

AN INVESTIGATION OF THE ELECTRIC MOMENTS OF SOME
COMPOUNDS OF FLUORINE

By

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I. INTRODUCTION

Electric dipole moment data provide important information in structural chemistry. Combined with other structural data, dipole moments provide information concerning the shape of molecules and the bond angles, as well as details of the electronic structures of molecules such as ionic-covalent bond resonance and resonance among valence-bond structures.

Because of the high reactivity and general nature of the halogen fluorides, very little work had been done with them before 1946. The dipole moments of only two of these compounds, chlorine monofluoride and chlorine trifluoride, had been measured directly at microwave frequencies, and none had been measured at radio frequencies.

As a result of the present interest in fluorine chemistry, both in industry and in the government, many halogen fluorides, fluorocarbons, and fluorocarbon derivatives are now available for study. The dipole moments of several of these compounds were measured in the vapor phase. Equipment was built with which to carry out these measurements, both on compounds that possess sufficient vapor pressure at room temperature, and on compounds that boil considerably above room temperature. Special methods for handling and purifying the halogen fluorides have been developed and additional equipment constructed with which their dipole moments could be determined.

The data thus obtained shed further light on the molecular structures of the halogen fluorides and fluorocarbon derivatives studied in this investigation.

II. HISTORICAL REVIEW

Interhalogens

An excellent summary of the chemical and physical properties of the halogen fluorides has been presented by Thompson (1). Booth and Pinkston have written a chapter on the halogen fluorides in the book Fluorine Chemistry (2), and several review articles on the chemistry and physical properties of these compounds have appeared (3,4,5).

Relatively few direct measurements of the electric moments of the interhalogen compounds, especially the halogen fluorides, have been reported. This is due to their high reactivity, difficulties in handling and purification, and lack of availability.

The first dipole moment of an interhalogen compound was obtained by Townes (6) who reported a moment of 0.65 D for iodine monochloride from microwave studies. Gilbert and Roberts (7) obtained a moment of 0.881 D for chlorine monofluoride, the first halogen fluoride to be measured. This result was obtained from microwave data, as was the moment of 1.29 D for bromine monofluoride reported by Smith, Tidwell and Williams (8). Sheka (9) reported the dipole moment of iodine monobromide to be 1.21 D from dielectric constant and density data of solutions of iodine monobromide in bromine. A value of 0.6 D for the moment of bromine monochloride was estimated by Frohlich and Jost (10) from dielectric constant measurements in the liquid state at different

temperatures. Chlorine trifluoride, according to Magnuson (11), has a moment of 0.554 D at microwave frequencies.

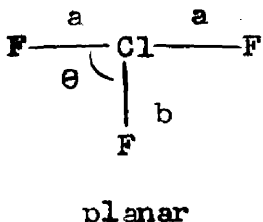
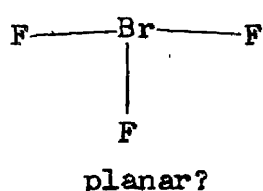
The structures of the interhalogen compounds have been studied by electron diffraction, infrared and Raman spectroscopy, and crystal structure methods. The results of some of these studies are summarized in Table I.

Fluorocarbons

Between 1900 and 1925 the foundations of modern organic fluorine chemistry were laid by the Belgian chemist Swartz. He devised general methods for the preparation of fluorine compounds, and it was his work which rendered possible, about 1930, the commercial application of aliphatic polyfluorohalocompounds as refrigerants. During the past twenty years Bigelow (2,14), Cady and Simons (2) developed methods for the controlled interaction of fluorine with organic compounds, resulting in the synthesis of a large number of members of a new class of compounds, the fluorocarbons.

Physical properties. Fluorocarbons having molecular weights less than perfluorobutane have higher boiling points than hydrocarbons with the same carbon structure; for those with higher molecular weights the reverse is true (2). Fluorocarbons are much more volatile than hydrocarbons of the same molecular weight; thus perfluoromethane with molecular weight 88 boils at -128°C , while hexane, molecular weight 86, boils at 69°C . Fluorocarbons boil only slightly higher than the noble gases

TABLE I
STRUCTURAL DATA FOR SOME OF THE INTERHALOGEN COMPOUNDS

Compound	Dipole Moment	Bond Distance	Configuration	Reference
ClF	0.88 D	1.628 Å	---	7
ClF ₃	0.554	a=1.698 b=1.598 θ=87° 29'	 planar	12
BrF	1.29	1.759	---	8
BrF ₃	---	1.78	 planar?	13
ICl	0.65	2.303	---	15
IBr	1.21	---	---	9
BrCl	0.6	---	---	10

of similar molecular weight. This fact emphasizes the low intermolecular attractive forces of the fluorocarbons.

As is shown in Table II, a comparison of melting points of saturated fluorocarbons with those of saturated hydrocarbons with the same carbon skeleton shows that the fluorocarbons have higher melting points.

Table II shows that a fluorocarbon has a density about twice that of the parent hydrocarbon. The rate of change of density with temperature is about three times that for hydrocarbons. Like the density, the viscosity and temperature coefficient of viscosity are appreciably higher than those for hydrocarbons.

Their surface tensions are extremely low, far lower than those of the corresponding hydrocarbons, and include the lowest values recorded. This is another result of the low intermolecular forces present.

As indicated in Table II, fluorocarbons have very low refractive indices, lower than those of any other known type of compound. The atomic refractivity of the fluorine atom varies with the type of compound; for aliphatic monofluorides it is 0.95, and for perfluorocarbons is 1.23 to 1.25. Likewise, their dielectric constants are somewhat lower than those of the corresponding saturated hydrocarbons.

Their diamagnetic susceptibilities are abnormally low and the lowest ultrasonic velocity yet measured in liquids at normal temperatures has been recorded in perfluoroheptane.

The fluorocarbons are practically insoluble in water, anhydrous hydrogen fluoride, and hydroxylic organic solvents. This last fact has

TABLE II
COMPARISON OF SOME PHYSICAL PROPERTIES OF
FLUOROCARBONS AND HYDROCARBONS

Compound	Boiling Point	Melting Point	Density, g/ml	Refractive Index	Dielectric Constant(20°C)
CF ₄	-128°C	-184°C	1.62 (-130°C)	---	---
CH ₄	-161	-184	0.415 (-164)	---	---
C ₂ F ₆	-78.3	-100	1.291 (-100)	---	---
C ₂ H ₆	-88.3	-172	0.561 (-100)	---	---
n-C ₆ F ₁₂	+29.3	-125.6	1.695 (+20)	1.245	1.68
n-C ₆ H ₁₂	36.2	-131.5	0.626 (20)	1.3570	1.828
n-C ₇ F ₁₆	82.4	---	1.733 (20)	1.2618	1.765
n-C ₇ H ₁₆	98.5	---	0.684 (20)	1.3867	1.971

been utilized in their purification, since alcohol extraction removes much of the partly-fluorinated material. Fluorocarbons are slightly soluble in hydrocarbons and somewhat more soluble in ethers and chlorocarbons.

Since the fluorocarbons are chemically inert, their physical properties have been utilized for purity determinations. Analysis by infrared methods is very useful since the presence of isomers can be detected. This is important since many of the isomers have essentially the same boiling points. Determinations of dielectric constants are also valuable as a means of checking purity (16).

A comparison of some of the physical properties of the fluorocarbons and the hydrocarbons is given in Table II. A more complete list of the principal physical properties of the known fluorocarbons and a more thorough discussion of them has been presented by Brice (2), and by Hasseldine and Sharpe (17).

Molecular properties. Determinations of bond distances in fluorocarbons have resulted in a variety of values for the C-F and C-C bonds. It appears certain that the C-F bond distance is not necessarily the same in different molecules. Values of $1.33 \text{ \AA}$ to $1.38 \text{ \AA}$ have been reported for the bond distance in three simple fluoroethanes. In many cases, serious discrepancies exist in the values reported for the C-C bond distance. Values from $1.46 \text{ \AA}$ (18) to $1.52 \text{ \AA}$ (2) have been reported, while the usual value in aliphatic hydrocarbons is $1.55 \text{ \AA}$. A list of bond distances, bond angles, and bond energies of some simple fluorocarbons

is presented in Table III. A more extensive table of bond distances and bond angles has been compiled by Glockler (2).

The thermochemistry of the fluorocarbons has not yet been studied to any extent. The average C-F bond strength in perfluoromethane has been found to be 109.9 kcal./mole. However, it has been indicated that the C-F bond in a molecule such as methyl fluoride may be much weaker. An estimate of 89.7 kcal./mole based on dipole moment data has been reported for the C-F bond in this compound (2). Likewise, the C-F bond energy in difluoromethane is approximately 105.3 kcal./mole. Heats of formation have been estimated from the above approximations.

As more information becomes available concerning bond energies, internuclear distances, and force constants, it will be possible to discuss quantitatively resonance, hyperconjugation, and steric effects in the fluorocarbons.

Dipole moments of several fluorocarbons have been determined. Some of these are listed in Table IV. Since the dipoles in fluorocarbons are very close together, they will affect one another by induction. The greater moment of ethyl fluoride compared to methyl fluoride is due to the moment induced on the second carbon by the principal dipole in the C-F bond. Secondary alkyl fluorides have larger moments than primary fluorides and tertiary fluorides have larger moments than secondary compounds (19). Smyth (20) has studied the question of induction and resonance from dipole moment data. Leonard and Sutton (21) have measured dipole moments of aromatic fluorine compounds and used the results to estimate bond angles.

TABLE III
MOLECULAR CONSTANTS OF SOME FLUOROCARBONS

Compound	C-F Bond Distance	C-C Bond Distance	FCF Bond Angle	Estimated C-F Bond Energy
CH_3F	1.38 Å ^o	---	---	89.7 kcal/mol
CH_2F_2	1.36	---	110°	105.6
CHF_3	1.33	---	109° 28'	103.3
CF_4	1.36	---	109° 28'	109.9
$\text{CF}_3\text{-CH}_3$	1.37	1.52 Å ^o	107° 30'	---
$\text{CHF}_2\text{-CHF}_2$	1.33	1.46	108°	---
$\text{CF}_3\text{-CF}_3$		1.51	108°	---

TABLE IV
DIPOLE MOMENTS OF SOME FLUOROCARBONS

Compound	Dipole Moment	Reference
Methyl fluoride	1.808 D	19
Difluoromethane	1.93	22
Trifluoromethane	1.645	18
Ethyl fluoride	1.92	19
1,1-Difluoroethane	2.24	23
1,1,1-Trifluoroethane	2.321	24
Hexafluoroethane	0.0	25
Trifluoroacetic acid	2.28	23
3,3,3-Trifluoropropyne	2.36	18
Cyclopentyl fluoride	1.86	26
n-Amyl fluoride	1.85	27
n-Perfluoropentane	0.0	23
iso-Perfluoropentane	0.0	23

III. THEORETICAL BACKGROUND

In 1912, Peter Debye (28,29) postulated the existence of permanent electric dipole moments in certain molecules and developed the theory which has been the basis for all subsequent dipole moment work. Debye's theoretical treatment is briefly outlined below.

When a dielectric material is placed between the plates of a condenser, the capacitance is increased by a factor ϵ , the dielectric constant of the medium. The capacitance C of a condenser with a dielectric between the plates is given by

$$C = \epsilon C_0$$

where C_0 is the capacitance of the condenser with a vacuum between the plates. Since the charges on the plates are unchanged, the original electric field E_0 between the plates is reduced by the factor ϵ , so that

$$E = \frac{E_0}{\epsilon}$$

gives the new electric field E . The field is reduced because the induced dipoles are aligned so as to produce an over-all dipole moment that cuts down the field strength. The vector quantity $\underline{P}$ called the polarization vector is the dipole moment per unit volume, and reduces the net charge σ on the plates so that the field in the dielectric is

$$\underline{E} = 4\pi(\sigma - \underline{P}). \quad (1)$$

The displacement vector $\underline{D}$ is defined as

$$\underline{D} = 4 \pi \sigma = \epsilon \underline{E} \quad (2)$$

and the equation

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

results from substitution in Equation 1.

The magnitude of the dipole moment $\underline{m}$ induced in a molecule by an electric field is proportional to the intensity of the field $\underline{F}$, so that

$$\underline{m} = \alpha_0 \underline{F} \quad (4)$$

where the proportionality constant α_0 is called the distortion polarizability. The field that polarizes a molecule is the local field immediately surrounding it, and this is different from the average field $\underline{E}$ throughout the dielectric. For an isotropic substance this local field has been shown to be

$$\underline{F} = \underline{E} + \frac{4 \pi \underline{P}_i}{3} \quad (5)$$

where $\underline{P}_i$ is the induced, or distortion, polarization.

The induced polarization, or the induced dipole moment per unit volume, is the number of molecules per cubic centimeter, n , multiplied by the average moment induced in a molecule $\bar{m}$. Thus

$$\underline{P}_i = n \bar{m} = n \alpha_0 \underline{F} = n \alpha_0 \left(\underline{E} + \frac{4 \pi \underline{P}_i}{3} \right) \quad (6)$$

results from substitution in Equations 4 and 5.

From Equations 2 and 3

$$\underline{E} (\epsilon - 1) = 4 \pi \underline{P}_i$$

which combined with Equation 6 gives

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4 \pi n \alpha_0}{3}$$

which is known as the Clausius-Mosotti Equation. Multiplying both sides of this equation by the ratio of molecular weight to density M/d , gives

$$\frac{(\epsilon - 1) M}{(\epsilon + 2) d} = \frac{4 \pi n M \alpha_0}{3 d} = \frac{4 \pi N \alpha_0}{3} = P_A \quad (7)$$

where the quantity P_A is called the molar induced polarization, and includes contributions from induced dipoles only. In order to obtain the total molar polarization a term due to the permanent dipoles must be added.

The induced moment is independent of temperature since, if the molecular position is disturbed by thermal collisions, the dipole is at once induced again in the field direction. The contribution to the polarization caused by the permanent dipoles, however, is smaller at higher temperatures since the random thermal collisions of the molecules oppose the tendency of the dipoles to line up in the electric field.

For a permanent dipole in the absence of a field, all orientations are equally probable, and the number of dipoles directed within a solid

angle $d\omega$ is $A d\omega$, where A is a constant depending on the number of molecules under observation. If a dipole moment μ is oriented at an angle θ to a field strength F , its potential energy is

$$U = - \mu F \cos \theta.$$

According to the Boltzmann distribution law, the number of molecules oriented within the solid angle $d\omega$ is

$$A e^{-\frac{U}{kT}} d\omega = A e^{\mu F \cos \theta / kT} d\omega$$

and the average value of the dipole moment in the direction of the field can be shown to be

$$\bar{m} = \frac{\int A e^{\mu F \cos \theta / kT} \mu \cos \theta d\omega}{\int A e^{\mu F \cos \theta / kT} d\omega}. \quad (8)$$

To evaluate this expression, let

$$\frac{\mu F}{kT} = x \quad \text{and} \quad \cos \theta = y \quad (9)$$

then

$$d\omega = 2\pi \sin \theta d\theta = 2\pi dy. \quad (10)$$

Substituting Equations 9 and 10 in Equation 8 gives

$$\frac{\bar{m}}{\mu} = \frac{\int_{-1}^{+1} e^{xy} y dy}{\int_{-1}^{+1} e^{xy} dy} = \coth x - \frac{1}{x} = L(x)$$

where $L(X)$ is known as the Langevin function. In most cases,

$$x = \frac{\mu F}{kT}$$

is a very small number so that on expanding $L(x)$ in a power series, only the first term need be retained, leaving

$$L(x) = \frac{x}{3} \quad \text{and} \quad \bar{m} = \frac{\mu^2}{3kT} F.$$

The total polarizability α of a dielectric is found by adding the orientation polarizability, due to the permanent dipoles, to the distortion polarizability, and may be written

$$\alpha = \alpha_0 + \mu^2 / 3kT.$$

The total polarization is therefore

$$P_M = \frac{4\pi N}{3} \left(\alpha_0 + \frac{\mu^2}{3kT} \right) \quad (11)$$

where P_M is the total molar polarization. This equation is known as the Debye equation. Combining this with the Clausius-Mosotti Equation (Equation 7) gives

$$P_M = \frac{(\epsilon - 1) M}{(\epsilon + 2) d} = \frac{4\pi N}{3} \left(\alpha_0 + \frac{\mu^2}{3kT} \right) \quad (12)$$

which can be written in the form of an equation for a straight line as

$$P_M = P_A + \frac{B}{T} \quad (13)$$

where

$$P_A = \frac{4 \pi N \alpha_0}{3}, \quad B = \frac{4 \pi N \mu^2}{9k} \quad (14)$$

P_A is the intercept and B the slope of the straight line defined by Equation 13. When values of the dielectric constant at several temperatures are available the total molar polarization is calculated using Equation 12 and plotted against the reciprocal of the absolute temperature. The slope B is evaluated from the graph and the dipole moment calculated from Equation 14. When the values of the constants are inserted this equation becomes

$$\mu = 0.01218 \times 10^{-18} \sqrt{B} \quad \text{esu} \quad (15)$$

Dipole moments are usually given in Debye units where

$$1 \text{ Debye} = 1 \text{ D} = 1 \times 10^{-18} \text{ electrostatic units (esu).}$$

An alternate method of calculating dipole moments is possible using the Maxwell relation

$$\epsilon = n_r^2$$

where n_r is the refractive index. This relation is strictly true only if the refractive index is measured with radiation of infinite wavelength and for a polar substance is true only at infinite temperatures. Combining the Maxwell equation with the Clausius-Mosotti equation gives the Lorenz-Lorentz equation:

$$\frac{(n_r^2 - 1) M}{(n_r^2 + 2) d} = R = P_A \quad (16)$$

where R is the molar refraction. If the dielectric constant is measured at only one temperature and the refractive index is known, B/T can be determined from Equation 13, and the dipole moment from Equation 14. When the values of the constants are inserted, Equation 14 becomes

$$\mu = 0.01281 \sqrt{(P_M - P_A) T} \times 10^{-18} \text{ esu.} \quad (17)$$

IV. APPARATUS AND METHOD

Review of Methods

The first measurements of dielectric constants from which dipole moments can be calculated were made by Silow (30) in 1875. His method involved measuring the angle through which an electrometer needle was turned by a given potential, first in air and then in the material under investigation. The ratio of the angles in the two cases was used to calculate the ratio of the forces involved and from this the dielectric constant of the medium. This early method was improved upon by other investigators and the same principles used as late as 1924 by Carman (31) and also Fuerth (32).

Many other methods have been developed since, but, like the one mentioned above, most are applicable to measuring dielectric constants of liquids and solutions only, and will not be discussed in detail here. These methods include the measurement of the velocity of propagation of electromagnetic waves through the medium, and measurements of capacitance by either bridge circuits or the resonance method. Smyth (33) has described and compared all of these methods and a few other methods not widely used.

Where extreme accuracy is desired, as in the case of gases, the most commonly used and most adaptable method is the heterodyne-beat method of measuring capacitance. This is the method employed in this

investigation and is also generally used for measurement of dielectric constants of liquids and solutions. Among the investigators to use and develop this method are Herweg (34), Williams (35,36), Zahn (37), and Watson (38). A detailed description of this method is given later.

Other methods are also employed for determining dipole moments in the vapor phase. The most accurate of these depends on the Stark effect as observed at microwave frequencies. The present method of calculating moments from this effect was developed by Golden and Wilson (39). Hyde and Hornig (40) have determined bond moments from infrared intensities using a pressure-broadening technique developed by Wilson and Wells (41). The dipole moment for chlorine trifluoride was calculated by Magnuson (11) from dielectric constant determinations at microwave frequencies which were made by measuring the change in resonance frequencies of a cavity when it was filled with the gas. The molecular-beam method (42) has been used for compounds of low volatility and low solubility which are stable at high temperatures.

Heterodyne-Beat Apparatus

General Principles

The general principle of the heterodyne-beat method is schematically represented in Figure 1. Two radio-frequency signals of frequencies f_0 and f , generated by a fixed oscillator and by a variable oscillator, respectively, are fed into a "mixer" tube, in the output of which is produced a beat note of frequency $f-f_0$. If f and f_0 are nearly equal,

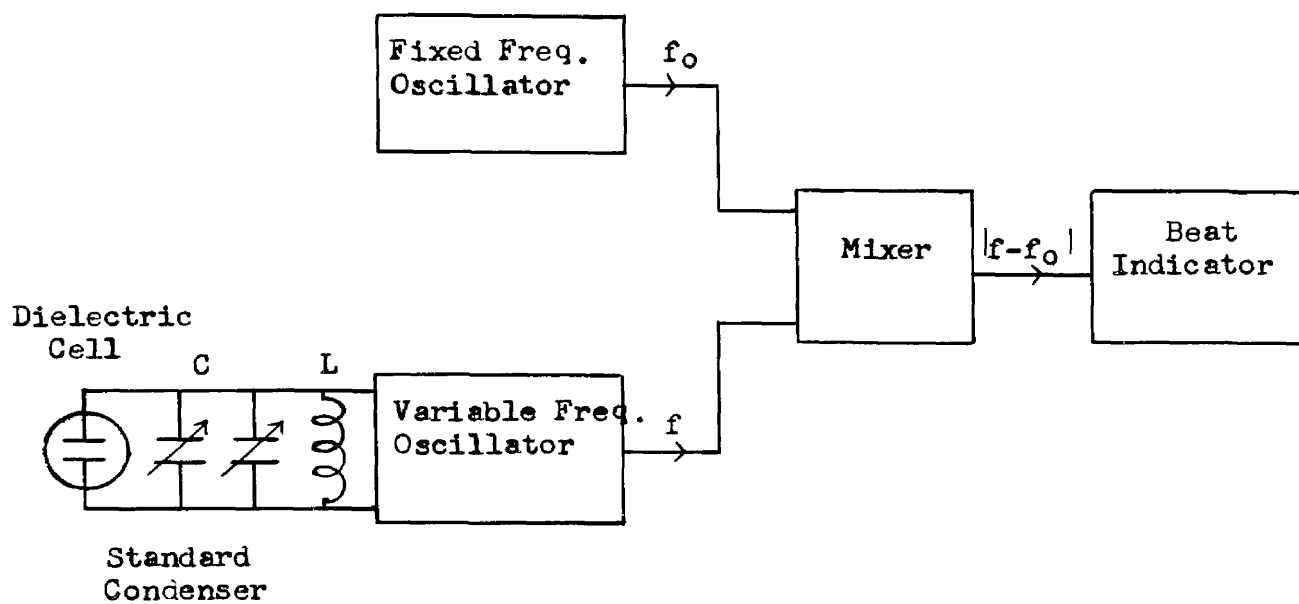


Figure 1. Block diagram illustrating the principle of the heterodyne-beat apparatus

the beat note will lie in the audio range. The frequency of the signal generated by the variable oscillator is approximately equal to

$$f = \frac{1}{2 \pi \sqrt{L C}} \quad (18)$$

where L and C are, respectively, the inductance and capacitance in the tuning circuit.

If f is greater than f_0 for a certain total capacitance C in the tuning circuit of the variable frequency oscillator (Figure 1), than an increase in the total capacitance will decrease the frequency of the beat note, changing it from inaudible to audible, from high pitch to low pitch, until f and f_0 are exactly equal and the beat frequency is zero. On further increase of capacitance, a beat note will again arise, this time increasing in frequency with increasing capacitance until it lies beyond the audible range. A capacitance setting corresponding to zero beat, or to a definite frequency difference of, say, 400 cycles, can be used as the reference point for capacitance increment measurements by this method. A reference frequency other than the zero beat is usually desirable since a common defect found in heterodyne-beat apparatus is the phenomenon called "locking-in" of the oscillators. That is, when f is brought close to f_0 , low frequency beats cannot be observed because the more stable of the two oscillators exerts a synchronizing action on the less stable, and over a considerable range the two oscillators are locked in step with one another and a sharp zero beat cannot be obtained. In this investigation a constant frequency source

of 400 cycles was used as reference and compared with the beat-frequency on a cathode-ray oscilloscope. When the beat frequency was also 400 cycles, a one-to-one Lissajous figure (a circle) was observed on the oscilloscope.

With the above method of beat-frequency detection, the heterodyne-beat method offers the most precise method of capacitance measurement. The precision can be shown by differentiation of the frequency equation. Since the inductance L is fixed, differentiation of Equation 18 gives

$$\frac{\Delta f}{f} = - \frac{\Delta C}{2 C}$$

where Δf and ΔC are the errors in the frequency and capacitance, respectively. A frequency of 500 kilocycles was generated by the fixed oscillator, and a change of one cycle in a hundred seconds, or 0.01 cycle per second, was easily detected on the oscilloscope. Thus the detectable change of capacitance of the circuit was two parts in fifty million. The total capacitance needed in a tuning circuit was of the order of 500 micromicrofarads, and the capacitance increments measured were about one micromicrofarad. Therefore the precision of measurement attainable was two-thousandths of one percent. Actually a change in beat frequency of much less than 0.1 cycle per second was detectable, so that the precision of capacitance measurements by the heterodyne-beat method was limited in practice by the stability of the variable and fixed oscillators, and the precision of the setting and calibration of the standard condenser. A heterodyne-beat circuit designed from the

point of view of oscillator stability has been presented by Chien (43). The circuits he designed for a variable frequency oscillator, frequency mixer, and a power supply were used in building the heterodyne-beat apparatus used in this investigation.

Variable Oscillator

The circuits of the heterodyne-beat apparatus and the voltage-regulated power supply are presented in Figures 2 and 3, respectively. The variable frequency oscillator made use of a 6A8-type pentagrid-converter tube which exhibits a negative transconductance between the signal grid and the anode grid. Under these conditions, the screen current remained fairly constant for wide variations in signal-grid voltage, and the frequency at which the tube oscillates was relatively independent of stray signal feedback through the plate. This design resulted in an oscillator of high frequency stability, and one which should not be affected by the frequency of the fixed oscillator, or exhibit the "locking-in" phenomenon at low frequencies.

Crystal Oscillator

The crystal oscillator employed was of an unusual type. It was a modification of the Pierce oscillator (44) designed by Thompson (45). The crystal replaced the tuning circuit found in most oscillators and thus the oscillator required no tuning adjustment and would work without change of components over a wide range of crystal frequencies.

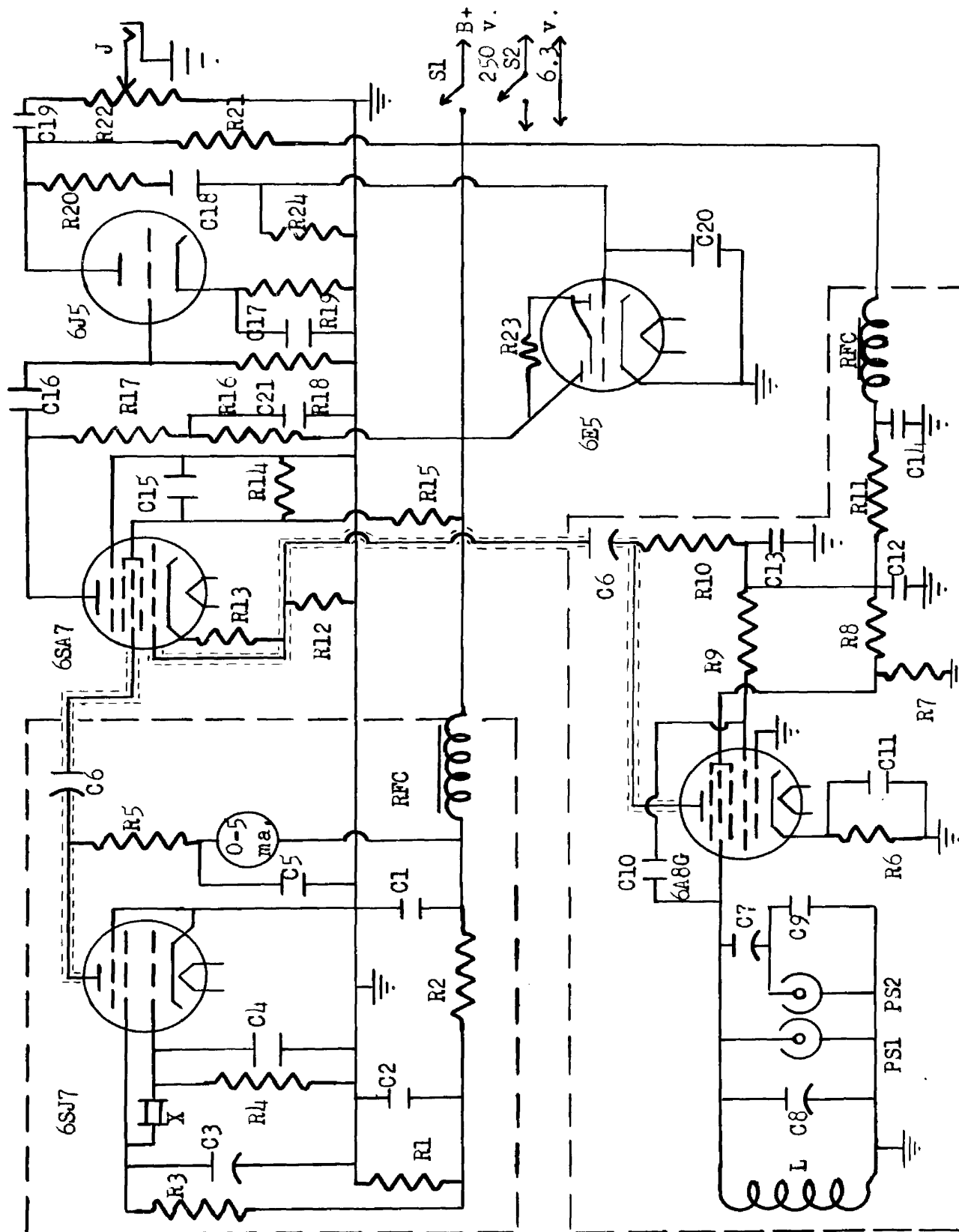


Figure 2. Circuit of the heterodyne-beat apparatus.

Figure 2. (continued) Legend

<u>Resistors</u>		<u>Condensers</u>	
R1	33,000 ohms	C1	0.005 μ f mica
R2	22,000 ohms	C2,C5,C15	0.1 μ f 600-volt paper
R3,R4,R18	0.1 megohm	C3,C8	335 $\mu\mu$ f var. air cond.
R20,R12		C4	25 $\mu\mu$ f mica
R5,R9,R20	47,000 ohms	O6	0-50 $\mu\mu$ f air trimmer
R17,R21,		C7	175 $\mu\mu$ f var. air cond.
R6	680 ohms	C9	0.010 μ f mica decade
R7	6800 ohms	C10,C14	0.005 $\mu\mu$ f 500-volt paper
R8,R14	15,000 ohms	C11,C18,C19	0.01 μ f 600-volt paper
R11	27,000 ohms	C12	10 μ f 450-volt electrolytic
R13	150 ohms	C13	0.0025 μ f mica
R15	82,000 ohms	C16	0.25 μ f 600-volt paper
R16	25,000 ohms	C17	10 μ f 25-volt electrolytic
R19	2000 ohms	C20	300 μ f mica
R22	0.5 megohm	C21	4 μ f 450-volt electrolytic
R23	potentiometer		
R24	1 megohm		
	4.7 megohm		

Miscellaneous

S1,S2	S.P.S.T. switches
PS1	Socket for coaxial wire connection to dielectric cell
PS2	Socket for coaxial wire connection to standard condenser
J	Phone jack for lead to cathode-ray oscilloscope

Since excitation otherwise was not adjustable, the condenser C₃ (Figure 2) was required to obtain satisfactory operation. The 6SJ7 pentode tube was used as a triode oscillator, with the cathode and suppressor grid grounded. This provided screening against capacitance coupling of the oscillator to later stages, so that the frequency of oscillation was less affected by feedback through the plate.

Each oscillator was shielded by enclosure in a separate metal box and the signal output of each was fed to the mixer tube through coaxial leads. The entire apparatus was enclosed in a thermally insulated aluminum box. Temperature control of the apparatus was provided for, but was not found to increase the stability of the beat-frequency output.

Precision Condenser

A General Radio Type 722-N precision condenser, with a capacitance range of 1100 micromicrofarads was used as the standard condenser. Since the capacitance increments measured were less than four micromicrofarads, it was necessary to place the precision condenser in series with another condenser, thereby decreasing the effective capacitance of the standard from 1100 to 4 micromicrofarads. That was the role of the condenser C₇ in Figure 2, a variable condenser with a lock setting and with a maximum capacitance of 175 micromicrofarads.

The total capacitance C of the standard condenser C_S plus the air condenser C₇ is given by the equation

$$C = \frac{C_S C_7}{C_S + C_7}$$

which shows that the reading on the standard condenser would be very non-linear with the total capacitance change, since C_S was as large or larger than C_7 . This was highly undesirable and to avoid this, a condenser (C_9 in Figure 2) of relatively large capacitance was placed in parallel with the standard condenser. This had the advantage that one side of both the mica and standard condenser were grounded. C_9 was a General Radio Type 380-N mica decade condenser with a capacitance range of 0.01 to 0.001 microfarads. With this arrangement the total capacitance of the three condensers is

$$C = \frac{C_7^2}{(C_S + C_9 + C_7)}$$

and differentiation with respect to C_S gives

$$\frac{dC}{dC_S} = \frac{C_7^2}{(C_S + C_9 + C_7)^2}$$

Thus if C_9 is large compared to C_S the change of the total capacitance with respect to the standard condenser scale will be much more linear than in the previous case. The calibration curve for the standard condenser (Figure 5) indicates the approach to linearity achieved by this combination of condensers.

By variation of the capacitance of C_7 and C_9 the standard condenser could be made to cover any capacitance range from around one up to eleven-hundred micromicrofarads. For this investigation C_9 was set at

0.004 microfarads and C_7 adjusted such that 10,000 dial units on the standard condenser represented a capacitance change of 3.700 micromicrofarads, or approximately 0.0003 micromicrofarads per dial unit.

Calibration of Precision Condenser

A primary standard capacitor built by J. L. Speirs (46) from a design by Conner (47) was used for the calibration of the General Radio precision condenser. This primary standard is shown in Figure 4 and in Plate I. It consisted of a coaxial cylinder arrangement such that a center rod, the opposite ends of which were inserted in cylinders of different diameters, could be moved along its axis to produce minute capacitance changes. The capacitance change per inch of travel was calculated from the geometry of the capacitor with a maximum error of less than one percent. The inner rod turned on a threaded center block and the drum at the center was ruled with 1400 units per inch. The capacitance change per inch of travel was 1.4800 micromicrofarads, or 0.0001057 micromicrofarads per drum unit. The one percent maximum error would not affect the dielectric constant measurements as long as the relative values of the calibration units were constant, since the dielectric constant depends on the ratio of two capacitance measurements. With this in mind, the calibration of the General Radio precision condenser was accomplished using the center portion of the scale on the primary standard capacitor, since it was shown that this was the most linear part of the scale.

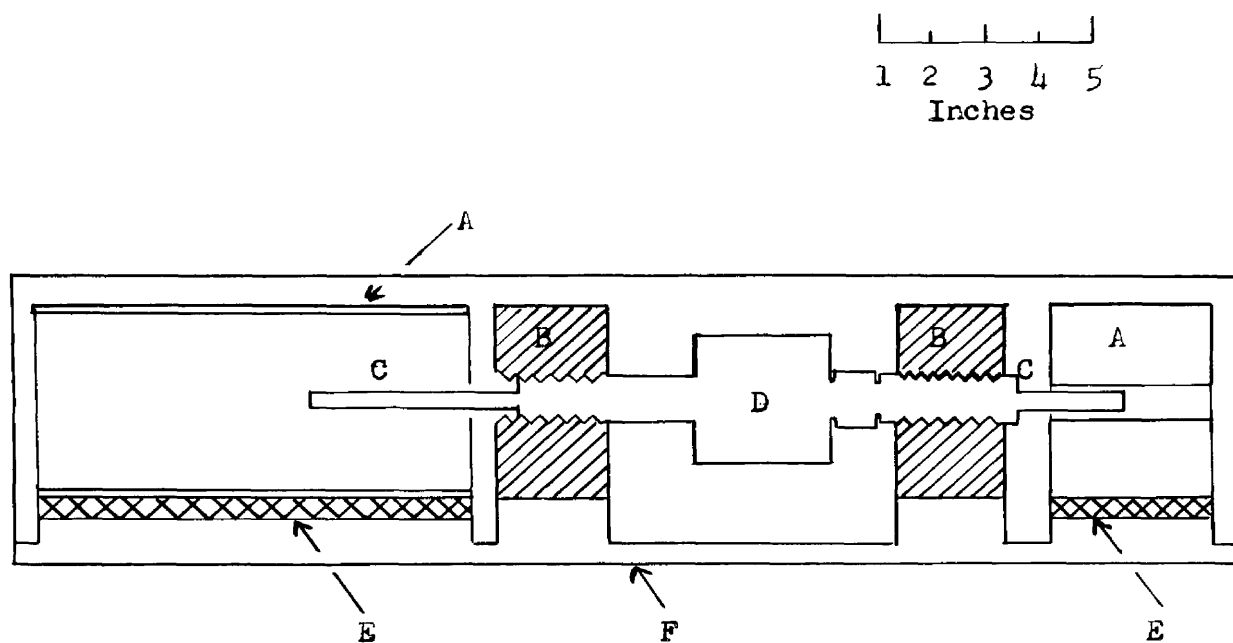


Figure 4. Primary standard capacitor used for calibrating General Radio precision condenser.

- | | |
|---------------------|--------------------------|
| A Coaxial cylinders | D Graduated drum |
| B Threaded blocks | E Mycalex insulators |
| C Center rod | F Grounded base and case |

Plate I. Primary standard capacitor used for
calibrating precision condenser.



The precision condenser was calibrated at the frequency used for the dielectric constant measurements. The calibrating capacitor was substituted for the dielectric cell using the same coaxial leads so that all indeterminate capacitance in the circuit was identical with that present under actual operating conditions. By this means, the calibration was made in terms of only one condenser, the General Radio precision condenser, and its calibrated capacitance change was exactly equal to changes of capacitance in the dielectric cell.

A replica of the calibration curve, drawn one-sixteenth of the actual size used in the investigation, is shown in Figure 5.

Reference Frequency

A reference frequency standard¹ of 400 cycles was used for comparison with the beat frequency on a cathode-ray oscilloscope. This frequency standard consisted of a thermally-compensated bimetallic fork such that large frequency deviations did not occur with changes in ambient temperatures. The frequency was also independent of external factors such as supply voltage, tube aging, and change in component values. Its frequency stability at 400 cycles was rated at $\pm 0.002\%$ between 15°C and 35°C . The signal from the frequency standard was fed to the horizontal input of a cathode-ray oscilloscope and the beat-frequency signal was supplied to the vertical input; the resulting Lissajous figure was used to determine a beat-frequency of 400 cycles.

¹ A Type R2003 frequency standard manufactured by the American Time Products, Inc., was used.

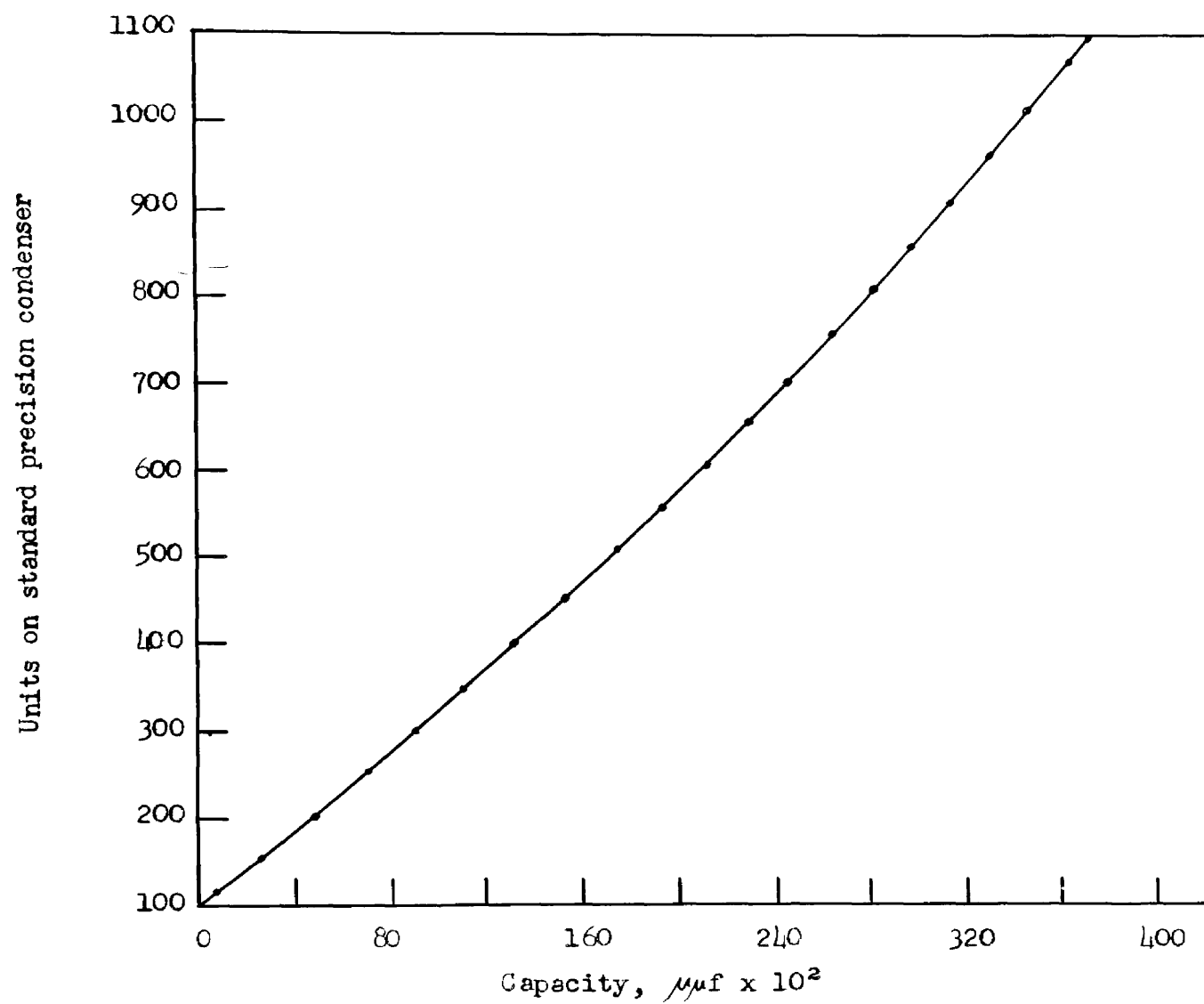


Figure 5. Calibration curve for standard precision condenser.

Dielectric Constant Cells

Cell I

The dielectric constant cell used for the fluorocarbon derivatives is shown in Figure 6. It consists of a series of nickel-plated copper cylinders insulated from one another by means of small Teflon spacers. The outer, middle, and innermost cylinders were connected and served as the grounded plates of the condenser. These cylinders were longer than the two electrically positive inner cylinders, which helped to diminish end effects. Platinum leads connected the cylinders to tungsten wires which were sealed through the glass casing. The tungsten wires were connected to the heterodyne-beat apparatus by a coaxial lead. The replaceable capacitance of the cell was approximately 350 micromicrofarads. Due to the construction of the cell and the character of the Teflon spacers the replaceable capacitance of the cell changed slightly with time, and it was necessary to calibrate the cell for each dielectric constant determination. Any change of the replaceable capacitance with temperature was not detectable within the precision of the calibrations. This cell could be used for compounds which were not corrosive to glass or nickel. Since the gas-handling system used in conjunction with the cell was not constructed to handle gases at temperatures other than room temperature, this cell could only be used for compounds that had sufficient vapor pressure at room temperature for dielectric constant measurements to be made.

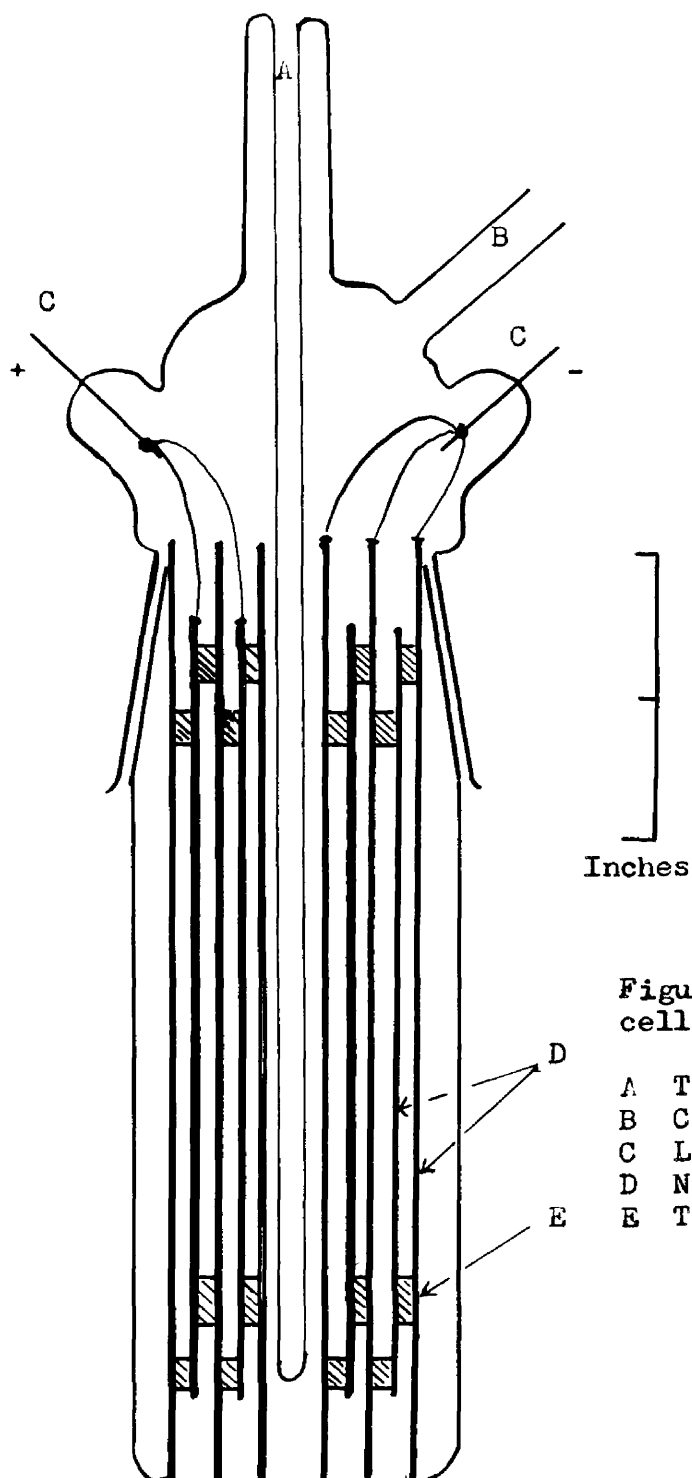


Figure 6. Cell I, dielectric constant cell for non-corrosive gases.

- A Thermocouple well
- B Connection to vacuum line
- C Leads to heterodyne-beat apparatus
- D Nickel-plated copper cylinders
- E Teflon insulators

Cell II

The dielectric constant cell used for the halogen fluoride work is illustrated in Figure 7, and its component parts pictured in Plate II. In order to give the cell a large replaceable capacitance, a spacing of only 0.013 inches between the inner and outer cylinders was first used. It was found that adsorption of gases on the surface of the cylinders was great enough to introduce large errors in the dielectric constant measurements. To reduce the adsorption error, smaller inner cylinders were used, thereby increasing the spacing between the cylinders. For the lower boiling compounds, chlorine trifluoride and bromine pentafluoride, a spacing of 0.040 inches was used; for the higher boiling compounds, iodine pentafluoride and bromine trifluoride, it was necessary to increase the spacing to 0.087 inches. The replaceable capacitance decreased with increased spacing, but for a given spacing was found to be independent of temperature, and because of the rigidity of the construction of this cell, compared to cell I, the replaceable capacitance was constant with time.

Although the cell was equipped with a coolant circulating system, this was not used; instead the cell was placed in a temperature-regulated bath which is described below. This cell could be used for all compounds except those which would react with Monel metal. It could be heated to a temperature of 200°C, and the gas handling system connected with it could be heated to a temperature of 130°C. For most compounds, a minimum pressure of around 200 mm. of mercury was required for

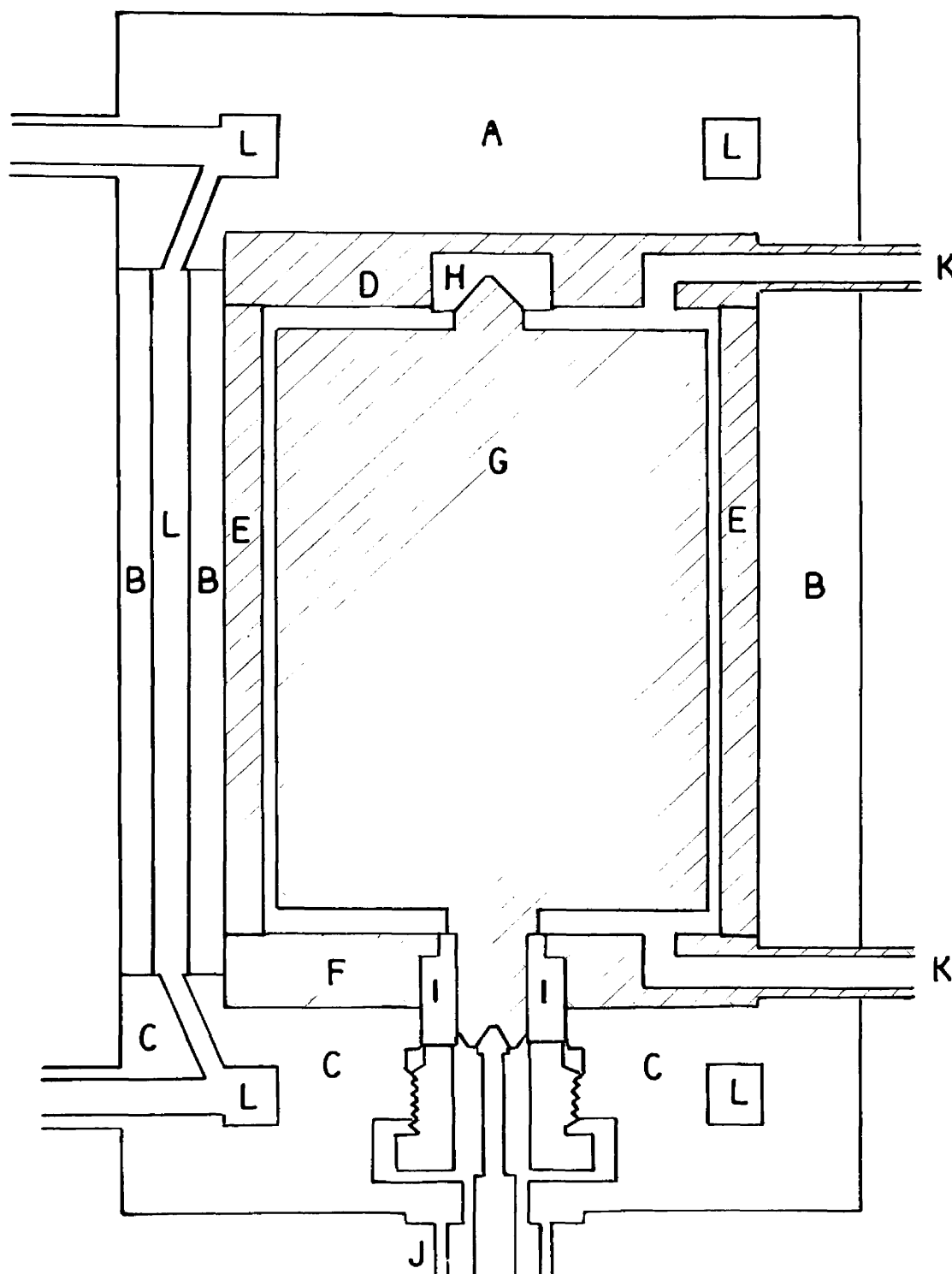


Figure 7. Section through the cylindrical cell **II**: A, B, C, jacket (three parts); D, E, F, outer cylinder (three parts); G, inner cylinder; H, I, Teflon insulating spacers; J, coaxial connector (to bridge); K, inlet tubes for samples (valves not shown); L, portions of coolant-circulating system.

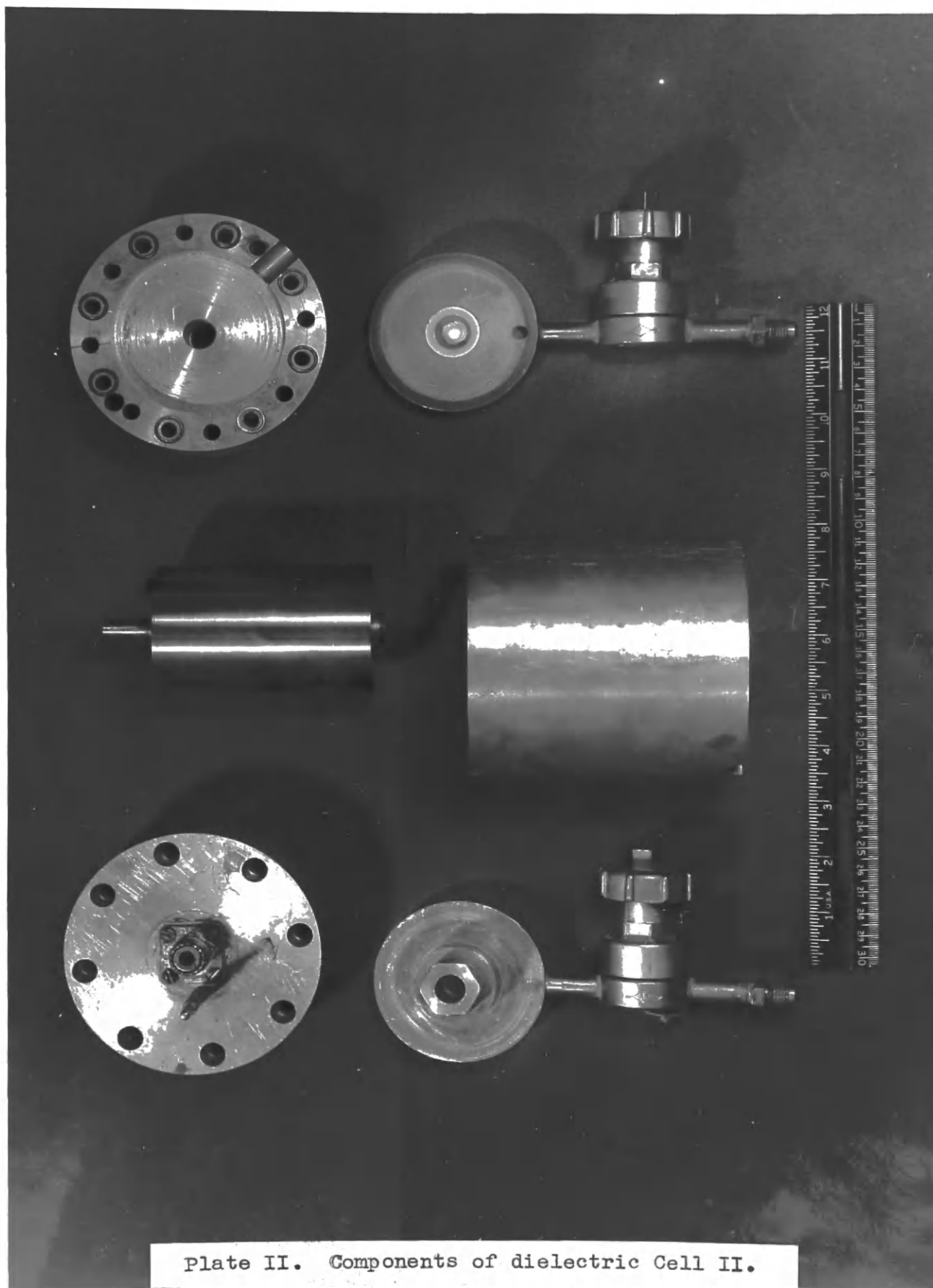


Plate II. Components of dielectric Cell II.

dielectric constant measurements. Thus this cell could be used for any compound which had a vapor pressure of 200 mm. of mercury, or more, at 130°C.

Gas-Handling Systems

Vacuum Line I

The glass vacuum system used for handling both the fluorocarbon derivatives and the gases used for calibrating the cells is shown schematically in Figure 8. Long tubes filled with Drierite were used to dry the air and gases used for standardization. Traps were cooled with Dry Ice-isopropanol mixtures or liquid air. The manometer¹ used could be read to ± 0.05 mm. of mercury. It was designed (46) such that the ratio of the diameter of the manometer tube and the reservoir exactly counteracted the increase in the mercury height due to the lower density of mercury at room temperature than at 0°C. The scale was made of Saran, which had a temperature coefficient of expansion that compensated for changes in mercury density due to room temperature variations.

Vacuum Line II

The vacuum system used for the halogen fluoride work is schematically illustrated in Figure 9. The traps A and B could be removed from the Helicoid gage² and filled with halogen fluoride samples by use of

¹ Manufactured by the Emil Greiner Company, New York, N. Y.

² Manufactured by the Helicoid Gage Division, American Chain and Cable Company, Bridgeport, Conn.

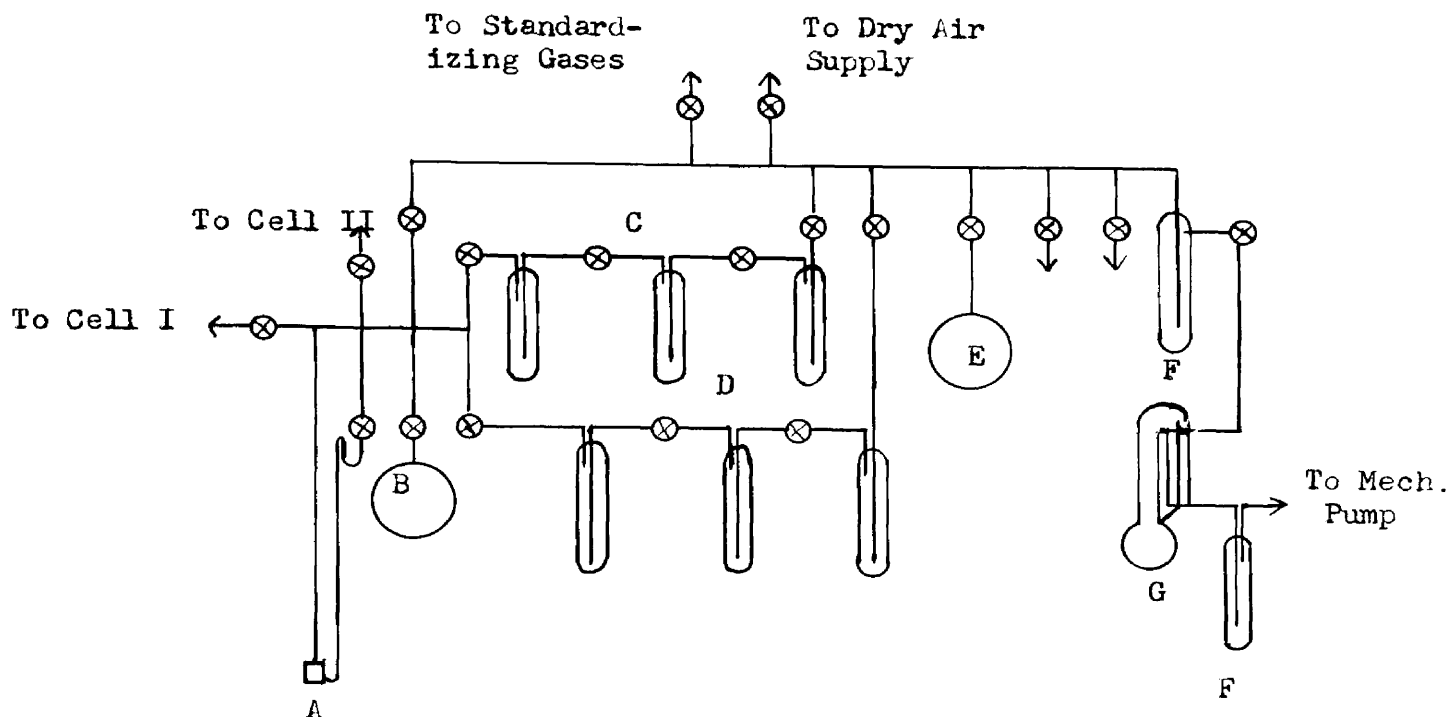


Figure 8. Gas handling system for non-corrosive gases (Vacuum Line I)

- A Emil Greiner Model G10719 absolute and differential manometer
- B McLeod gage, range: 0.001-1.0 mm. of mercury (Kontes Glass Company Type A)
- C Series of traps used for distilling and storing liquid ammonia used for calibration
- D Series of traps for distilling and storing gases being measured
- E McLeod gage, range: 0.2-1 x 10⁻⁵ mm. of mercury
- F Glass cold traps for pump protection
- G Mercury diffusion pump
- ⊗ Glass vacuum stopcocks

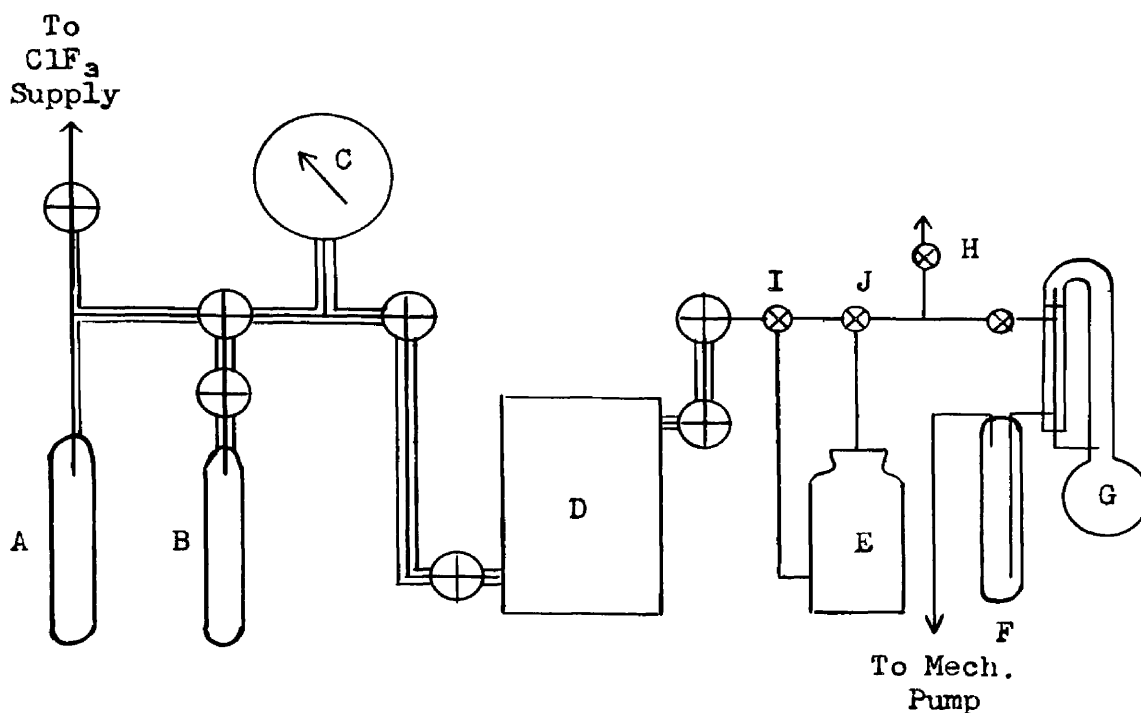


Figure 9. Vacuum system for handling halogen fluorides (Vacuum Line II).

- A,B Monel traps for distilling and storing halogen fluorides
- C Helicoid pressure gage: 0-760 mm. of mercury
- D Monel dielectric cell (Cell II).
- E Absorbing bottle, filled with soda-lime.
- F Glass cold-trap for pump protection
- G Mercury diffusion pump
- H Connection to Vacuum Line I
- = Electrically heated nickel tubing
- Glass tubing
- ⊕ Metal stopcocks, phosphor-bronze bellows
- ⊕ Glass vacuum stopcocks

a separate handling system. When placed in the position shown, chlorine trifluoride could be passed through the system to remove small amounts of water or other contaminants which might be present, and with which the halogen fluorides would react. The Bourdon tube in the Helicoid gage was electrically heated to the same temperature as the other parts of the metal system. Before each dielectric constant measurement the pressure gage was calibrated against the manometer shown in Figure 8, using dry air as a source of pressure. The two vacuum systems were connected through the stopcock H shown in Figure 9. During calibration of both the pressure gage and dielectric cell, the stopcocks I and J were turned to by-pass the halogen fluoride absorbing bottle. The pressure calibration was dependent on the atmospheric pressure; therefore the gage had to be calibrated before each series of runs. Calibration curves were reproducible over a period of an hour or more to within ± 1 mm. of mercury. The gage was always calibrated at the temperature at which the measurements were to be made.

The halogen fluoride upon which measurements were being made was stored in trap B, and trap A, which was kept cold with Dry Ice-isopropanol mixtures, was used to withdraw the vapor during a measurement. It was impossible to remove the last trace of the corrosive vapors by this means, and they were pumped out through the absorbing bottle E. This part of the system was glass, and corrosion in stopcock I necessitated it being replaced occasionally.

Temperature Measurement and Control

Temperature-Controlled Bath I

A schematic representation of the relative positions of Cell I and the various elements of the heating system in the bath is shown in Figure 10. The bath was contained in a copper can which provided an electrostatic shield for the dielectric cell. The liquid used in the bath was Arochlor 1248,¹ a chlorinated biphenyl which is liquid from below room temperature to above 300°C. Since it is a good dielectric, the heating wires could be wound directly in the bath. This bath was used from room temperature to around 100°C.

Temperature-Controlled Bath II

The temperature-regulated bath used for the high temperature work is illustrated in Figure 11. This bath was considerably larger than the one described above. The same liquid was used for the heating medium, with knife heaters serving as the heating elements. An auxiliary heater of 500-watt capacity was used in conjunction with the 250-watt heater, to relieve the load controlled by the thermoregulator at high temperatures. The voltage to the 500-watt heater was adjusted at each temperature such that only a small amount of regulated current through the 250-watt heater was needed to maintain the temperature at the desired value. Cell II required a small amount of fluorothene wax

¹ Monsanto Chemical Co., St. Louis, Mo.

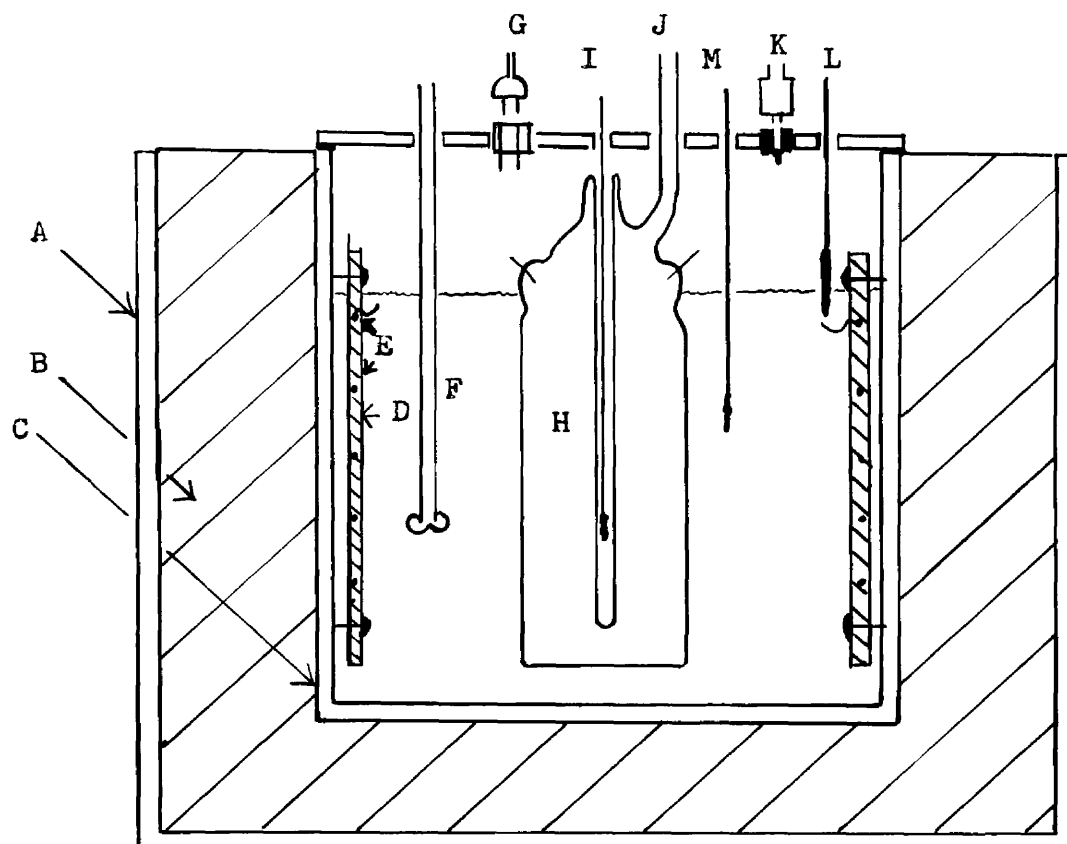


Figure 10. Temperature-regulated bath (Bath I) for glass-enclosed dielectric cell (Cell I).

- A Wooden outer box
- B Foam-glass insulation
- C Copper container for bath liquid
- D Mycalex strips for holding heater wires
- E Nichrome heating wires that are connected to G
- F Glass stirrer
- G Heater connection to temperature regulator
- H Dielectric constant cell
- I, M Thermocouple wires
- J Glass connection to vacuum system
- K Coaxial connector from cell leads to heterodyne-beat apparatus
- L Thermistor

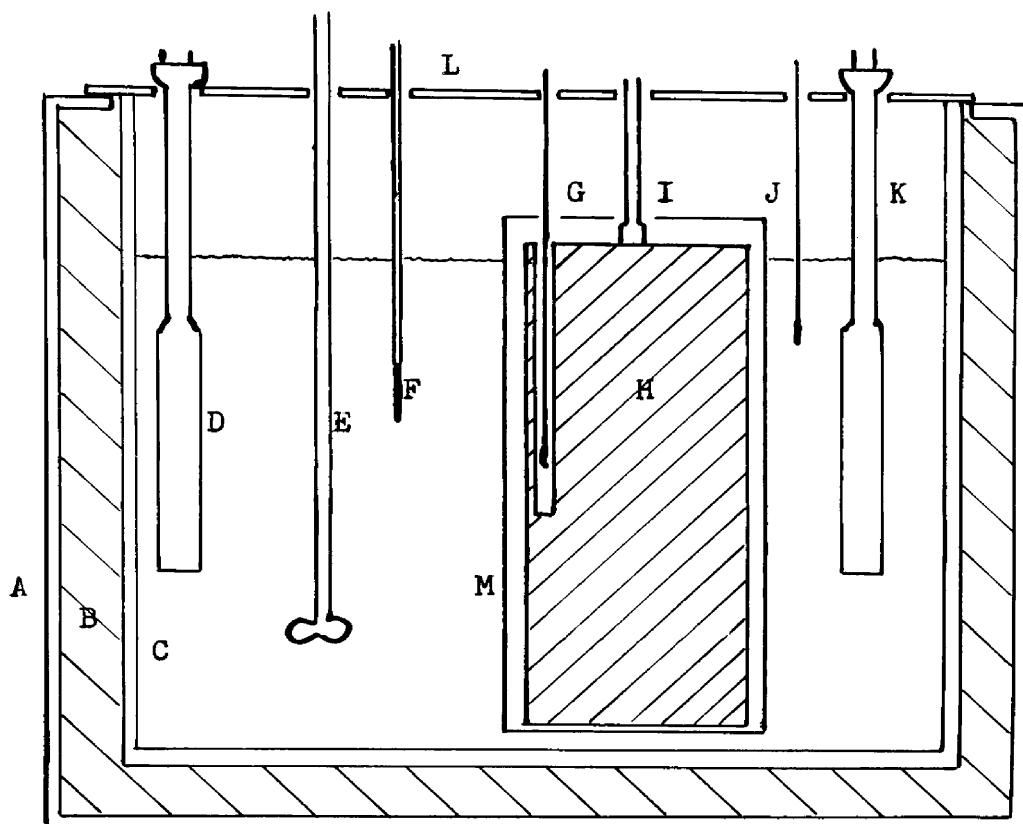


Figure 11. Temperature-regulated Bath II for Cell II.

- A Wooden outer bath
- B Glass cotton insulation
- C Glass jar
- D 500-watt auxiliary heating knife, not controlled by regulator
- E Metal stirrer
- F Thermistor
- G, J Thermocouples
- H Cell II
- I Coaxial lead to heterodyne-beat apparatus
- K 250-watt heating knife, controlled by regulator
- L Water-cooled brass cover
- M Metal container enclosing dielectric cell

to make it vacuum-tight. Arochlor 1248 is an excellent solvent for anything organic in nature, and was found to dissolve the fluorothene wax and leak into the cell. To prevent this, the cell was enclosed in a metal container and the whole assembly was placed in the bath. With this arrangement, temperature control of the cell was excellent, even with an air space between it and the bath liquid. The only disadvantage was the length of time required for the cell to attain the equilibrium temperature, which was usually slightly below that of the bath.

The vapors of Arochlor 1248 are toxic and quite corrosive to paints, varnishes, etc. To reduce the amount of vaporization of the Arochlor 1248 into the room, a water-cooled cover was placed on the bath, and an air blower pulled the remaining vapors into the hood. Under these conditions, the bath could be safely heated to 200°C or slightly above.

The Thermoregulator

The circuit shown in Figure 12 was an adaptation of a thermoregulator designed by Burwell, Peterson, and Kathmann (49). The temperature-sensitive element was a thermistor¹ in a Wheatstone bridge circuit, while the heater current was controlled by means of a saturable reactor in series with the heater. With this regulator, and the baths described above, the temperature of either cell could be controlled to less than $\pm 0.05^\circ\text{C}$.

¹ A type 14B thermistor, manufactured by the Western Electric Company, New York, N. Y. was used.

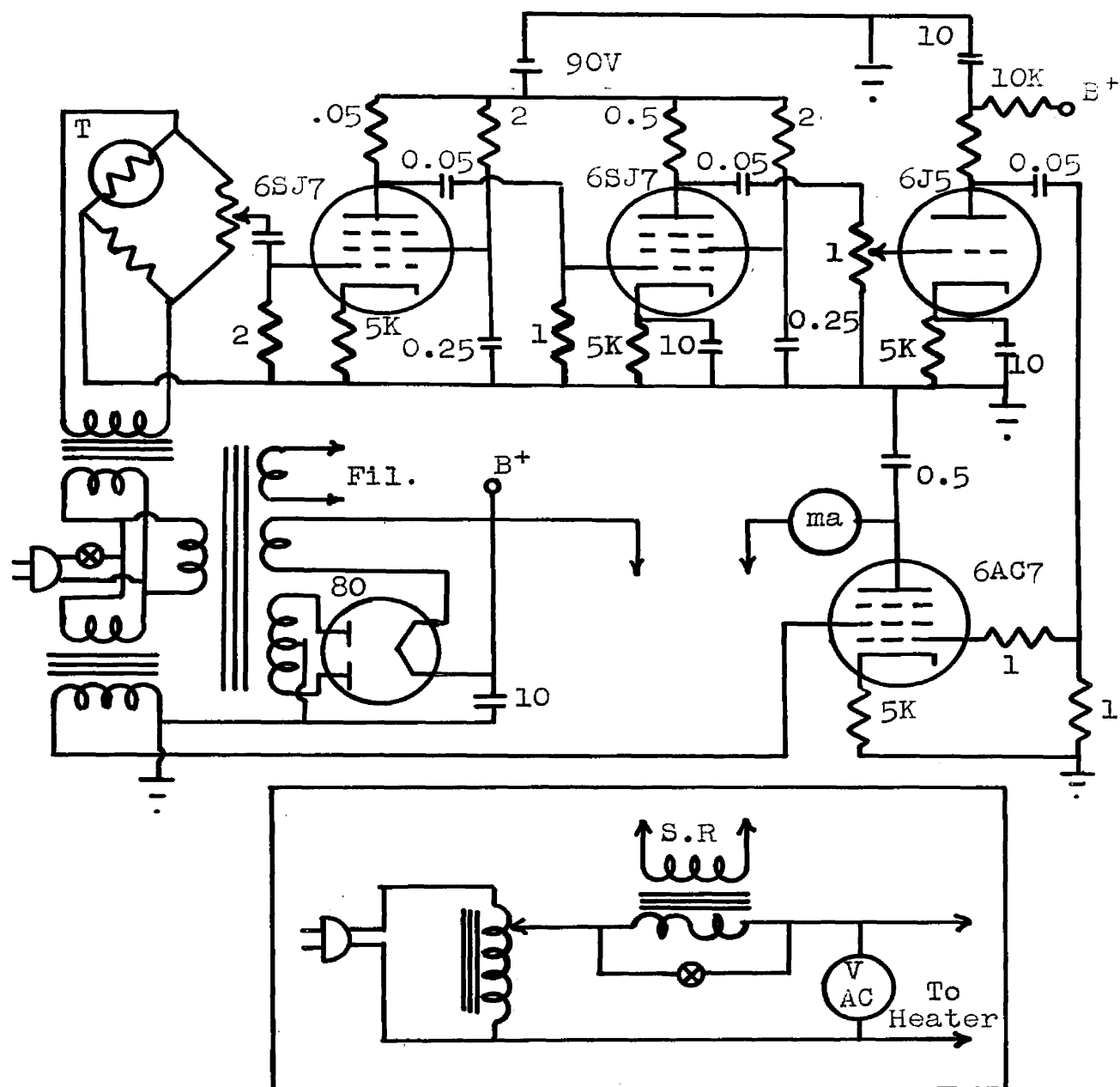


Figure 12. Thermistor thermoregulator circuit: T, thermistor; S.R., saturable reactor. The saturable reactor circuit shown within the box was placed in a separate metal cabinet. Sizes of capacitors are given in microfarads; resistors are given in megohms (10^6 ohms) unless otherwise indicated; K indicates thousands of ohms.

Temperature Measurement

All temperature measurements were made with thermocouples; a precision potentiometer¹ was used to measure their output. The thermocouples were prepared by fusing together the ends of number 22 copper wire and number 22 constantan wire.² Two thermocouples were used in each bath, one immersed in the bath and one placed in the cell. The wiring was so arranged that either thermocouple could be connected to the precision potentiometer or to an electronic recording potentiometer.³ The use of the recording potentiometer was convenient for following the bath and cell temperatures while the bath temperature was being changed. All switches and connections to both measuring devices were made of copper so that the only junctions of different metals were those of the thermocouples. The ice-point reference used for the cold-junction thermocouple consisted of finely crushed and washed ice mixed with distilled water and placed in a Dewar flask. The potentials measured were converted to degrees Centigrade by interpolation on a large plot of copper-constantan potential versus temperature.⁴

¹ A type K-2 potentiometer, made by the Leeds and Northrup Company, Philadelphia, Pa. was used.

² The thermocouple wires were purchased from the Wheelco Instruments Company, Chicago, Ill.

³ A Leeds and Northrup Speedomax Type G electronic recorder was used.

⁴ From the Reference Table For Thermocouples, National Bureau of Standards Circular 508.

Materials

Halogen Fluorides

Iodine pentafluoride was purified by distillation in a Monel still as described by Thompson (1). The impurity content was determined from freezing point curves, and the molal concentration of impurities was found to be 0.0025.

Bromine pentafluoride was purified by distillation as described by Speirs and Rogers (50), and the concentration of impurities found by freezing point measurements to be 0.02 molal.

Bromine trifluoride has not been obtained as pure as the other compounds. For this investigation, bromine trifluoride was distilled from the iron shipping tank into a trap on an all-nickel vacuum line; three successive trap-to-trap distillations were made, the appropriate fraction being taken for the measurements. This process should largely eliminate the two chief impurities, hydrogen fluoride and bromine pentafluoride, because of the large differences in boiling points. The impurity of the bromine trifluoride sample on which the dielectric constant measurements were made was probably less than two mole percent.

Chlorine trifluoride was likewise purified by trap-to-trap distillations. The sample used was frozen in a trap cooled by a Dry Ice-propanol mixture and evacuated to remove chlorine. The impurity of the samples obtained in this manner was probably less than one mole percent.

Fluorocarbon Derivatives

Purified samples of perfluorotetramethylene oxide, perfluoroethyl ether, and 1,1,1,2,2,3,3-heptafluoropropane were furnished through the courtesy of W. H. Pearlson of the Minnesota Mining and Manufacturing Company. These compounds contained only traces of impurities and these impurities were of a very similar nature to the compounds. The compounds were further distilled from trap-to-trap in the glass vacuum system shown in Figure 6, and the center fraction from each of three successive distillations was used for the dielectric constant measurements.

A sample of purified chlorotrifluoroethylene was obtained from the Union Carbide and Carbon Corporation. The center fraction of three successive distillations was used for the measurements.

Gases Used For Cell Standardization

The materials used for the determination of the replaceable capacitances of the cells were ammonia and carbon dioxide. The ammonia used was from a cylinder supplied by the Ohio Chemical and Surgical Company. It was passed through a drying tube into the glass vacuum system, where it was successively distilled three times, each distillation using the center fraction of the previous distillation. The last center fraction was used for the calibrations.

The carbon dioxide was a commercial grade specified to be 99.5% pure. It was passed from the cylinder through a long tube of Drierite

directly into the vacuum system and into the cell, where it was used for the calibration of Cell II.

Procedure

Cell Calibration

The replaceable capacitances of the cells were obtained by measurements on a gas whose dielectric constant was accurately known. Ammonia and carbon dioxide were selected because several measurements of high precision had been reported in the literature for their dielectric constants.

Cell I. Ammonia was used as the calibrating gas for Cell I. The cell was allowed to attain temperature equilibrium, evacuated for some time, washed with ammonia vapors, and then filled with ammonia to a pressure of 700-800 mm. of mercury. Sufficient time was allowed for the gas to reach the temperature of the cell. The pressure of the gas was then read, and the reading on the standard condenser, corresponding to a beat frequency of 400 cycles, was recorded. Next, ammonia was withdrawn until the pressure dropped approximately 100 mm. of mercury, the standard condenser was adjusted to bring the beat frequency back to 400 cycles, and the new condenser reading and the pressure were recorded. This was continued until the ammonia was completely removed, the last set of data for a run being taken with the cell evacuated. The temperature was observed at the beginning and end of each run. This procedure was repeated at each temperature that the dielectric constants of the

fluorocarbons were measured, and on the same day, since the replaceable capacitance was found to change slightly over a long period of time.

Cell II. The calibration of the cell used for the halogen fluoride measurements was accomplished using exactly the same procedure outlined above, except that carbon dioxide was used as the calibrating gas. Ammonia was found to give somewhat inconsistent results, probably as a result of adsorption on the Monel cylinders. Since the replaceable capacitance of Cell II was found to be independent of temperature, and constant with time, fewer calibrations were made than with Cell I. Carbon dioxide has a low dielectric constant and more accuracy was attainable at low temperatures. Therefore the replaceable capacitance was usually determined at temperatures lower than those used for the dielectric constant measurements of the halogen fluorides.

Dielectric Constant Measurements

Exactly the same procedure used for the cell calibrations was used for obtaining dielectric constant data. Three or more runs were usually made at each temperature, until good agreement between runs was obtained. The dielectric cells were always evacuated for some time before introducing the gas to be measured, then washed a few times with the gas, and again evacuated for a while before the actual measurements were made.

After each run the bath temperature was changed to the next temperature at which measurements were to be made. Considerable time was necessary for the cell to attain the new equilibrium temperature.

When the cells reached equilibrium temperature the beat frequency ceased to drift. The drift of the beat frequency was the result of the outer cylinder changing temperature more rapidly than the inner cylinder, thus changing the cell capacitance. When the inner cylinder reached the temperature of the outer cylinder, the capacitance of the cell was the same as before and the beat frequency ceased to drift.

With the high boiling halogen fluorides pressures of only 200-300 mm. of mercury of the vapor were used to start a run, compared to a starting pressure of 700-800 mm. of mercury for the lower boiling halogen fluorides and the fluorocarbon derivatives.

Treatment of Data

Calibration of Cells

The calibration of the dielectric constant cells consists in the determination of their capacitance when they are evacuated. If the evacuated cell consisted of a pure geometrical capacitance C_0 , the determination would be greatly simplified, for the capacitance of the empty cell could be measured directly, the capacitance C_g of the condenser when filled with a gas would be

$$C_g = \epsilon C_0$$

and the dielectric constant ϵ of the gas could be determined. Unfortunately, the cell always has a certain fixed capacitance C_f associated with its leads and with parts which cannot be filled with

a gas. The total capacitance C_t of the empty cell is therefore

$$C_t = C_o + C_f \quad (19)$$

and that of the cell when it is filled with a gas is

$$C_g = \epsilon C_o + C_f \quad (20)$$

The capacitance of the cell C_o which is affected by the introduction of a gas in the cell is called the replaceable capacitance and in order to determine it C_f must be eliminated from the calculations. By subtracting Equation 19 from Equation 20 and solving for C_o , C_f is eliminated and the equation

$$C_o = \frac{C_g - C_t}{\epsilon - 1} = \frac{\Delta C}{\epsilon - 1} \quad (21)$$

results, where ΔC is the capacitance change in the cell when a gas with dielectric constant ϵ is placed in the evacuated cell. This is the equation which was used to evaluate the replaceable capacitance of the cells.

Cell I. Dielectric constants of ammonia at one atmosphere pressure over a temperature range had been accurately measured by van Itterbeck and de Clippeleir (51) and were used to obtain the dielectric constants of ammonia at the temperatures at which the cell was calibrated. A large plot of dielectric constant versus temperature between 20°C and 120°C was made for this purpose, using their data (Table V).

TABLE V
DIELECTRIC CONSTANTS OF AMMONIA VAPOR
AT SEVERAL TEMPERATURES (51)

Temperature °C	$(\epsilon - 1) \times 10^6$
29.95	5826
38.72	5522
47.59	5240
58.63	4916
71.44	4581
80.33	4369
92.21	4062
116.12	3498

The values of ΔC in Equation 21 were obtained by measuring the change in capacitance with pressure of the gas. Values read on the precision condenser for each pressure were changed to micromicrofarads by interpolation on the calibration curve for the precision condenser. A plot of micromicrofarads against pressure was then made and the capacitance change from zero pressure to one atmosphere was read on the graph. This gave ΔC for one atmosphere of ammonia. The dielectric constant of ammonia at the temperature at which ΔC was measured was then used to calculate the replaceable capacitance C_0 by substitution of ΔC and ϵ in Equation 21.

Cell II. Carbon dioxide was the gas used for the calibration of this cell. A value for the dielectric constant of carbon dioxide at 20°C and one atmosphere pressure has been given as

$$\epsilon = 1.000922 \pm 0.000001$$

by the National Bureau of Standards (52). This is the mean value of several results obtained at radio- and microwave frequencies.

The molar volume of carbon dioxide at 20°C and one atmosphere pressure was calculated. At each temperature the pressure which corresponded to this molar volume was calculated using the ideal gas law. Deviations from ideality at the temperatures and pressures used were insignificant. From the plot of capacitance versus pressure, the capacitance change from zero pressure to the calculated pressure was read and the replaceable capacitance calculated.

Dipole Moments

Plots of capacitance versus pressure for each compound were used to obtain the capacitance change between zero pressure and one atmosphere of the gas. Using Equation 30 and the values of the replaceable capacitance of the cell, the dielectric constants of the gas at the various temperatures were calculated.

In order to calculate the molar polarization the molar volume had to be obtained. Values of the critical constants of chlorine trifluoride were available (53), so the Berthelot equation was used to calculate the molar volumes at the various temperatures. No equation-of-state data were available for the other compounds investigated; therefore, the ideal gas law was used to calculate the molar volumes.

Using the dielectric constants and the molar volumes, the molar polarizations were calculated by means of Equation 12. A plot of the molar polarization against the reciprocal of the absolute temperature was then made, and the slope determined both graphically and by a least-squares method. The dipole moment was then calculated from the slope using Equation 15, and the induced molar polarization P_A which was the intercept of the plot at $1/t = 0$, was found by a least-squares method.

V. RESULTS

Halogen Fluorides

Bromine Pentafluoride

The complete data for the determination of the dipole moment of bromine pentafluoride are given and the details of the calculations are presented. The data and calculations for the other compounds studied will be presented in a more condensed form.

Data. The original data obtained for bromine pentafluoride are given in the first and third columns of Table VI. The second and fourth columns of this table are the values of pressure and capacitance obtained from the calibration curves for the Helicoid gage and the precision condenser, respectively. The data for the calibration of the precision condenser are presented in Table VII, and the calibration data for the Helicoid gage are given in Table VIII. A plot of the calibration data for the precision condenser has already been presented in Figure 5. An example of a typical calibration curve for the Helicoid gage is shown in Figure 13.

Data for the calibration of the cell are given in Table IX. An example of the capacitance versus pressure plots made using these data is shown in Figure 14. The values of ΔC obtained from the graphs at each temperature are tabulated in Table X. The average value of ΔC

thus obtained is

$$\Delta C_{ave} = 0.123 \mu\mu f$$

which, combined with the dielectric constant of carbon dioxide, gives

$$C_0 = 133 \mu\mu f$$

for the replaceable capacitance of the cell.

A typical plot of capacitance versus pressure for bromine pentafluoride is shown in Figure 15. At each temperature, the value of the capacitance change when the atmosphere of the vapor was introduced into the cell was read from the graphs (Table XI). These values were combined with that of the replaceable capacitance of the cell obtained above, and the dielectric constants at the various temperatures calculated using Equation 30. These are presented in the fourth column of Table XII along with the calculations of the molar polarization.

Dipole moment. The plot of the molar polarization versus the reciprocal of the absolute temperature is shown in Figure 16. The slope of this line was calculated by a least-squares method (54) using the equation

$$B = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2} \quad (22)$$

where B is the slope, n is the number of terms, and x and y are the terms plotted on the abscissa and the ordinate, respectively. Substituting the appropriate values in the equation gives a slope $B = 12,022$ for the straight line in Figure 16. Using Equation 15, this value of the slope results in a dipole moment of

$$\mu = 1.4 \text{ D.}$$

TABLE VI
DIELECTRIC CONSTANT DATA FOR BROMINE PENTAFLUORIDE

Helicoid Gage	Pressure mm. of Mg	Precision Condenser Reading	Capacitance, $\mu\mu\text{f}$
Measurements at 72.5°C			
30	689	192.6	0.437
111	613	214.4	0.534
198	528	237.0	0.634
318	420	268.0	0.767
403	325	291.1	0.865
509	220	319.6	0.980
604	126	344.6	1.082
696	36	368.7	1.178
730	<1	379.0	1.220
32	691	192.7	0.437
107	618	212.7	0.527
204	522	239.2	0.644
312	416	267.8	0.765
407	322	292.5	0.871
502	228	318.3	0.975
601	129	344.1	1.080
695	36	368.5	1.177
730	<1	379.3	1.220

TABLE VI (CONTINUED)

Helicoid Gage	Pressure mm. of Hg	Precision Condenser Reading	Capacitance, μmf
Measurements at 89.5°C			
28	703	203.2	0.484
75	656	214.6	0.534
126	605	227.2	0.591
175	557	238.4	0.641
252	480	257.3	0.721
329	404	275.2	0.798
401	332	292.8	0.872
481	253	312.4	0.951
559	176	330.8	1.026
649	87	352.8	1.114
700	37	365.8	1.164
735	<1	372.8	1.195
32	699	202.9	0.482
103	628	220.9	0.563
199	533	243.3	0.661
308	425	269.6	0.773
402	331	292.8	0.872
505	229	318.0	0.971
681	55	360.1	1.145
735	<1	371.9	1.195
38	692	203.9	0.486
101	630	220.1	0.561
185	547	240.0	0.647
300	433	277.6	0.807
402	331	292.6	0.871
503	231	317.6	0.973
595	140	339.7	1.062
683	52	361.7	1.150
735	<1	374.3	1.200

TABLE VI (CONTINUED)

Helicoid Gage	Pressure mm of Hg	Precision Condenser Reading	Capacitance MMF
Measurements at 101.8°C			
28	701	151.2	0.251
91	638	165.4	0.315
197	533	188.8	0.419
272	459	205.7	0.495
337	394	219.4	0.557
405	326	234.2	0.623
470	261	248.8	0.684
568	165	270.5	0.777
664	69	292.6	0.871
734	<1	308.1	0.934
34	695	148.7	0.238
99	630	163.0	0.305
200	530	185.7	0.405
277	453	202.1	0.479
359	372	220.1	0.560
431	300	235.9	0.629
519	213	255.6	0.713
595	138	272.6	0.782
674	59	291.0	0.864
734	<1	304.7	0.920
37	692	148.4	0.238
118	611	166.2	0.319
210	520	186.6	0.409
318	412	209.9	0.513
401	330	228.6	0.598
510	221	252.9	0.701
595	138	271.6	0.782
675	58	290.4	0.862
734	<1	303.1	0.914

TABLE VI (CONTINUED)

Helicoid Gage	Pressure mm. of Hg	Precision Condenser Reading	Capacitance $\mu\mu f$
Measurements at 115.8°C			
32	694	147.8	0.234
109	618	163.6	0.307
201	528	183.4	0.395
322	408	207.7	0.504
408	323	225.6	0.585
508	223	246.6	0.675
600	133	266.1	0.757
686	47	283.9	0.834
732	<1	293.5	0.875
37	690	148.4	0.238
100	627	161.7	0.229
207	522	183.7	0.397
314	417	205.9	0.496
403	328	224.7	0.580
512	220	247.4	0.679
605	127	266.5	0.760
691	42	284.8	0.838
732	<1	293.3	0.875
23	703	145.2	0.224
116	611	164.0	0.309
206	523	183.0	0.395
318	412	205.9	0.495
410	321	225.0	0.582
512	220	246.7	0.676
603	129	266.0	0.758
680	53	282.0	0.826
732	<1	292.8	0.872

TABLE VI (CONTINUED)

Helicoid Gage	Pressure mm. of Hg	Precision Condenser Reading	Capacitance $\mu\mu\text{f}$
Measurements at 129.2°C			
35	683	140.4	0.201
108	611	154.2	0.264
202	518	172.6	0.346
297	425	190.1	0.426
401	321	210.3	0.516
506	218	230.6	0.607
609	112	250.6	0.692
698	30	267.2	0.763
727	<1	274.3	0.794
31	687	133.9	0.170
108	611	148.4	0.238
202	518	166.4	0.320
310	412	186.4	0.405
407	316	205.9	0.495
510	214	226.0	0.586
610	116	244.8	0.667
690	37	260.8	0.736
727	<1	268.4	0.769
Measurements at 144.1°C			
32	685	191.4	0.431
108	610	206.1	0.497
215	505	225.7	0.585
310	411	243.7	0.663
411	311	262.2	0.742
500	223	279.2	0.815
589	135	295.4	0.883
680	45	312.4	0.951
725	<1	320.8	0.985
39	679	189.4	0.422
113	605	203.4	0.485
203	517	220.4	0.561
311	410	240.2	0.648
402	320	257.1	0.720
506	217	276.7	0.802
601	122	294.6	0.879
681	43	309.4	0.939
725	<1	317.6	0.972

TABLE VI (CONTINUED)

Helicoid Gage	Pressure mm. of Hg	Precision Condenser Reading	Capacitance μmf
Measurements at 157.7°C			
31	686	148.4	0.283
111	607	162.5	0.303
200	520	177.3	0.369
311	411	196.2	0.453
409	314	212.8	0.527
505	218	229.6	0.601
692	33	261.6	0.739
725	<1	267.4	0.764
30	687	138.0	0.190
100	618	150.5	0.248
206	513	168.0	0.327
310	411	186.1	0.408
418	304	204.1	0.488
506	217	219.8	0.588
593	131	234.8	0.627
682	43	250.4	0.691
725	<1	257.6	0.722
32	685	132.3	0.164
112	606	146.6	0.229
199	521	161.6	0.298
311	410	180.3	0.382
406	316	196.5	0.454
502	221	213.9	0.532
600	123	230.5	0.606
685	40	235.0	0.669
725	<1	251.8	0.697

TABLE VII

DATA FOR THE CALIBRATION OF THE GENERAL RADIO PRECISION CONDENSER

Units on Precision Condenser	Units on Primary Standard Capacitor	A [*]	Capacitance $\mu\mu f \times 10^2$
97.4	1100	0	0.0
108.1	1150	50	5.28
119.8	1200	100	10.57
131.1	1250	150	15.85
142.6	1300	200	21.14
154.2	1350	250	26.42
165.0	1400	300	31.71
178.0	1450	350	36.99
189.9	1500	400	42.28
201.5	1550	450	47.56
213.3	1600	500	52.85
213.3	1000	500	52.85
224.9	1050	550	58.13
237.1	1100	600	63.42
249.1	1150	650	68.70
262.0	1200	700	73.99
274.2	1250	750	79.27
286.8	1300	800	84.56
299.3	1350	850	89.84
312.7	1400	900	95.13
325.4	1450	950	100.41
339.0	1500	1000	105.70
352.1	1550	1050	110.98
365.0	1600	1100	116.27
377.7	1650	1150	121.55
391.4	1700	1200	126.84
403.9	1750	1250	132.12
417.5	1800	1300	137.41
430.2	1850	1350	142.69
443.7	1900	1400	147.98
455.8	1950	1450	153.26
469.5	2000	1500	158.55
469.5	1000	1500	158.58
483.3	1050	1550	163.83
496.4	1100	1600	169.12
510.3	1150	1650	174.40
524.6	1200	1700	179.69
538.9	1250	1750	184.97
553.2	1300	1800	190.25
567.4	1350	1850	195.54

TABLE VII (CONTINUED)

Units on Precision Condenser	Units on Primary Standard Capacitor	A*	Capacitance $\mu\text{mf} \times 10^2$
582.0	1400	1900	200.82
596.2	1450	1950	206.11
611.2	1500	2000	211.39
625.7	1550	2050	216.68
640.8	1600	2100	221.96
655.9	1650	2150	227.25
670.8	1700	2200	232.53
685.1	1750	2250	237.82
700.9	1800	2300	243.10
715.3	1850	2350	248.39
731.1	1900	2400	253.67
745.4	1950	2450	258.96
760.9	2000	2500	264.24
760.9	1000	2500	264.24
776.7	1050	2550	269.53
791.6	1100	2600	274.81
807.8	1150	2650	280.10
824.2	1200	2700	285.38
840.6	1250	2750	290.67
857.7	1300	2800	295.95
873.7	1350	2850	301.24
890.8	1400	2900	306.52
907.8	1450	2950	311.81
925.1	1500	3000	317.09
941.8	1550	3050	322.36
960.2	1600	3100	327.65
976.3	1650	3150	332.95
995.0	1700	3200	338.23
1011.4	1750	3250	343.52
1029.8	1800	3300	348.80
1046.8	1850	3350	354.09
1064.5	1900	3400	359.37
1080.9	1950	3450	364.66
1100.0	2000	3500	369.94

*Column A gives the total number of units on the primary standard capacitor that correspond to the number of units covered on the precision condenser.

TABLE VIII
CALIBRATION DATA FOR THE HELICOID GAGE

Helicoid Gage Reading	Pressure mm. of Hg	Helicoid Gage Reading	Pressure mm. of Hg
Calibration at 72.5°C		Calibration at 115.8°C	
36	689.5	30	698.8
95	630.0	98	630.5
190	525.9	183	543.5
293	433.5	265	463.8
376	353.1	357	372.3
458	270.0	432	299.9
549	183.0	510	220.4
623	107.1	600	134.3
678	52.8	673	59.0
730	<1.0	732	<1.0
Calibration at 89.5°C		Calibration at 129.2°C	
27	704.9	21	699.6
95	635.4	165	554.1
215	516.5	239	482.2
286	446.1	340	381.8
381	353.2	431	295.0
470	265.2	513	211.0
569	166.8	585	140.7
649	87.0	658	70.1
735	<1.0	727	<1.0
Calibration at 101.8°C		Calibration at 144.1°C	
19	711.1	19	701.6
82	646.6	102	616.0
168	562.7	170	549.4
271	459.1	278	442.8
370	362.0	352	367.7
450	281.3	443	280.0
533	200.0	533	188.8
604	129.7	621	102.6
670	63.7	679	46.8
734	<1.0	725	<1.0

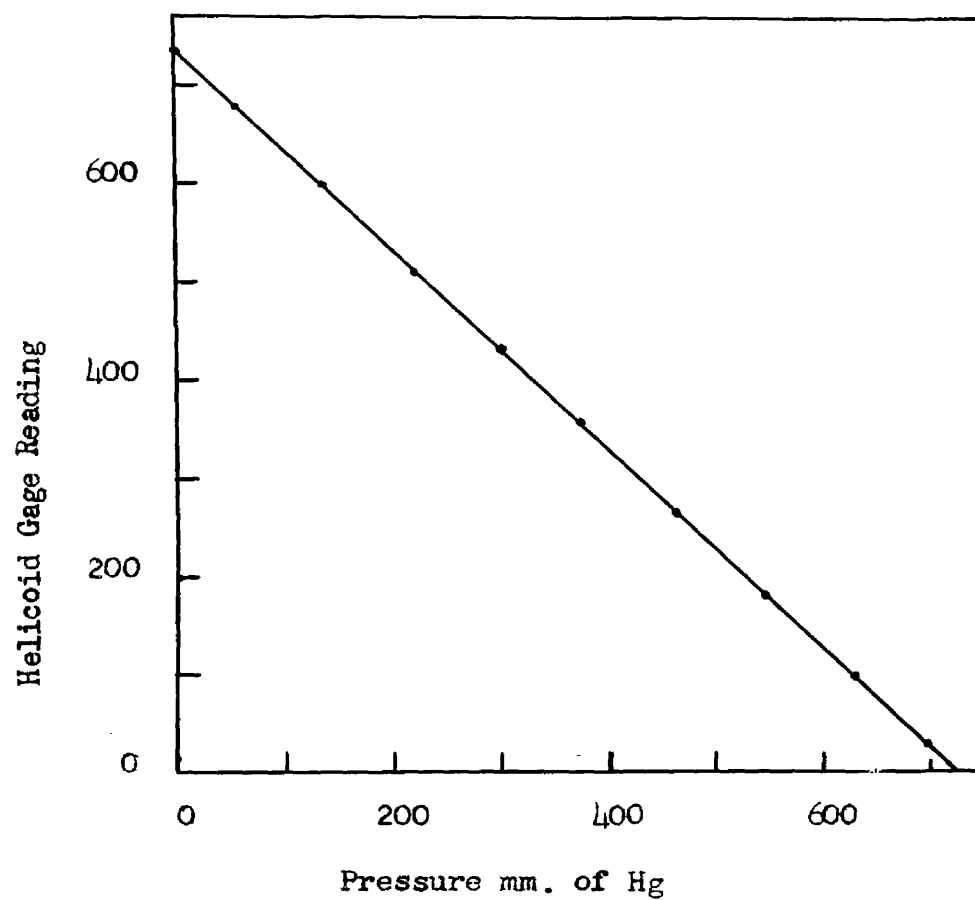


Figure 13 Typical calibration curve for the Helicoid pressure gage. Calibration at 115.8°C.

TABLE IX
CALIBRATION DATA FOR DIELECTRIC CELL II

Pressure mm. of Hg	Condenser Reading	Capacitance $\mu\mu f$	Pressure mm. of Hg	Condenser Reading	Capacitance $\mu\mu f$
Calibration at 72.5°C			Calibration at 115.7°C		
785.0	159.0	0.287	792.2	186.3	0.409
535.3	166.5	0.320	695.8	189.6	0.423
464.5	169.0	0.331	596.4	192.3	0.435
391.2	171.3	0.341	435.0	196.7	0.455
307.1	173.7	0.352	347.8	198.9	0.464
208.0	176.8	0.366	247.7	201.7	0.477
99.0	180.2	0.381	136.0	204.9	0.491
<1.0	183.1	0.394	<1.0	208.5	0.508
Calibration at 89.5°C			Calibration at 128.8°C		
787.0	162.6	0.303	783.9	149.0	0.240
683.6	165.5	0.315	702.8	151.2	0.251
586.4	168.6	0.329	603.5	153.7	0.261
478.8	171.5	0.342	472.6	157.1	0.279
398.8	174.0	0.353	385.1	159.4	0.288
297.3	177.4	0.369	289.8	162.1	0.301
196.7	180.0	0.380	185.7	164.3	0.311
91.8	183.3	0.395	86.0	167.0	0.322
<1.0	185.9	0.406	<1.0	168.9	0.330
Calibration at 101.9°C			Calibration at 144.1°C		
781.8	161.5	0.298	789.8	182.7	0.392
673.5	164.8	0.312	700.7	184.8	0.401
550.3	168.1	0.327	569.5	187.5	0.414
464.0	170.8	0.339	481.0	190.0	0.425
361.2	174.0	0.353	386.6	192.5	0.436
270.1	176.9	0.366	299.3	194.6	0.445
185.0	179.2	0.377	205.8	197.0	0.456
99.5	181.8	0.388	98.4	199.9	0.469
<1.0	184.2	0.399	<1.0	202.6	0.481
779.8	287.2	0.849			
702.4	289.8	0.859			
699.4	292.8	0.872			
497.2	296.0	0.885			
396.1	299.1	0.898			
302.7	302.1	0.910			
199.6	305.2	0.923			
105.4	308.2	0.935			
<1.0	311.4	0.948			

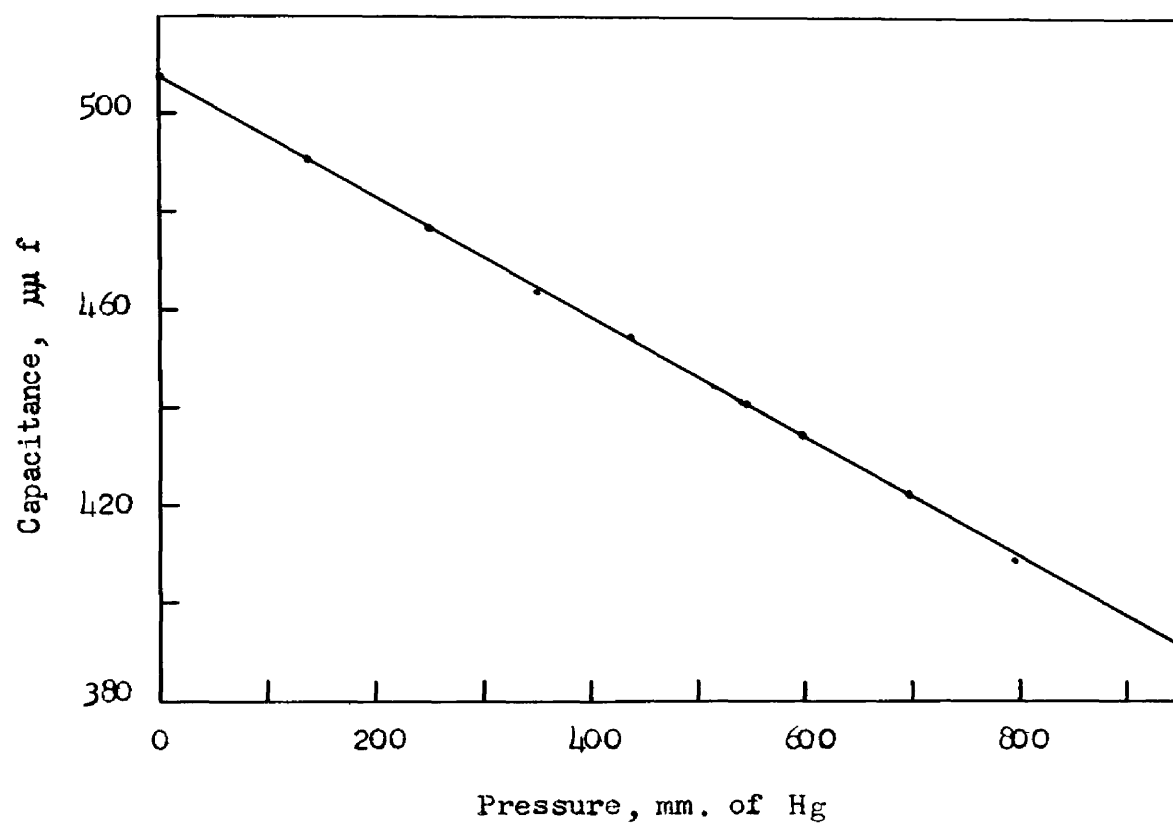


Figure 14. Typical plot of cell calibration data.
Calibration of Cell II at 115.7°C.

TABLE X
VALUES OF ΔC FOR CARBON DIOXIDE
FROM DATA IN TABLE IX

Temperature °C	Corrected* Pressure mm. of Hg	C mm f
72.5	895.1	0.122
89.5	940.1	0.123
89.5	940.1	0.123
101.9	971.2	0.123
115.7	1007.0	0.123
128.8	1040.9	0.122
144.1	1072.8	0.124
ΔC Average = 0.123		

*Pressure exerted at t°C by the molar volume of carbon dioxide at 20°C.

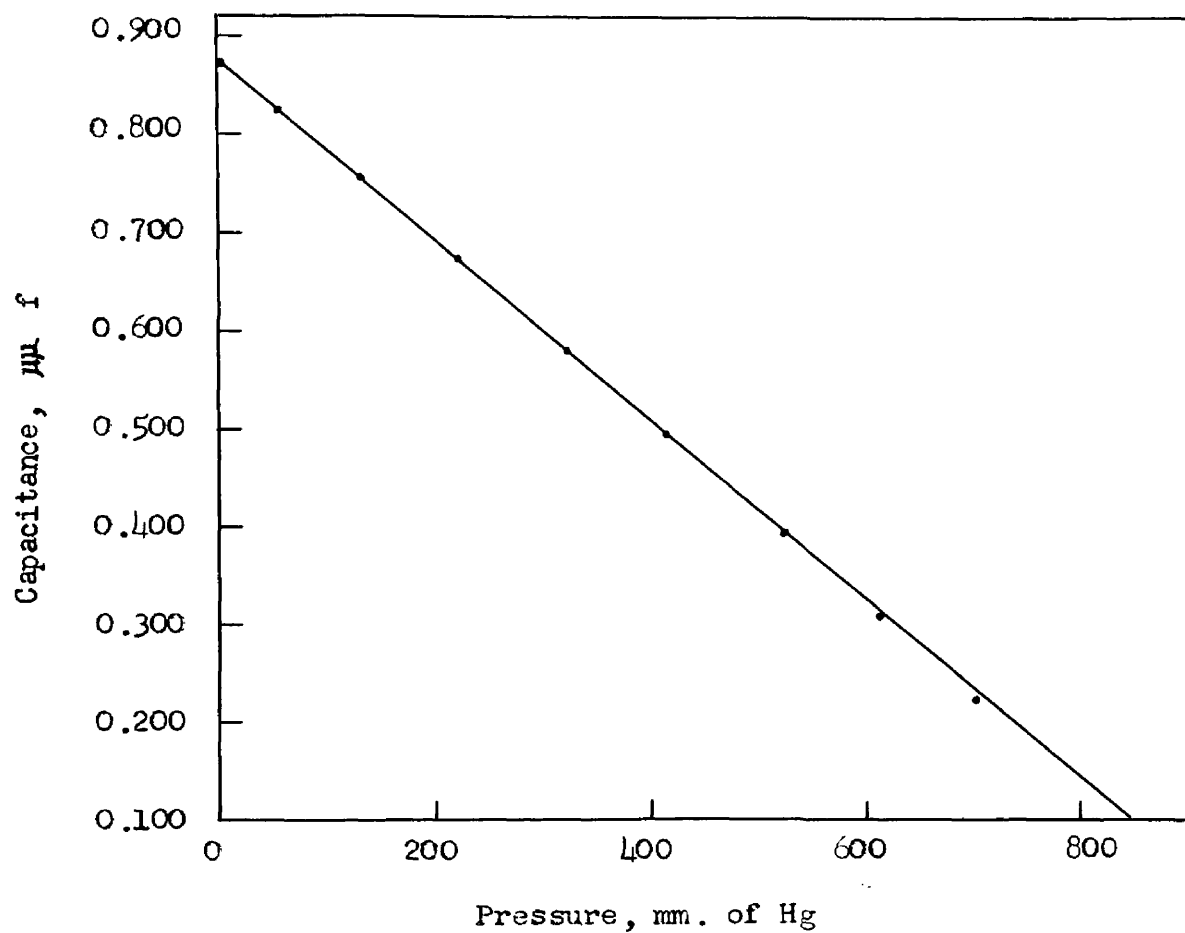


Figure 15. Typical plot of capacitance versus pressure for bromine pentafluoride at 115.8°C.

TABLE XI
VALUES OF ΔC FOR BROMINE PENTAFLUORIDE
FROM THE DATA IN TABLE VI

Temperature °C	$\Delta C \text{ } \mu\mu f$ (0-1 atm of BrF_5)			Average ΔC $\mu\mu f$
72.5		0.844	0.842	0.843
89.5	0.775	0.777	0.777	0.777
101.9	0.735	0.738	0.739	0.737
115.8	0.691	0.692	0.690	0.691
129.2		0.654	0.656	0.655
144.1		0.613	0.615	0.614
157.7	0.580	0.586	0.586	0.584

TABLE XII

CALCULATIONS OF MOLAR POLARIZATION FOR BROMINE PENTAFLUORIDE

Temp. °C	Temp. °K	ΔC $\mu\mu f$	$(\epsilon - 1) \times 10^6$	$\frac{(\epsilon - 1)}{(\epsilon + 2)} \times 10^6$	V_M^* cc./mole	P_M cc./mole	$\frac{1}{T^\circ K} \times 10^3$
72.5	345.6	0.843	6320	2102	28,374	59.6	2.893
89.5	362.6	0.777	5824	1938	29,769	57.7	2.758
101.8	374.9	0.737	5525	1838	30,779	56.6	2.667
115.8	388.9	0.691	5180	1724	31,929	55.0	2.571
129.2	402.4	0.655	4910	1634	33,029	54.0	2.468
144.1	417.2	0.614	4603	1532	34,252	52.5	2.397
157.7	430.8	0.584	4378	1457	35,369	51.5	2.321

* The molar volume obtained from $PV_M = RT$.

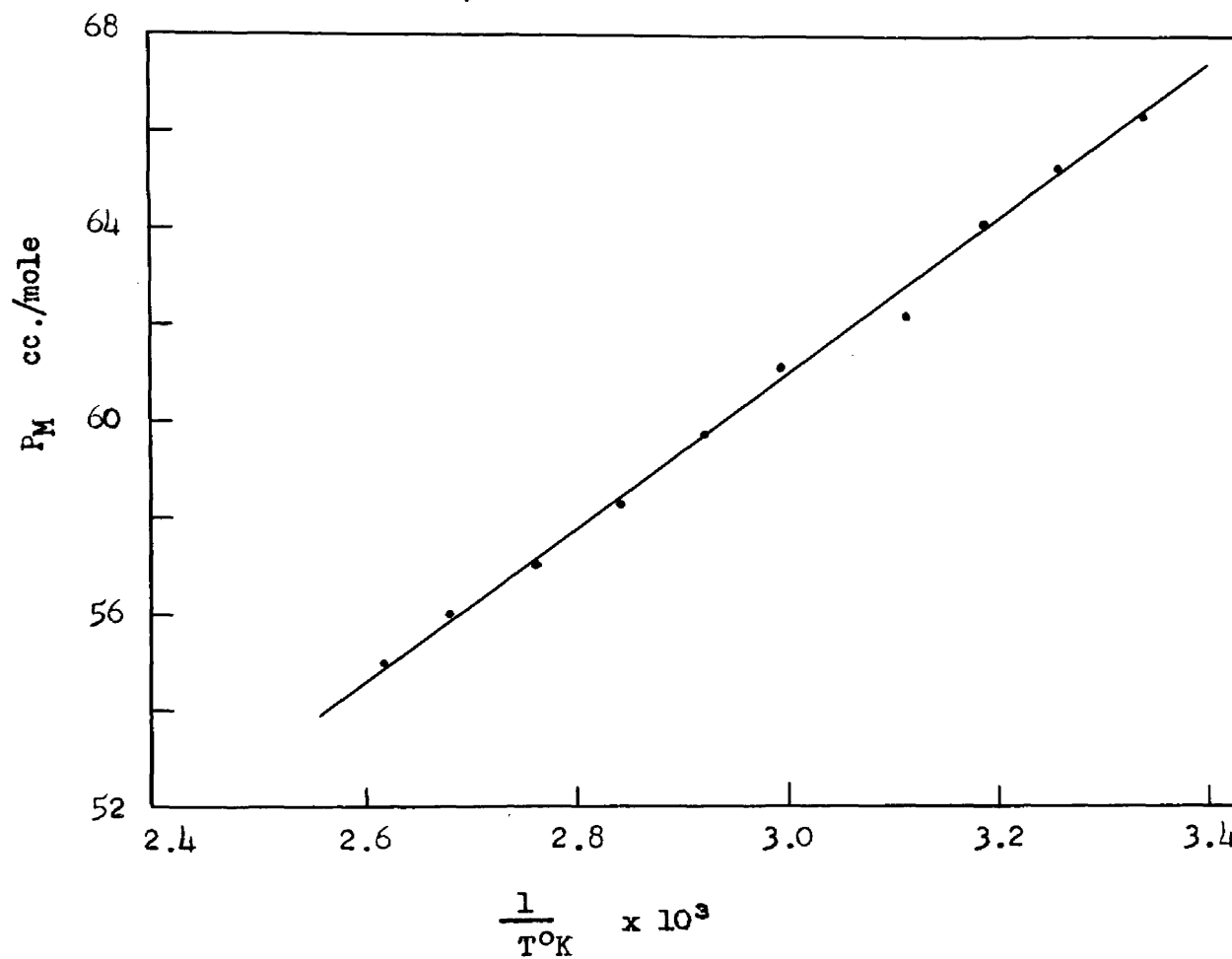


Figure 16. Molar polarization versus the reciprocal of the absolute temperature for bromine pentafluoride.

Chlorine Trifluoride

Data. The data for plotting the capacitance-versus-pressure curves for chlorine trifluoride are presented in Table XIII. The data for the calibration of the cell and Helicoid gage are not shown. The average value of ΔC at each temperature is given in Table XIV, along with the dielectric constant at each temperature and the molar polarization. The molar volume of the chlorine trifluoride was obtained using the Berthelot equation-of-state,

$$V_M = \frac{RT}{P} \left[1 + \frac{9 P T_C}{128 P_C T} \left(1 - \frac{6 T_C^2}{T^2} \right) \right]$$

and the critical constants estimated by Grisard, Bernhardt, and Oliver (53).

Dipole moment. The plot of molar polarization against the reciprocal of the absolute temperature is shown in Figure 17. The slope of the straight line as determined by the least-squares method (3,364) corresponds to value for the dipole moment of

$$\mu = 0.74 \text{ D}$$

The calculation of the dipole moment using the molar refraction gave a slightly different value. Malik (55) has determined the molar refraction of chlorine trifluoride from refractive index measurements on the gas, and gives a value of $R = 10.3 \pm 0.5$. Substituting this value and the molar polarization at each temperature into Equation 17 gives the results shown in Table XV. The average value of the moment obtained

TABLE XIII
DIELECTRIC CONSTANT DATA FOR CHLORINE TRIFLUORIDE

Pressure mm. of Hg	Capacitance $\mu\mu f$	Pressure mm. of Hg	Capacitance $\mu\mu f$
Measurements at 46.2°C		Measurements at 102.2°C	
733	0.330	755	0.540
651	0.370	683	0.565
596	0.399	608	0.592
533	0.431	515	0.629
455	0.469	406	0.671
394	0.499	299	0.709
315	0.537	201	0.746
202	0.592	92	0.798
87	0.648	<1	0.849
<1	0.696		
		721	0.527
736	0.315	661	0.553
662	0.353	609	0.576
602	0.382	518	0.616
524	0.422	424	0.654
458	0.454	310	0.700
393	0.486	199	0.746
295	0.532	83	0.801
194	0.583	<1	0.847
85	0.634		
<1	0.679	729	0.522
		656	0.554
Measurements at 78.7°C		553	0.601
732	0.831	450	0.644
621	0.879	349	0.696
504	0.927	250	0.726
448	0.951	148	0.752
401	0.976	<1	0.850
314	1.006		
205	1.054	Measurements at 140.8°C	
94	1.099	724	0.401
<1	1.143	678	0.418
		621	0.437
731	0.827	563	0.455
644	0.865	496	0.478
540	0.911	423	0.498
489	0.935	329	0.534
428	0.956	231	0.566
343	0.995	104	0.610
247	1.036	<1	0.650
149	1.078		
81	1.109		
<1	1.147		

TABLE XIV

MOLAR POLARIZATION CALCULATIONS FOR CHLORINE TRIFLUORIDE

Temperature, °K	$\Delta C,^*$ $\mu\mu f$	$(\epsilon - 1) \times 10^6$	Molar Volume, cc/mole	P_M cc/mole	$\frac{1}{T} \times 10^3$ °K
319.3	0.372	2825	25,756	24.2	3.132
351.8	0.328	2490	28,488	23.6	2.842
375.8	0.302	2293	30,512	23.3	2.661
413.3	0.254	1929	33,707	21.7	2.416

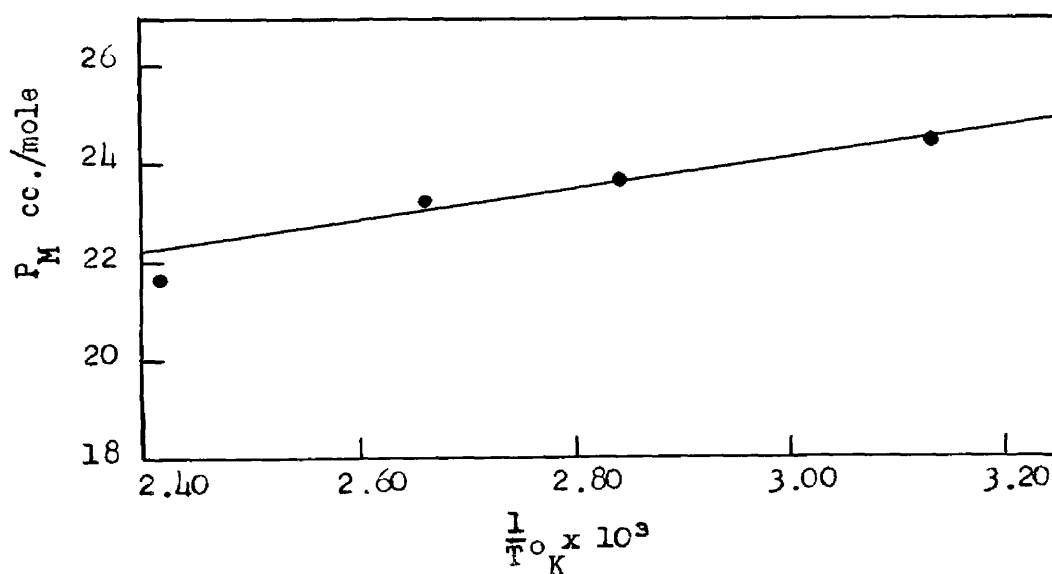
* Replaceable capacitance, $C_0 = 132 \mu\mu f$.

Figure 17. Molar polarization versus the reciprocal of the absolute temperature for chlorine trifluoride.

in this manner is

$$\mu = 0.85 \text{ D.}$$

This agrees with the value obtained from the plot of the molar polarization versus the reciprocal of the absolute temperature within the accuracy of the measurements. (See Discussion of Errors)

TABLE XV
DIPOLE MOMENT OF CHLORINE TRIFLUORIDE CALCULATED
USING THE MOLAR REFRACTION

Temperature °K	Dipole Moment D
319.3	0.83
351.8	0.86
375.8	0.87
413.3	0.85

Iodine Pentafluoride

Data. The dielectric constant data are presented in Table XVI, and the results of the various plots and calculations are summarized in Table XVII. Because of the high boiling point of this compound, the dielectric constant could not be measured over a large temperature range. Therefore it was not possible to obtain sufficient data for a plot of molar polarization versus the reciprocal of the absolute temperature.

TABLE XVI

DIELECTRIC CONSTANT DATA FOR IODINE PENTAFLUORIDE

Pressure mm. of Hg	Capacitance $\mu\mu f$	Pressure mm. of Hg	Capacitance $\mu\mu f$
Measurements at 119.6°C		Measurements at 135°C (cont'd)	
239	0.840	221	0.756
146	0.968	196	0.790
59	1.074	174	0.817
<1	1.152	151	0.849
		123	0.884
246	0.850	104	0.908
216	0.891	65	0.956
188	0.927	35	0.992
168	0.955	<1	1.041
142	0.992		
113	1.031	231	0.753
81	1.073	210	0.784
63	1.095	181	0.827
<1	1.173	151	0.866
		122	0.910
293	0.763	92	0.948
252	0.825	57	0.992
220	0.871		
195	0.907	Measurements at 150.4°C	
170	0.947	205	0.875
147	0.974	177	0.913
116	1.020	144	0.949
96	1.051	112	0.991
60	1.098	82	1.026
<1	1.177	52	1.063
		16	1.103
Measurements at 135.0°C		<1	1.107
253	0.732		
221	0.773	218	0.837
197	0.806	194	0.863
171	0.841	171	0.891
147	0.868	147	0.917
118	0.906	118	0.953
90	0.942	90	0.987
53	0.983	61	1.021
19	1.026	39	1.046
<1	1.052	<1	1.107

TABLE XVI (CONTINUED)

Pressure mm. of Hg	Capacitance $\mu\mu f$	Pressure mm. of Hg	Capacitance $\mu\mu f$
Measurements at 150.4°C		Measurements at 172.9°C (continued)	
210	0.799	205	1.043
191	0.825	168	1.080
171	0.845	139	1.111
141	0.880	116	1.137
113	0.916	88	1.167
92	0.943	60	1.198
58	0.975	38	1.221
34	1.011	17	1.243
<1	1.066	<1	1.261
Measurements at 172.9°C			
		198	1.033
424	0.846	173	1.059
364	0.917	149	1.084
283	1.001	111	1.124
213	1.068	82	1.155
157	1.125	53	1.185
114	1.169	31	1.208
73	1.213	14	1.226
55	1.234	<1	1.240
<1	1.292		
209	1.064		
180	1.093		
155	1.116		
131	1.129		
98	1.175		
64	1.208		
37	1.238		
15	1.257		
<1	1.273		

TABLE XVII

DIPOLE MOMENT CALCULATIONS FOR IODINE PENTAFLUORIDE
BY THE REFRACTIVITY METHOD

Temp. °K	ΔC^* $\mu\mu f$	$(\epsilon - 1) \times 10^6$	V_M cc./mole	P_M cc./mole	$(P_M - R)T$	μ D
392.7	1.011	9108	32,241	97.6	30,787	2.24
408.1	0.940	8468	33,505	94.3	30,648	2.24
423.5	0.885	7973	34,769	92.2	30,915	2.25
446.0	0.792	7135	36,617	86.9	30,194	2.23

* Replaceable capacitance of cell $C_0 = 111 \mu\mu f$

Dipole Moment. Malik (55) has obtained a value of 19.2 cc./mole for the molar refraction R of iodine pentafluoride. This value was used to obtain the value of B in Equation 17 at each temperature, from which the dipole moment was calculated. The details of the calculations are given in the last three columns of Table XVII. The excellent agreement between these values indicates the precision which is possible in measuring compounds which possess a high dipole moment. The average value for the dipole moment of iodine pentafluoride is

$$\mu = 2.24 \text{ D.}$$

Bromine Trifluoride

Data. The dielectric constant data for bromine trifluoride are presented in Table XVIII. This was the highest boiling compound measured, and therefore a very small temperature range was available over which the dielectric constant data could be obtained. The calculations are summarized in Table XIX.

Dipole moment. The dipole moment was calculated using the value of 12.9 cc./mole for the molar refraction obtained by Malik (55). The average value of the dipole moment at three different temperatures is

$$\mu = 1.33 \text{ D.}$$

TABLE XVIII
DIELECTRIC CONSTANT DATA FOR BROMINE TRIFLUORIDE

Pressure mm. of Hg	Capacitance μmf	Pressure mm. of Hg	Capacitance μmf
Measurements at 142.4°C		Measurements at 151.6°C	
197	0.247	121	0.683
182	0.252	73	0.705
151	0.270	36	0.723
125	0.280	<1	0.740
89	0.300		
59	0.315	296	0.568
21	0.332	247	0.591
<1	0.344	196	0.615
		148	0.639
198	0.236	108	0.656
171	0.249	61	0.679
143	0.256	20	0.698
115	0.283	<1	0.707
87	0.299		
57	0.315	Measurements at 175.1°C	
29	0.332	290	0.592
<1	0.348	250	0.610
		216	0.625
215	0.259	158	0.649
191	0.273	121	0.661
162	0.285	78	0.680
131	0.304	29	0.706
105	0.319	<1	0.718
80	0.330		
56	0.343	302	0.571
23	0.363	265	0.588
<1	0.373	221	0.607
		186	0.622
Measurements at 151.6°C		118	0.651
290	0.630	81	0.667
227	0.661	29	0.690
183	0.679	<1	0.702
137	0.700		
90	0.722	310	0.536
42	0.744	262	0.553
<1	0.763	218	0.579
		171	0.597
278	0.609	123	0.618
220	0.636	79	0.637
163	0.663	27	0.660
		<1	0.672

TABLE XIX

DIPOLE MOMENT CALCULATIONS FOR BROMINE TRIFLUORIDE

Temp. °K	ΔC^* $\mu\mu f$	$(\epsilon - 1) \times 10^6$	V_M cc./mole	P_M cc./mole	$(P_M - R)/T$	μ_D
415.5	0.416	3748	34,113	42.6	12,340	1.40
424.7	0.354	3189	34,679	37.0	10,235	1.29
448.2	0.329	2964	36,797	36.3	10,488	1.30

* Replaceable capacitance $C_0 = 111 \mu\mu f$

Fluorocarbon Derivatives

1,1,1,2,2,3,3-Heptafluoropropane

Data. The dielectric constant data are presented in Table XX. The cell used for the fluorocarbon derivative work (Cell I) had a much larger replaceable capacitance than Cell II, therefore larger capacitance changes were observed upon placing a gas between the plates. This increased the precision of the measurements. The calculations of the molar polarization are summarized in Table XXI.

Dipole moment. The plot of molar polarization versus the reciprocal of the absolute temperature is shown in Figure 19. The slope of the line B obtained by the least-squares method is equal to 15,960 and the dipole moment calculated from this is

$$\mu = 1.62 \text{ D.}$$

Perfluorotetramethylene Oxide

Data. The dielectric constant data are presented in Table XXII, and the calculations are summarized in Table XXIII.

Dipole moment. The plot of molar polarization versus the reciprocal of the absolute temperature is shown in Figure 19. The slope of the line B determined by a least-squares method is 1931, and the dipole moment calculated from this is

$$\mu = 0.56 \text{ D.}$$

TABLE XX
DIELECTRIC CONSTANT DATA FOR
1,1,1,2,2,3,3-HEPTAFLUOROPROPANE ($n\text{-C}_3\text{F}_7\text{H}$)

Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$	Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$
Measurements at 26.7°C		Measurements at 48.4°C	
788.0	0.261	787.2	0.257
704.0	0.586	704.7	0.548
607.3	0.954	599.0	0.904
507.3	1.332	491.1	1.260
394.7	1.763	393.6	1.581
298.0	2.332	297.9	1.898
195.8	2.502	201.2	2.209
100.0	2.865	104.5	2.527
0.5	3.216	0.1	2.864
Measurements at 34.2°C		Measurements at 61.1°C	
780.3	0.510	792.1	0.495
690.8	0.844	696.9	0.797
600.4	1.165	603.4	1.085
498.6	1.541	497.2	1.415
397.5	1.908	390.0	1.751
293.2	2.279	293.0	2.049
198.4	2.624	199.2	2.343
106.3	2.951	100.4	2.653
0.2	3.309	0.2	2.949
Measurements at 41.0°C		Measurements at 69.4°C	
785.0	0.453	790.9	0.497
702.7	0.745	699.9	0.776
605.8	1.084	599.8	1.071
502.3	1.448	503.2	1.357
394.0	1.826	398.2	1.677
303.5	2.116	295.3	1.979
194.0	2.512	199.5	2.256
98.3	2.844	97.2	2.561
0.1	3.163	0.1	2.838

TABLE XX (CONTINUED)

Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$	Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$
Measurements at 79.3°C		Measurements at 109.0°C	
791.9	0.508	789.7	0.568
704.0	0.762	704.5	0.780
601.6	1.052	600.5	1.028
487.8	1.368	486.8	1.309
403.0	1.616	384.5	1.569
299.0	1.904	292.1	1.795
189.0	2.206	201.8	2.015
100.5	2.459	102.4	2.254
0.2	2.738	0.2	2.499
Measurements at 89.8°C		Measurements at 99.8°C	
780.3	1.056	784.1	0.522
699.2	1.210	698.1	0.746
576.7	1.448	598.8	1.000
491.6	1.618	483.1	1.293
390.5	1.811	398.7	1.516
276.7	2.027	301.3	1.767
203.2	2.163	185.2	2.059
109.0	2.344	102.2	2.267
0.2	2.567	0.2	2.520

TABLE XXI

MOLAR POLARIZATION CALCULATIONS FOR 1,1,1,2,2,3,3-HEPTAFLUOROPROPANE

Temperature °K	ΔC^* μmf	$(\epsilon - 1) \times 10^6$	V_M cc/mole	P_M cc/mole	$\frac{1}{T} \times 10^3$
299.8	2.860	8104	24,614	66.3	3.336
307.3	2.745	7778	25,229	65.2	3.254
314.1	2.640	7481	25,788	64.1	3.184
321.5	2.500	7084	26,395	62.2	3.110
334.2	2.364	6699	27,438	61.1	2.992
342.5	2.254	6387	28,119	59.7	2.920
352.5	2.136	6053	28,932	58.3	2.838
362.3	2.032	5758	29,745	57.0	2.760
372.9	1.940	5497	30,615	56.0	2.682
382.1	1.860	5271	31,370	55.0	2.617

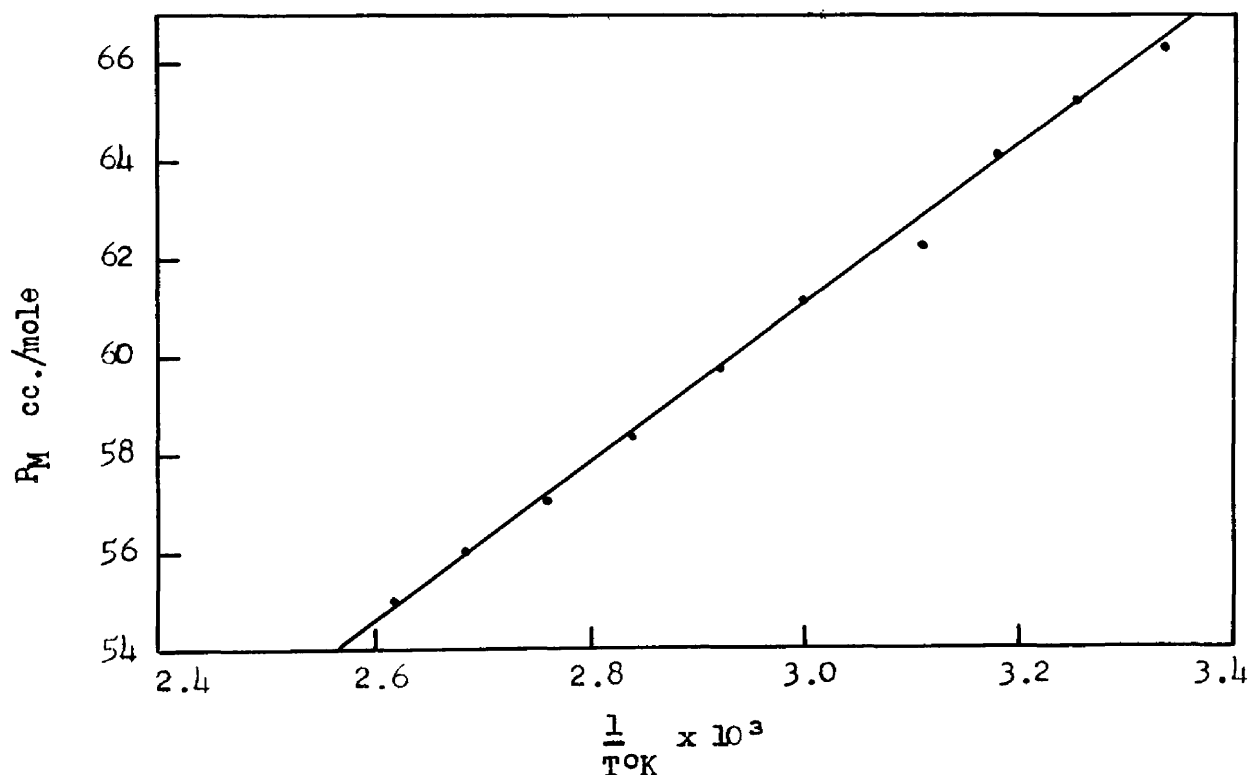
* Replaceable capacitance, $C_0 = 353 \mu\text{mf}$.

Figure 18. Molar polarization versus the reciprocal of the absolute temperature for 1,1,1,2,2,3,3-heptafluoropropane.

TABLE XXII
DIELECTRIC CONSTANT DATA
FOR PERFLUOROTETRAMETHYLENE OXIDE (cyclic-(CF₂)₄O)

Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$	Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$
Measurements at 26.1°C		Measurements at 56.0°C	
781.4	1.010	783.4	1.382
720.8	1.125	697.0	1.540
642.0	1.270	591.3	1.721
551.0	1.439	521.1	1.834
456.1	1.634	236.5	1.976
372.2	1.787	368.5	2.089
280.8	1.954	287.2	2.221
193.3	2.110	207.2	2.350
121.2	2.240	128.7	2.480
45.6	2.378	58.1	2.600
6.7	2.455	0.6	2.693
Measurements at 36.9°C		Measurements at 66.7°C	
790.8	0.707	792.8	1.423
712.1	0.895	725.0	1.541
646.5	1.017	657.0	1.657
581.1	1.134	573.5	1.788
511.4	1.260	492.7	1.919
447.8	1.376	407.0	2.048
369.6	1.522	331.4	2.176
290.0	1.671	223.1	2.314
206.4	1.818	163.0	2.444
129.3	1.953	84.8	2.569
64.2	2.068	0.7	2.706
0.5	2.179		
Measurements at 44.7°C		Measurements at 74.6°C	
783.0	1.137	787.1	0.629
717.3	1.254	717.5	0.738
662.3	1.354	649.0	0.846
595.5	1.473	576.0	0.959
515.8	1.620	501.3	1.073
426.7	1.773	412.8	1.207
352.3	1.904	325.0	1.347
265.3	2.053	235.2	1.489
174.4	2.206	149.4	1.627
81.0	2.364	70.3	1.744
0.7	2.497	0.3	1.853

TABLE XXII (CONTINUED)

Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$	Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$
Measurements at 82.9°C		Measurements at 101.8°C	
789.8	0.693	787.8	0.769
716.7	0.809	710.7	0.880
652.0	0.905	645.0	0.972
586.3	1.005	566.7	1.086
508.8	1.118	492.0	1.190
430.9	1.234	440.4	1.261
358.1	1.342	372.1	1.360
268.9	1.472	311.0	1.450
192.0	1.598	344.4	1.562
118.9	1.708	160.7	1.667
56.2	1.800	72.5	1.784
0.3	1.884	0.4	1.809
Measurements at 93.2°C		Measurements at 111.1°C	
784.9	0.705	788.7	0.793
711.1	0.814	701.8	0.916
645.2	0.910	642.8	1.004
572.3	1.014	569.6	1.097
508.5	1.107	483.5	1.216
424.1	1.228	397.0	1.337
343.5	1.346	310.6	1.459
266.6	1.459	224.5	1.578
194.8	1.566	149.8	1.681
119.5	1.677	76.8	1.780
49.7	1.773	0.2	1.884
0.5	1.847		

TABLE XXIII

MOLAR POLARIZATION CALCULATIONS FOR PERFLUOROMETHYLENE OXIDE

Temperature °K	ΔC^* $\mu\mu f$	$(\epsilon - 1) \times 10^6$	V_M cc/mole	P_M cc/mole	$\frac{1}{T} \text{°K} \times 10^3$
299.2	1.413	4039	24,564	33.0	3.342
310.1	1.362	3894	25,451	32.9	3.226
317.2	1.313	3753	26,042	32.5	3.153
329.1	1.255	3588	27,019	32.3	3.039
339.8	1.219	3485	27,898	32.4	2.943
347.7	1.184	3385	28,546	32.2	2.876
356.1	1.145	3273	29,236	31.9	2.808
366.3	1.108	3167	30,073	31.8	2.730
375.4	1.088	3110	30,820	31.9	2.664
384.2	1.055	3016	31,543	31.6	2.603

* Replaceable capacitance $C_0 = 350 \mu\mu f$.

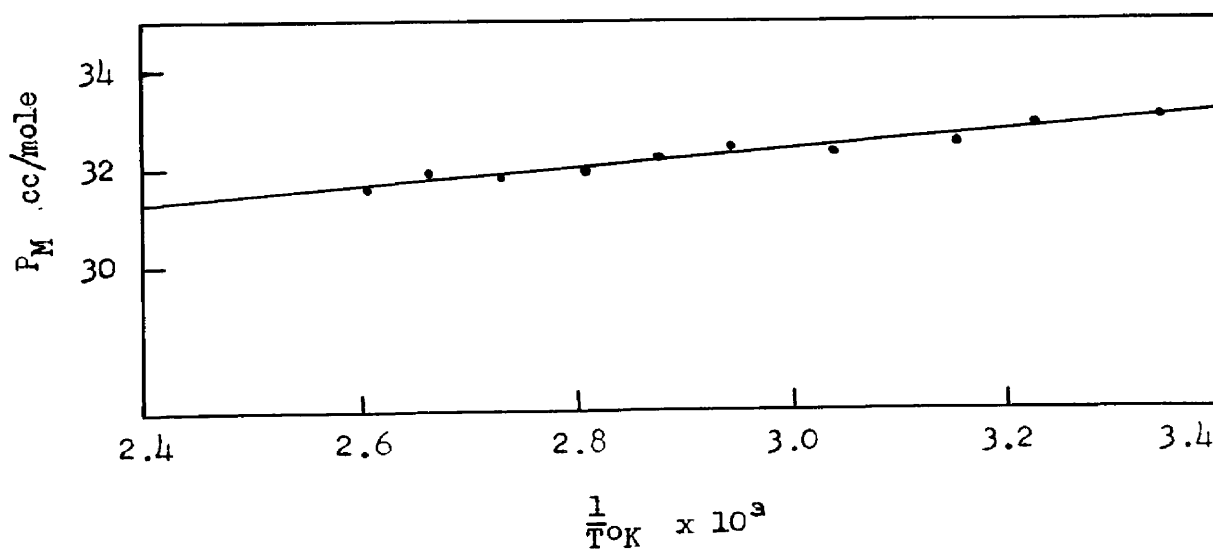


Figure 19. Molar polarization versus the reciprocal of the absolute temperature for perfluorotetramethylene oxide.

Perfluoroethyl Ether

Data. The dielectric constant data are presented in Table XXIV, and the calculation of the molar polarization at each temperature is summarized in Table XXV.

Dipole moment. The plot of the molar polarization versus the reciprocal of the absolute temperature is shown in Figure 20. The slope of the line B is 1643 and the dipole moment calculated from this is

$$\mu = 0.51 \text{ D.}$$

Chlorotrifluoroethylene

Data. The dielectric constant data are given in Table XXVI, and the calculations are summarized in Table XXVII.

Dipole moment. The plot of molar polarization versus the reciprocal of the absolute temperature is shown in Figure 21. The slope of the line B is 904, and the dipole moment calculated from this is

$$\mu = 0.38 \text{ D.}$$

TABLE XXIV
DIELECTRIC CONSTANT DATA FOR PERFLUOROETHYL ETHER
($(C_2F_5)_2O$)

Pressure mm. of Hg	Capacitance $\mu\mu f$	Pressure mm. of Hg	Capacitance $\mu\mu f$
Measurements at 26.0°C		Measurements at 47.0°C	
787.5	1.021	787.9	1.222
721.2	1.149	698.2	1.380
639.9	1.303	598.2	1.564
540.0	1.497	505.2	1.727
426.5	1.714	399.3	1.909
308.3	1.932	303.3	2.071
199.4	2.126	197.0	2.248
96.0	2.311	103.7	2.409
0.5	2.486	0.2	2.581
Measurements at 34.8°C		Measurements at 55.0°C	
791.1	1.113	787.3	1.360
700.4	1.282	688.1	1.535
596.0	1.479	598.2	1.691
490.5	1.677	497.7	1.859
399.0	1.841	397.4	2.028
294.6	2.027	295.2	2.194
192.8	2.203	193.7	2.359
97.8	2.373	99.5	2.517
0.2	2.541	0.3	2.683
Measurements at 40.9°C		Measurements at 62.3°C	
794.6	0.878	796.1	1.425
703.9	1.037	702.9	1.585
597.5	1.226	598.9	1.760
490.6	1.420	500.4	1.923
400.0	1.584	399.1	2.086
296.8	1.763	298.1	2.252
200.0	1.930	197.3	2.415
98.8	2.102	99.4	2.576
0.1	2.263	0.2	2.738

TABLE XXIV (CONTINUED)

Pressure mm. of Hg	Capacitance $\mu\mu f$	Pressure mm. of Hg	Capacitance $\mu\mu f$
Measurements at 72.7°C		Measurements at 91.8°C	
794.4	1.427	787.4	0.920
699.0	1.585	696.0	1.058
596.9	1.747	599.8	1.199
502.7	1.892	499.4	1.349
398.1	2.057	397.9	1.502
297.8	2.212	295.8	1.655
197.0	2.368	199.8	1.793
104.3	2.514	99.0	1.940
0.1	2.686	0.3	2.080
Measurements at 82.2°C		Measurements at 100.6°C	
782.9	0.451	783.0	0.989
695.4	0.600	693.9	1.122
599.9	0.746	597.1	1.267
505.4	0.895	501.7	1.404
399.1	1.052	396.2	1.562
296.4	1.206	288.5	1.715
199.0	1.355	194.0	1.852
112.0	1.504	99.8	1.983
0.2	1.662	0.3	2.123

TABLE XXV

MOLAR POLARIZATION CALCULATIONS FOR PERFLUOROTHYL ETHER

Temperature °K	ΔC^* $\mu\mu f$	$(\epsilon - 1) \times 10^6$	V_M cc/mole	P_M cc/mole	$\frac{1}{T} \times 10^3$ °K
299.3	1.413	4004	24,556	32.7	3.343
307.9	1.374	3893	25,279	32.8	3.248
314.0	1.345	3811	25,779	32.7	3.184
320.1	1.291	3658	26,280	32.0	3.124
328.1	1.266	3587	26,973	32.2	3.048
335.4	1.242	3519	27,536	32.2	2.981
345.8	1.191	3375	28,390	31.9	2.892
355.3	1.159	3284	29,170	31.9	2.814
364.9	1.123	3182	29,958	31.7	2.740
373.7	1.097	3108	30,681	31.7	2.676

* Replaceable capacitance $C_0 = 353 \mu\mu f$.

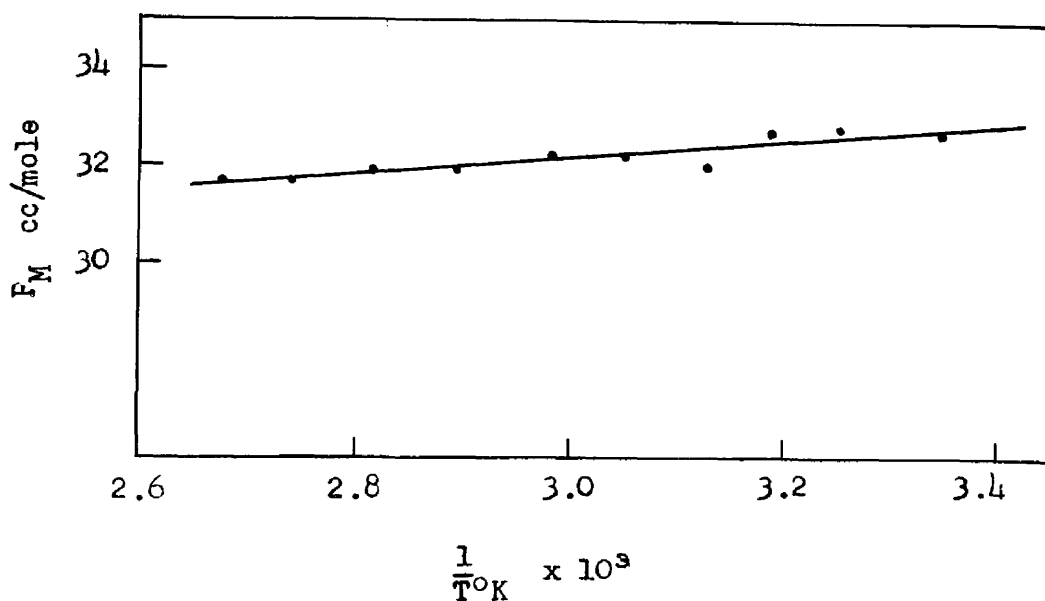


Figure 20. Molar polarization versus the reciprocal of the absolute temperature for perfluoroethyl ether.

TABLE XXVI

DIELECTRIC CONSTANT DATA FOR CHLOROTRIFLUOROETHYLENE
(CClF=CF₂)

Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$	Pressure mm. of Hg	Capacitance $\mu\mu\text{f}$
Measurements at 28.2°C		Measurements at 54.4°C	
781.3	1.522	788.2	1.093
701.2	1.632	705.8	1.192
601.0	1.759	599.1	1.319
498.5	1.893	495.0	1.444
406.8	2.025	407.7	1.551
303.9	2.150	297.0	1.687
200.4	2.284	187.9	1.809
95.0	2.421	107.3	1.906
0.5	2.545	0.8	2.030
Measurements at 34.7°C		Measurements at 63.6°C	
783.5	1.864	776.8	1.237
700.0	1.973	704.3	1.318
584.3	2.120	584.7	1.462
494.9	2.234	486.0	1.577
401.2	2.359	393.7	1.685
296.8	2.498	302.4	1.788
205.9	2.619	191.1	1.913
107.3	2.747	99.0	2.020
0.8	2.881	0.1	2.127
Measurements at 44.5°C		Measurements at 76.5°C	
784.3	1.307	779.8	1.555
688.0	1.432	695.7	1.651
605.6	1.537	597.4	1.759
493.7	1.677	494.1	1.873
393.3	1.803	399.2	1.980
294.6	1.923	297.5	2.088
194.0	2.048	195.5	2.200
100.0	2.166	101.4	2.305
0.5	2.287	0.2	2.418

TABLE XXVI (CONTINUED)

Pressure mm. of Hg	Capacitance $\mu\mu f$
Measurements at 84.2°C	
783.2	1.569
703.8	1.659
608.8	1.758
500.0	1.877
383.1	2.003
287.0	2.105
208.5	2.190
117.3	2.293
0.8	2.422
Measurements at 92.6°C	
781.6	2.003
692.2	2.096
589.6	2.200
503.1	2.296
392.1	2.416
242.5	2.576
135.9	2.689
0.5	2.837
Measurements at 104.2°C	
777.3	0.655
699.5	0.733
596.5	0.841
500.7	0.936
390.5	1.047
294.8	1.144
190.8	1.248
101.6	1.340
0.5	1.448

TABLE XXVII

MOLAR POLARIZATION CALCULATIONS FOR CHLOROTRIFLUOROETHYLENE

Temperature °K	ΔC^* $\mu\mu f$	$(\epsilon - 1) \times 10^6$	V_M cc/mole	P_M cc/mole	$\frac{1}{T_0} \times 10^3$
301.3	0.992	2729	24,737	22.5	3.319
307.8	0.986	2712	25,270	22.8	3.249
317.6	0.951	2616	26,075	22.7	3.149
327.5	0.912	2508	26,888	22.5	3.053
336.7	0.907	2495	27,643	22.9	2.970
349.6	0.841	2314	28,702	22.1	2.860
357.5	0.823	2264	29,351	22.1	2.797
365.7	0.813	2367	30,024	22.3	2.734
377.3	0.778	2140	30,976	22.0	2.650

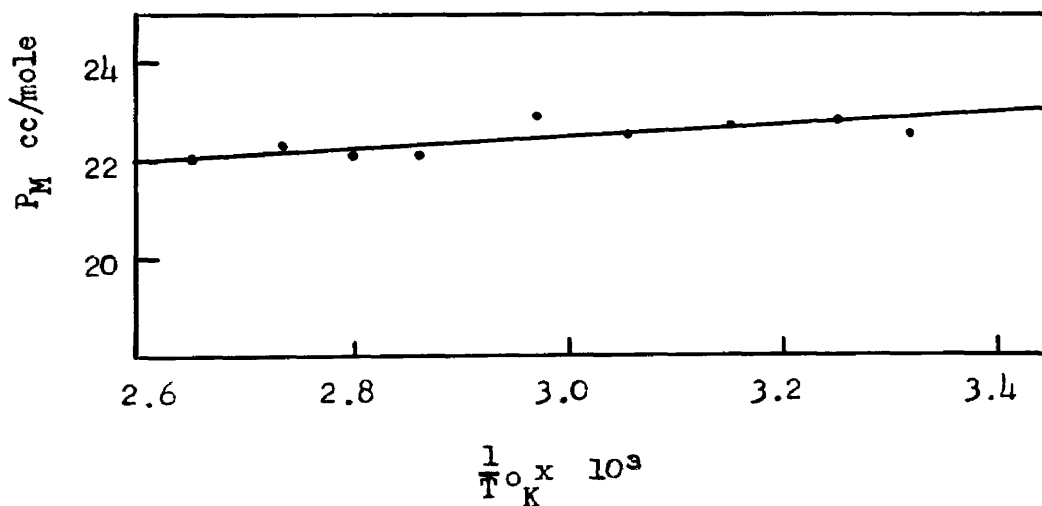
* Replaceable Capacitance $C_0 = 363 \mu\mu f$.

Figure 21. Molar polarization versus the reciprocal of the absolute temperature for chlorotrifluoroethylene.

Discussion of Errors

The largest factor governing the accuracy of the dielectric constant measurements was the "drift" of the beat frequency. This was due in part to the instability of the oscillators, but was mostly due to small vibrations in the dielectric cells caused by the bath stirrers. When the stirrers were not in operation the drift was observed to be negligible. The drift was more pronounced in Cell I, because of its delicate construction, than in Cell II which was more rigidly built. It was therefore necessary to carry out separate error analyses, one for the fluorocarbon derivatives for which Cell I was used, and one for Cell II and the halogen fluorides.

Halogen Fluorides

The sensitivity of the capacitance measurements had as an upper limit the smallest capacitance increment which could be read on the precision condenser. This increment was equal to $0.0003 \mu\mu f$. The beat-frequency drift during the period of several runs was of the order of $0.0005 \mu\mu f$, so that the total uncertainty in each reading was slightly less than $\pm 0.001 \mu\mu f$. Thus the total probable error in the capacitance measurements was 100% for increments of $\Delta C = 0.001 \mu\mu f$, decreasing asymptotically to about one percent for values equal to $0.100 \mu\mu f$. A plot of the probable error versus ΔC for Cell II is shown in Figure 22.

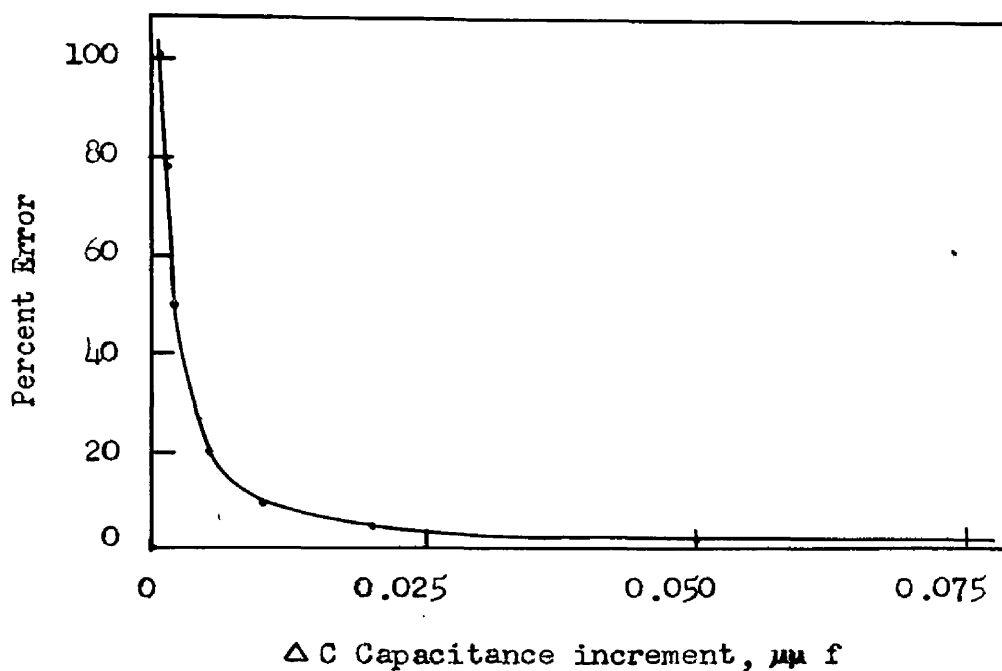


Figure 22. Probable error as a function of capacitance increment, ΔC for a single observation using Cell II.

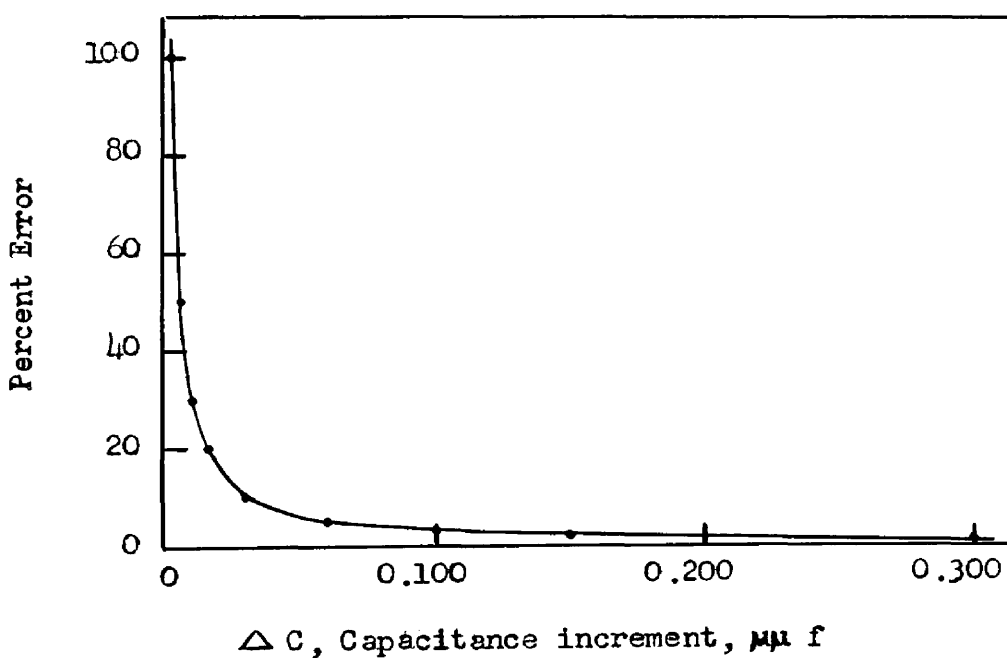


Figure 23. Probable error as a function of capacitance increment, ΔC for a single observation using Cell I.

Cell calibration. The maximum probable error in the calibration of the dielectric cell was determined by differentiation of Equation 21 which gives

$$\Delta C_0 = \frac{\Delta C}{(\epsilon - 1)^2} \Delta(\epsilon - 1) + \frac{\Delta(\Delta C)}{(\epsilon - 1)} \quad (23)$$

where ΔC_0 , $\Delta(\epsilon - 1)$, and $\Delta(\Delta C)$ represent the errors in these terms. As indicated in Table IX, the average capacitance increment during a run was equal to 0.014 $\mu\mu f$. This corresponds to a probable error of seven percent as shown in Figure 22. The value for ΔC was taken as the total capacitance change during a run, 0.123 $\mu\mu f$ (Table X), and seven percent of this or 0.009 $\mu\mu f$ was the value of $\Delta(\Delta C)$. The mean value for the dielectric constant of carbon dioxide reported by Maryott and Buckley (52) is $(\epsilon - 1) \times 10^6 = 922 \pm 1$, hence

$$\Delta(\epsilon - 1) = 1 \times 10^{-6}.$$

The errors in the pressure measurements were negligible since the error in each pressure reading was ± 0.05 mm. of mercury which corresponded to $\pm 1 \times 10^{-6}$ $\mu\mu f$.

Substituting the above value in Equation 23 gives an uncertainty of six percent in the replaceable capacitance C_0 of Cell II, or

$$C_0 = 133 \pm 9 \mu\mu f.$$

Dielectric constant measurements. Solving Equation 21 for $(\epsilon - 1)$ and again differentiating gives

$$\Delta(\epsilon - 1) = \frac{\Delta C}{C_0^2} \Delta C_0 + \frac{\Delta(\Delta C)}{C_0} \quad (24)$$

where the terms are the same as in Equation 23. The data for chlorine trifluoride show the average capacitance increment during a run to be 0.030 $\mu\mu\text{f}$, corresponding to an error of three percent, or $\Delta(\Delta C) = 0.009 \mu\mu\text{f}$ since the average value of the capacitance change for an atmosphere of the gas was 0.300 $\mu\mu\text{f}$. The errors in the pressure measurements were slightly larger here, ± 1 mm. of mercury, since the Helicoid gage was used. However this corresponded to only 0.0003 $\mu\mu\text{f}$ and is again negligible. These values, substituted in Equation (24) give an average error in the dielectric constant measurements of chlorine trifluoride of

$$\Delta(\epsilon - 1) = \pm 200 \times 10^{-6}$$

or eight percent.

Molar polarization. Differentiation of Equation 12 gives

$$\Delta P_M = \frac{(\epsilon - 1)}{(\epsilon + 2)^2} V_M (\Delta(\epsilon + 2)) + \frac{(\epsilon - 1)}{(\epsilon + 2)} V_M (\Delta(\epsilon - 1)) + \frac{(\epsilon - 1)}{(\epsilon + 2)} \Delta V_M$$

where ΔV_M is the error in the molar volume calculation, and the other terms are the same as in the above equations. The error in the molar volume was assumed to be no more than 0.1% for chlorine trifluoride, since the Berthelot equation-of-state was used. For all other molar volume calculations the ideal gas law was used and the error assumed to be no more than one percent. This was justifiable since in most cases

pressures were less than 200 mm. of mercury. Substituting in the above equation an average value of V_M (30,000 cc./mole), ΔV_M (30 cc./mole), and $\Delta(\epsilon - 1)$ (200×10^{-6}), the average error in the molar polarization of chlorine trifluoride was found to be ± 0.4 cc./mole.

Dipole moment. The errors in those dipole moments which were determined from the slopes of the plots of P_M versus $1/T$ were found by differentiation of the equation

$$\mu = 0.0128 \sqrt{\frac{P'_M - P_M}{1/T' - 1/T}}$$

where the term under the square-root sign is the slope in Equation 15.

Differentiation of this equation gives

$$\Delta\mu = 0.0064 \left[\frac{(P'_M - P_M)^{\frac{1}{2}}}{(1/T' - 1/T)^{\frac{3}{2}}} \left(\frac{\Delta T'}{T'^2} + \frac{\Delta T}{T^2} \right) + \frac{\Delta P'_M + \Delta P_M}{((1/T' - 1/T)(P'_M - P_M))^{\frac{1}{2}}} \right]$$

where the values of P'_M at T' and P_M at T were found from the plots of P_M versus $1/T$. These values were taken at the lower and upper ends of the temperature range, respectively. Since errors in the temperature measurements $\Delta T'$ and ΔT , are equal to $\pm 0.05^\circ\text{C}$, the first term in the equation is negligible and the last term in the equation is the contributing factor in the error. The last term indicates that the percentage error will be much greater when the dipole moment is small, or $(P'_M - P_M)$ is small, and when the temperature range is small.

Substitution of the appropriate terms in this equation shows that the error in the dipole moment of chlorine trifluoride is ± 0.11 D.

The error in those dipole moments calculated using molar refraction data was found by differentiation of Equation 17, which gives

$$\Delta \mu = 0.0064 \frac{(P_M - R) \Delta T + (\Delta P_M + \Delta R) T}{\sqrt{(P_M - R) T}}$$

where ΔR is the error in the molar refraction. The value substituted for ΔR included an estimate of the discrepancy between molar refraction, which depends only on the electronic polarization, and molar induced polarization, which is the sum of the electronic polarization plus the atomic polarization. In many cases, especially with the fluorides, experimental values of R and P_A differ by as much as twenty percent. This nevertheless causes very little error in the dipole moment of a compound with a relatively large moment, as indicated by calculations made on iodine pentafluoride. Assuming the error in the molar refraction to be that reported by Malik (55) ($R = 19.2 \pm 0.3$ cc./mole), the error calculated using the above equation was found to be ± 0.07 D. Assuming the discrepancy between the molar refraction and the molar induced polarization to be as much as 25% gave an error of only ± 0.09 D.

Fluorocarbon Derivatives

The errors in the dipole moment determinations of the fluorocarbon derivatives were calculated by the same method as was used for the halogen fluorides. The maximum probable error for a single capacitance measurement using Cell I is plotted versus ΔC in Figure 23. The error in the replaceable capacitance of Cell I was found to be $\pm 4 \mu\mu f$.

Although the errors for small capacitance measurements were larger for Cell I than Cell II, the larger replaceable capacitance of Cell I more than compensated for this.

The errors calculated were in every case the maximum probable errors. The precision of the measurements was much greater than this and indicated that the actual errors were probably less than those calculated. However, since there was a possibility that adsorption of gases on the plates of the dielectric cells introduced errors which were indeterminate, and because the errors due to the deviations from ideality of the gases were unknown, all the dipole moments are reported with the errors calculated for the upper limit of uncertainty.

The dipole moments of the compounds studied in this investigation, and their maximum probable errors, are presented in Table XXVIII. The values of the induced molar polarization, calculated by means of a least-squares treatment of the P_M versus $1/T$ data, are also given for those compounds for which these data were obtained, and compared with the molar refractions found by Malik (55).

TABLE XXVIII
 DIPOLE MOMENTS AND MOLAR INDUCED POLARIZATIONS
 DETERMINED IN THIS INVESTIGATION

Compound	Dipole Moment, D	Maximum Probable Error, D	Molar Induced Polarization	Molar* Refraction
BrF ₅	1.40	⁺ 0.14	21.8 cc./mole	15.48 cc./mole
ClF ₃	0.74	0.11	13.6	10.34
IF ₅	2.24	0.09	--	--
BrF ₃	1.33	0.14	--	--
n-C ₃ F ₇ H	1.62	0.10	13.0	16.67
cyclic-(CF ₂) ₄ O	0.56	0.12	26.5	--
(C ₂ F ₅) ₂ O	0.51	0.12	27.2	23.49
CClF=CF ₂	0.38	0.10	20.2	15.77

* Reference (55)

VI. DISCUSSION OF RESULTS

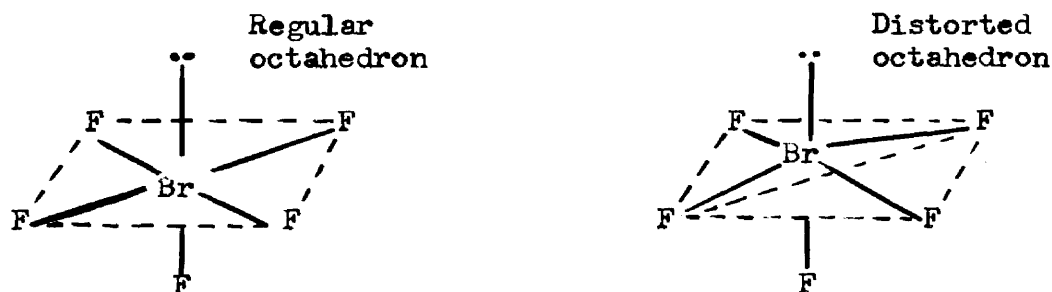
Halogen Fluorides

Chlorine trifluoride. The structure of chlorine trifluoride has been accurately determined from microwave-spectral data (12). This is the only halogen fluoride, except the diatomic compounds, for which bond distances and bond angles have been assigned. This structure has already been presented in Table I. With this information and the dipole moment of chlorine monofluoride, the theoretical value for the dipole moment of chlorine trifluoride can be calculated. The dipole moment of chlorine trifluoride should be that of chlorine monofluoride plus the small contributions from the two Cl-F bonds which are at an angle of $87^{\circ} 29'$ with the center Cl-F bond. These contributions were calculated to be +0.04 for each bond, resulting in a value for the total dipole moment of 0.96 D, which is somewhat higher than the observed value. However, the bond contributing the most to the total moment is shorter by 0.03 Å than that in chlorine monofluoride which could account for the difference since the shorter bond should be associated with greater covalent character and lower moment.

Bromine trifluoride. The structure of bromine trifluoride is probably planar with a structure similar to that of chlorine trifluoride, although the bond distances and angles have not been accurately determined. It was assumed that the bond angles in bromine trifluoride were the same

as those in chlorine trifluoride, and that the bond moment of the Br-F bonds was equal to the dipole moment of bromine monofluoride. These assumptions gave a calculated value for the dipole moment of 1.40 D which agrees with the experimental value of 1.33 ± 0.14 within the experimental error.

Bromine pentafluoride. Several structures for bromine pentafluoride are possible, including a trigonal bipyramid, a tetragonal pyramid with the bromine atom above the plane of the base, and a planar pentagon. The relatively large dipole moment observed (1.40 D) eliminates any of the above structures, as they would exhibit either no dipole moment or a very small moment at the most. A regular octahedron, with the bromine atom in the plane of the four fluorine atoms and an unshared electron pair occupying the sixth corner should have a dipole moment essentially equal to that of bromine monofluoride (1.29 D), since the four Br-F bonds in a plane would not contribute to the total dipole moment. If the bromine atom is slightly above the plane of the four fluorine atoms so that the four F-Br-F angles have the same value as the F-Cl-F angles



in chlorine trifluoride, then a larger dipole moment for bromine pentafluoride would be expected. A structure of this type would indicate that

two fluorine atoms add symmetrically about the bromine atom of bromine trifluoride to form bromine pentafluoride. The calculated value for the dipole moment for this structure is 1.52 D which agrees with the experimental value of 1.40 ± 0.14 D about as well as does the value calculated for the regular octahedral structure (1.29 D). Some support for the distorted structure is found in the dipole moment data for iodine pentafluoride.

Iodine pentafluoride. The large value for the dipole moment of iodine pentafluoride can best be explained by a structure similar to the distorted octahedral arrangement suggested for bromine pentafluoride. Assuming the dipole moment of the I-F bond to be equal to the electronegativity difference (1.5), since the electric moment of iodine monofluoride is unknown, and assuming a structure similar to the distorted octahedron shown above for bromine pentafluoride, the dipole moment is calculated to be 1.9 D. This is considerably lower than the experimental value of 2.24 ± 0.09 D. However, an octahedral structure in which the iodine lies in the plane of the four fluorines would give an even lower calculated moment of 1.5 D. Since the bond moments obtained from electronegativity differences occasionally differ from the observed bond moments by as much as 0.3 to 0.4 D, the discrepancy may be only apparent. The high value of the observed moment could also be due in part to the iodine and fluorine exhibiting unusual electronegativities in a compound of this type, where a large number of highly electronegative groups surround a highly electropositive central atom; however, in this case one would expect a smaller rather than a larger moment.

Frequently proposed symmetrical structures, such as the trigonal bipyramid and the tetragonal pyramid, are definitely excluded by the high dipole moments observed for both iodine pentafluoride and bromine pentafluoride.

Fluorocarbon Derivatives

1,1,1,2,2,3,3-Heptafluoropropane. The dipole moment of this compound

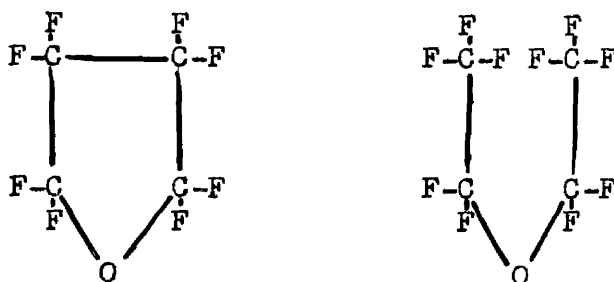


would be expected to be the same as that of trifluoromethane, as was found to be the case. The moment of trifluoromethane is 1.645 D (Table IV) and the observed moment of 1,1,1,2,2,3,3-heptafluoropropane is 1.60 ± 0.10 D. However, both of these compounds would be expected to have dipole moments higher than those observed.

The completely fluorinated compounds have zero moments, so the substitution of a hydrogen for a fluorine atom should produce a moment equal to the sum of a C-F dipole and a C-H dipole since they are oppositely directed. The C-F bond moment is 1.4 D and the C-H bond moment is 0.4 D (56) hence the moment of a fluorocarbon with a single C-H bond should be approximately 1.8 D. However, just as the moments of methyl- and ethyl fluoride are higher than predicted because of inductive effects, the moments of 1,1,1,2,2,3,3-heptafluoropropane and trifluoromethane are lower due to the induced positive character of the

carbon atom in the C-H bond, which reduces the magnitude of the C-H dipole. This effect tends to lower the over-all moment of these compounds.

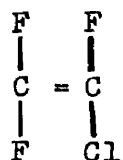
Perfluorotetramethylene oxide and perfluoroethyl ether. These two



compounds should have essentially the same dipole moment since the contributing dipoles lie mainly along the two C-O axes at the same angle, about 108° , in each compound. The value of the dipole moment for 1,1,1,2,2,3,3-heptafluoropropane indicates that the group moment of the perfluoropropyl group is the same as the moment of a perfluoromethyl group. Therefore it is assumed that the perfluoroethyl group has the same moment, and is equal to the moment of the C-H bond subtracted from the moment of 1,1,1,2,2,3,3-heptafluoropropane, or 1.3 D. The C-O bond moment (0.8 D) is oppositely directed to that of the perfluoroethyl group, so that the difference between the two gives the moment directed along the C-O axis in perfluorotetramethylene oxide and in perfluoroethyl ether, and is equal to 0.5 D in each case. There are two of these moments at an angle of about 108° which results in a total calculated moment of 0.55 D for each of the two compounds.

This value is in good agreement with the observed values of 0.56 ± 0.12 D for perfluorotetramethylene oxide and 0.51 ± 0.12 for perfluoroethyl ether.

Chlorotrifluoroethylene. The dipole moment of this compound would be



expected to be the difference between a C-F bond moment (1.4 D) and a C-Cl bond moment (1.5 D), or 0.1 D. The observed value of 0.38 ± 0.1 D is higher than this. This may be explained by the increase in the positive character of the carbon atom in the C-Cl bond induced by the electronegative fluorine atoms attached to it and the adjacent carbon atom. The observed electric moments of trichlorofluoromethane and chlorotrifluoromethane, which should each be equal to the difference between the C-F and the C-Cl bond moments, are 0.45 and 0.39 D respectively.

VII. SUMMARY

Equipment for measuring the dielectric constants of compounds in the vapor phase over a range of temperatures was constructed, and used to determine the dipole moments of eight compounds containing fluorine. Dielectric cells and auxiliary equipment were constructed both for measurements on high-boiling corrosive liquids and for measurements on ordinary low-boiling liquids.

The compounds studied and the values of their dipole moments, were: bromine pentafluoride, 1.40 ± 0.14 D; chlorine trifluoride, 0.74 ± 0.11 D; iodine pentafluoride, 2.24 ± 0.09 D; bromine trifluoride, 1.33 ± 0.14 D; 1,1,1,2,2,3,3-heptafluoropropane, 1.62 ± 0.10 D; perfluorotetramethylene oxide, 0.56 ± 0.12 D; perfluoroethyl ether, 0.51 ± 0.12 D; and chlorotrifluoroethylene, 0.38 ± 0.10 D.

The dipole moment of chlorine trifluoride agreed reasonably well with that predicted from its known structure. The observed electric moment supports a similar structure for bromine trifluoride. The high dipole moments observed for bromine pentafluoride and iodine pentafluoride show that they cannot have symmetrical structures. The large moments can be accounted for on the basis of either a regular octahedral structure or a distorted octahedral structure, although the latter gives better agreement with the data for iodine pentafluoride.

Dipole moments were calculated for the fluorocarbon derivatives from bond moments, and compared with the experimental values. The calculated values agreed with the observed moments if the inductive effects of the strong C-F dipoles were considered.

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