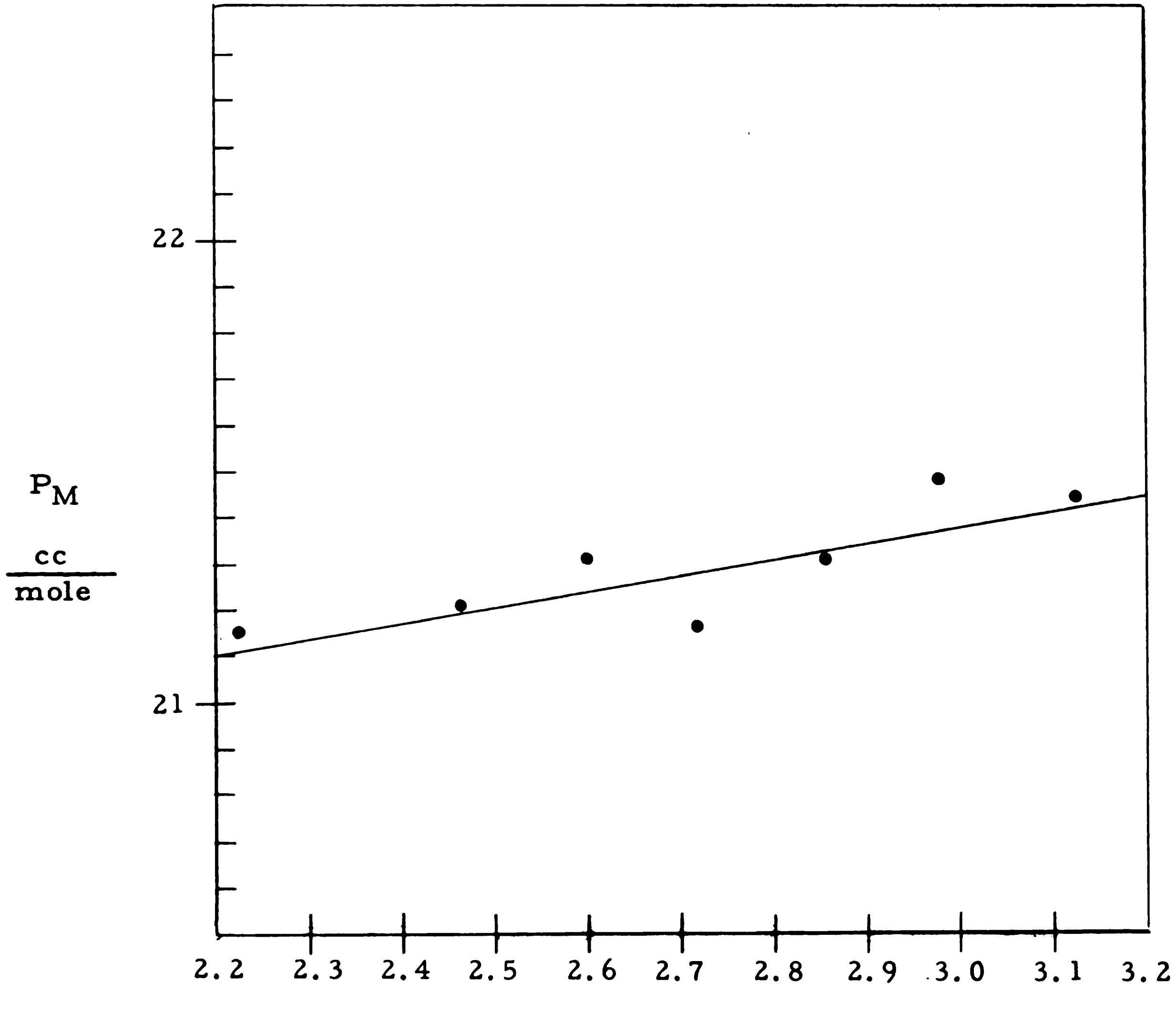


Figure 12. Molar polarization versus the reciprocal of the absolute temperature for cis-2-butene.

Table XII--Capacitance-Pressure Data for trans-2-Butene

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 451.20°K | | T = 425.03°K | | T = 385.11°K | |
| | | (cont.) | | | |
| 0.074 | 99.60 | 0.072 | 99.11 | 0.306 | 348.92 |
| 0.078 | 102.04 | 0.066 | 87.86 | 0.320 | 360.87 |
| 0.079 | 103.48 | 0.080 | 102.21 | 0.320 | 365.80 |
| 0.081 | 103.33 | 0.119 | 153.61 | 0.319 | 357.78 |
| 0.079 | 125.77 | 0.071 | 98.21 | 0.321 | 370.48 |
| 0.102 | 149.00 | 0.077 | 106.52 | 0.315 | 369.23 |
| 0.070 | 101.29 | 0.083 | 105.33 | 0.317 | 358.18 |
| 0.078 | 102.49 | 0.087 | 112.79 | 0.301 | 346.52 |
| 0.074 | 105.33 | 0.081 | 104.03 | 0.318 | 366.14 |
| 0.082 | 108.69 | 1.433 | 1847.75 | 0.332 | 373.80 |
| 0.065 | 93.32 | | | 0.309 | 356.93 |
| 0.070 | 93.87 | dC/dP = 0.776 x $10^{-3}$ | | 0.320 | 354.50 |
| 0.086 | 114.69 | | | 3.798 | 4329.15 |
| 0.115 | 154.13 | | | | |
| 0.063 | 85.11 | | | dC/dP = 0.877 x $10^{-3}$ | |
| 0.071 | 94.17 | T = 405.78°K | | | |
| 0.083 | 112.45 | | | | |
| 1.350 | 1828.76 | 0.313 | 375.61 | | |
| | | 0.296 | 358.76 | T = 367.76°K | |
| dC/dP = 0.738 x $10^{-3}$ | | 0.302 | 358.61 | | |
| | | 0.317 | 377.60 | 0.324 | 360.70 |
| | | 0.313 | 375.96 | 0.330 | 357.78 |
| | | 0.299 | 360.57 | 0.333 | 358.27 |
| T = 425.03°K | | 0.306 | 370.23 | 0.329 | 353.60 |
| | | 0.197 | 231.05 | 0.355 | 379.69 |
| 0.080 | 100.52 | 0.299 | 349.14 | 0.355 | 380.98 |
| 0.086 | 101.81 | 0.285 | 344.33 | 0.257 | 299.17 |
| 0.083 | 106.44 | 0.277 | 348.95 | 0.254 | 276.12 |
| 0.083 | 102.61 | 3.204 | 3850.81 | 0.355 | 379.79 |
| 0.077 | 99.67 | | | 0.360 | 385.16 |
| 0.074 | 96.67 | dC/dP = 0.832 x $10^{-3}$ | | 0.331 | 356.38 |
| 0.075 | 94.73 | | | 0.326 | 351.85 |
| 0.066 | 90.50 | | | 3.909 | 4219.49 |
| 0.073 | 96.13 | | | | |
| | | | | dC/dP = 0.926 x $10^{-3}$ | |

Table XII - Continued

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 350.52°K | | T = 335.67°K | | T = 320.07°K | |
| 0.355 | 358.62 | 0.364 | 354.54 | 0.384 | 357.56 |
| 0.357 | 367.24 | 0.359 | 356.98 | 0.379 | 363.63 |
| 0.370 | 378.89 | 0.353 | 354.39 | 0.383 | 359.55 |
| 0.363 | 379.88 | 0.369 | 358.78 | 0.384 | 349.69 |
| 0.353 | 367.64 | 0.366 | 362.11 | 0.373 | 352.38 |
| 0.368 | 366.49 | 0.354 | 349.81 | 0.370 | 344.71 |
| 0.343 | 369.38 | 0.362 | 351.80 | 0.364 | 339.68 |
| 0.355 | 369.08 | 0.360 | 360.42 | 0.382 | 364.97 |
| 0.371 | 384.42 | 0.362 | 353.54 | 0.393 | 365.77 |
| 0.360 | 378.69 | 0.358 | 355.24 | 0.385 | 353.07 |
| 0.368 | 365.50 | 0.358 | 355.84 | 0.376 | 356.44 |
| 0.363 | 377.25 | 0.369 | 354.94 | 0.387 | 365.32 |
| 4.326 | 4473.08 | 4.334 | 4268.39 | 4.560 | 4272.74 |
| dC/dP = 0.967 x $10^{-3}$ | | dC/dP = 1.015 x $10^{-3}$ | | dC/dP = 1.067 x $10^{-3}$ | |

Table XIII--Molar Polarization Data for trans-2-Butene.

| T°K | ΔC μμf/atm | $10^6$x(ε-1) | $10^6$x $\frac{(\epsilon-1)}{(\epsilon+2)}$ | $\widetilde{V}$ cc/mole | $P_M$ cc/mole | $10^3$x 1/T (°K)$^{-1}$ |
|---|---|---|---|---|---|---|
| 451.20 | 0.5609 | 1661 | 553.4 | 36760 | 20.34 | 2.216 |
| 405.78 | 0.6323 | 1870 | 623.0 | 33000 | 20.56 | 2.464 |
| 385.11 | 0.6665 | 1933 | 657.2 | 31290 | 20.56 | 2.597 |
| 367.76 | 0.7038 | 2057 | 685.2 | 29850 | 20.45 | 2.719 |
| 350.52 | 0.7349 | 2148 | 715.5 | 28410 | 20.33 | 2.853 |
| 335.67 | 0.7714 | 2252 | 751.1 | 27180 | 20.42 | 2.979 |
| 320.07 | 0.8109 | 2370 | 789.4 | 25880 | 20.43 | 3.124 |

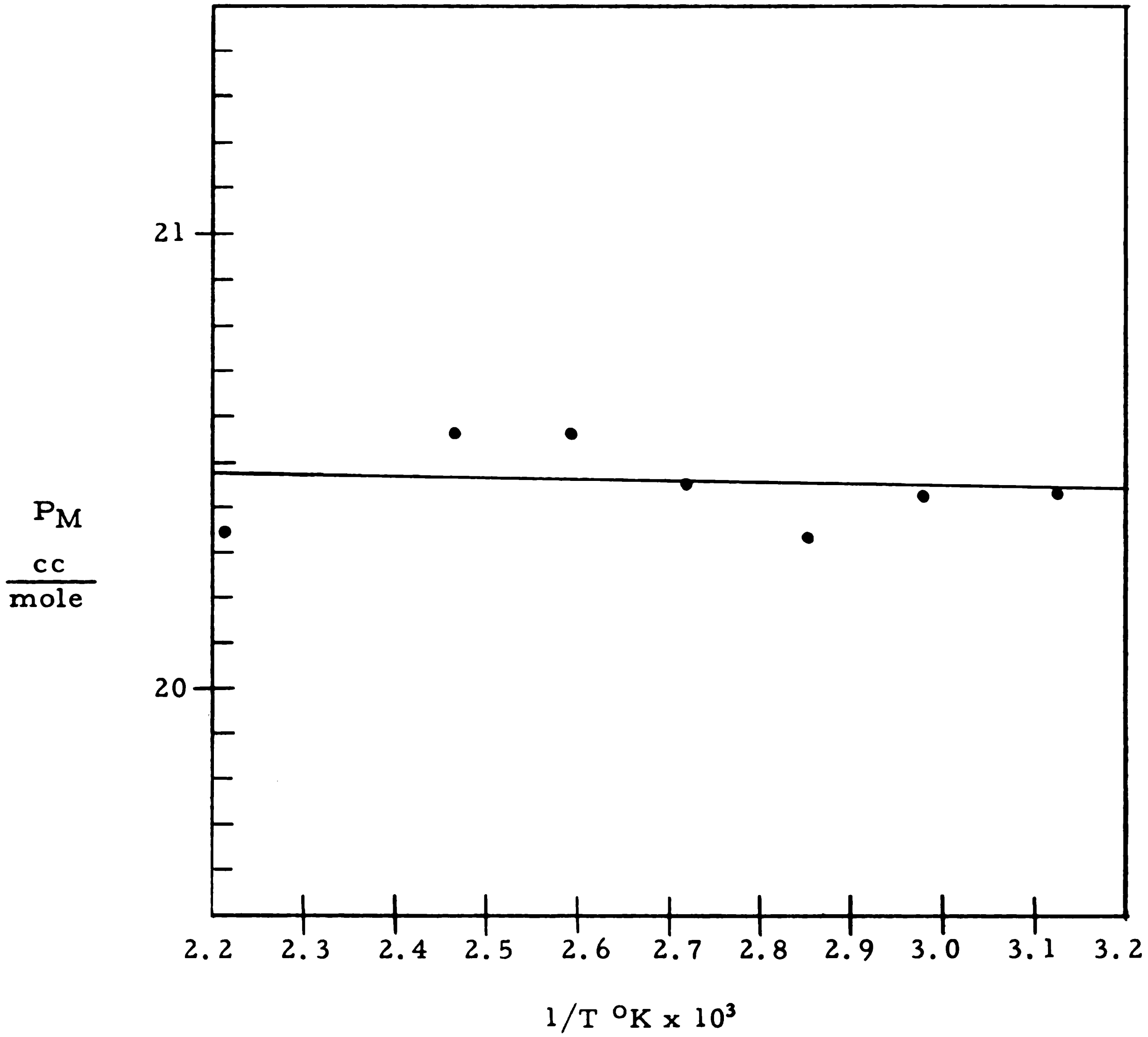


Figure 13. Molar polarization versus the reciprocal of the absolute temperature for <u>trans</u>-2-butene.

Table XIV--Capacitance-Pressure Data for 3-Methyl-1-Butyne

| dC $\mu\mu$f | dP mm | dC $\mu\mu$f | dP mm | dC $\mu\mu$f | dP mm |
|---|---|---|---|---|---|
| T = 433.50$^{\circ}$K | | T = 381.53$^{\circ}$K | | T = 367.50$^{\circ}$K | |
| 0.127 | 101.93 | 0.158 | 104.39 | 0.148 | 95.17 |
| 0.132 | 106.06 | 0.135 | 91.68 | 0.148 | 94.72 |
| 0.132 | 106.41 | 0.151 | 106.77 | 0.146 | 94.92 |
| 0.128 | 104.52 | 0.144 | 103.14 | 0.153 | 94.67 |
| 0.141 | 114.03 | 0.144 | 102.09 | 0.136 | 103.68 |
| 0.127 | 101.38 | 0.142 | 103.04 | 0.173 | 99.95 |
| 0.132 | 105.32 | 0.144 | 98.35 | 0.149 | 97.51 |
| 0.131 | 105.12 | 0.143 | 101.00 | 0.149 | 95.30 |
| 0.125 | 99.64 | 0.149 | 91.10 | 0.157 | 101.16 |
| 0.127 | 102.93 | 1.461 | 1006.19 | 0.117 | 95.33 |
| 0.125 | 100.34 | | | 0.158 | 94.34 |
| 1.427 | 1147.68 | dC/dP = 1.452 x $10^{-3}$ | | 0.146 | 96.53 |
| | | | | 0.145 | 95.54 |
| dC/dP = 1.243 x $10^{-3}$ | | | | 0.139 | 92.75 |
| | | | | 0.147 | 97.08 |
| | | T = 375.70$^{\circ}$K | | 0.149 | 99.02 |
| | | | | 2.243 | 1452.44 |
| T = 411.98$^{\circ}$K | | 0.591 | 367.64 | | |
| | | 0.558 | 366.00 | dC/dP = 1.544 x $10^{-3}$ | |
| 0.144 | 97.38 | 0.571 | 356.34 | | |
| 0.122 | 89.26 | 0.549 | 346.83 | | |
| 0.118 | 97.13 | 0.554 | 353.05 | | |
| 0.115 | 97.03 | 0.551 | 352.85 | T = 350.55$^{\circ}$K | |
| 0.125 | 97.83 | 0.575 | 358.47 | | |
| 0.141 | 107.29 | 0.549 | 346.68 | 0.633 | 380.18 |
| 0.138 | 106.79 | 0.515 | 337.87 | 0.575 | 347.17 |
| 0.149 | 109.18 | 0.541 | 335.18 | 0.481 | 290.95 |
| 0.134 | 102.26 | 0.538 | 335.03 | 0.502 | 303.80 |
| 0.131 | 105.69 | 6.092 | 3855.94 | 0.532 | 320.78 |
| 0.130 | 104.10 | | | 0.520 | 331.71 |
| 0.133 | 103.85 | dC/dP = 1.580 x $10^{-3}$ | | 0.669 | 398.08 |
| 1.600 | 1217.79 | | | 0.642 | 382.75 |
| | | | | 0.568 | 343.47 |
| dC/dP = 1.314 x $10^{-3}$ | | | | 0.614 | 364.33 |

Table XIV - Continued

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 350.55°K (cont.) | | T = 335.68°K (cont.) | | T = 320.03°K | |
| 0.577 | 347.00 | 0.586 | 336.34 | 0.677 | 359.25 |
| 0.570 | 342.47 | 0.638 | 366.14 | 0.618 | 332.96 |
| 6.883 | 4152.66 | 0.637 | 366.44 | 0.638 | 342.52 |
| | | 0.590 | 339.75 | 0.682 | 361.24 |
| dC/dP = 1.657 x $10^{-3}$ | | 0.591 | 338.75 | 0.589 | 371.93 |
| | | 0.449 | 258.34 | 0.581 | 311.85 |
| | | 0.465 | 261.63 | 0.660 | 352.78 |
| | | 6.904 | 3947.92 | 0.627 | 337.74 |
| T = 335.68°K | | | | 0.626 | 330.22 |
| | | dC/dP = 1.749 x $10^{-3}$ | | 0.622 | 333.61 |
| 0.603 | 341.47 | | | 0.466 | 251.66 |
| 0.581 | 334.80 | | | 0.492 | 263.06 |
| 0.592 | 335.40 | | | 7.228 | 3894.82 |
| 0.589 | 338.34 | | | | |
| 0.583 | 330.52 | | | dC/dP = 1.869 x $10^{-3}$ | |

Table XV--Molar Polarization Data for 3-Methyl-1-Butyne.

| T°K | ΔC μμf/atm | $10^6 x(\ -1)$ | $10^6 x \frac{(\epsilon-1)}{(\epsilon+2)}$ | $\tilde{V}$ cc/mole | $P_M$ cc/mole | $10^3$ x 1/T $(^\circ K)^{-1}$ |
|---|---|---|---|---|---|---|
| 433.50 | 0.9447 | 2798 | 931.8 | 35280 | 32.87 | 2.307 |
| 411.98 | 0.9986 | 2955 | 984.0 | 33500 | 32.96 | 2.427 |
| 381.53 | 1.104 | 3256 | 1084.0 | 30970 | 33.57 | 2.621 |
| 375.70 | 1.201 | 3308 | 1102.0 | 30490 | 33.80 | 2.662 |
| 367.50 | 1.159 | 3439 | 1145.0 | 29800 | 34.12 | 2.721 |
| 350.55 | 1.259 | 3680 | 1225.0 | 28400 | 34.79 | 2.843 |
| 335.68 | 1.329 | 3885 | 1293.0 | 27160 | 35.12 | 2.979 |
| 320.03 | 1.420 | 4151 | 1382.0 | 25850 | 35.73 | 3.125 |

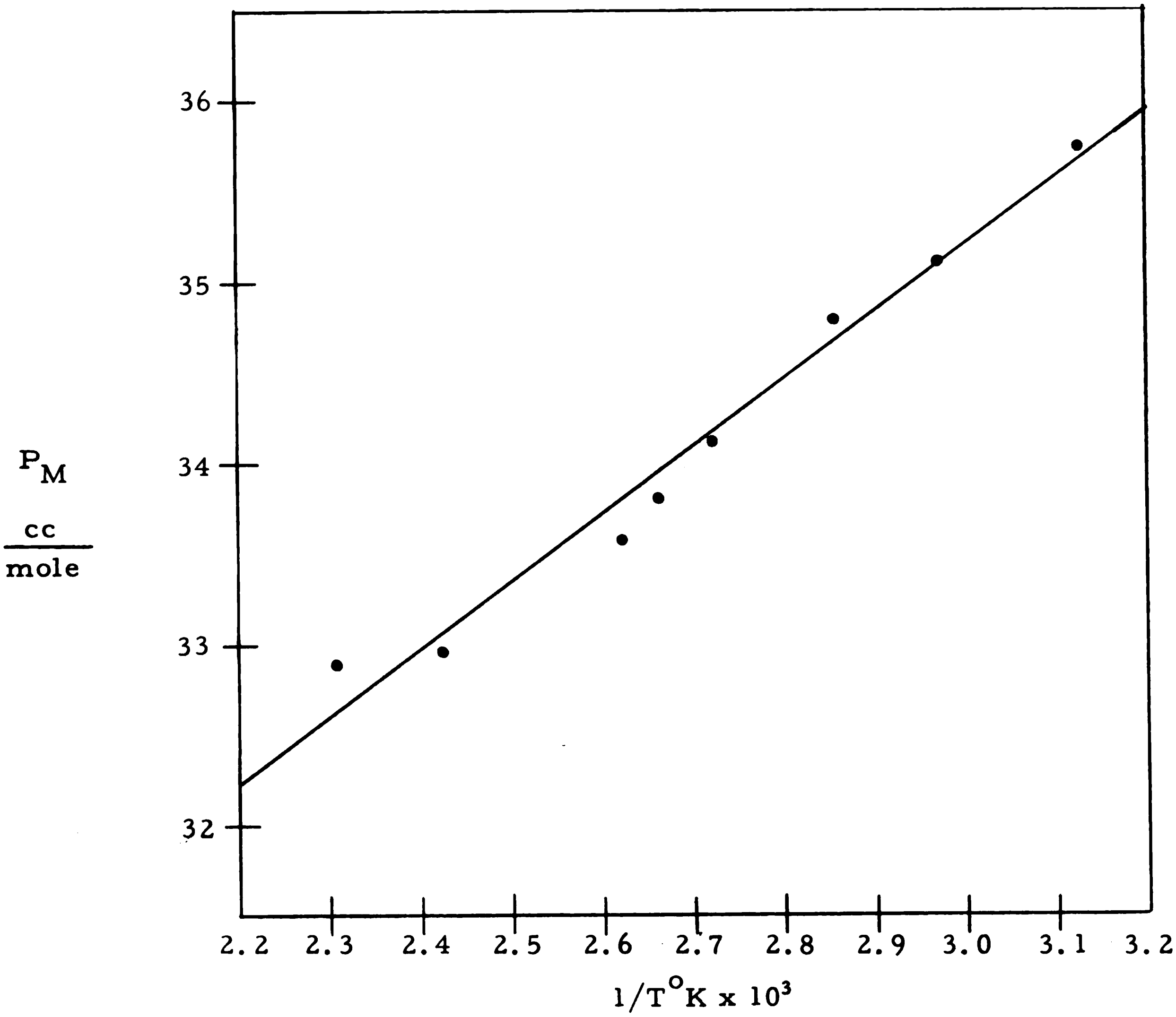


Figure 14. Molar polarization versus the reciprocal of the absolute temperature for 3-methyl-1-butyne.

Table XVI--Capacitance-Pressure Data for 3, 3-Dimethyl-1-Butyne

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 433.98°K | | T = 381.55°K | | T = 375.70°K (cont.) | |
| 0.138 | 103.57 | 0.137 | 86.50 | 0.573 | 320.25 |
| 0.132 | 95.46 | 0.164 | 95.77 | 0.589 | 324.73 |
| 0.138 | 96.10 | 0.165 | 97.36 | 7.332 | 4044.32 |
| 0.135 | 97.80 | 0.166 | 102.99 | | |
| 0.151 | 105.86 | 0.193 | 111.25 | dC/dP = 1.812 x $10^{-3}$ | |
| 0.129 | 95.66 | 0.172 | 95.07 | | |
| 0.127 | 95.81 | 0.164 | 101.69 | | |
| 0.140 | 97.90 | 0.171 | 104.78 | | |
| 0.118 | 85.71 | 0.161 | 102.79 | T = 367.45°K | |
| 0.113 | 88.74 | 0.166 | 99.50 | | |
| 1.341 | 962.61 | 0.130 | 79.12 | 0.171 | 93.56 |
| | | 0.155 | 96.35 | 0.160 | 92.22 |
| dC/dP = 1.393 x $10^{-3}$ | | 0.154 | 96.15 | 0.175 | 97.60 |
| | | 0.164 | 102.33 | 0.178 | 97.60 |
| | | 0.162 | 100.04 | 0.156 | 90.82 |
| | | 2.424 | 1471.69 | 0.175 | 102.63 |
| T = 412.10°K | | | | 0.165 | 97.00 |
| | | dC/dP = 1.647 x $10^{-3}$ | | 0.171 | 99.89 |
| 0.139 | 97.78 | | | 0.166 | 96.23 |
| 0.129 | 88.92 | | | 0.154 | 90.86 |
| 0.138 | 87.22 | | | 0.153 | 87.47 |
| 0.141 | 89.76 | T = 375.70°K | | 0.154 | 90.21 |
| 0.142 | 95.89 | | | 0.157 | 88.73 |
| 0.157 | 106.79 | 0.626 | 343.05 | 0.151 | 86.99 |
| 0.162 | 109.93 | 0.658 | 366.79 | 2.286 | 1321.81 |
| 0.150 | 104.30 | 0.622 | 342.80 | | |
| 0.147 | 95.39 | 0.603 | 334.84 | dC/dP = 1.741 x $10^{-3}$ | |
| 0.162 | 109.18 | 0.631 | 345.89 | | |
| 0.167 | 107.54 | 0.619 | 341.61 | T = 350.54°K | |
| 0.159 | 104.20 | 0.614 | 337.52 | | |
| 1.793 | 1196.90 | 0.601 | 327.82 | 0.560 | 294.63 |
| | | 0.590 | 325,83 | 0.567 | 300.15 |
| dC/dP = 1.498 x $10^{-3}$ | | 0.606 | 333.19 | 0.560 | 297.81 |

Table XVI - Continued

| dC μμf | dP mm | dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|---|---|
| T = 350.54$^{\circ}$K | | T = 343.22$^{\circ}$K | | T = 333.45$^{\circ}$K | |
| (cont.) | | (cont.) | | (cont.) | |
| 0.548 | 291.49 | 0.189 | 97.78 | dC/dP = 2.000 x $10^{-3}$ | |
| 0.598 | 316.18 | 0.198 | 102.06 | | |
| 0.661 | 352.78 | 0.193 | 101.31 | | |
| 0.679 | 357.61 | 0.210 | 106.64 | | |
| 0.650 | 343.47 | 1.565 | 816.07 | T = 320.12$^{\circ}$K | |
| 0.658 | 354.32 | | | | |
| 0.613 | 329.28 | dC/dP = 1.918 x $10^{-3}$ | | 0.719 | 340.08 |
| 0.636 | 339.83 | | | 0.704 | 339.08 |
| 0.562 | 303.14 | | | 0.672 | 318.91 |
| 7.292 | 3880.69 | | | 0.672 | 317.32 |
| | | T = 333.45$^{\circ}$K | | 0.729 | 343.72 |
| dC/dP = 1.879 x $10^{-3}$ | | | | 0.661 | 312.95 |
| | | 0.201 | 101.68 | 0.659 | 311.10 |
| | | 0.188 | 94.86 | 0.692 | 328.78 |
| | | 0.207 | 104.47 | 0.720 | 338.49 |
| T = 343.22$^{\circ}$K | | 0.167 | 83.59 | 0.754 | 353.67 |
| 0.196 | 103.35 | 0.185 | 90.70 | 0.761 | 356.76 |
| 0.196 | 103.30 | 0.193 | 97.43 | 0.721 | 336.85 |
| 0.197 | 103.35 | 0.208 | 101.36 | 8.464 | 3997.71 |
| 0.186 | 98.28 | 1.556 | 777.91 | | |
| | | | | dC/dP = 2.117 x $10^{-3}$ | |

Table XVII--Molar Polarization Data for 3, 3-Dimethyl-1-butyne.

| $T^{o}K$ | $\Delta C$ $\mu\mu f/atm$ | $10^6x( \; -1)$ | $10^6x\frac{(\epsilon-1)}{(\epsilon+2)}$ | $\widetilde{V}$ cc/mole | $P_M$ cc/mole | $10^3x \; 1/T$ $(^{o}K)^{-1}$ |
|---|---|---|---|---|---|---|
| 433.98 | 1.059 | 3137 | 1045 | 35250 | 36.84 | 2.304 |
| 412.10 | 1.139 | 3371 | 1122 | 33420 | 37.50 | 2.427 |
| 381.55 | 1.252 | 3692 | 1229 | 30890 | 37.96 | 2.621 |
| 375.70 | 1.377 | 3792 | 1262 | 30400 | 38.37 | 2.662 |
| 367.45 | 1.323 | 3926 | 1307 | 29720 | 38.84 | 2.721 |
| 350.54 | 1.428 | 4174 | 1389 | 28290 | 39.30 | 2.853 |
| 343.22 | 1.458 | 4276 | 1423 | 27680 | 39.39 | 2.914 |
| 333.45 | 1.520 | 4458 | 1484 | 26860 | 39.86 | 3.000 |
| 320.12 | 1.609 | 4703 | 1565 | 25750 | 40.30 | 3.124 |

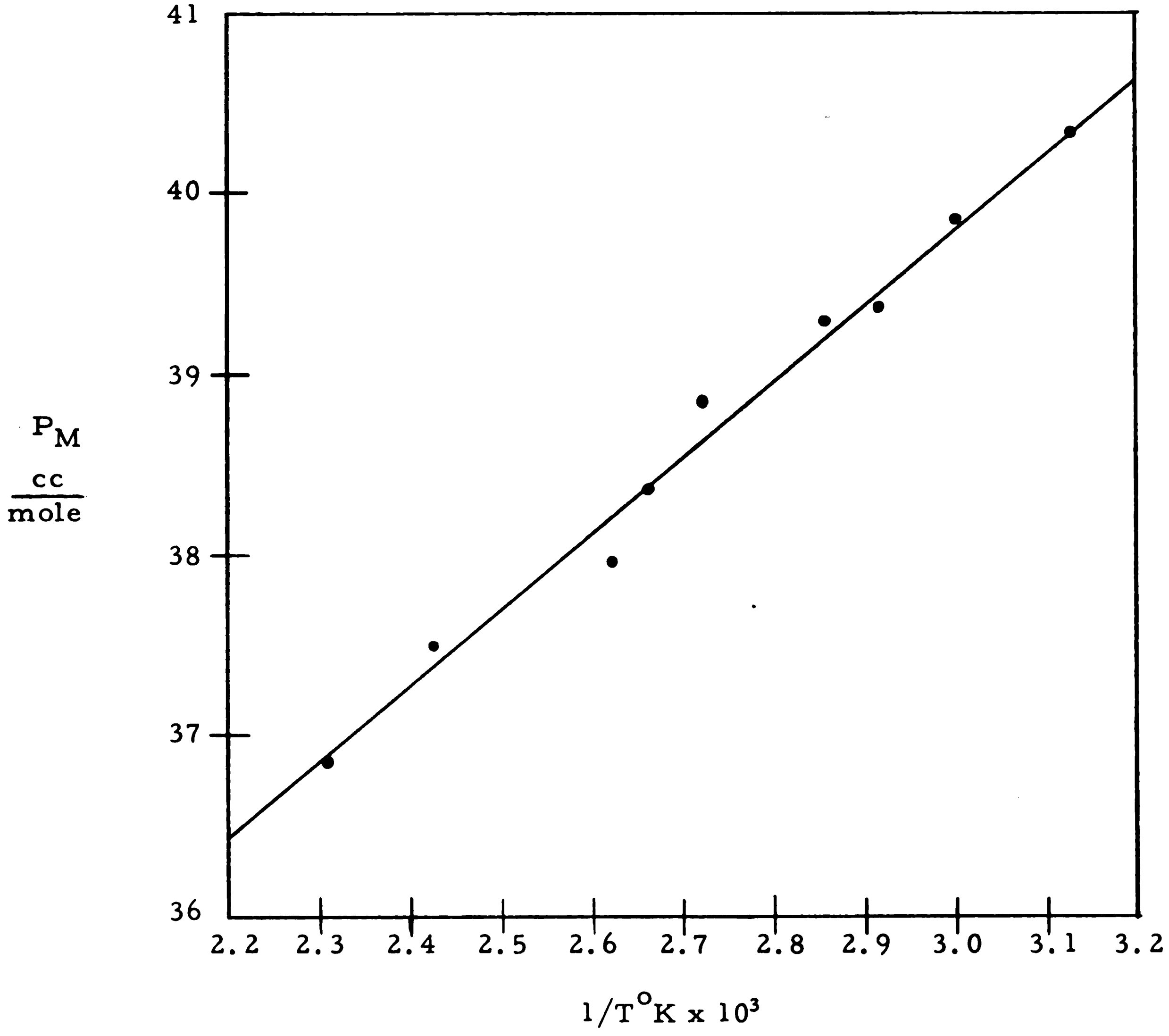


Figure 15. Molar polarization versus the reciprocal of the absolute temperature for 3, 3-dimethyl-1-butyne.

Table XVIII--Capacitance-Pressure Data for 1, 2-Dibromocyclohexane.

| dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|
| T = 448.46°K | | T = 467.53°K | |
| 0.467 | 122.7 | 0.461 | 125.4 |
| 0.464 | 119.7 | 0.432 | 119.8 |
| 0.459 | 118.2 | 0.524 | 146.6 |
| 0.454 | 115.2 | 0.494 | 139.5 |
| 0.539 | 142.0 | 0.467 | 128.9 |
| 0.501 | 132.1 | 0.445 | 125.9 |
| 0.465 | 122.7 | 0.505 | 143.4 |
| 0.453 | 120.4 | 0.478 | 137.2 |
| 3.802 | 993.0 | 3.806 | 1066.7 |
| dC/dP = $3.820 \times 10^{-3}$ | | dC/dP = $3.568 \times 10^{-3}$ | |

Table XIX--Molar Polarization Data for 1, 2-Dibromocyclohexane.

| T°K | ΔC μμf/atm | $10^6 x \frac{(\epsilon-1)}{(\epsilon+2)}$ | $\widetilde{V}$ cc/mole | $P_M$ cc/mole | $10^3 x 1/T$ $(°K)^{-1}$ | $P_o$ $\text{ccmole}^{-1}$ |
|---|---|---|---|---|---|---|
| 448.46 | 2.910 | 2707 | 36120 | 97.78 | 2.230 | 43.26 |
| 467.53 | 2.717 | 2516 | 37720 | 94.90 | 2.139 | 43.26 |

Table XX--Capacitance-Pressure Data for 1-Bromo-2-Chlorocyclohexane.

| dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|
| T = 448.46°K | | T = 467.53°K | |
| 1.009 | 236.1 | 0.680 | 178.0 |
| 0.988 | 236.1 | 0.673 | 178.0 |
| 1.035 | 240.3 | 0.673 | 183.2 |
| 1.010 | 240.3 | 0.682 | 183.2 |
| 1.046 | 253.3 | 0.965 | 243.8 |
| 1.051 | 253.3 | 0.959 | 243.8 |
| 0.604 | 145.9 | 0.900 | 237.5 |
| 0.606 | 145.9 | 0.921 | 237.5 |
| 7.349 | 1751.2 | 6.453 | 1685.0 |
| dC/dP = $4.196 \times 10^{-3}$ | | dC/dP = $3.829 \times 10^{-3}$ | |

Table XXI--Molar Polarization Data for 1-Bromo-2-Chlorocyclohexane.

| T°K | ΔC μμf/atm | $10^6 x \frac{(\epsilon-1)}{(\epsilon+2)}$ | $\tilde{V}$ cc/mole | $P_M$ cc/mole | $10^3$x 1/T (°K)$^{-1}$ | $P_o$ ccmole$^{-1}$ |
|---|---|---|---|---|---|---|
| 448.46 | 3.189 | 2966 | 36100 | 107.07 | 2.230 | 40.36 |
| 467.53 | 2.910 | 2694 | 37700 | 101.56 | 2.139 | 40.36 |

Table XXII--Capacitance-Pressure Data for 1, 2-Dichlorocyclohexane.

| dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|
| T = 441.83°K | | T = 468.22°K | |
| 0.703 | 283.1 | 0.649 | 291.1 |
| 0.702 | 283.1 | 0.638 | 291.1 |
| 0.733 | 309.4 | 0.885 | 405.5 |
| 0.728 | 309.4 | 0.885 | 405.5 |
| 0.776 | 323.5 | 0.557 | 246.8 |
| 0.775 | 323.5 | 0.548 | 246.8 |
| 0.844 | 329.2 | 4.162 | 1885.8 |
| 0.824 | 329.2 | | |
| 6.086 | 2490.4 | dC/dP = $2.207 \times 10^{-3}$ | |
| dC/dP = $2.443 \times 10^{-3}$ | | | |

Table XXIII--Molar Polarization Data for 1, 2-Dichlorocyclohexane.

| T°K | ΔC μμf/atm | $10^6 \times \frac{(\epsilon-1)}{(\epsilon+2)}$ | $\tilde{V}$ cc/mole | $P_M$ cc/mole | $10^3 \times 1/T$ $(^\circ K)^{-1}$ | $P_o$ cc mole$^{-1}$ |
|---|---|---|---|---|---|---|
| 490.25 | 1.493 | 1355 | 39570 | 53.62 | 2.040 | 27.73 |
| 468.17 | 0.844 | 1400 | 37720 | 52.81 | 2.136 | 27.73 |

Table XXIV--Capacitance-Pressure Data for 1,4-Cyclohexanedione.

| dC μμf | dP mm | dC μμf | dP mm |
|---|---|---|---|
| T = 490.25°K | | T = 468.17°K | |
| 0.136 | 75.0 | 0.085 | 70.9 |
| 0.146 | 75.0 | 0.072 | 70.9 |
| 0.167 | 84.7 | 0.076 | 59.5 |
| 0.172 | 84.7 | 0.061 | 59.5 |
| 0.110 | 53.5 | 0.084 | 70.1 |
| 0.100 | 53.5 | 0.067 | 70.1 |
| 0.111 | 54.1 | 0.445 | 401.0 |
| 0.109 | 54.1 | | |
| 1.051 | 534.6 | dC/dP = 1.110 x $10^{-3}$ | |
| dC/dP = 1.965 x $10^{-3}$ | | | |

Table XXV--Molecular Polarization Data for 1,4-Cyclohexanedione.

| T°K | ΔC μμf/atm | $10^6 \text{x} \frac{(\epsilon-1)}{(\epsilon+2)}$ | $\widetilde{V}$ cc/mole | $P_M$ cc/mole | $10^3$x a/T (°K)$^{-1}$ | $P_o$ cc mole$^{-1}$ |
|---|---|---|---|---|---|---|
| 490.25 | 1.493 | 1355 | 39570 | 53.62 | 2.040 | 27.73 |
| 468.17 | 0.844 | 1400 | 37720 | 52.81 | 2.136 | 27.73 |

# RESULTS

Dipole moments and values of $P_o$ and $P_E$ of the hydrocarbons are given in Table XXVI. Dipole moments and differences between $E_a$, the energy of the isomer having substituents oriented axially to the ring, and $E_e$, the energy of the isomer with equatorially oriented substituents in the substituted cyclohexanes, are listed in Table XXVII.

Table XXVI--Dipole Moments of Hydrocarbons

| Compound | $\mu$ Debye | $P_o$ cc | $P_E$* cc |
|---|---|---|---|
| 2-Methylpropane | 0.18 | 19.74 | 20.67 |
| 2-Methylbutane | 0.10 | 24.78 | 25.29 |
| trans-2-Butene | 0 | 20.44 | 20.17 |
| cis-2-Butene | 0.24 | 20.35 | 20.17 |
| 3-Methyl-1-butyne | 0.78 | 24.07 | 23.29 |
| 3, 3-Dimethyl-1-butyne | 0.83 | 27.15 | 27.91 |

*Calculated by Equation 23.

Table XXVII--Dipole Moments and Isomeric Energy Differences of Substituted Cyclohexanes

| Compound | T, °C | $\mu$ Debye | $\Delta E = E_{aa} - E_{ee}$ Cal/mole |
|---|---|---|---|
| trans-1, 2-Dibromo cyclohexane | 177 | 2.00 | -332 |
| | 196 | 1.99 | -358 |
| trans-1, 2-Dichlorocyclohexane | 170 | 2.28 | 102 |
| | 196 | 2.30 | 152 |
| trans-1-Bromo-2-chlorocyclohexane | 196 | 2.17 | -72 |
| | 219 | 2.21 | -19 |
| 1, 4-Cyclohexanedione | 196 | 1.39 | --- |
| | 218 | 1.44 | --- |

# ANALYSIS OF ERROR

Uncertainty in the values of $\mu$ calculated by Equation 20 were determined from the total differential of $\mu$ given by;

$$\mu = 0.0128\ b^{\frac{1}{2}}$$

$$d\mu = \frac{0.0064\ db}{b^{\frac{1}{2}}}$$

in which b is the slope, defined in the case of the hydrocarbons as;

$$b = \frac{u}{v}$$

$$u = P_M - P'_M$$

$$v = \frac{1}{T} - \frac{1}{T'}$$

The differential of the slope is

$$db = \frac{vdu-udv}{v^2}$$

$$du = dP_M - dP'_M$$

$$dv = \left(\frac{1}{T'^2} - \frac{1}{T^2}\right) dT$$

$$db = \frac{\left(\frac{1}{T} - \frac{1}{T'}\right)(dP_M - dP'_M) - (P_M - P'_M)\left(\frac{1}{T'^2} - \frac{1}{T^2}\right) dT}{\left(\frac{1}{T} - \frac{1}{T'}\right)^2}$$

Taking the two $\Delta P_M$ as equal and maximizing the term gives

$$\delta b = \frac{2\ \delta\ P_M}{\left(\frac{1}{T} - \frac{1}{T'}\right)} + (P_M - P'_M)\left(\frac{1}{T^2} - \frac{1}{T'^2}\right)\ \delta T$$

for the uncertainty of the slope and

$$\delta\mu = \frac{0.0064}{\frac{1}{b^2}} \quad \frac{2\,\delta P_M}{(\frac{1}{T} - \frac{1}{T'})} + (P_M - P_M')\,(\frac{1}{T^2} - \frac{1}{T'^2})\;\delta T \qquad (37)$$

for the uncertainty of $\mu$.

The quantity $\delta P_M$ was determined by recalculating values of $P_M$ using the equations used for the original calculations, and values altered by the amount of the experimental uncertainty in the appropriate direction to yield the greatest change in $P_M$.

Uncertainty in the values of $(\epsilon - 1)_{NH_3}$ consists of possible systematic error resulting from the use of erroneous values of $\mu$ and $P_o$ in the calculation and random error associated with the determination of values of $(\epsilon - 1)_{NH_3}$ from the plot.

The first of these was shown to be negligible by comparing values of the cell constant measured using ammonia, carbon dioxide and sulfur dioxide. The second was judged on the basis of the smallest increment which could be read, to be not more than

$$\delta(\epsilon - 1)_{NH_3} = \pm 3 \times 10^{-6}$$

Error in the value of $\Delta C$ depended upon the precision with which the capacitance and pressure could be read, and, to a somewhat greater extent, upon drift of the apparatus. Since the latter source of error does not lend itself to arbitrary analysis, deviations from the mean dC/dP for each of the hydrocarbons and ammonia at each temperature were averaged to obtain an experimental value for the overall uncertainty of $\delta\Delta C$. This value is;

$$\delta\Delta C_{NH_3} = \delta\Delta C_x = \pm 0.01 \mu\mu f/\text{atm}$$

Using these values and data taken at the median temperatures, the uncertainty in the cell constant was found to be

$$\delta C_O = \pm 2.8 \mu\mu f$$

Error in the determination of $\widetilde{V}$ resulting from the use of inexact values of Vander Waal's parameters has little effect upon the value of the dipole moment because approximately the same correction is applied to each value of $P_M$ and the whole line is lowered relatively uniformly. Thus a difference of about 0.5% of the volume occurred between corrections, amounting to over 1% of the volume, calculated at the extremes of temperature for 2-methylbutane. This corresponds to a contribution of less than 0.05% of the volume by a given molar volume. Assuming that this increment is in error by not more than 50%, the value of $\widetilde{V}$ was taken as 0.03%.

Values of $\delta\mu$ for the hydrocarbons calculated using these values are listed in Table XXVIII.

Errors in values of $P_o$ derived from the calculated intercept of $P_M$ vs 1/T plots are heavily dependent upon the accuracy of molar volume calculations. In view of the uncertainty associated with determining the Vander Waal's parameters from critical data the error in $P_o$ is difficult to estimate. However, the precision may be estimated by differentiating the total molar polarization expression.

$$P_M = P_o + b\frac{1}{T}$$

$$dP_M = dP_o + b(d\frac{1}{T}) + \frac{1}{T}\,db$$

Dropping the second term on the right which is insignificant, rearranging the maximizing gives

$$\delta P_o = \delta P_M + \frac{1}{T}\,\delta b$$

Values computed by this method are listed in Table XXVIII.

Dipole moments of the substituted cyclohexanes were calculated, at each temperature, by the following equation;

$$\mu = 0.0128 \sqrt{T(P_M - P_o)}$$

in which $P_o$ was calculated by Equation 22. The uncertainty in $\mu$ in this case is given by;

$$\delta\mu = \frac{0.0064\,[T\,\delta\,(P_M - P_o) + (P_M - P_o)\,\delta T]}{[T(P_M - P_o)]^{\frac{1}{2}}}$$

Which, since the uncertainty of $P_o$ is indeterminate and the second term in the numerator is small, becomes;

$$\delta\mu = \frac{0.0064\ T\delta P_M}{[T(P_M - P_o)]^{\frac{1}{2}}}$$

Mean of values of $\delta\mu$ calculated at each temperature for each compound are listed in Table XXVIII.

Uncertainty in values of $\Delta E$ calculated by Equation 28 could only be estimated because of the indeterminate error in $m_1$ and $m_2$. This estimate was made by the following equation which was derived by differentiating Equation 28 and assuming $\delta m_i$ to be zero.

$$\delta\Delta E = 2RT\mu\ \left(\frac{1}{m_1^2 - \mu^2} + \frac{1}{\mu^2 - m_2^2}\right)\ \delta\mu$$

Values of $\delta\Delta E$ calculated from mean moments are listed in Table XXVIII.

It should be noted that the uncertainty in dipole moments as calculated by Equation 37 increases as the slope of $P_M$ vs 1/T plot decreases, regardless of the precision of the measurement. In the case of the hydrocarbons the resulting values of the uncertainty are unreasonably large. Thus, Equation 37 predicts that 2-methylpropane might have a moment as high as 0.51 D., and 2-methylbutane a moment of 0.66 D. On the other hand a molecule actually having a moment of 0.65 D. could not, according to Equation 37, be found to have a value lower than 0.5 D. if the precision of measurement were the same as that of the present measurements.

Table XXVIII--Experimental Error

| Compound | $\delta \mu$ Debye | $\delta P_o$ cc | $\delta \Delta E$ Cal/mole |
|---|---|---|---|
| 2-Methylpropane | ±0.32 | ±2.2 | |
| 2-Methylbutane | ±0.56 | ±2.2 | |
| cis-2-Butene | ±0.25 | ±2.2 | |
| trans-2-Butene | ----- | | |
| 3-Methyl-1-Butyne | ±0.07 | ±2.1 | |
| 3,3-Dimethyl-1-butyne | ±0.07 | ±2.2 | |
| trans-1,2-Dibromocyclohexane | ±0.06 | | ± 80 |
| trans-1,2-Dichlorocyclohexane | ±0.05 | | ±110 |
| trans-1-Bromo-2-chlorocyclohexane | ±0.07 | | ±130 |
| 1,4-Cyclohexanedione | ±0.16 | | ----- |

If it is assumed that the upper limit of uncertainty of a $\mu$ value is that value for which the error, as calculated by Equation 37, includes the $\mu$ value, then $\delta \mu$ values may be obtained for the first three hydrocarbons which seem much more realistic than those listed in Table XXVIII. These values are as follows:

| | $\delta \mu$ |
|---|---|
| 2-methylpropane | 0.16 |
| 2-methylbutane | 0.19 |
| <u>cis</u>-2-butene | 0.15 |

# DISCUSSION OF RESULTS

## HYDROCARBONS

The electric moments of 2-methylpropane and 2-methylbutane obtained here are zero within the indicated experimental error. However, the value obtained for 2-methylpropane is in quite good agreement with one obtained from microwave measurements (46). Since the error as calculated by Equation 37 tends to increase without limit as the slope of the $P_M$ vs 1/T plot becomes small, it is possible that values so calculated are excessive and that moments of the order of 0.1 to 0.2 Debye exists in these molecules.

A rough relation may be established between moments of 2-methylbutane and 2-methylpropane if it is assumed that the butyl skeleton of 2-methylbutane is in a perfect skew conformation and that a uniform gradation of C-H bond dipoles, m, occurs such that

$$m_{\text{tert.C-H}} > m_{\text{sec.C-H}} > m_{\text{prim.C-H}}$$

and

$$m_{\text{tert.C-H}} - m_{\text{prim.C-H}} = 2(m_{\text{sec.C-H}} - m_{\text{prim.C-H}})$$

Let the vector bond moments be

$$\underline{m}_{\text{tert.C-H}} = \underline{A}$$

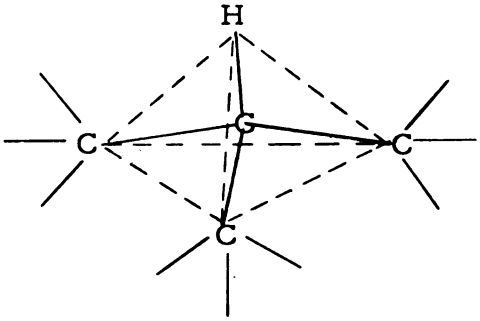
$$\underline{m}_{\text{sec.C-H}} = \underline{B}$$

$$\underline{m}_{\text{prim.C-H}} = \underline{D}$$

so that

$$A\text{-}B = B\text{-}D = \frac{A\text{-}D}{2}$$

The tetrahedrally disposed bonds about the central atom in 2-methylpropane may be resolved into two colinear vectors A and D since, as a result of the tetrahedral bonding, the resultant of the three D bond vectors about each methyl group is another D bond vector lying along the respective fourth bond. The resultant of these three D bond vectors is in turn a D bond vector lying along the A bond.



2-Methylpropane

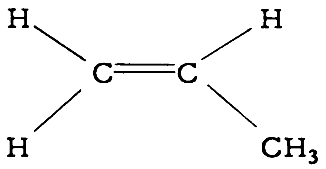
The A and D bond vectors are thus anti-parallel (assuming uniformity of orientation of the bond dipoles) and the moment of 2-methylpropane is A-D.

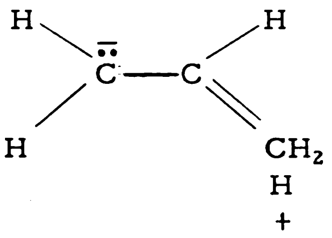
The situation in 2-methylbutane is somewhat different because of the absence of symmetry. However, the two methyl groups at the ends of the butyl chain have C-C bonds which are parallel, cancelling their D bond vectors and leaving only a D bond vector and an A bond vector on the second carbon, opposed (by virtue of the stipulation of the skewed conformation) by two B bond vectors on the third carbon. The result is a vector on carbon number 2 of value A-B making an angle of 70 degrees with one on carbon number 3 of value B-D. Since both of these are equal to one-half (A-D) the moment of 2-methylbutane is the sum of two vectors at an angle of 70 degrees each equal to one-half the moment of 2-methylpropane. The value of 2-methylbutane calculated from this relation is

2-methylbutane $\mu$ calc. = 0.15 D.

which is in good agreement with the observed value.

The occurrence of electric moments in ethylenic hydrocarbons is usually explained on the basis of hyperconjugation structures of type II.


I


II

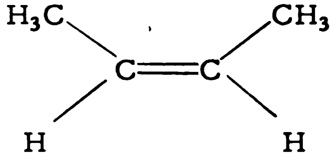
Propene

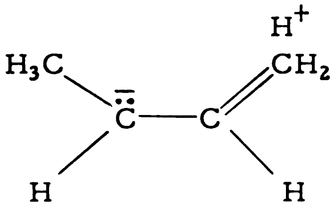
Since three structures of type II may be drawn for propene while only two may be drawn for 1-butene it may be concluded that the contribution of polar forms is more significant to the resonance hybrid in the case of propene than in the case of 1-butene. Propene would therefore be expected to exhibit the larger electric moment, which, indeed, proves to be the case (11).

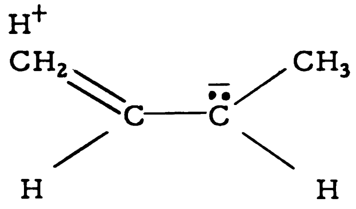
Propene $\mu$ = 0.35 D.

1-Butene $\mu$ = 0.30 D.

In the case of cis 2-butene three structures of type IV and three of type V may be drawn.

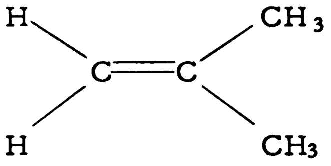

III


IV

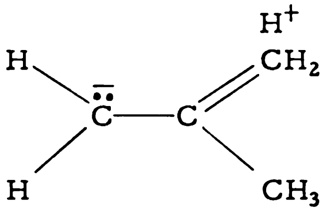

V

cis-2-Butene

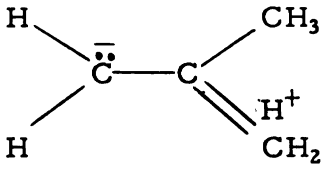
Each of these forms would be expected to result in a dipole moment about equal to that of propene. If each form made a contribution equal in importance to the contribution of II to the propene molecule the electric moment of cis-2-butene would be expected to be somewhat larger than that of propene. The present work has shown it to be equal or somewhat smaller. By way of explanation of this result, it should be noted that, to the extent to which these forms contribute, the hybrid molecule must support negative charges on adjacent carbon atoms. It is to be expected, therefore, that such forms will play a smaller role in the 2-butenes than in propene. Further indications of the importance of this effect may be had from consideration of the moment of 2-methylpropene which has the same number and type of resonance structures (VI, VII, VIII) as cis-2-butene;



VI



VII



VIII

but which has only one negative charge site. The moment of this compound is 0.49 D. (14), which is in agreement with the expected value of about 0.6 Debye.

The trans-2-butene molecule has a center of symmetry and as a result would be expected to have a zero net moment, which the present work has shown to be the case.

The moments of 3-methyl-1-butyne and 3, 3-dimethyl-1-butyne are somewhat lower than was anticipated in view of the values reported by Krieger and Wenzke (15) for other mono-acetylenes. It should be noted, however, that these authors in effect forced the $P_M$ vs 1/T plots to intercept the $P_M$ axis at the calculated value of the molar refraction. This procedure ignores the atomic polarization, which increases with the number of C-C and C-H bonds, and, consequently, leads to results which are increasingly in error on the high side as the molecular weight increases.

The direction of the variation of the electric moments in 3-methyl-1-butyne and 3, 3-dimethyl-1-butyne may be explained on the basis of either hyperconjugative effects or dipole induced-dipole interactions if it is assumed for both arguments that the principal bond moment in the molecule is in the acetylenic C-H bond.

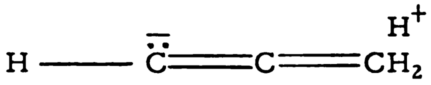
$$\mathrm{H} \;{+}\!\!\!\longrightarrow \mathrm{C}\equiv\mathrm{C}-\mathrm{R}$$

VI'

On the basis of hyperconjugation three forms such as VIII' may be drawn for this molecule while only one such form may be drawn for 3-methyl-1-butyne and none may be drawn for 3, 3-dimethyl-1-butyne.

$$\mathrm{H}-\mathrm{C}\equiv\mathrm{C}-\mathrm{CH_3}$$

VII'



$$\mathrm{H}-\overset{-}{\ddot{\mathrm{C}}}=\mathrm{C}=\overset{\mathrm{H}^+}{\mathrm{CH_2}}$$

VIII'

The moment resulting from forms such as VIII' opposes that resulting from VI', and, because of the greater number of such forms which may be drawn for propyne, the moment of that molecule, which has been reported to be about 0.74 D. (14, 21), would be expected to be smaller than that of either 3-methyl-1-butyne or 3, 3-dimethyl-1-butyne. Similarly the moment of 3-methyl-1-butyne would be expected to be smaller than that of 3, 3-dimethyl-1-butyne. In both cases the experimental moments vary in the expected direction.

Shifting now to consideration of induced dipoles, it may be argued that any contribution to the permanent electric dipole resulting from polarization of the alkyl groups of these molecules by the field of the principal dipole would be in the same direction as that dipole and would result in an increase in the total moment. A rough calculation of such a contribution may be made by assuming that the contribution of the principal dipole is the same in each case, that is, that its value and field are the same in each case. The group polarization, $\rho g$, is the product of the group polarizability, $\alpha g$, by the effective field, $E_{dp}$, and is equal to the induced dipole moment, $m_i$ (Equations 1, 8, 11).

$$\rho g = \alpha_g E_{dp} = m_i$$

The components of polarizability in the plane of the $\equiv C - C$ bond are given in Table XXIX (20).

Table XXIX--Group Polarizabilities

| | Methyl | Ethyl | Isopropyl | t-Butyl |
|---|---|---|---|---|
| Polarizability (x $10^{-25}$ cm$^3$) | 27 | 46 | 65 | 84 |

The sum of the unknown principal contribution and the product of the polarizability by the unknown $E_{dp}$ may be taken as equal to the experimental electric moment for two compounds of known $\mu$. These equations may then be solved simultaneously and the resulting values of the principal moment and $E_{dp}$ used to calculate the electric moment in other cases.

This calculation was made solving the equations for propyne and 3-methyl-1-butyne simultaneously and calculating the moment of 3, 3-dimethyl-1-butyne as follows;

$$\mu_1 = m_x + \alpha_1 E_{dp}$$

$$\mu_2 = m_x + \alpha_2 E_{dp}$$

$$E_{dp} = \frac{\mu_1 - \mu_2}{\alpha_1 - \alpha_2}$$

$$m_x = \mu_1 \frac{\alpha_1(\mu_1 - \mu_2)}{\alpha_1 - \alpha_2}$$

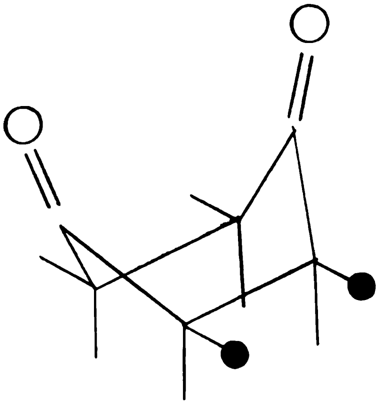
$$\mu_3 = m_x + \alpha_3 E_{dp}$$

3, 3-Dimethyl-1-butyne $\mu_{calc.} = 0.81$ D.

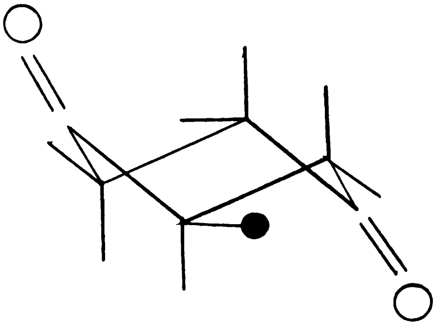
The agreement between this value and the observed value lends considerable support to the interpretation of variations of the moments of these molecules in terms of dipole induced-dipole interactions.

## 1, 4-Cyclohexanedione

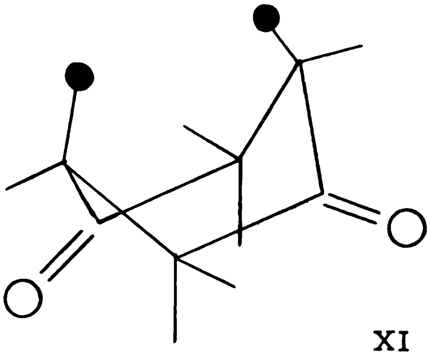
Calculation of the energy differences between conformational isomers by Equation 28 requires that the number of energy levels be limited to two and hence, that the number of possible conformations of the molecule under study be limited to two. Examination of the 1, 4-cyclohexanedione molecule reveals that as well as forms IX and X a pair of enantiomorphic forms, XI, may be imagined for the molecule.



IX



X



XI

The moment of the molecule in the chair conformation, X, may be estimated to be zero by inspection, and those of the two boat forms calculated by taking the vector sum of two cyclohexanone moments at an angle of 76 degrees in IX and 128 degrees in XI. Thus;

$$m_{IX} = 4.2 \text{ D.}$$

$$m_{X} = 0$$

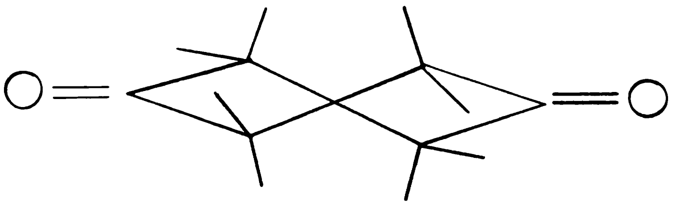
$$m_{XI} = 2.3 \text{ D.}$$

If the energies of the various boat and chair forms were equal, the net or measured moment would be the root mean square of these (giving $m_{XI}$ a statistical weight of two). This mean is 2.66 D., considerably larger than the measured moment, indicating that in the actual molecule the chair form is favored over one or both of the boats.

Inspection of the molecular models of this molecule reveals that in the chair form, X, the intramolecular interactions, other than those between hydrogen atoms oriented in the skew configuration, consist of interaction between four hydrogen atoms in the eclipsed conformation with respect to the two oxygen atoms ($O_1$-$H_1$ in X). The interactions in form IX consist of those between eight hydrogen atoms eclipsed in pairs ($H_1$-$H_2$ in IX), four hydrogen-oxygen interactions of the type found in form X, and, probably, an interaction between the two oxygen atoms. In either form XI enantiomorph there are two hydrogen-oxygen interactions of the same type found in the other two forms, interaction between the two axial hydrogen atoms at the peaks of the boat ($H_1$-$H_2$ in XI), and perhaps, a small interaction between the two oxygen atoms. The energies of the three forms would, on the basis of these considerations, be expected to be in the following order;

$$E_X < E_{IX} < E_{XI}$$

It is also possible that a form such as XII has a role in



XII

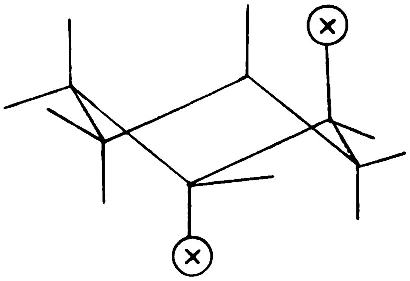
the determination of the net moment (41). The $CH_2COCH_2$ bond angle in this form is calculated to be 111°20' on the basis of a tetrahedral angle of 109°28' for the other bonds. This is very close to the value of the $C-\overset{O}{\overset{\|}{C}}-C$ angle found in a large number of compounds (40), indicating that the energy of the molecule in this form would not be greatly increased by bond strain. Furthermore the intramolecular interactions in this molecule are practically identical to those found in the chair form X.

No means is available by which the various possible combinations may be sorted out, since no relation is known by which the energy of one form may be expressed in terms of another except the simple two level relation of Equation 28. An estimate may be made, however, of the difference in energy between the chair form X, and the composite boat form which has been termed the flexible form (41). If it is assumed that only the three unstrained forms need be considered and that the energies of IX and XI are the same, the approximate value of $\Delta E$ is

$$\text{1, 4-Cyclohexanedione } \Delta E = E_F - F_C = 2.11 \frac{\text{kcal}}{\text{mole}}$$

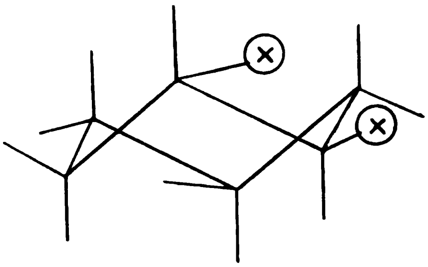
## *trans*-1, 2-Dihalogenocyclohexanes

In the *trans*-1, 2-dihalogenocyclohexanes, as in other substituted cyclohexanes, the distinguishable conformations of the chair forms are denoted by reference to the orientation of the substituents with respect to the threefold symmetry axis in the chair form of cyclohexane. An axial orientation (a) is parallel to this axis, while an equatorial orientation (e) forms angles of 110 and 70 degrees with it. Each of the molecules studied here has a polar (e-e) and a nonpolar (a-a) conformation.



a-a

XIII



e-e

XIV

The moment of the polar form, XIV, of these molecules may be estimated from bond moments, or measured directly as the moment of the cis isomer of the molecule in question. A value of 3.13 D. has been used here for the moment of this form of all three molecules. This value is the mean of the moments of the three molecules measured in solution (19), all of which are the same within experimental error.

In Table XXX values of $\Delta E$ between these forms calculated from vapor phase measurements are compared with values determined from solution measurements (19), corrected for the decrease in energy of the polar form in solution. This correction is given by (48)

$$E_R = \frac{-(\epsilon - 1)\mu^2}{(2\epsilon + 1)a^3}$$

in which $E_R$ is the loss of energy resulting from the transfer of a dipole of moment $\mu$ from vacuum($\epsilon = 1$) to a medium of dielectric constant $\epsilon$, where 'a' is the molecular radius.

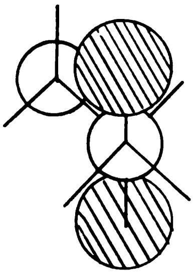
Table XXX--Energy Differences Between Conformational Isomers for Some trans-1,2-Dihalogenocyclohexanes.

| | $\Delta E = (E_{aa} - E_{ee})$kcal mole$^{-1}$ | | |
|---|---|---|---|
| | Vapor | Benzene Solution | Corr. Benzene Solution |
| trans-1,2-dichlorocyclohexane | 0.13 | 0.65 | -0.05 |
| trans-1-bromo-1-chlorocyclohexane | -0.05 | 0.37 | -0.18 |
| trans-1,2-dibromocyclohexane | -0.35 | -0.07 | -0.43 |

Values of $\Delta E$ have also been calculated for these compounds from measurements in $CCl_4$ (see Table II), which are generally in somewhat better agreement with the vapor values reported here. However, when the correction cited here is applied this agreement disappears.

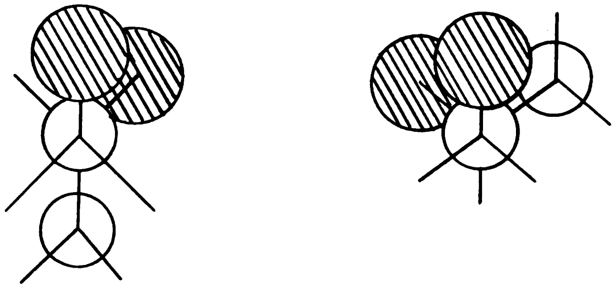
That the values of $\Delta E$ reported here, as well as those calculated from solution measurements are approximately correct may be demonstrated by consideration of the results of similar measurements on 1, 2-dichloroethane and 1, 2-dichloropropane.

For 1, 2-dichloropropane the three possible stable configurations are represented by the diagrams below, in which the reader is looking directly along the 1, 2-carbon-carbon bond.



anti

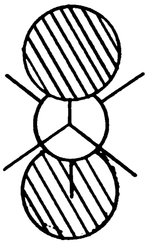
XV



gauche-1 gauche-2

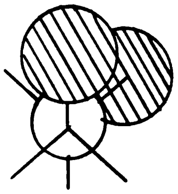
XVI

The gauche-2 form apparently has a much higher energy than either of the other two forms, and consequently would be expected to exist in only negligible amounts at ordinary temperatures, an observation which is in accord with the results of Raman measurements (42). The energy difference, $\Delta E$, between the anti and the gauche-1 forms of this molecule, calculated (43) from vapor phase moments (44), and that between the anti and gauche forms, XVII and XVIII,



anti

XVII



gauche

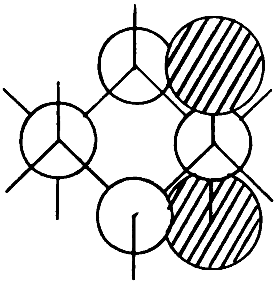
XVIII

of 1, 2-dichloroethane (45) are;

| | $\Delta E = E_g - E_a$ kcal mole$^{-1}$ |
|---|---|
| 1, 2-Dichloroethane | 1.21 kcal |
| 1, 2-Dichloropropane | 1.0 kcal |

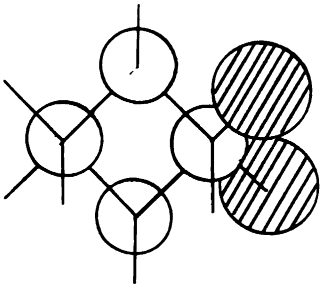
The difference of 0.2 kcal can only be attributed to the interaction between the halogen on carbon number one and the methyl group, carbon number three, in 1, 2-dichloropropane.

Consideration of the diagrams, XIX and XX of the conformational isomers of the trans-1, 2-dihalogenocyclohexanes reveals that an analogous situation prevails, except that instead of one such halogen-methyl interaction there are four, two of which occur without the sacrifice of a halogen-hydrogen interaction. The difference between the energies of the e-e and a-a conformations of trans-1, 2-dichlorocyclohexane would be predicted on this basis to be somewhat over 0.8 kcal less than that of the anti and gauche forms of 1, 2-dichloroethane, which proves to be the case, the difference between vapor phase values being about 1 kcal.



a-a

XIX



e-e

XX

# SUMMARY

The electric moments of two series of compounds were measured in the vapor phase by the heterodyne-beat method at radio frequency.

One of the series consisted of six hydrocarbons; two alkanes, 2-methylpropane and 2-methylbutane; two alkenes, *cis*-2-butene and *trans*-2-butene; and two alkynes, 3-methyl-1-butyne and 3, 3-dimethyl-1-butyne. Small moments, confirming published microwave results, were found in the alkanes. The moment of *trans*-2-butene was found to be zero, as anticipated in view of its symmetry, while *cis*-2-butene was found to have a moment which could be explained, qualitatively, on the basis of hyperconjugation. The moments of the alkynes were discussed in terms of both hyperconjugation and dipole induced dipoles.

The second series of compounds consisted of four substituted cyclohexanes; *trans*-1, 2-dichlorocyclohexane, *trans*-1-bromo-2-chlorocyclohexane, *trans*-1, 2-dibromocyclohexane, and 1, 4-cyclohexanedione. The moments of these substances were measured over a short range of high temperatures, and the differences in energy between conformational isomers calculated in each case. These results were compared to the results obtained from measurements made on these compounds in solutions of various solvents.

# LITERATURE CITED

1. P. Debye, Physik. Z., 13, 97 (1912).

2. J. J. Thompson, Phil. Mag., 45, 513 (1923).

3. C. P. Smyth, Phil. Mag., 45, 849 (1923); Phil. Mag., 47, 530 (1924); J. Am. Chem. Soc., 46, 2151 (1924).

4. J. Errara, J. Phys. Radium, [6] 6, 390 (1925); Physik. Z., 27, 764 (1926).

5. C. P. Smyth, S. O. Morgan and J. C. Boyce, J. Am. Chem. Soc., 50, 1536 (1928).

6. A. Eucken and L. Meyer, Physik. Z., 30, 397 (1929).

7. N. V. Sidgwick, "The Covalent Link in Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1933, p. 146.

8. C. P. Smyth and C. T. Zahn, J. Am. Chem. Soc., 47, 2501 (1925).

9. C. P. Smyth and K. B. McAlpine, J. Chem. Phys., 2, 571 (1934).

10. K. B. McAlpine, and C. P. Smyth, J. Am. Chem. Soc., 55, 453 (1933).

11. H. E. Watson, A. G. Rao and K. L. Ramaswamy, Proc. Roy. Soc. (London), A143, 558 (1934).

12. M. Kubo, Sci. Papers Inst. Phys. Chem. Res. (Tokyo), 26, 242 (1935).

13. See C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York (1955).

14. H. E. Warson, G. P. Kane and K. L. Ramaswamy, Proc. Roy. Soc. (London), A156, 130 and 144 (1936).

15. F. J. Krieger and H. H. Wenzke, J. Am. Chem. Soc., 60, 2115 (1938).

16. A. Tulinskie, A. DiGiacomo and C. P. Smyth, J. Am. Chem. Soc., 75, 3552 (1953).

17. W. Kwestroo, F. A. Meijer and E. Havinga, Rec. trav. Chim. 73, 717 (1954).

18. K. Kozima, K. Sakashita and S. Maeda, J. Am. Chem. Soc., 76, 1965 (1954).

19. P. Bender, D. L. Flowers and H. L. Goering, J. Am. Chem. Soc., 77, 3463 (1955).

20. C. G. LeFèvre and R. J. W. LeFèvre, J. Chem. Soc., 1996, (1935).

21. S. N. Ghosh, R. Trambarulo and W. Gordy, Phys. Rev., 87, 172 (1952).

22. O. F. Mosotti, Mem.di Mathem. e di Fisica in Modena, 24, II, 49, (1850).

23. R. Clausius, "Die Mechanische Warmetheorie," Vol. II, p. 62, Vieweg, 1879.

24. P. Langevin, J. de Phys., [4] 4, 678 (1905).

25. H. A. Lorentz, Ann. Physik., 9, 641 (1880).

26. M. P. Ivitsky, Bull. Soc. Chim. France, 35, 357 (1924).

27. H. Greengard in "Organic Synthesis" John Wiley and Sons, New York, Vol. III, p. 26.

28. C. T. Zahn, Phys. Rev., 27, 455 (1926).

29. J. M. A. deBruyne and C. P. Smyth, J. Am. Chem. Soc., 57, 1203 (1935).

30. D. K. Coles, W. E. Good, J. K. Bragg and A. H. Sharbaugh, Phys. Rev., 82, 877 (1951).

31. van Itterbeck and de Clippelier, Physica, 14, 349 (1948).

32. R. D. Pruett, Ph. D. Dissertation, Michigan State College, (1954).

33. J. Chien, J. Chem. Educ., 24, 494 (1947).

34. J. A. Conner, Electronics, 24, 250 (1951).

35. R. L. Burwell, A. H. Peterson and G. B. Rathman, Rev. Sci. Intr. 19, 608 (1948).

36. S. Cromer MDDC-803, United States Atomic Energy Commission, Technical Information Branch, Oak Ridge, Tenn.

37. "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 31st ed., p. 1833.

38. M. Smith, and G. Hanson, Oil and Gas Journal, 44, 10, 119 (1945).

39. T. L. Brown, J. Am. Chem. Soc., 81, 3229 (1959).

40. L. Pauling, "The Nature of the Chemical Bond," Third Ed., Cornell Univ. Press, Ithaca, New York, 1960, p. 136 ff.

41. P. Hazebrock and L. J. Costerhoff, Disc. Faraday Soc., 10, 82 (1951).

42. L. Kahovec and J. Wagner, Z. phys. chem., (B) 47, 48 (1940).

43. Y. Morino, I. Mijagawa and A. Wada, J. Chem. Phys., 20, 1976 (1952).

44. R. A. Oriani and C. P. Smyth, J. Chem. Phys., 17, 1174 (1949).

45. S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, 1954, pp. 34-38.

46. D. R. Lide, J. Chem. Phys., 29, 914 (1958).

47. D. R. Lide, J. Chem. Phys., 33, 1514 (1960).

48. S. Mizushima and H. Okazaki, J. Am. Chem. Soc., 71, 3411 (1949).