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Title FLUOROBORANES. I. PREPARATION AND PROPERTIES
OF TRIFLUOROMETHYLDI-n-BUTYLBORANE. II. A STUDY OF
DIBORON TETRAFLUORIDE

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Abstract approved

(Major professor)

A large-scale preparative method for potassium di-n-butylborate in triethylamine solvent has been developed. The reaction of potassium di-n-butylborate I with trifluoromethyl iodide has been shown to yield trifluoromethyl di-n-butylborane and other products. Reaction of this substance with boron trifluoride gave trifluoromethyl boron difluoride. Reactions of diboron tetrafluoride, boron tribromide, and di-n-butylboron chloride with trifluoromethyl mercury iodide and bis(trifluoromethyl) mercury have also been studied. In each case a free radical mechanism leads to extensive decomposition of the trifluoromethyl group.

The design and operation of an all-glass, excepting the stainless steel detector unit, gas chromatograph is given. The instrument was operative on both a preparative and analytical scale handling

samples that range in size from less than 0.25 ml up to five ml.

The experimental equipment and technique for the determination of the infrared spectrum of volatile compounds and compounds of marginal stability is described. The apparatus and technique were used to determine the infrared spectrum of diboron tetrafluoride.

FLUOROBORANES.
I. PREPARATION AND PROPERTIES OF
TRIFLUOROMETHYLDI-*n*-BUTYLBORANE.
II. A STUDY OF DIBORON TETRAFLUORIDE.

by

JAMES MAURICE SELF

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FLUOROBORANES.
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I. PREPARATION AND PROPERTIES OF
TRIFLUOROMETHYLDI-n-BUTYLBORANE.

INTRODUCTION

The preparation and study of unusual chemical species has long interested the chemist. Many compounds of boron show chemical and physical properties not expected from a rudimentary study of the element. The ability of boron to nominally violate the octet rule and yet form stable compounds is one of the most striking examples of its departure from the ordinary. The vacant p_z orbital of the boron atom in its trivalent state confers upon it the ability to form strong dative bonds with any substance capable of donating a pair of electrons. This vacant p_z orbital also gives rise to a strong electrophilic effect in a boron compound. A reason for the stability of boron compounds has been suggested by Pauling (120). Pauling states that by a process of charge redistribution and partial double bonding, a molecule such as boron trifluoride can satisfy the octet rule and thus stabilize itself. Even so the boron atom in such molecules can still form strong dative bonds. If one or more of the groups sigma bonded to the boron atom possesses properties not conducive to this charge redistribution and/or partial double bonding, the effect on the thermodynamic stability of the molecule and its chemical behavior may be extensive.

The trifluoromethyl group fits the requirements inasmuch as it is highly electrophilic, does not possess non-bonding electrons on the atom adjacent to the bonding site to allow back-coordination, nor is it capable of back-donation of electron density by a hyperconjugative mechanism. Its properties will be discussed in more detail later.

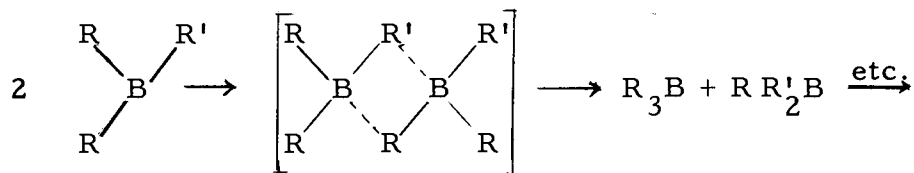
Development of the organic chemistry of boron has occurred in large part since 1950. The work of A. Stock and E. Krause in Germany and H. I. Schlesinger in the United States in the period 1920-1940 laid the foundation for this development. Various types of organoborons have been prepared such as trialkylboranes, alkyl-diboranes, metal tetraalkylborates and borohydrocyclics. This work has been reviewed by Gerrard (58) and discussed by Baker (8) and Schaad (139)

Theories have been proposed to explain the fact that halogens, hydrogen, and small alkyl groups, all of which are normally monovalent, can form bonds with two groups to yield a stable dimer in trimeric compounds of Group III elements. The most popular of these are those expounded by Pitzer (132), Sanderson (136; 137) and Rundle (135). Rundle's concept, the three-center bond, was applied to the boron hydrides with slight modifications by Eberhardt et al. (47). The three-center bond model allows partial delocalization of electron density by considering bonds in which an electron pair occupies the region of overlap of three atomic orbitals from three

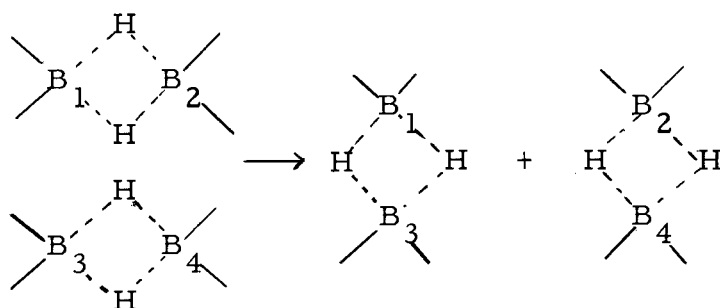
atoms. In this nomenclature a normal covalent bond would be termed a two-center bond. The model rather successfully accounts for molecular stabilities and structures in electron-deficient species such as the boron hydrides, but gives somewhat erroneous values for molecular dipoles and other observable physical constants.

A molecular orbital treatment of B_9H_{15} by Dickerson et al. (45) and of $B_{10}H_{14}$, B_4H_{10} and B_5H_{11} by Moore et al. (120) gave models which are in a little better agreement with experimental chemical and physical properties of the higher hydrides of boron than is the three-center bond model.

Mechanisms for the disproportionation of many unsymmetrically substituted boron atoms have been proposed by Long et al. (104), Parsons et al. (124) and Sanderson (137). Long et al. (104) and Parsons et al. (124) proposed a disproportionation mechanism that requires the formation of a bridge structure in a transient state, followed by an electronic shift to give symmetrical products. R and R' = different halogen atoms, hydrogen atoms, or small alkyl groups.



Sanderson (137) suggested that it involves a bimolecular reaction.



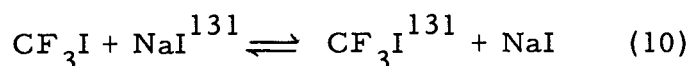
This mechanism is possible for dimers but the probability of its occurrence in the disproportionation of monomers is low.

The chemistry of the known compounds formed by the various elements with completely fluorinated alkyl groups has been reviewed recently by Clark (34) and earlier by Emel us (47), Lagowski (101) and Emel us and Haszeldine (50). Complete replacement of fluorine for hydrogen on an alkyl group considerably alters the electronegativity of the group. The electronegativity of the normal alkyl group is approximately 2.2 on the Pauling scale (121). Lagowski (102), using bond dissociation energies and infrared absorption frequencies, has calculated the electronegativity of the trifluoromethyl group to be approximately 3.3 on Pauling's scale. As a consequence, in virtually all cases, the trifluoromethyl group will be bonded to an element or radical of electronegativity less than itself. The high electronegativity of the trifluoromethyl group gives rise to a considerable decrease in the availability of electrons on the atom or group to which it is attached as compared to a methyl group and other potential substituents, excepting fluoride and a few other groups.

The trifluoromethyl group differs from both fluoride and methyl groups in at least one other respect that is of considerable importance in boron derivatives. Substituents such as fluoride can enhance the stability of particular boranes by back-coordination of non-bonding electrons to the p_z orbital of boron as was pointed out earlier. The same behavior is expected for other substituents with non-bonding electrons including all substituents in which the bonding atom is an oxygen, nitrogen or other Group V, VI or VII elements. Primary and secondary alkyl groups can also back-coordinate via a hyperconjugation mechanism. Neither mode of behavior is possible with perfluoroalkyl groups. Perfluoroalkyl groups, therefore, not only reduce sigma bonding electron density in the region of the boron but cannot contribute electrons to the boron atom through any known electronic redistribution process. It is expected, then, that trifluoromethyl substituents will considerably enhance the electron-deficiency and therefore the Lewis acidity of a boron atom. Since intermolecular interactions to form stable borane dimers and to form similar species in the transition state of disproportionation reactions are highly dependent upon the Lewis acidity of the boron atom, it is expected that trifluoromethyl boranes will behave quite differently from other known boranes in these respects. Hopefully a series of these compounds will give valuable information about the factors that influence dimer formation.

The synthesis of trifluoromethyl boranes offers many difficulties because those very properties that lead to the interest in the compounds contribute to their thermodynamic instability. In order to properly select those potential syntheses that are most promising, the chemical and physical behavior of the trifluoromethyl group and its known derivatives will be reviewed in some detail.

Trifluoroiodomethane and iodomethane both show strong continuous absorptions in the near ultra-violet with trifluoroiodomethane showing a maximum at about 2680 Å. Trifluorochloromethane and trifluorobromomethane do not absorb above 2300 Å (10; 35). Ultra-violet spectra studies of trifluoroiodomethane in basic solvents (Et₃N, Et₂O, etc; Et = Ethyl) showed shifts of approximately 20 μ to shorter wavelengths, as compared with the same materials in light petroleum oil solutions. It is postulated that this shift is due to formation of species of the type (R_FI)B or (R_FI)⁻B⁺ (R_F=CF₃) (B = base). This would indicate that reactions occurring by ionic mechanism would be facilitated in basic solvents (68; 69). For example:



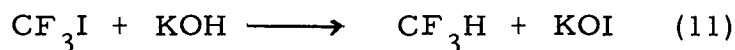
The exchange takes place in alcoholic solutions but more work is needed to determine for certain that an ionic mechanism occurs.

From this it is apparent that even if an ionic mechanism cannot occur, the stability of the trifluoromethyl group is enhanced in

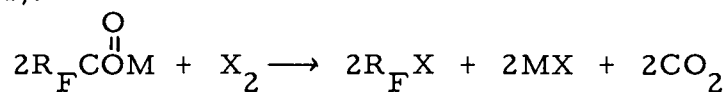
a basic medium.

The conductivity of liquid CF_3I at -45°C is less than 4×10^{-9} $\text{ohm}^{-1}\text{cm}^{-1}$ indicating that CF_3I is not appreciably ionized (11). A study of the solvent properties of CF_3I confirm that it is not ionized (40).

In perfluoroiodoalkanes the extreme electron withdrawing effect of the perfluoroalkyl group is so strong that the iodine characteristically behaves as a positive halogen in solvolytic reactions. For example:



The perfluoroalkylhalogens are usually prepared by the reaction of a halogen with a metallic salt of the respective perfluoroalkyl acid (38; 70; 74; 81).



(R_F = completely fluorinated alkyl group, X = halogen)

Endeavors to develop a general method for the synthesis of perfluoroalkyl derivatives of the various elements led to attempts to prepare a Grignard reagent of the perfluoroalkyl iodides or bromides. With carbon chains of three carbons or larger these attempts have been rather successful (71; 72; 84; 85; 110; 115; 128; 130). There has been one report of a perfluoroethyl Grignard reation (122).

Attempts to prepare a Grignard reagent of the trifluoromethyl

group have not been so successful (67; 114). The evidence for the existence of such a compound is based on the formation of small amounts of fluoroform upon addition of protonic substances.

Similarly perfluoroalkyl derivatives of zinc (79; 119) and lithium (93; 116; 129) have been prepared with carbon chains of three carbons or greater, but as yet these species have not proven to be useful reagents for other syntheses. The existence of a trifluoromethyl derivative of zinc or lithium has not been proven. Perfluoroalkyl derivatives of lead, tin and silicon have been prepared and studied (95; 97; 98; 125; 145; 30; 32; 33). In the case of these three elements the trifluoromethyl derivatives are known. Perfluoroalkyl derivatives of mercury (9; 49; 50; 51; 52; 53; 63; 80; 134) are potentially useful reagents because they are reactive and in general not hard to handle. As yet, they have not been successfully applied to the synthesis of perfluoroalkyl derivatives of other elements. The most widely studied group of perfluoroalkyl derivatives is the perfluoroalkyl derivatives of the group five elements of the periodic chart (14; 17; 46; 76; 78; 153; 154). Excepting the halogen derivatives, these elements are the most stable and easiest to handle. Their stability is unquestionably due to the presence of non-bonding electrons in their valence shell.

Recently, Knungants (101) has made a study of pseudohalogen properties of the trifluoromethyl group. In some of its properties

the trifluoromethyl group can be considered a pseudohalogen but the comparison is only superficial and not useful for an extrapolation of physical and chemical behavior from the derivatives of pseudohalogen to trifluoromethyl derivatives (35).

In many of the reactions of the CF_3 group, as in the pyrolysis of tris (trifluoromethyl) arsine (7), difluorocarbene is generated.

Difluorocarbene polymerizes to C_2F_4 , $\text{F}_2\text{C}=\text{CF}_2$, and higher polymers (7; 105).

Difluorocarbene can be produced by several methods (18; 45; 56; 86; 105; 141). The heat of formation of difluorocarbene is small for a specie of this type, AX_2 , ($\text{X} = \text{hydrogen or halogen}$). The values reported are $\Delta H_f = -20 \text{ kcal mole}^{-1}$ (86), $-35 \text{ kcal mole}^{-1}$ (106), $-17 \text{ kcal mole}^{-1}$ (107) and $-45 \pm \text{ kcal mole}^{-1}$ (110). Even though there is considerable deviation among these reports they are all much less than any known heat of formation of other species of formula AX_2 .

Physical studies of difluorocarbene such as the vibrational spectra (109), electron spin resonance (1), and absorption spectrum (13) indicate that there is a considerable contribution to the stability of the carbene by π bonding and in the ground state the electrons are paired. This is supported by the fact that difluorocarbene has a relatively long half-life (5×10^{-4} to 1×10^{-3} seconds) in solution (55; 106; 141). These observations suggest a synthetic method for trifluoromethylboranes wherein a compound containing a B-F bond

is added across difluorocarbene. Anduades (3) gives evidence for the analagous insertion of difluorocarbene in an N-F bond. However, Mahler (105) reports that $(CF_3)_3PF_2$, a substance known to produce difluorocarbene readily, does not react with boron trifluoride.

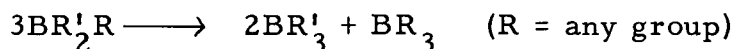
Early attempts to prepare perfluoroalkyl boranes failed (12; 103). Lagowski et al. (103) predicted that perfluoroalkyl derivatives of the group III elements, especially boron and aluminum, would be impossible to synthesize because of rapid disproportionation to yield BF_3 and some other specie. His prediction was based on the lack of stabilization of the p_z orbital of boron in trimeric compounds by a perfluoroalkyl group. Shortly after his prediction reports of such species appeared. Parsons et al. (123) reported trifluoromethylborondifluoride. Brinkman, Stone, Kaesy, and Stafford reported compounds of the type $CF_2 = CFBX_2$ (24; 96; 144), and Chambers et al. reported on the synthesis of trifluoromethylfluoroborate anion (29; 31).

The stability and even the existence of the perfluorovinylboranes, Brinkman (24; 96; 144) reported, is attributed to the higher electron density around the double bond in the vinyl group. Resonance stabilization of the p_z orbital of the boron is possible. The stability of the trifluoromethylfluoroborate anion is attributed to the complete saturation of valence on both the carbon and boron so that there is no electron deficiency in this ion; it is analagous to

the fluoborate anion, BF_4^- . The only saturated perfluoroalkyl derivative of trivalent boron that has been isolated is trifluoromethylboron difluoride. This substance does not readily disproportionate to symmetrically-substituted species but does eliminate difluorocarbene readily to form boron trifluoride and fluorocarbon polymer in the presence of catalysts (123).

Haupttschein et al. (82) reported the preparation of $\text{LiAl}(\text{CF}_3)_2\text{H}_2\text{I}$. As of yet, no additional chemistry or data is available.

The question of the stability of unsymmetrically-substituted boranes toward disproportionation reactions



is unresolved. There are many conflicting reports in the literature on the stability of particular boranes. There are, apparently, very active catalysts for the disproportionation reactions so that stability is a function of the manner of preparation and state of purity of the compound in many cases. For example, it has long been the predominant opinion in the field, based on numerous observations, that substances of the type $\text{BX}_2\text{X}'$ ($\text{X}, \text{X}' = \text{halogen}$) could not exist. Coyle et al. (36; 37) recently reported from N. M. R. studies the existence of BBrClF , BF_2Cl , and BF_2Br at low temperature. Brinkman et al. (23) have shown that halogen exchanges rapidly on species of the type RBX_2 and R_2BX while alkyl radical exchange could not be detected. Cotton et al. (34) have correlated through

theoretical considerations of acceptor properties, reorganization energies and π bonding in boron and aluminum halides the experimental data available on exchange of halogen and alkyl groups on boron.

From the previous discussion of literature reports, some generalizations can be made about the most promising methods to attack the problem of synthesizing trifluoromethyl boranes. A basic solvent should be used to enhance the stability of the trifluoromethyl group and to complex the boron specie. In this manner, the boron can be preserved in a tetravalent state until in a final step the desired compound can be displaced from the basic solvent by another Lewis acid. The probability of bond formation with the electron withdrawing trifluoromethyl group is also enhanced if the electric field of the trifluoromethyl group is increased. The solvent must be a liquid at readily accessible temperatures and have sufficient volatility at room temperature to facilitate easy handling in a vacuum system. The solvent should also form a very stable compound with some Lewis acid other than a borane in order that it be displaced readily from a boron-containing compound. A solvent that satisfies all of these requirements is triethylamine.

An attractive synthetic method utilizes potassium di-n-butylborate-I as an intermediate. Auten et al. (6) prepared this substance and observed that it reacted with iodomethane to yield di-n-butylmethylborane (Bu = the n-butyl group).



An analogous reaction utilizing trifluoroiodomethane in place of iodomethane should serve to attach a trifluoromethyl group to the boron (8).

Another promising synthetic method is the reaction of di-n-butylboron chloride with trifluoromethylmercury iodide.



A third method that may yield the desired compound is the reaction of diboron tetrafluoride with trifluoromethyl mercury iodide or bis(trifluoromethyl) mercury. The method depends upon the reducing power of diboron tetrafluoride, an unknown quantity.



Since the mercury in both $(\text{CF}_3)_2\text{Hg}$ and CF_3HgI is easily activated by ultraviolet radiation, such irradiation may catalyze the reaction.

Baker (8) attempted to prepare Bu_2BCF_3 by the reaction of trifluoromethyl iodide with potassium di-n-butylborate I. He was never able to isolate trifluoromethyl di-n-butyl borane, partially because of the small scale preparation that he used in following Auten's directions (6) and partially because of the difficulty in separating the air-sensitive, slightly volatile trifluoromethyl di-n-butylboron from a complex mixture of unreacted starting materials and by-products such as tri-n-butyl borane and tetra-n-butyl diboron. These latter materials were reported to be formed by Booth (22) in other reactions of potassium di-n-butyl borate I. The same

synthesis will be carried out on a much larger scale in an attempt to separate di-n-butyltrifluoromethyl borane. A high-temperature preparative scale gas chromatograph will be constructed and used for the ultimate purification of the product.

It is also the purpose of this work to initiate a study of the properties of the trifluoromethyl boranes. Of prime importance is the stability of this type of compound toward both disproportionation and elimination of difluorocarbene in a variety of molecular environments. The Lewis acid strength of any trifluoromethylboranes produced will also be investigated.

EXPERIMENTAL

Apparatus and Technique

Vacuum Manipulation

All reactions and purifications of products were carried out using a conventional vacuum apparatus as described by Sanderson (138). Special apparatus were constructed when necessary and they will be described in connection with the experiment where used.

Fractional condensation was generally used for the separation of volatile mixtures. The method depends upon the fact that the residual vapor pressure of different compounds becomes negligible at different temperatures. Since a logarithmic relationship exists between vapor pressure and temperature, the rate of change of vapor pressure is greatest at high pressure (or temperature). A vapor pressure of .1 mm mercury or less was considered negligible.

The apparatus used in this technique is a fractionation train, Sanderson (138, p. 88-90). The fractionation is achieved by placing cold baths of decreasing temperature around U-tubes (Sanderson, 138, p. 88) in the direction of gas flow. Each component condenses in the first U-tube at which its vapor pressure is negligible so that proper selection of cold baths allows separation provided the

components differ sufficiently in volatility. This method of separation is roughly equivalent in efficiency to a distillation separation using a column of one theoretical plate. A complete description of this technique is given in Sanderson (138, p. 90). Gas chromatography was used where high purity of materials was required.

Gas Chromatography

The problems encountered in preparative scale gas chromatography are, in some respects, parallel to those of analytical gas chromatography, but in general these problems grow larger exponentially as the columns are enlarged. By definition, preparative scale gas chromatography means the separation of large samples, 1-25 ml, but in a more practical aspect, 1-5 ml.

A major problem in preparative scale work is the rapid volatilization of a sample to give plug injection. A lot of energy is consumed when 5 ml of a liquid is volatilized in a short time. If a sample is not completely volatilized in the vaporizer, it passes to the column packing where it withdraws the necessary heat and in doing so lowers the column temperature. Therefore, the vaporizer must supply a large amount of heat rapidly. Atkinson and Tuey (4) give statistics on the requirements.

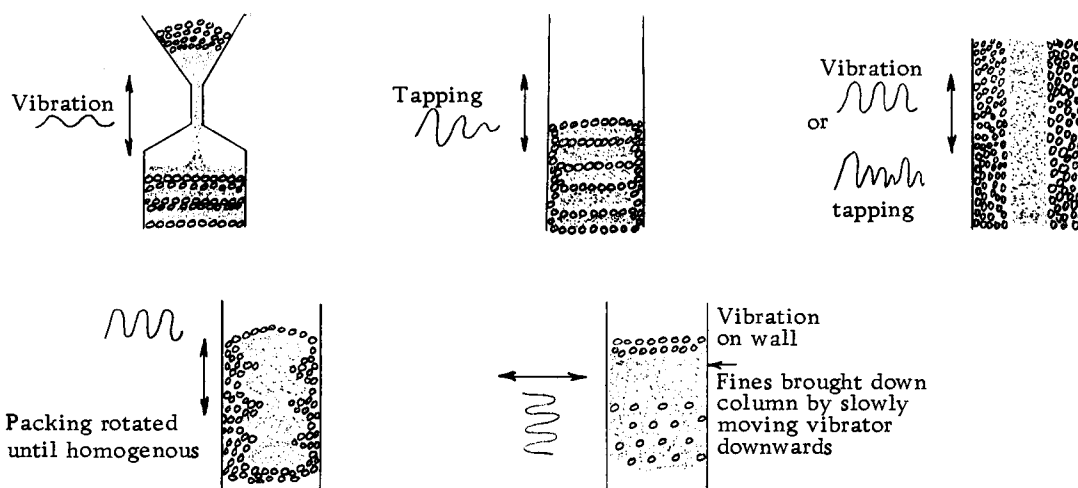
Filling a vaporization chamber with a material to increase the heat capacity or placing a demand type heating unit in the vaporizer

have been used to supply the necessary heat of vaporization.

The pressure created by the vaporization of the sample may force the sample upstream against the carrier gas flow. This can be prevented in some cases by a non-return valve (91). Huyten et al. (88) reported no problem with the vaporization of 1 ml samples.

A very important consideration is the technique used to pack the column. In a small diameter column an irregularity in the uniformity of the packing does not present too much of a problem, but on the preparative scale it does. The variation of the gas flow pattern across a cross section of a larger column (3-5 inches) can give rise to serious distortions. As the column diameter gets larger the velocity profile gets worse. The diffusion of gas perpendicular to the direction of flow cannot compensate for these variations as it does in small diameter columns (88).

Huyten et al. (88) have studied flow variation across a three inch column. It was found that flow down the outside of the column was as much as 1.5 times that in the center. In the same report an account is given of a study of the various approaches to pouring, vibrating and beating a column while packing. Lateral and vertical variations in the density of the solid support were observed. Pypker (133) made a similar study using mixtures of differently colored 20/40 and 70/120 mesh celite. The results of these studies are shown on the following page.



Golay (59), from theoretical considerations, postulated that restrictions placed along a column which forced the sample front to straighten out would prove beneficial. A restriction lengthens the path along the walls without affecting the path-length in the body of the column. Amy et al. (2) demonstrated the validity of this theory. Huyten et al. (88) also obtained better results by using small diameter connecting tubes between sections of their column. Amy et al. (2) have shown that if these connectors are not packed, pressure surges are noted as predicted by Weinstein (151; 152).

The detector for preparative scale work presents no special problem. All of the gas stream can go through the detector, or a given fraction. Preparative scale gas chromatography usually uses a heavy liquid loading to increase capacity (42).

The preparative scale gas chromatograph usually gives the efficiency of the analytical chromatograph. There is considerable

disagreement as to whether or not results worsen because of increasing diameter (21; 42; 43; 54; 61; 89; 90; 100; 147).

The problems of greatly increased sample to area ratio and larger diameter work together to lead to several difficulties. A fortunate aspect is that one can trap out the center portion of a peak when a clean separation cannot be achieved. A very stable liquid phase is necessary in preparative scale work to avoid contaminating samples.

The Gas Chromatograph

A gas chromatograph was constructed with these considerations in mind, in order to facilitate the separation of larger quantities of material than an analytical chromatograph can handle with special provisions for the particular chemical nature of the boranes. A general schematic of the Gas Chromatograph is given in Figure 1.

The Oven (Air Bath)

A cross section of the wall of the oven is given in Figure 2. All six faces of the rectilinear parallelepiped were constructed in the same manner. The oven was made in two fitting halves with geometry and dimensions as shown in Figure 3. Figures 4 and 5 show the basic air flow inside the oven. Figure 6 gives the dimensions and construction of the 100 watt heating element for the oven. The two halves of

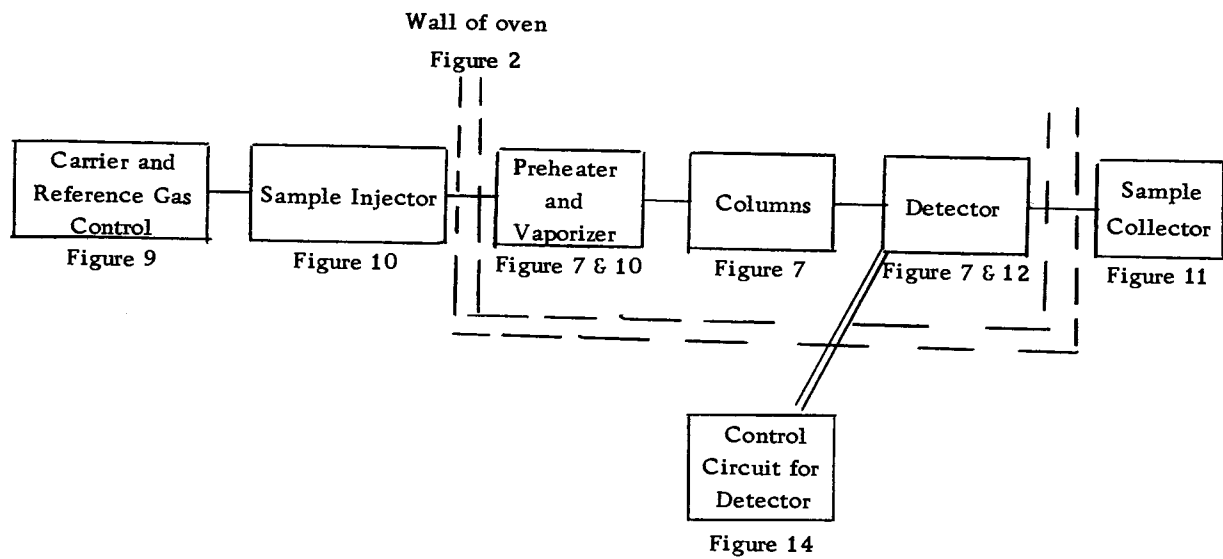


Figure 1. Gas Chromatograph.

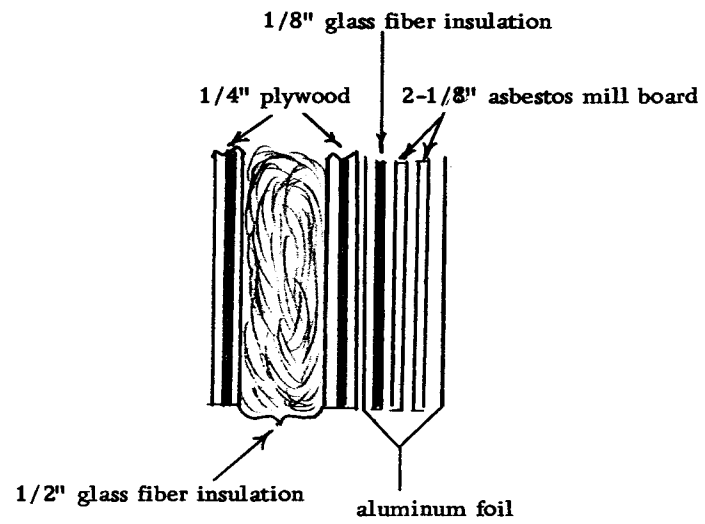


Figure 2. Wall of Oven.

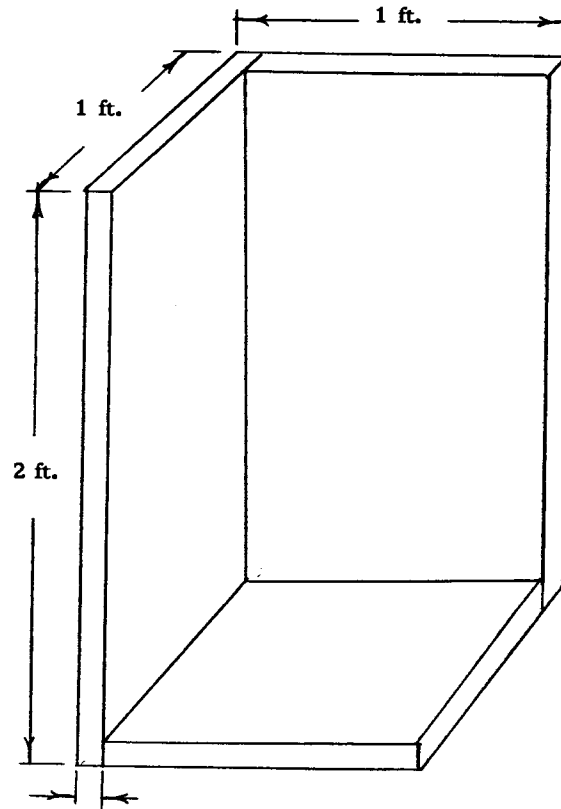
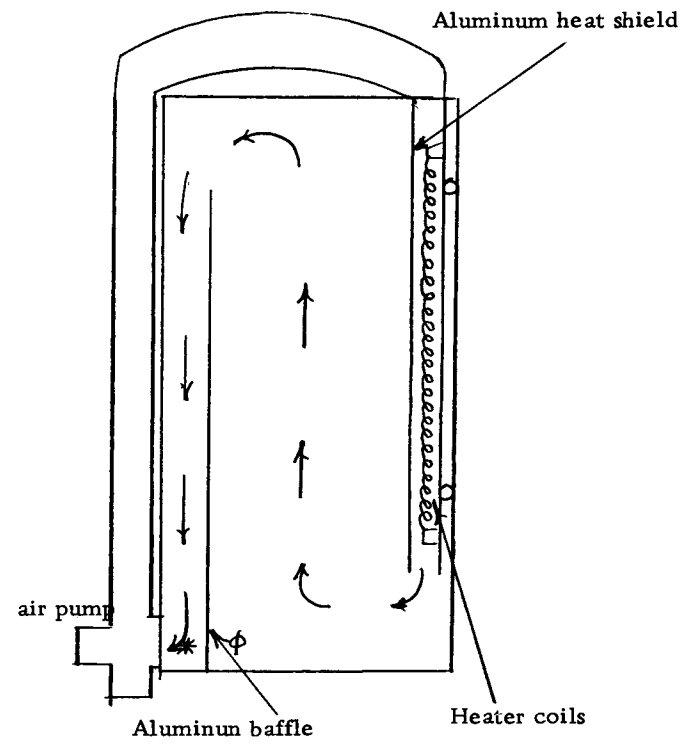
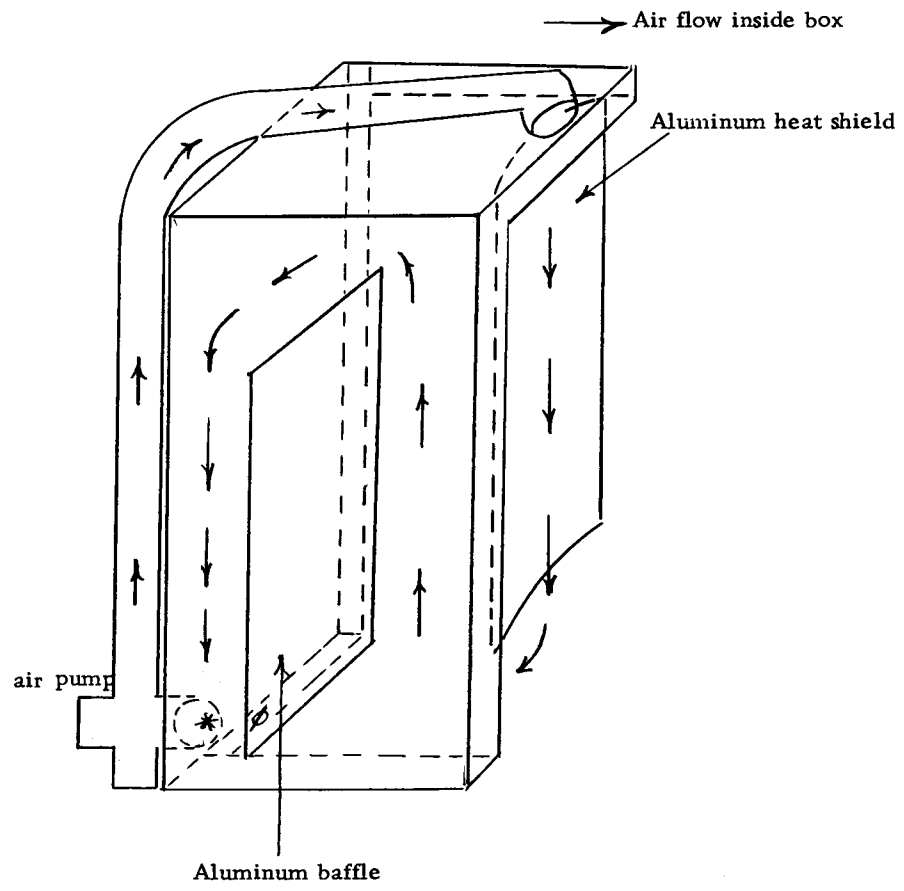


Figure 3. Dimensions of Oven.



Figures 4 and 5. Basic air flow inside oven.

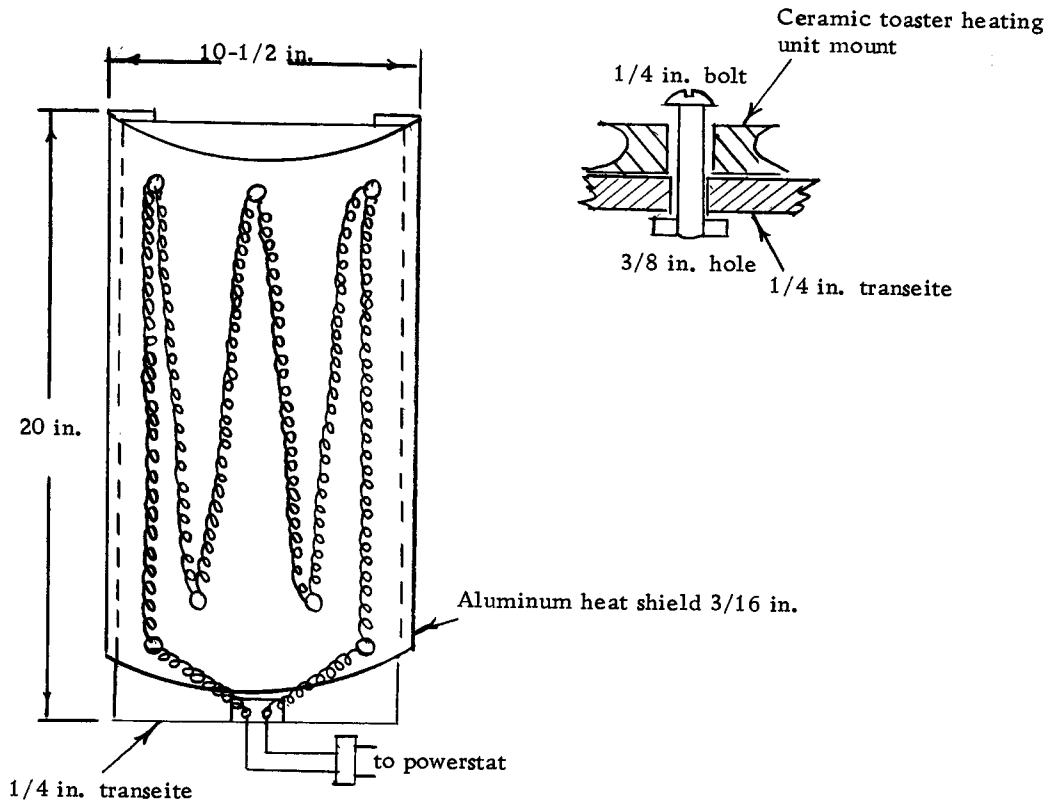


Figure 6. Heater Construction.

the oven are held together by eight loop and clasp latches.

Figure 7 shows the arrangement of the (Gow-Mac) Gas Density Balance, the preheater and vaporization chamber, 100 watt oven heater, the aluminum baffle, the thermoregulator (Quick set 4-238A, American Instrument Company, Silver Springs, Maryland), the 2 meter coil of 10 mm I D. pyrex tubing, and the electrical hook-up for the heater. The powerstat for the oven heater is turned on and off by a vacuum tube relay controlled by the thermoregulator. The powerstat for the preheater is set at a constant value which is just a little larger (approximately 10 percent) than the setting on the powerstat for the oven heater. This procedure gave a smooth heating and cooling cycle for the oven and insured that the gas passing through the preheater was raised to the temperature of the box. The recycling pump is a squirrel cage type with a continuous duty, 115 volt AC-3000 rpm motor (Figures 4 and 5).

Thermocouples (copper-constantan) were placed in the box at the position stated below and the temperature of respective positions was monitored with a potentiometric recorder. Figure 8 shows the switching circuit for the thermocouple and a potential bucking device. The bucking device was placed in the circuit to cut out part of the potential of the thermocouple so the potential could be read on the 1 MV scale of the recorder (Figure 14). The thermocouples were hooked up in this way so that it would be easy to monitor the

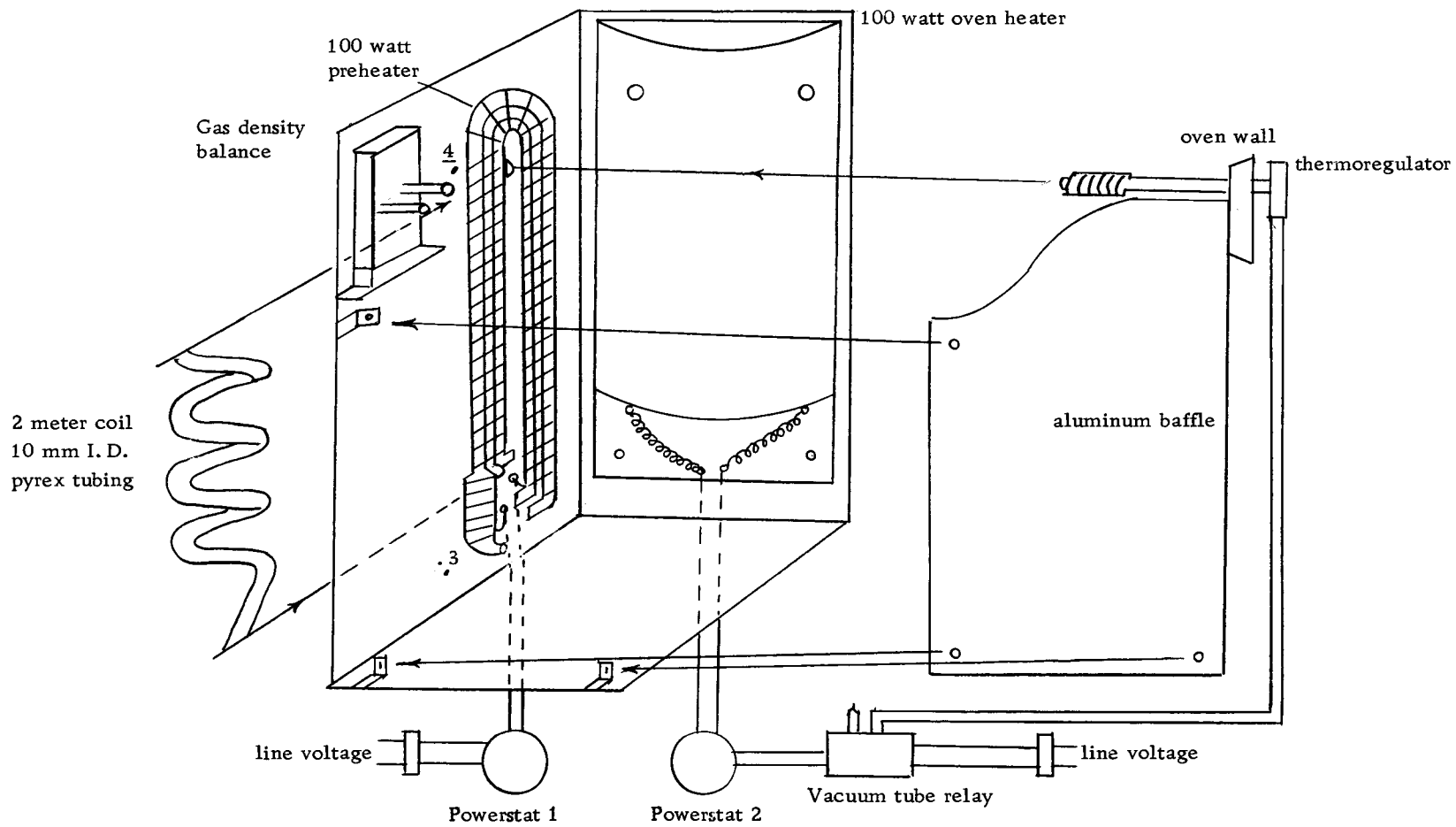


Figure 7. Placement of components inside oven.

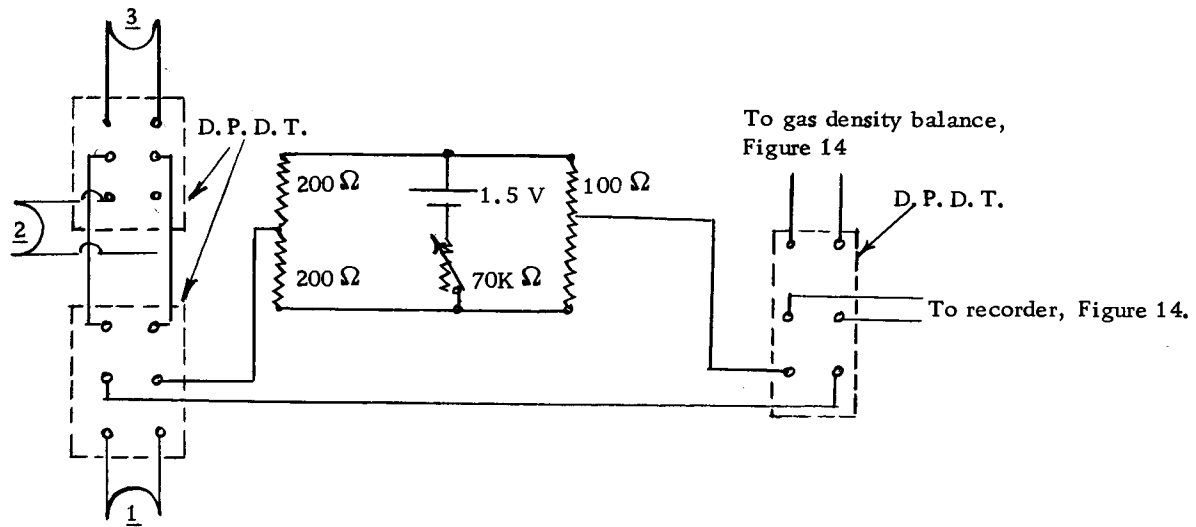


Figure 8. Thermocouple control circuit.

temperature at various positions while the chromatograph was operating.

Temperature control and variation was determined by placing four thermometers, which had been calibrated at 100°C , at various points in the oven. Thermometer (1) was placed near the air outlet inside the chamber (the * in Figures 4 and 5); (2) on the opposite side of the aluminum baffle from thermometer (1) (\emptyset in Figures 4 and 5); (3) approximately 2 cm from the vaporization chamber (Figure 7); (4) midway between the Gas Density Balance and preheater (Figure 7).

After the circulation system had operated for 12 hours (thermoregulator set at 100°C), the four thermometers read (1) 99.5°C , (2) 100°C , (3) 100.5°C and (4) 104°C . The value for (4) is high, apparently due to the fact that the thermometer was so close to the preheater. When thermometer (4) was pushed into the box 3 or 4 cm it read 100.5°C . As the 100 watt heating unit switched on and off there was no change in the thermometer reading. Thermocouples were placed (1) in the Gas Density Balance, (2) on the column, (3) in the approximate geometric center of the box in order to measure the temperature of these areas and the variation in temperature as the heating element cycled. Thermocouple (1) read 103°C with a variation of less than $.088^{\circ}\text{C}$. The maximum variation is assigned on the basis that $.088^{\circ}\text{C}$ change represents the width of a recorder chart

line at a full scale response of 1 MV and no change was observed. The high reading of 103°C was presumed to arise from the close proximity of thermocouple (1) and the preheater. Thermocouple (2) read 102°C with a maximum variation of $\pm .09$ and (3) $102 \pm .17$ as the heating element cycled.

Figure 9 shows the control system for the carrier gas.

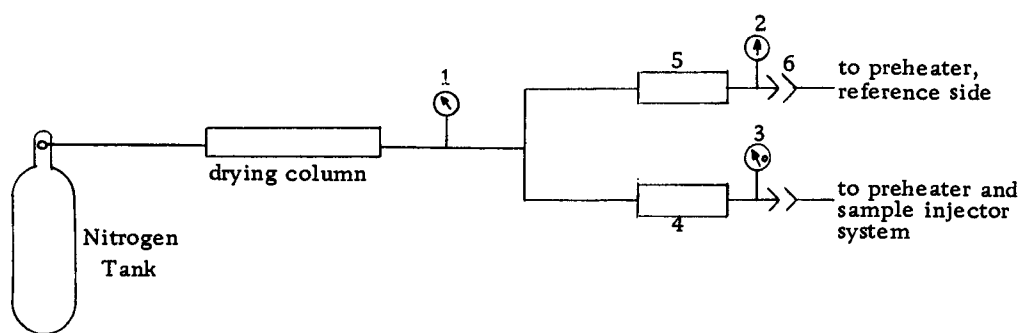


Figure 9. Control system for the carrier gas.

The nitrogen used was Matheson prepurified (99.5 percent). The drying column contained P_2O_5 on glass bends. One, 2 and 3 are pressure gauges; 4 and 5 are 63BU-L Constant Differential type flow controllers (Moore Products Company, Spring House, Pennsylvania); 6 is a break in the system where a flow meter could be attached to check the flow rate in each leg.

Figure 10 shows the sample injection system and preheater. The heating unit around the preheater and the vaporization chamber (C) is 100 watts. A sample is sealed on to the solid glass rod D in a fracture bulb as shown in Figure 11. Reference carrier gas entered B and passed

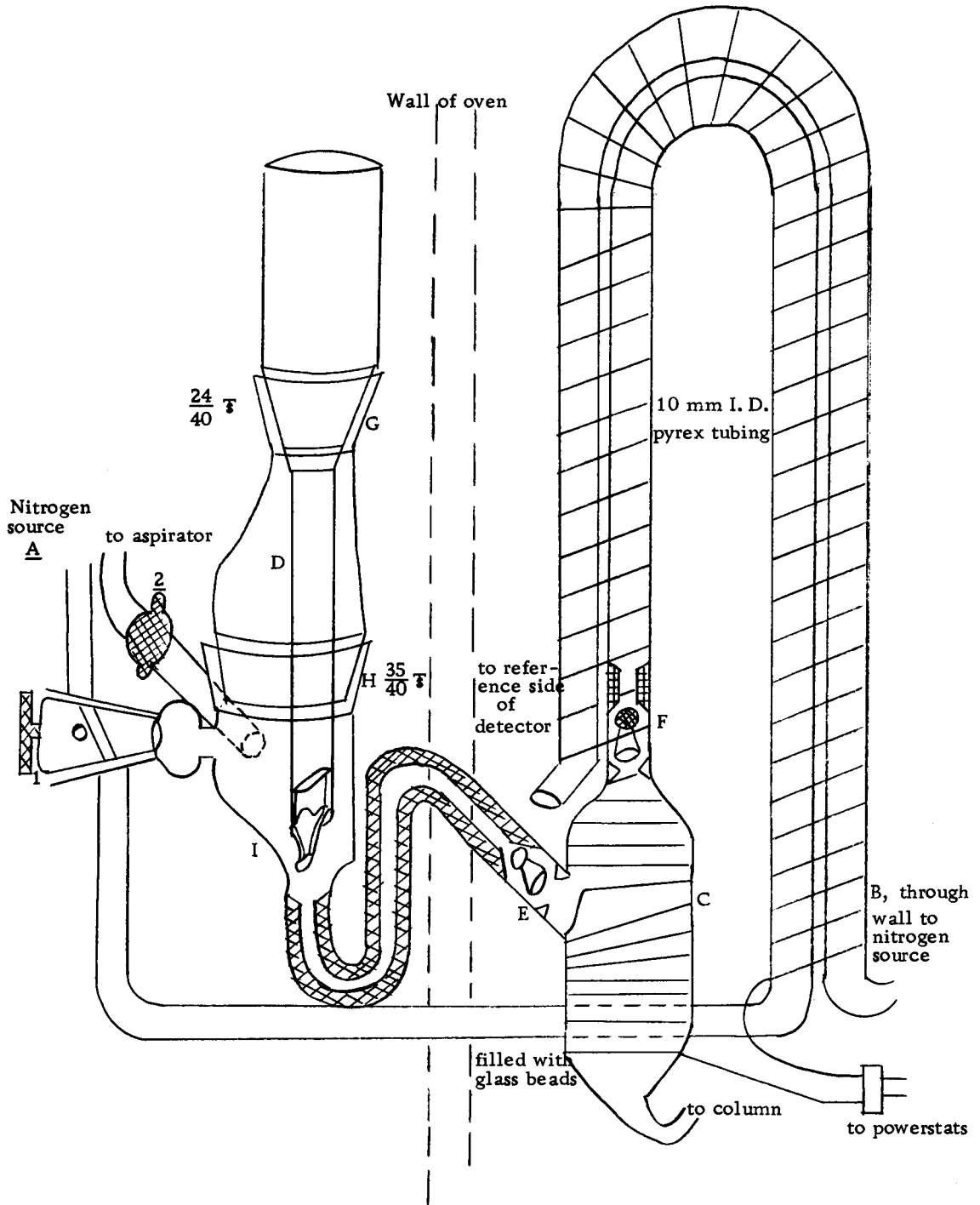


Figure 10. Preheater and sample injection system.

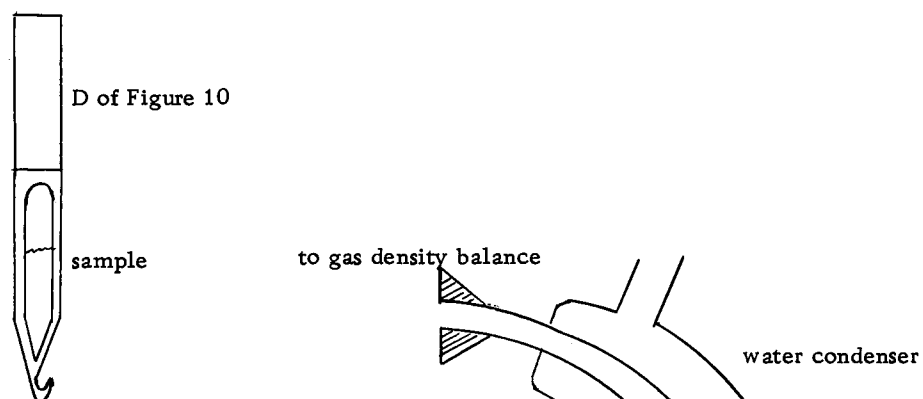


Figure 11. Sample injection bulb.

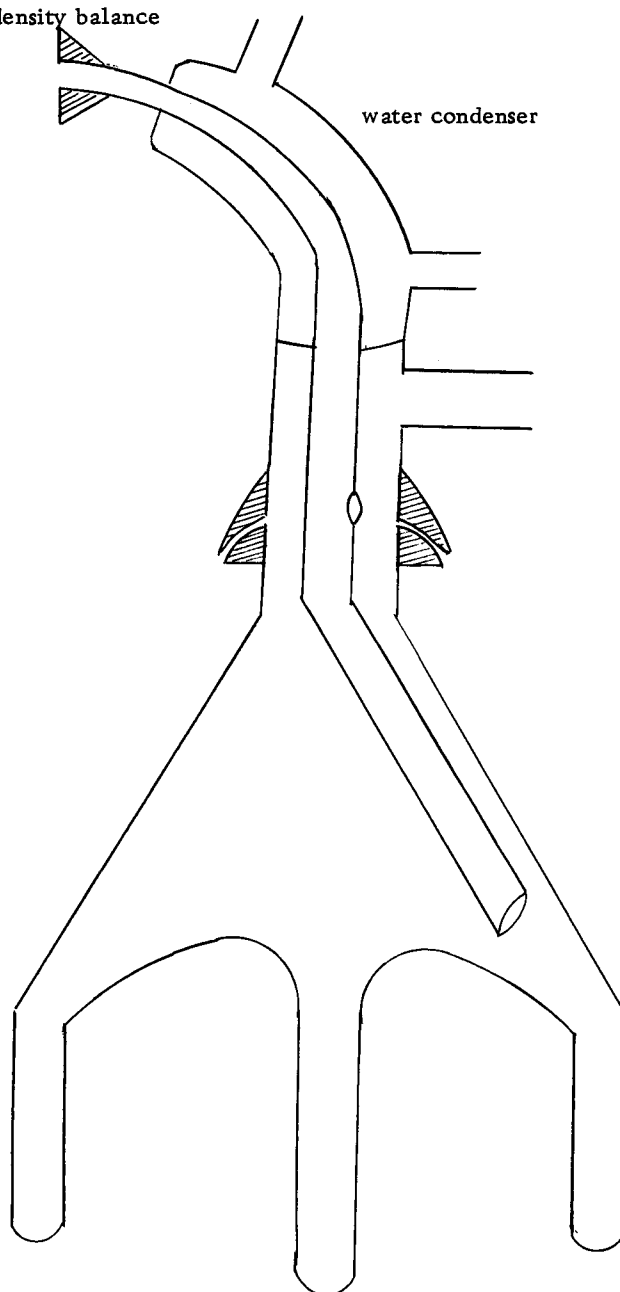


Figure 12. Sample Collector

through the preheater and on through a two meter 10 mm pyrex glass coil to the reference side of the detector. Sample carrier gas entered A through the preheater and passed on to the chromatographic column. The tip of the fracture bulb was broken off by rotation of D at G and H. In the event that the sample did not flow into the sample injection chamber I, stopcock 2 was opened and the pressure was reduced inside the chamber with the aid of an aspirator. During this operation the non-return valve, E, closed so as not to disturb the flow inside the column. Once the pressure was reduced, and the sample had flowed into the injection chamber, stopcock 2 was closed. Stopcock 1 was then rotated to direct the sample carrier gas into the injection chamber. The non-return valve E opened and non-return valve F closed. The sample was forced through the capillary tubing into the vaporization chamber C. This series of operations gave plug injection.

The sample receiver is illustrated in Figure 12.

Detector (Gas Density Balance)

The detector used in the chromatograph was the Gow-Mac 091 hot wire Gas Density Balance, of stainless steel construction (Gow-Mac Instrument Company, Madison, New Jersey). The gas inlets and outlet were fitted with stainless steel O ring connectors (Kontes Glass Company, Vineland, New Jersey) which matched pyrex glass

0 ring connectors fitted with viton O rings. The entire system is pyrex except for the detector.

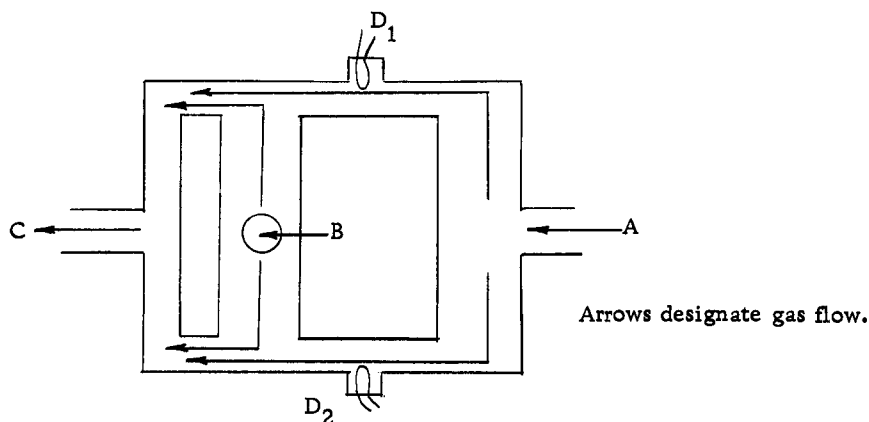


Figure 13. The gas density balance.

Review of Theory and Operation of Gas Density Balance (60; 64; 111; 127)

The reference gas enters the detector (Figure 13) at A and the sample carrier gas at B; C is a common exit for both streams. As shown in Figure 13, the gases coming in at A and B are each split into two streams and then brought together at outlet C. The hot-wire detectors (D_1 and D_2) are placed in a measuring bridge in the two streams.

The detector is mounted vertically as drawn in Figure 7 in order to give a differential flow rate of the gases entering at A and B, which have different densities. If the gas entering the detector at B has the same density as the gas entering at A, the flow of gas across D_1 and D_2 will be the same, therefore the rate of cooling at

D_1 and D_2 will be the same. D_1 and D_2 have the same resistance with the same temperature dependence.

If the gas entering at B has a density greater than the gas entering at A the relative flow rate of the reference gas across D_2 is less than across D_1 . Consequently, cooling rate will change and D_2 will be hotter (have greater resistance) than D_1 , causing an unbalance in the measuring bridge. If the gas entering at B has a density less than the gas entering at A, the reverse of the situation described above will occur and a signal of opposite sign will be generated.

In all cases described above the flow rate of the gas leaving the detector at C is constant, and only the flow rate of the interior gas stream varies. These changes in differential flow rate result in pressure changes in the various pathways but the total pressure drop across the detector will remain constant. The quantitative relation of pressure drop, density and flow are based on Bernoulli's theorem as shown in Equation 1.

$$\begin{aligned}
 (1) \quad \Delta P_1 &= \rho_1 (X_A - X_B) - F'U_1 = 0 \\
 \Delta P_2 &= \rho_2 (X_A - X_B) - F'U_2 = 0 \\
 \hline
 \Delta(\Delta P) &= \Delta \rho (X_A - X_B) - F'\Delta U = 0
 \end{aligned}$$

where

$$\begin{aligned}
 P &= \text{pressure} \\
 \rho &= \text{density} \\
 (X_A - X_B) &= \text{height of column of gas} \\
 F' &= \text{coefficient of friction} \\
 U &= \text{flow rate}
 \end{aligned}$$

The first term in each equation is the pressure drop developed by a change in density. The second term is the pressure drop expended as friction accompanying the change in flow rate.

To determine the parameters that make up the constant F' , Poiseuille's equation is applied, assuming flow is laminar and the change in viscosity is negligible.

$$F' U = \frac{128\mu L U}{g\pi D^4}$$

where

U = flow rate

L = length of conduit

g = gravity constant

D = diameter of conduit

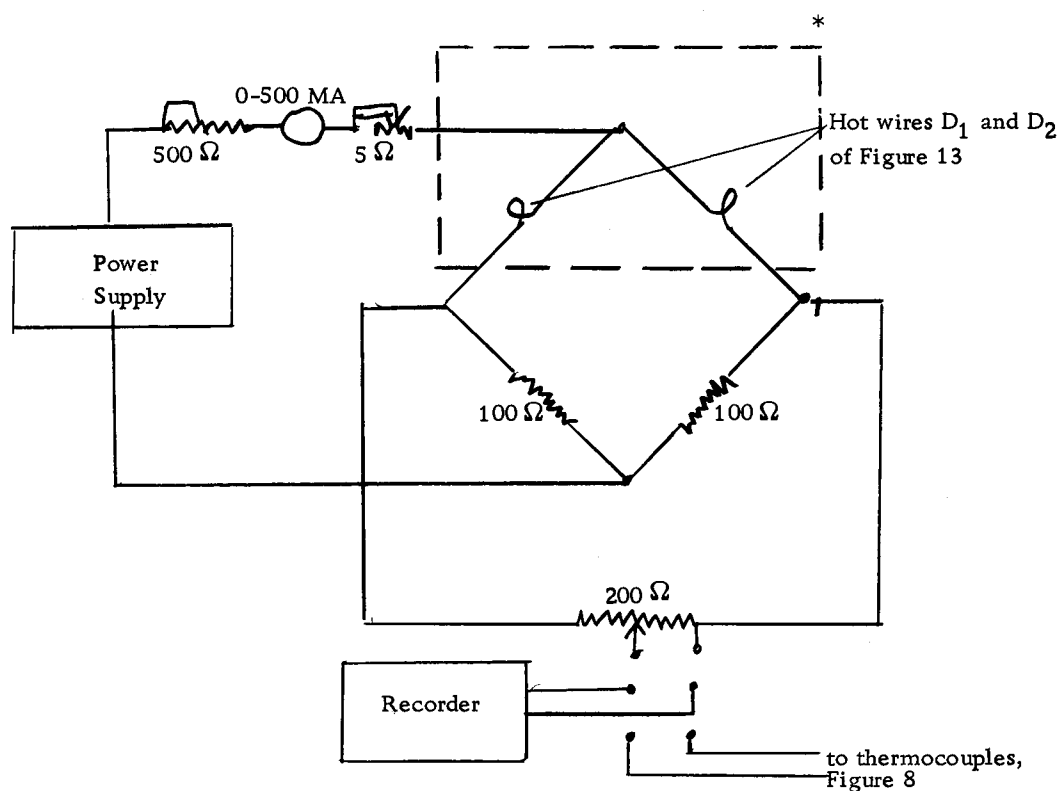
μ = viscosity

The circuitry for the detector is shown in Figure 14.

In order to test the operation of the chromatograph, a column of five sections of 12 mm I. D. pyrex glass 1-1/2 feet long, connected with "U's" of 6 mm I. D. pyrex glass was constructed. Alternate "U's" were packed and left free of packing. The column was packed with chromosorb P (Johns-Manville), coated with 20 percent by weight Dow Corning Silicon 710 fluid.

The column was packed by the vacuum technique in an attempt to avoid beating, tapping, and vibrating to keep the density of a cross section of the column as uniform as possible.

When the oven was thermostatted at $92.0^{\circ}\text{C} \pm <.1^{\circ}$ with



* Part of circuit inside oven.

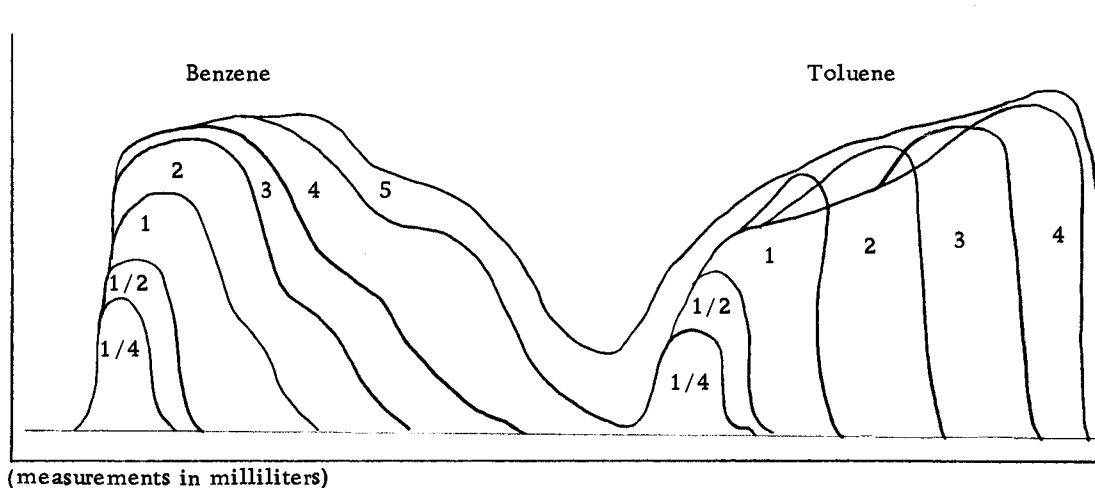
Recorder: Varian Associates. Graphic Recorder Model G. 14

Power Supply: Wilkens Instrument and Research, Inc., Walnut Creek, California. Model A-191-B

Gas Density Balance: Gow Mac Instrument Company, 100 Kings Road, Madison, New Jersey. Hotwire W 2 Fil.

Figure 14. Gas density balance and controlling circuit.

injections of successively larger samples, the following curves were obtained for 50-50 by weight benzene-toluene mixtures.



From the shape of the curves it is obvious (59) that the vaporizer cannot efficiently vaporize (give plug injection) samples much larger than 2 ml. The curves (not drawn to exact scale) show that the column diameter should be increased and the amount of stationary liquid phase should be increased if samples larger than 5 ml are to be separated. The same effect could be produced by lengthening the column, but if this were done the peaks would still be broad (even broader). For samples 5-15 ml or greater the volume of the vaporizer should be increased approximately three fold, thereby increasing the heat capacity by approximately the same amount.

For small samples ($< 1/4$ ml) quantitative separations were obtained for benzene-toluene, diethyl ether-acetone, benzene-toluene-triethyl amine, and diethyl ether-acetone-triethyl amine.

Purity of Materials

Most generally materials were considered pure when they exhibited a vapor pressure within one percent of a value reported in the literature at the same temperature. On occasion, when the material was not volatile enough at room temperature or where the quantity of material was too small for such a measurement in a convenient volume, other methods were applied. Agreement between vapor pressures of a given sample measured in two different volumes of ratio 5:1 or greater at constant temperature was considered a criterion of purity. Under these circumstances a mixture of substances with different volatilities would show a change in vapor pressure because of the change in composition of the residual liquid phase. On other occasions a sample was split into two fractions by distilling away approximately half of the material. Coincidence of vapor pressures of the two fractions at the same temperature was indicative of purity. Finally, where critical, the purity was checked spectroscopically or by gas chromatography.

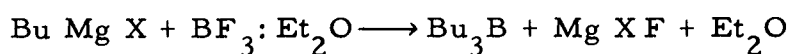
Preparation of Materials

1. Triethylamine. Reagent grade triethylamine was dried over CaH_2 for 24 hours and then P_2O_5 for 24 hours. Immediately before use, the triethylamine was distilled through a 24 inch long, 12 mm

diameter distilling column packed with pyrex glass helices.

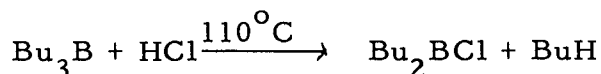
2. Diethyl ether. Reagent grade diethyl ether was dried over liquid sodium-potassium alloy and then distilled just prior to use as described in section 1.

3. Tri-n-butylborane. Tri-n-butylborane was prepared by the method of Johnson (92). (Bu = normal Butyl group, Et = ethyl group, X = halide.)



A quantity of tri-n-butylborane was also purchased from Callery Chemical Company, 201 North Braddock Avenue, Pittsburgh 8, Pennsylvania.

4. Di-n-butylboron chloride. Di-n-butylboron chloride was prepared according to the method of Booth et al. (22) with some modifications.



The tri-n-butylborane was placed in a 500 ml round bottom flask beneath the distilling column described in section 1. A magnetic-stirring hot plate was used to heat the paraffin bath in which the reaction vessel was placed. A magnetic-stirring bar (Teflon covered) was placed in the vessel. The hydrogen chloride was passed through the tri-n-butylborane at 110°C in such a way as to cause the bubbles of hydrogen chloride, as formed, to be struck by the stirring

bar. In this manner the time of reaction that Booth et al. (22) reported (22 hours) was shortened to eight hours. Once, by accident, some ferric oxide was present in the reaction vessel in contact with one mole of tri-n-butylborane. The ferric oxide dissolved as the hydrogen chloride was passed through the mixture at elevated temperature. In this case a virtually 100 percent conversion of tri-n-butylborane to di-n-butylboron chloride took place in less than four hours, indicating that ferric chloride catalyzed the reaction.

5. Sodium-potassium alloy. Sodium-potassium alloy was prepared by the method of Birmingham (20).

6. Trifluoromethyl iodide. Trifluoromethyl iodide was prepared according to the method of Haszeldine (74).

7. Trifluoromethyl mercury iodide. The trifluoromethyl mercury iodide was prepared according to the method of Banks et al. (9) and Emeléus et al. (50) with some modifications of apparatus as reported by Parsons (ONR report No. -2).

8. Bis(trifluoromethyl) mercury. Bis(trifluoromethyl) mercury was prepared by the method of Emeléus et al. (50).

9. Diboron tetrafluoride. The diboron tetrafluoride was prepared by the method described in Part II of this thesis.

10. Nitrogen. Nitrogen, Matheson prepurified 99.5 percent, was passed through a heated column of copper wire and then a

column of P_2O_5 on glass beads.

11. Other reagents. Hydrogen chloride and boron trifluoride were tank reagents from Matheson Company, purified by fractional condensation to vapor pressures in agreement with literature values.

Preparation of Potassium Di-n-Butylborate-I in Triethylamine

The potassium di-n-butylborate-I was prepared in a manner similar to that of Auten and Kraus (6) with some change in the apparatus (Figure 15). A typical preparation will be described. The apparatus was placed in a gloved box with a nitrogen atmosphere. The apparatus was purged with prepurified nitrogen (Matheson 99.5 percent) which was passed over hot copper and P_2O_5 on glass beads prior to use. After the system was purged 100 ml of triethylamine was added through A (Figure 15) followed by 20 ml of liquid sodium-potassium alloy. The mixture was then stirred until a slight blue color developed. At this time approximately 0.1 mole (16 grams) of di-n-butylboron chloride was added slowly through the by-pass dropping funnel with stirring. Immediately upon addition of the di-n-butylboron chloride the blue color of the mixture darkened. In 15 minutes all of the di-n-butylboron chloride was added and the mixture was a dark blue. Twelve minutes later the solution turned dark brown, almost black. The mixture was then stirred for 12 hours. At this time the apparatus was tipped and the material was

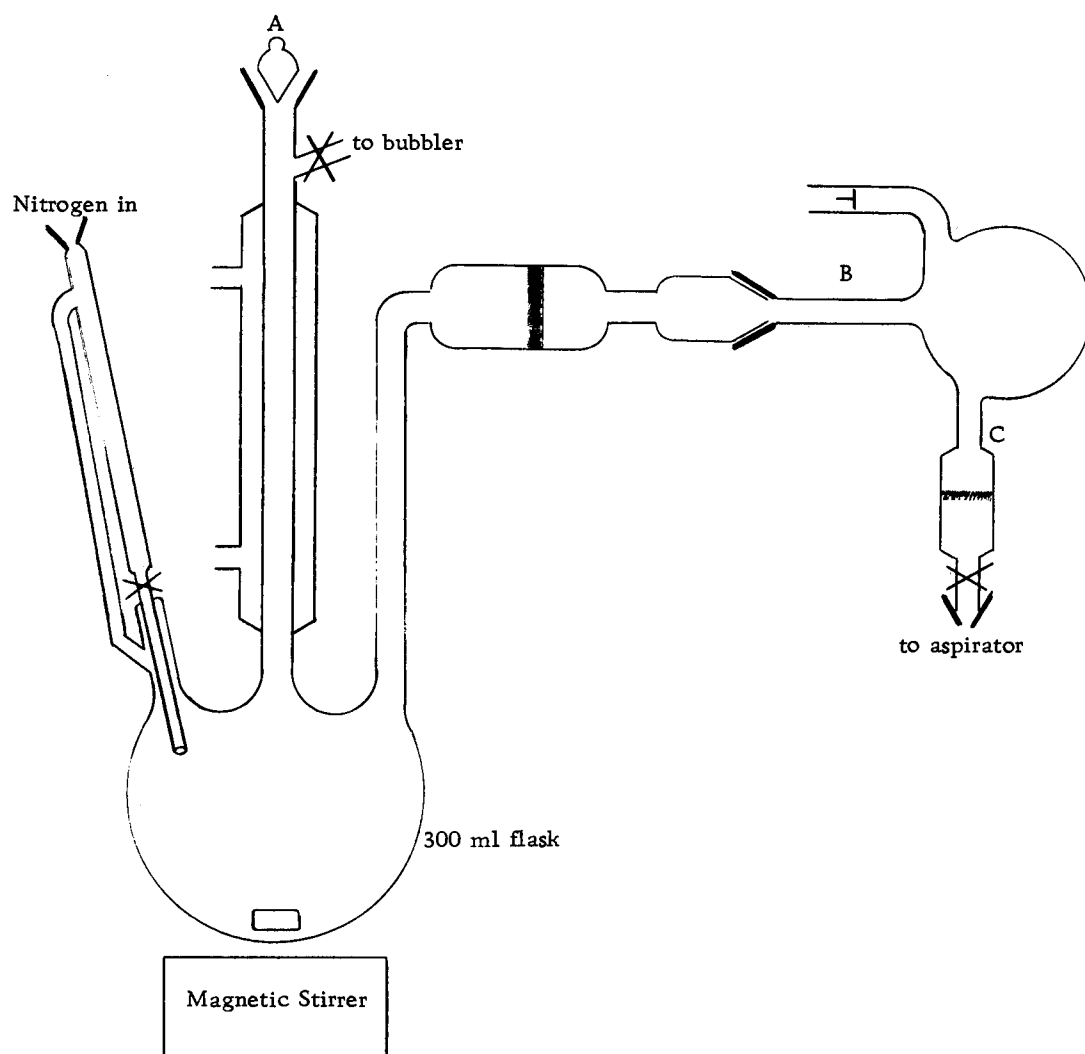
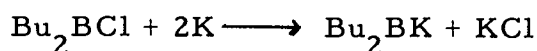


Figure 15. Reaction Vessel

filtered through the fritted glass filter to the receiver flask. The sodium-potassium alloy and the salt were washed four times with 50 ml portions of triethylamine, each added to the filtrate. While the apparatus was tipped on its side part of the excess Et_3N was distilled away with the aid of an aspirator. The receiver flask was removed from the apparatus and sealed off at B and C at reduced pressure. The salt remaining on the filter was light blue in color and gave a positive test for chloride. The assumed reaction is (Bu = the n-butyl group)



The percentage yield of Bu_2BK was 63.5 percent based on the amount of hydrogen evolved by reaction with hydrogen chloride.

The Reaction of Potassium Di-n-Butylborate-I with Trifluoromethyl Iodide in Triethylamine

The potassium di-n-butylborate-I container from the previous reaction was sealed onto the apparatus in Figure 16 at A separated by a medium porosity fritted glass filter. After filtration of the solution the apparatus was sealed off at A. The potassium di-n-butylborate-I, after the second filtration, gave a negative test for chloride. A sample of the small amount remaining on the filter was tested after the filter was sealed off and the material passed the filter.

Trifluoromethyl iodide, .13 moles, was distilled into bulb B.

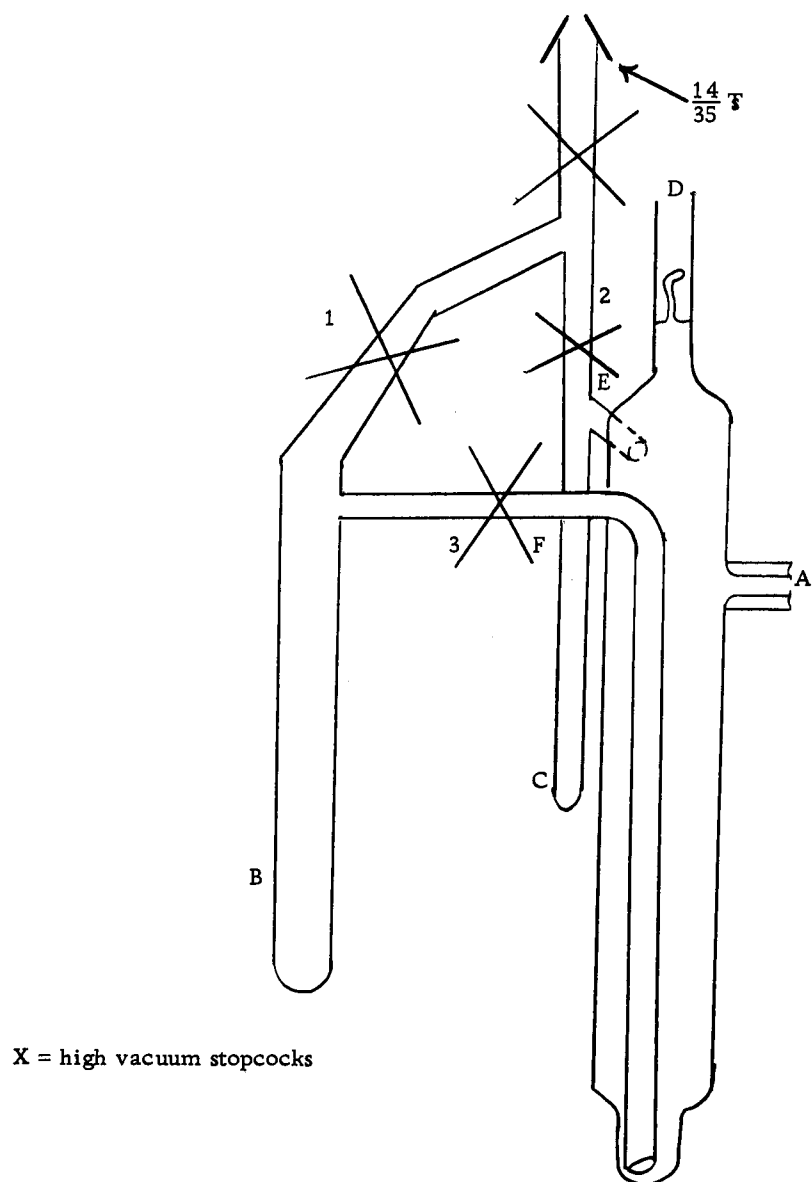
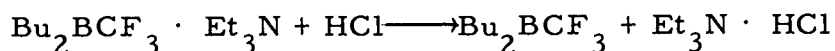
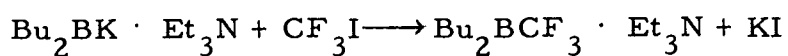


Figure 16. Reaction Vessel

A -80°C bath was placed around the bulb containing the potassium di-n-butylborate-I and liquid nitrogen around the trifluoromethyl iodide container. The stopcock 3 was opened and the trifluoromethyl iodide was allowed to warm slowly. The trifluoromethyl iodide passed by means of the dip tube through the potassium dibutylborate-I solution with the excess condensing in trap C, held at liquid nitrogen temperature. Trifluoromethyl iodide was recycled via stopcocks 1 and 2 to assure completeness of reaction. After sufficient trifluoromethyl iodide had been added the characteristic dark brown color of potassium di-n-butylborate-I had changed to a light amber. The excess triethylamine was removed from the light amber colored mixture and anhydrous hydrogen chloride was passed through the reaction vessel in a manner similar to that of the trifluoromethyl iodide.

The assumed predominate reactions are:



A fritted glass filter was then sealed on at D and the reaction tube sealed off at E and F. The non-volatile liquids, predominately trifluoromethyl di-n-butylborane, that formed with the hydrogen chloride treatment were filtered into a small container with a break seal on the side.

Over-all yield of trifluoromethyl di-n-butylborane was 30 per cent. This was determined by weighing the bulb in which the material was stored.

Several by-products were observed. After addition of trifluoromethyl iodide, trifluoromethane, 2.42 mmoles was identified by vapor pressure measurement and infrared spectrum. A very volatile compound, mixed with the trifluoromethane during storage, reacted with the mercury in the vacuum line to give a brown solid with no noticeable increase in pressure. Hydrogen, amount unknown, was identified by reaction with palladium chloride to produce hydrogen chloride. Butene, 1.16 mmoles, identified by vapor pressure and infrared spectrum. A fifth component was present, 3 mm Hg vapor pressure at 20°C, 5 mm Hg vapor pressure at 25°C with a molecular weight of 119.5. The least volatile component was tributylborane.

After addition of hydrogen chloride, traces of trifluoromethane, hydrogen, butene and tributyl boron were found. All of these were identified as before.

Purification and Identification of Trifluoromethyl Di-n-Butylborane

Impure di-n-butyltrifluoromethyl borane from the previous reaction was treated with triethylamine. Excess amine was removed, and the sample was heated to 50°C with a water bath, with pumping for 20 minutes. The material that was removed during

this treatment was almost entirely tri-n-butyl borane. Trifluoromethyl di-n-butylborane was then recovered from the amine complex by treatment with excess hydrogen chloride. It was distilled in vacuo at 60°C into small weighed bulbs.

Analysis for fluorine by the method used by Baker (8) gave 2.87 fluorines per molecule and 2.83 fluorines per molecule. Molecular weight was 190.7, calculated for trifluoromethyl di-n-butylborane 193.85.

Vapor Pressure Data:

Temperature °C	Vapor Pressure Obs.	Calculated*
145	71.6 mm	71.1 mm
140	64.1	58.0
130	44.3	42.7
125	32.6	33.0
120	27.0	26.3
115	20.5	20.1
105	13.1	13.5
96	9.6	9.0
90	6.9	6.7
85	5.3	5.2
74	2.9	2.9
65	1.8	1.76
57	1.2	1.1
40	.6	.4

$$*\log_{10} P_{\text{mm}} = 8.611 - \frac{2827}{T}$$

Determination of the Acid Strength of Trifluoromethyl Di-n-Butylborane

Trifluoromethyl di-n-butylborane (.112 m mole) was mixed with ammonia (.101 m mole) according to the method of Brown (26).

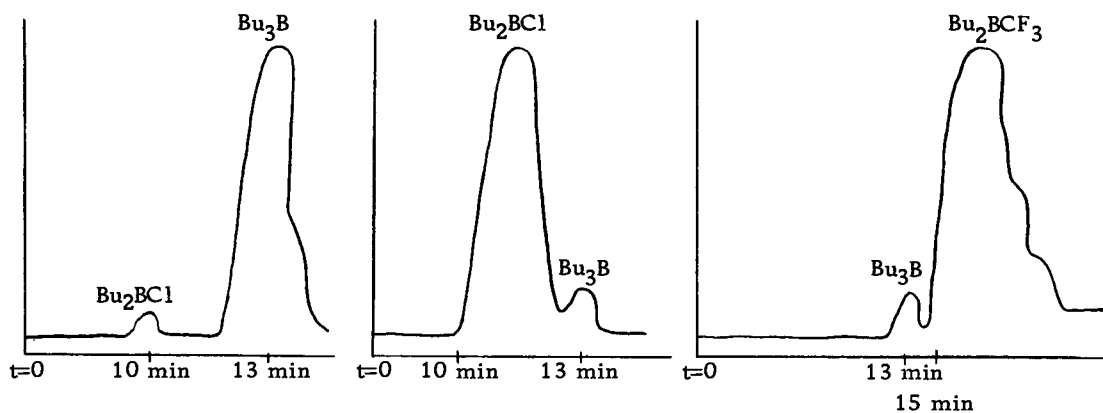
The pressure of the system was measured at two different temperatures.

Temperature °C	Observed Pressure	Calculated Pressure	Degree of Dissociation
23	.9 mm	.6 mm	.337
92	52.3 mm	8.1 mm	.845

This indicates that trifluoromethyl di-n-butylborane is a little stronger acid than trimethylborane. Brown (26) gives the degree of dissociation of trimethylborane-ammonia at 91.5°C to be .985. Calculated pressures were the vapor pressures of the trifluoromethyl di-n-butylborane as if it were the sole component.

The Gas Chromatographic Separation of Tri-n-Butylborane,
Di-n-Butylboron Chloride and Trifluoromethyl Di-n-Butylborane

Samples of volumes from .25 ml (approximately .26 g) to 1 ml (approximately 1.1 g) were separated on the gas chromatograph described. The chromatographs for the various separations are shown below.

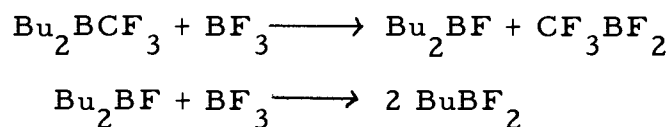


During the process of separation of tri-n-butylborane and trifluoromethyl di-n-butylborane the latter decomposed. This is indicated by the humps on the tailing side of the peak and the high background following once the peak is complete.

The Reaction of Trifluoromethyl Di-n-Butylborane with Boron Trifluoride

Trifluoromethyl di-n-butylborane, 4.73 grams (24.5 mmoles), and boron trifluoride were mixed and allowed to stand at room temperature for 24 hours. Separation of the products by fractional condensation gave boron trifluoride, 7.2 mmoles, identified by vapor pressure and its infrared spectrum; n-butylboron difluoride, 6.72 mmoles, identified by vapor pressure; and di-n-butylboron fluoride, amount undetermined. A fourth volatile component that passed a -112° trap slowly and condensed at -127° gave vapor pressures of 20 mm of Hg at -80° and 75 mm of Hg at -63° . The molecular weight by vapor density was 115. The material decomposed in the molecular weight bulb to give an equimolar amount of boron trifluoride. The infrared spectrum of the compound showed strong absorption peaks at 1080 cm^{-1} and 1190 cm^{-1} ; medium absorption peaks at 850 cm^{-1} , 845 cm^{-1} , 1040 cm^{-1} , 1255 cm^{-1} and 1460 cm^{-1} ; weak absorption peaks at 690 cm^{-1} , 725 cm^{-1} and 1160 cm^{-1} ; and a broad weak absorption from 1350 to 1400 cm^{-1} . A rerun of the spectrum showed

a large increase in the boron trifluoride level. The total quantity of material produced was 1.31 mmoles. On the basis of volatility, decomposition to boron trifluoride, and molecular weight the substance is identified as trifluoromethyl boron difluoride (calculated molecular weight 117.85).



About half of the volume of the original material was left in the reaction vessel after reaction and was assumed to be trifluoromethyl di-n-butylborane.

The Reaction of Diboron Tetrafluoride with Trifluoromethyl Mercury Iodide (a) When Irradiated with Ultraviolet Light, (b) In the Absence of Ultraviolet Radiation

a. This reaction gave varying results. Always boron trifluoride and diboron tetrafluoride were identified as reaction products. The amount of boron trifluoride present was always in excess of the amount that could be attributed to the natural decomposition of diboron tetrafluoride. A fraction intermediate in volatility between boron trifluoride and diboron tetrafluoride was isolated but attempts to transfer this material resulted in decomposition to boron trifluoride and other products. This material had a vapor pressure of 20 mm of Hg at -80° . Another substance was sometimes present among the products, less volatile than diboron tetrafluoride,

and this material condensed at -80° . On each occasion attempts to transfer and purify the material resulted in decomposition to boron trifluoride and other products.

b. Trifluoromethyl mercury iodide, 7.1 grams (2.77 mmoles), and diboron tetrafluoride (.73 mmoles) were mixed in an evacuated tube equipped with a breakseal. The material was allowed to stand for three weeks. In this time the trifluoromethyl mercury iodide crystals had turned dark gray. Separation of the volatile components by fractional condensation gave boron trifluoride (0.58 mmoles) boron tetrafluoride (0.31 mmoles), each identified by vapor pressure measurement and their infrared spectra. A third less volatile material that condensed at -80°C decomposed to boron trifluoride and other products when it was warmed above -80°C in a transfer process. This third component was always observed among the reaction products but could never be isolated because of its facile decomposition.

The tube was washed carefully three times with ether to remove excess trifluoromethyl mercury iodide. A large amount of dark gray material remained in the tube. Three drops of concentrated nitric acid were added and some of the dark gray material dissolved. The solution gave a positive test for mercury (II) and a negative test for iodide.

The Reaction of Diboron Tetrafluoride with Bis(Trifluoromethyl) Mercury When Irradiated with Ultraviolet Light

Bis(trifluoromethyl) mercury gave no apparent reaction with diboron tetrafluoride in the absence of ultraviolet radiation when the mixture was stored in a pyrex container for three days at room temperature (approximately 25°C). However, ultraviolet radiation initiated an extensive reaction involving the bis(trifluoromethyl) mercury.

Bis(trifluoromethyl) mercury, .361 grams (1.1 mmoles), was placed in a quartz tube, diboron tetrafluoride (.85 mmoles) was distilled in and the tube was sealed. The material was then irradiated with a General Electric U. A. 1100 ultraviolet source for 16 hours. The part of the tube contacted by bis(trifluoromethyl) mercury turned black during the course of the irradiation.

The tube was opened, the material was removed from the vessel and fractionated. The products were .61 mmole of boron trifluoride and .43 mmole of diboron tetrafluoride; identified by vapor pressure measurement and infrared spectrum.

A third product, isolated in trace quantities, had an infrared spectrum showing absorptions characteristic of the C-F and B-F fundamental vibration. This compound was never isolated in large enough quantities to allow identification.

The Reaction of Di-n-Butylboron Chloride with Trifluoromethyl Mercury Iodide

Trifluoromethyl mercury iodide, 8.5 grams (21.4 mmoles), was placed in a 1000 ml flask and 12 ml (approximately 75 mmoles) of di-n-butylboron chloride were distilled into the flask. Upon warming to room temperature, a reaction began immediately, and a red solid was formed (HgCl_2 , red salt). After standing for three days the volatile material was removed and separated by fractional condensation. The most volatile fraction was boron trifluoride (8.44 mmoles), identified by its vapor pressure (observed at -112°C 296 mm Hg, accepted value at -112.4 , 291.4 mm Hg), molecular weight (67.6, 68.0; calculated 67.85), and its infrared spectrum.

The next most volatile species was found to be n-butylboron difluoride; molecular weight 104.8 and 104; calculated 105.85. The infrared spectrum agreed very well with the spectrum Schaad (139) reports for this compound. Additional data appears later. The total amount of n-butylboron difluoride isolated was 0.955 mmoles.

The third most volatile fraction was found to be di-n-butylboron fluoride, molecular weight 142.1 and 144.8; calculated 143.85. Additional data appears later.

The excess di-n-butylboron chloride and remaining non-volatile material was separated on the gas chromatograph described previously.

The chromatogram showed the presence of di-n-butylboron chloride and tri-n-butylborane.

The solid material remaining in the flask, in time, had turned from a red to a dark brown or black. Qualitative tests for mercury (II), iodide, chloride and fluoride ions were positive.

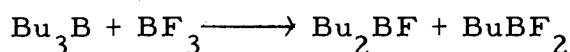
The Reaction of Trifluoromethyl Mercury Iodide with Excess Boron Tribromide

Trifluoromethyl mercury iodide, 5.1 grams (12.9 mmoles), was placed in a 1000 ml flask. After evacuation, 10 ml of boron tribromide was distilled into the flask. A slow reaction that began when the cold bath was removed from the vessel rapidly increased in vigor, culminating in a near explosion. The flask was cooled to -80°C and warmed slowly again. There was no visible reaction. After the flask stood for 24 hours the volatile material was removed and fractionated. The most volatile fraction was boron trifluoride, identified by vapor pressure and molecular weight. The amount of boron trifluoride present was 12.1 mmoles. The other volatile fractions were BBr_3 and a trace of some other material that could not be separated completely from boron tribromide by fractional condensation. The remaining solids were dark purple and black. These solids gave positive tests for bromide and iodide ions and a weak test for fluoride ion. One of the species present in the

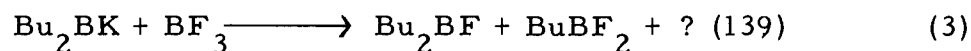
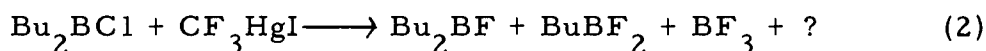
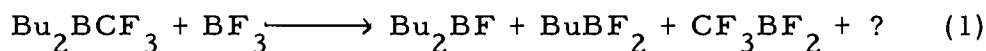
reaction flask during the course of the reaction attacked the mercury in the manometer attached to the flask.

Separation and Characteristics of n-Butylborondifluoride
and Di-n-Butylboronfluoride

n-Butylboron difluoride and di-n-butylboron fluoride have been prepared by the following reaction (26; 118).



In this laboratory the compounds have been prepared by these reactions.



Di-n-Butylboron fluoride

This material was separated from the most common impurities, boron trifluoride and n-butylboron difluoride by fractional condensation with cold baths at 0°C, -23°C, and -196°C. The di-n-butylboron-fluoride stops in the -23°C bath. The material is a colorless liquid with approximately 5 mm vapor pressure at room temperature.

Molecular weight determinations by vapor density were 142.5, 145, and 144. Calculated 143.85.

Vapor Pressure Data

Temp. °C	V. P. (Observed)	Calc. by equation*
87	109.2 mm	107 mm
73	63.1	63
54	27.3	25.7
38	12.9	11
25	5	5.35

*The values listed were calculated by $\log_{10} P_{\text{mm}} = 8.54 - \frac{2330}{T}$.
Boiling points are 139° by the equation of 140° by extrapolation on graph.

$$\Delta H_v = 10.7 \text{ kcal/mole}$$

$$\text{Trouton Constant} = 25.6$$

The infrared spectrum was determined using a Beckman I. R. 7 with NaCl and CsI interchanges from 200-4000 cm^{-1} . The spectrum is given in Figure 17.

n-Butylborondifluoride

n-Butylborondifluoride was isolated by fractional condensation as a product of two reactions given in equations 2 and 3.

The vapor pressure data, molecular weight data, and infrared spectrum agreed very well with that reported by Schaad (139). Schaad reported (139) the infrared spectrum from 600-4000 cm^{-1} reproduced in Figure 18 and one higher pressure scan. In addition, the infrared spectrum from 250-600 cm^{-1} is given in Figure 19. The only prominent bands in these spectra that were not previously discussed are the 480 and 518 bands in the CsI region. These are most likely

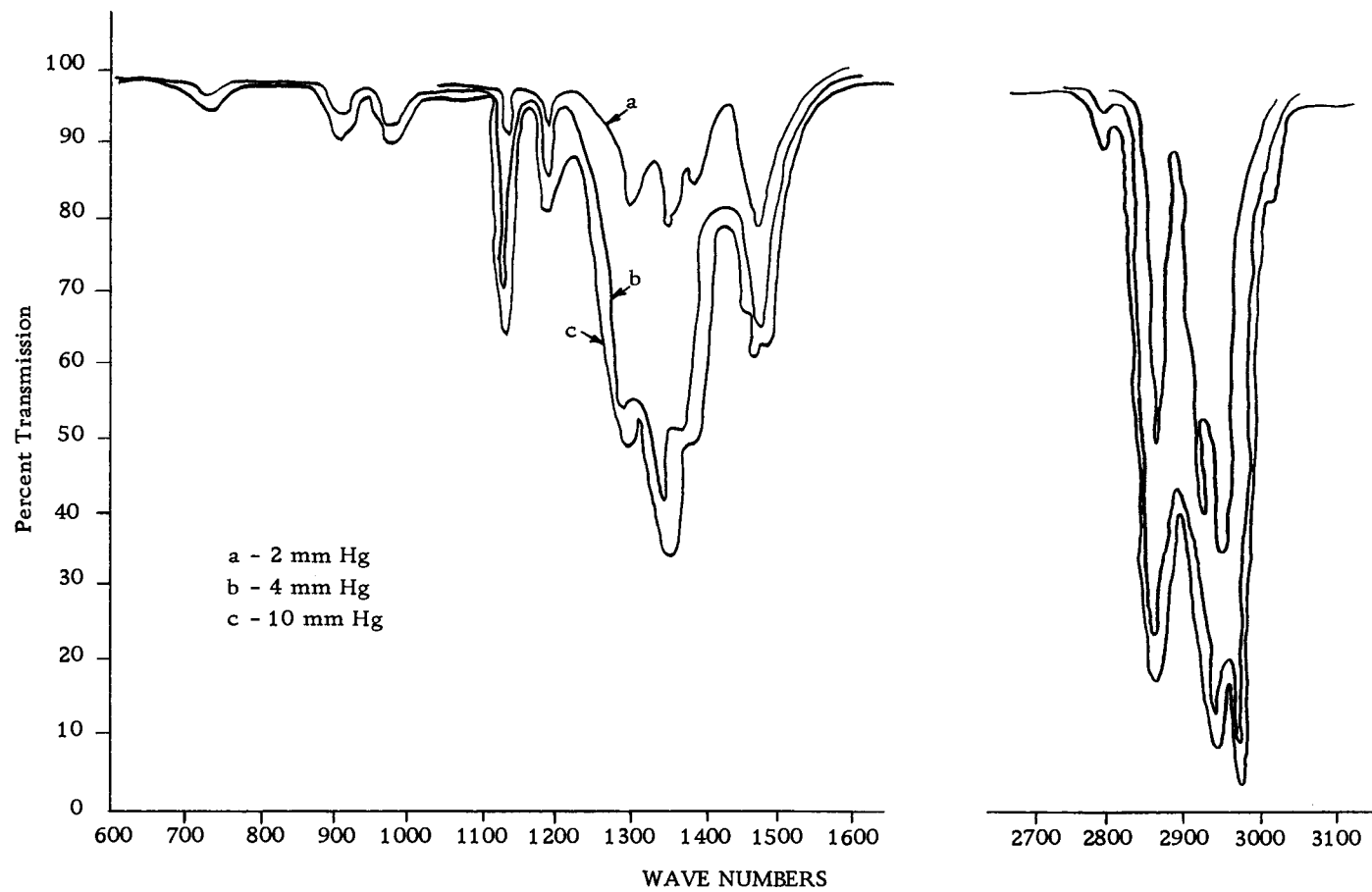


Figure 17. Infrared spectrum of Bu_2BF 600-4000 cm^{-1} .

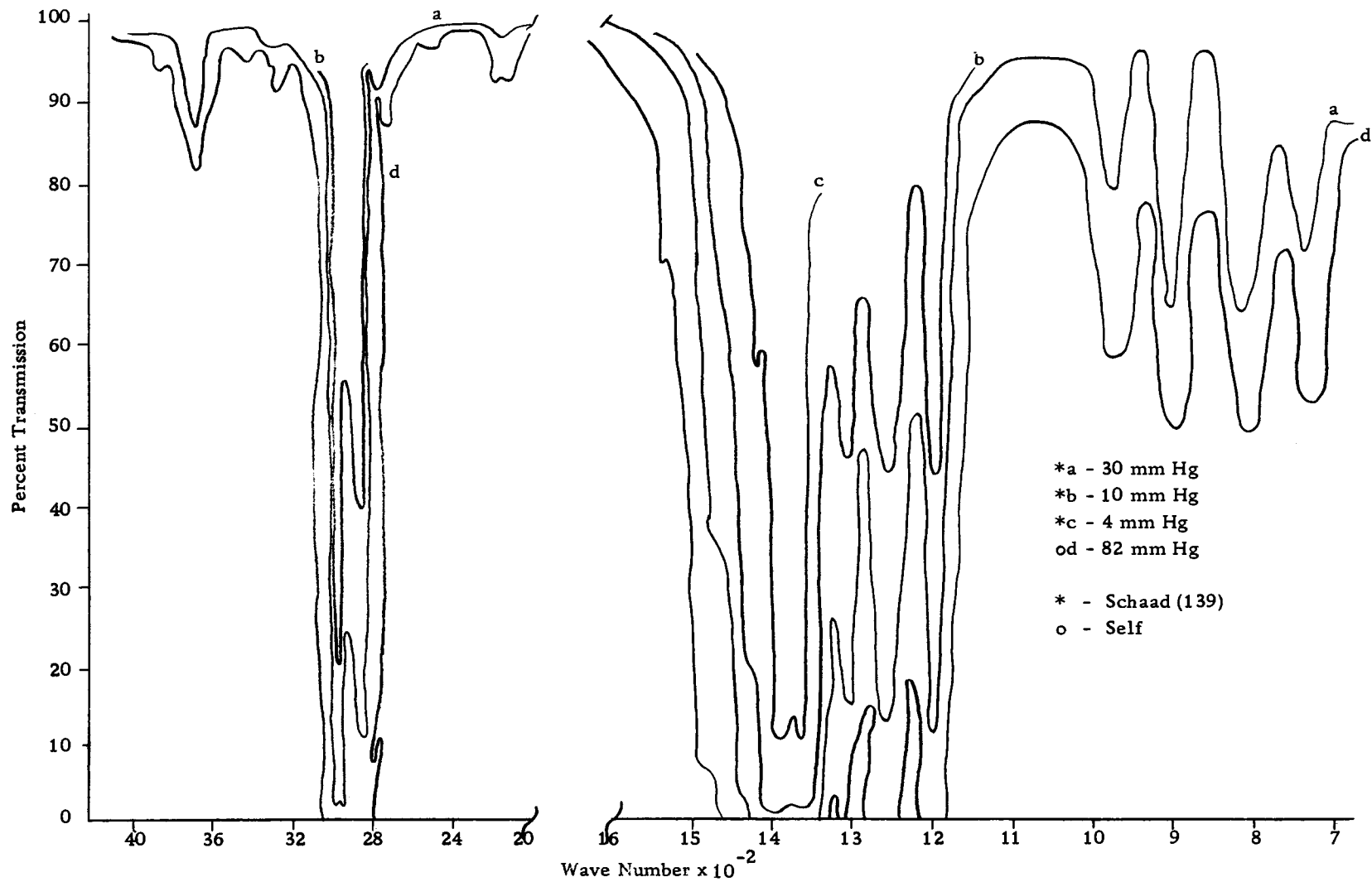


Figure 18. Infrared spectrum of BuBF_2

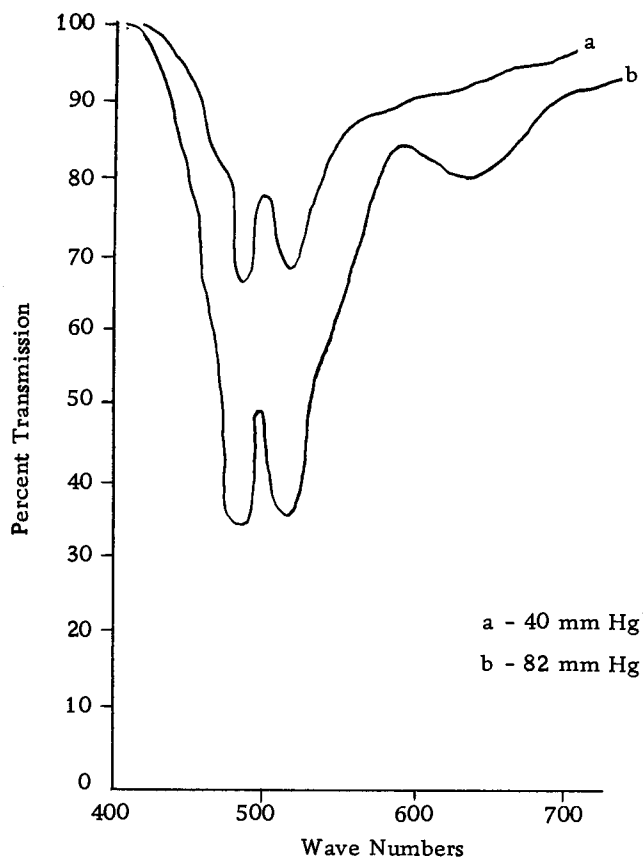


Figure 19. Infrared spectrum of BuBF_2 250-600 cm^{-1} .

generated by the out of the plane wagging motion of the BF_2 group.

The infrared spectra of these compounds were very similar to those given by Becher (15) for the compounds CH_3BF_2 and $(\text{CH}_3)_2\text{BF}$.

DISCUSSION OF RESULTS

Potassium di-n-butylborate I was prepared in large quantities (0.1 mole or greater) for use as an intermediate in the preparation of trifluoromethyl di-n-butylborane.



The physical and chemical properties of trifluoromethyl di-n-butylborane that have been experimentally determined may be summarized as follows. The compound gave an experimental molecular weight of 190.7; calculated 193.85. The vapor pressures of the compound correspond closely to the equation $\log_{10} P_{\text{mm}} = 8.609 - \frac{2825}{T}$. Trifluoromethyl di-n-butylborane is a moderately weak Lewis acid of about the same acid strength as trimethylborane as determined from the comparative degrees of dissociation of ammonia complexes at various temperatures. The trifluoromethyl di-n-butylborane is expected to be a slightly stronger Lewis acid than methyl di-n-butylborane because of the strong electrophilic character of the trifluoromethyl group. No quantitative knowledge is available about the acid strength of this hydrocarbon analogue of trifluoromethyl di-n-butylborane, but, qualitatively, it is known to be a much weaker Lewis acid than trimethylborane. Hence, the expected order of strengths is observed.

Trifluoromethyl di-n-butylborane reacts with boron trifluoride

to give trifluoromethylboron difluoride and other compounds. The reaction of greatest interest is represented by the equation:



It is not known whether the reaction represents a redistribution of groups attached to various boron atoms or a transfer of difluorocarbene in some equilibrium process. These alternatives will be discussed in more detail later.

Trifluoromethylboron difluoride, as observed in this work, decomposes rapidly to yield boron trifluoride and a white solid. Baker (8) reported that the compound is stable over long periods of time, in vacuo, although the same rapid decomposition was noted on occasion. The discrepancy is most likely due to the fact that many foreign species present in the vacuum system, in trace amount, could catalyze the decomposition. The experimental molecular weight is 115, calculated 117.8. The infrared spectrum of trifluoromethyl boron difluoride, not previously determined, shows absorptions characteristic of the C-F vibrations 1080 and 1190 cm^{-1} , and absorptions characteristic of the B-F vibrations 1255 and 1460 cm^{-1} .

Gas chromatography proved to be an efficient means of separating boranes on a large scale. The gas density balance is a very effective device for the detection of compounds of this type in a gas stream. The largest single factor for the utilization of the gas density balance is that the sample of material never contacts the

sensing elements. The trifluoromethyl di-n-butylborane decomposed during the process of separation, but this was most likely due to reaction with the column packing. A column packed with a more inert material should not give rise to this problem. An ideal packing for use in the separation of these substances appears to be a ten mesh cut 40/50 of ground teflon coated with a halocarbon wax, 15 to 20 percent by weight. The column that was used was effective in the fractionation of samples as large as five ml of mixtures of tri-n-butylborane and di-n-butylboron chloride. An impurity of about 4 percent of tri-n-butylborane was detected in a sample of trifluoromethyl di-n-butylborane.

The reaction between diboron tetrafluoride and trifluoromethyl mercury iodide indicated that the most probable mode of reaction is a mechanism involving the trifluoromethyl free radical or difluorocarbene. In either case, the radical probably attacks the B-B bond of diboron tetrafluoride inasmuch as carbon tetrafluoride is not observed among the products. Thus, fluorine abstraction apparently does not occur. The reaction was observed both with and without ultraviolet radiation when trifluoromethyl mercuric iodide was the reactant, since this substance can form free radicals easily at room temperature (11). Bis(trifluoromethyl) mercury, which does not form free radicals at room temperature, only reacted with diboron tetrafluoride when irradiated with ultraviolet light. The distribution

of reaction products was very similar to those obtained from the reaction of trifluoromethyl mercury iodide and diboron tetrafluoride.

In the reactions of di-n-butylboron chloride and of boron tribromide with trifluoromethyl mercury iodide, the trifluoromethyl group is completely degraded. This is indicated by the fact that 97 percent of the fluorine present in the trifluoromethyl mercury iodide was converted to boron trifluoride in the reaction with boron tribromide.

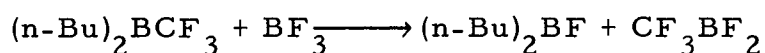
Difluorocarbene, if formed at all, must have been generated in an excited electronic state since its usual mode of decay to tetrafluoroethylene, hexafluorocyclopropane and higher polymers was not observed, nor was the diradical captured by the borane present in each case. Rather, complete degradation of the trifluoromethyl group was observed.

Additional data is given for physical properties of di-n-butylboron fluoride and n-butylboron difluoride. The experimental molecular weight was 144; calculated, 143.85. The vapor pressure correspond closely to the equation $\log_{10} P_{\text{mm}} = 8.54 - \frac{2330}{T}$. The infrared spectrum of di-n-butylboron fluoride is given from 250 cm^{-1} to 4000 cm^{-1} .

The infrared spectrum of n-butylboron difluoride is given from $250\text{-}600 \text{ cm}^{-1}$. The remainder of the data collected for this compound agreed very well with that reported by Schaad (139).

From the observations of the properties of trifluoromethylboranes it is apparent that further study of synthetic methods and reactions of these substances must be carried out under carefully controlled conditions. It is apparent that loss of difluorocarbene from the trifluoromethyl group is thermodynamically favored although at low temperatures and when the compound is in a high state of purity, the reaction is very slow. Stability was enhanced when the substances were complexed with Lewis bases, triethylamine specifically. Generation of the desired product from its complex in the last step of a synthesis, by displacement with hydrogen chloride, is also of considerable advantage, since the trifluoromethyl group is stabilized by the relatively high electron density in the region of the neighboring boron atom when complexed.

No definite conclusion can be drawn as to the ability of the trifluoromethyl group to participate in a group redistribution reaction by a bridge bond mechanism. In the one case where group redistribution involving trifluoromethyl apparently occurred, an alternate mechanism where difluorocarbene is transferred is also possible.



This reaction is worthy of considerable study. The mechanism might be elucidated by a nuclear magnetic resonance study, or by substituting some borane not containing fluorine for boron trifluoride in the reaction. Diborane, which undergoes redistribution

reactions readily, would be a logical choice.

The reaction between diboron tetrafluoride and trifluoromethyl mercury iodide or bis(trifluoromethyl) mercury should be investigated more fully. The mercury compounds are known to yield difluorocarbene under proper circumstances, to which diboron compounds should add. By use of a basic solvent the desired product might be preserved and isolated. In this work an indication that $\text{CF}_2(\text{BF}_2)_2$ was formed was noted, although decomposition occurred upon warming to room temperature.

The reactions between boron tribromide and trifluoromethylmercuric iodide and between di-n-butylboron chloride and trifluoromethyl mercury iodide warrant more study. The reaction should be carried out in a basic solvent such as triethylamine to moderate the reaction rate and increase the half-life of any difluorocarbene formed as an intermediate.

II. A STUDY OF DIBORON TETRAFLUORIDE

INTRODUCTION

The interesting point in the study of the molecular structure of B_2F_4 is to determine whether the two ends of the molecule are staggered or planar in the gaseous state. Figure 20 gives the three possible configurations of B_2F_4 and the irreducible representations corresponding to the three symmetries (V_d , V and V_h). A series of molecules that are isoelectronic with B_2F_4 have been studied. The observed vibrational spectra of this series (N_2O_4 , $C_2O_4^{=}$ and B_2Cl_4) lead to the conclusion that the members of the series have definite differences in their structures. Since this series is isoelectronic, on the surface, one would be inclined to think that they would all have the same structure. Differences do exist in the structures of the members of this series, but the reason for these differences is not fully understood.

Snyder et al. (143) concluded that N_2O_4 is planar in both the solid and gaseous state. Begun et al. (16) concluded that $C_2O_4^{=}$ is staggered in aqueous and solid solution. Mann and Fano (108) concluded that B_2Cl_4 is staggered in the gaseous phase. Hedberg (83) concluded by an electron diffraction study that B_2Cl_4 is staggered in the gaseous phase. Atoji et al. (5) found (from x-ray diffraction) that B_2Cl_4 is planar in solid phase. Trifonas et al. (146) found by

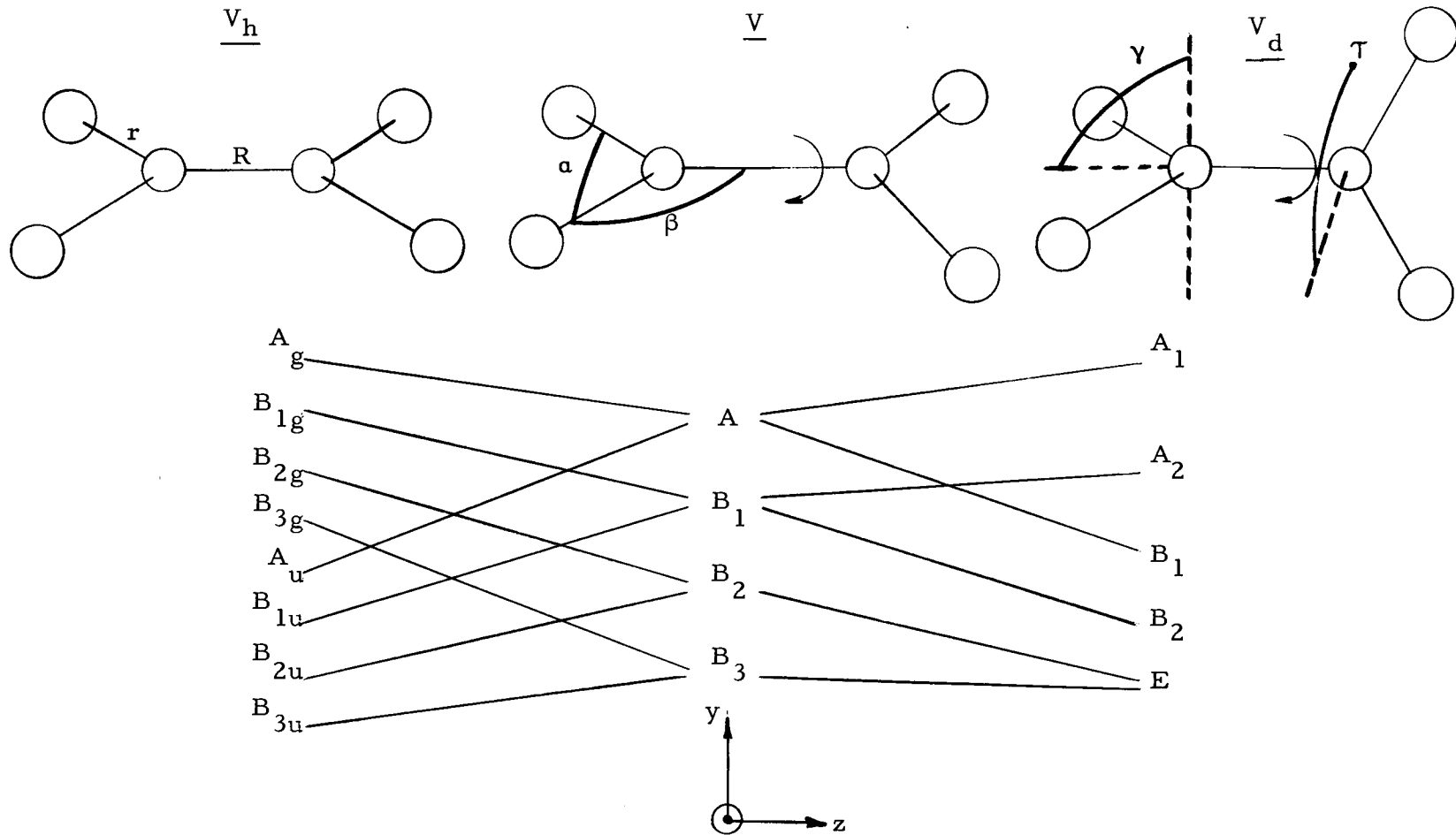


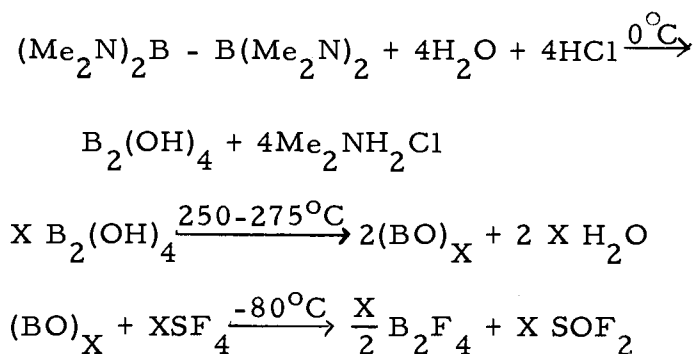
Figure 20. The possible configurations and their representations for B_2F_4

x-ray diffraction that B_2F_4 is planar in the solid phase. This study was undertaken in order to determine whether B_2F_4 is planar or staggered in the gaseous phase.

PREPARATION OF B₂F₄ AND DESCRIPTION OF
THE EXPERIMENT (I. R. SPECTRUM)

Preparation of B₂F₄

B₂F₄ was prepared by the method of Brotherton et al. (25).



Seventeen grams (86 mmoles) of (Me₂N)₄B₂ in 20 ml of H₂O at 0°C was hydrolyzed with 60 ml of 6.2 N HCl. The HCl was added slowly over a period of two hours. The B₂(OH)₄ was filtered and washed three times with .62 N HCl and placed in a vacuum dessicator over NaOH and Drierite for three days (yield 60 percent).

The B₂(OH)₄, a very light fluffy material, was dehydrated at 250°C for 24 hours at 1 mm pressure. (A glass wool plug was placed above the material to prevent its spreading through the vacuum system.) On heating of the B₂(OH)₄, noncondensable materials were generated.

When a sample of (BO)_X was heated to approximately 400°C a reaction occurred producing a quantity of noncondensable material and

a yellow solid (100; 155).

SF_4 (Dupont technical grade) was fractionated through baths at -80 , -124 , to -196°C . The -124°C fraction was used. Fifteen mmoles of SF_4 were added to the reaction vessel and allowed to stand at -80°C for 24 hours.

The volatile material was removed from the reaction vessel and fractionated through baths at -80 , -119 , to -196°C . The -119°C fraction was a mixture of B_2F_4 and SOF_2 ; the -196°C fraction was SOF_2 .

The material in the -119°C trap was refractionated slowly through baths at -95°C , -119°C , to -196°C . The material condensing at -119°C was found to be free of SOF_2 on the basis of the absence of the characteristic peaks in its infrared and mass spectrum; 6.5 mmoles of B_2F_4 was produced. The yield, on the basis of the SF_4 added, was 87 percent. The product was stored at -196°C .

B_2F_4 in contrast to B_2Cl_4 appears to be stable if the surfaces it comes into contact with are clean (140). Kel-F 90 grease (Minnesota Mining and Manufacturing Company, St. Paul, Minnesota) was used on all stopcocks the B_2F_4 contacted. A sample of B_2F_4 which remained in the I. R. cell with NaCl windows, showed no detectable increase in the BF_3 level after 16 hours. It was not possible to obtain BF_3 -free spectra with CsBr, CsI, KI windows. The presence of the BF_3 in the cell whenever CsBr, CsI, or KI windows were

employed may be due to a reaction between B_2F_4 and the more polarized atoms at the surface of the salt windows.¹

The separation of B_2F_4 and SOF_2 is difficult. This may be due to the formation of a low temperature adduct between B_2F_4 and SOF_2 similar to the adduct that forms between BF_3 and SOF_2 (62).

The I. R. Cells

Previous attempts to take the I. R. Spectrum of B_2F_4 have failed due to the reactivity of the compound. B_2F_4 reacts with all of the compounds usually used to seal on salt windows to form BF_3 and some other specie. Elucidation of the spectrum of B_2F_4 was impossible since some of the vibrational frequencies of BF_3 and B_2F_4 were so close. For this reason a radically different method for the sealing of salt windows was utilized.

The salt windows of the cell used for the study of the gaseous spectrum were sealed on by Ag-(Hg)Pb seal method (66), Figure 21

The flange of the cell was silvered by Brashear's Process (65).

The lead gasket was prepared by cutting an annular gasket from .005 inch thick Pb foil. The surface was cleaned with dilute HNO_3 , then washed several times with distilled water. The surface of the gasket was polished with a soft cloth or tissue to a metallic luster. Mercury was placed on the lead gasket in a drop-wise manner and

¹A small amount of iodine was detected in the cell.

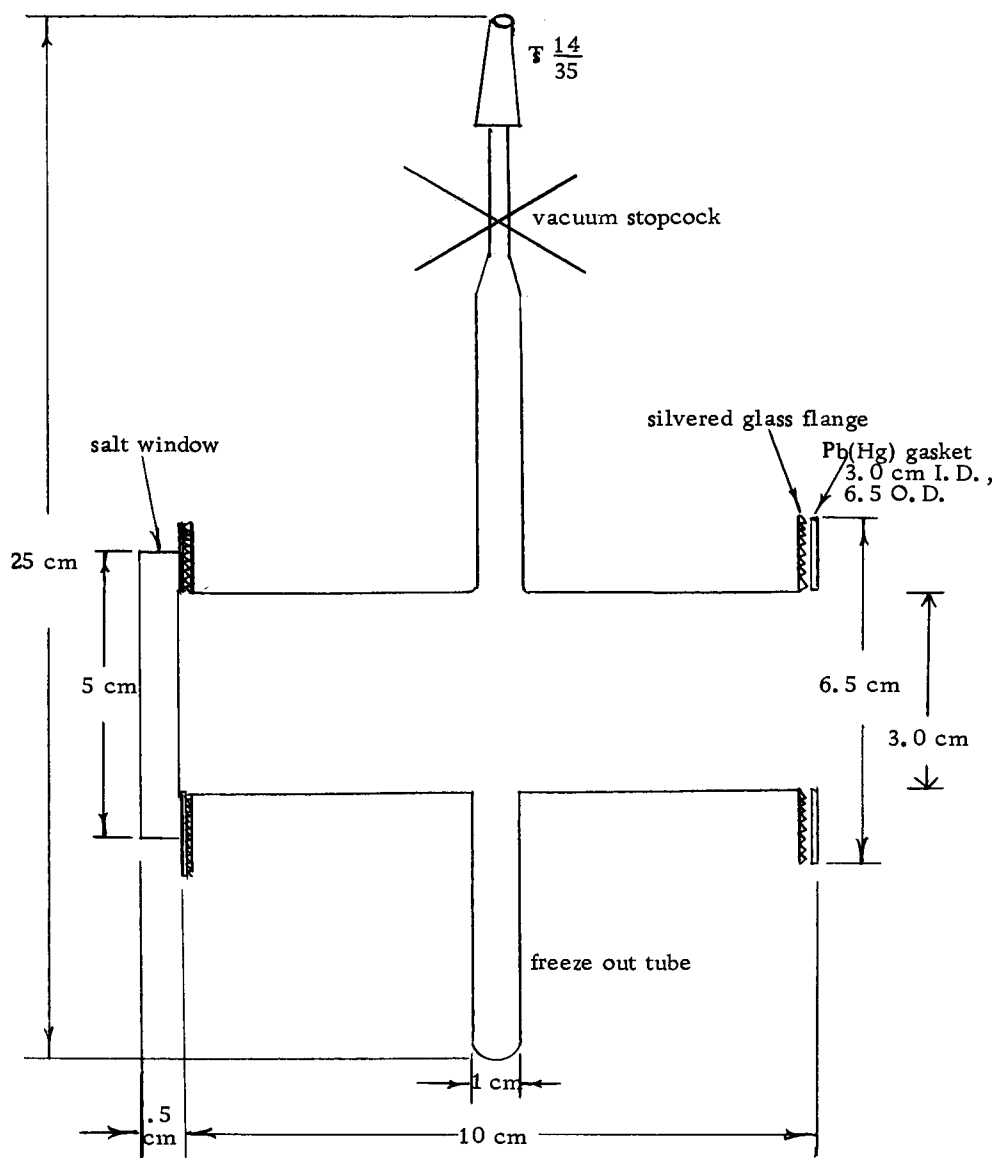


Figure 21. Gas infrared cell.

distributed evenly by rubbing with a soft cloth. The operation was repeated on the reverse side of the gasket and it was allowed to stand for 15 to 30 minutes. The amount of mercury on the surface is critical. Too much mercury will make the gasket spongy, too little will not wet the silver and salt (NaCl or CsBr) surface properly. The lead gasket must be free of scratches and punctures.

The cell was assembled as illustrated in Figure 21 and clamped under pressure (15-20 pounds) between two aluminum rings held together by threaded aluminum rods. The cell was allowed to stand under pressure for 48 hours before it was evacuated. At this time the contact surfaces had a mirror-like appearance. Cells sealed in this manner held a vacuum for periods up to two months or longer.

The low temperature cell (149) was constructed as shown in Figures 22 and 23. All stopcocks are Eck and Krebs (Long Island City, New York) high vacuum hollow plugs, oblique bore. All stopcocks were greased with Kel-F 90. The large T joint ($\frac{50}{50}$) was greased with Dow Corning high vacuum grease. The two $\frac{19}{38}$ joints were greased with Kel-F 90.

The end of the cooling finger was covered with a thick coating of Dow Corning high vacuum grease to assure good thermal contact. The sides of the salt plate that fit into the brass block were also covered with a layer of Dow Corning high vacuum grease to insure good thermal contact. The hole in the side of the window where the

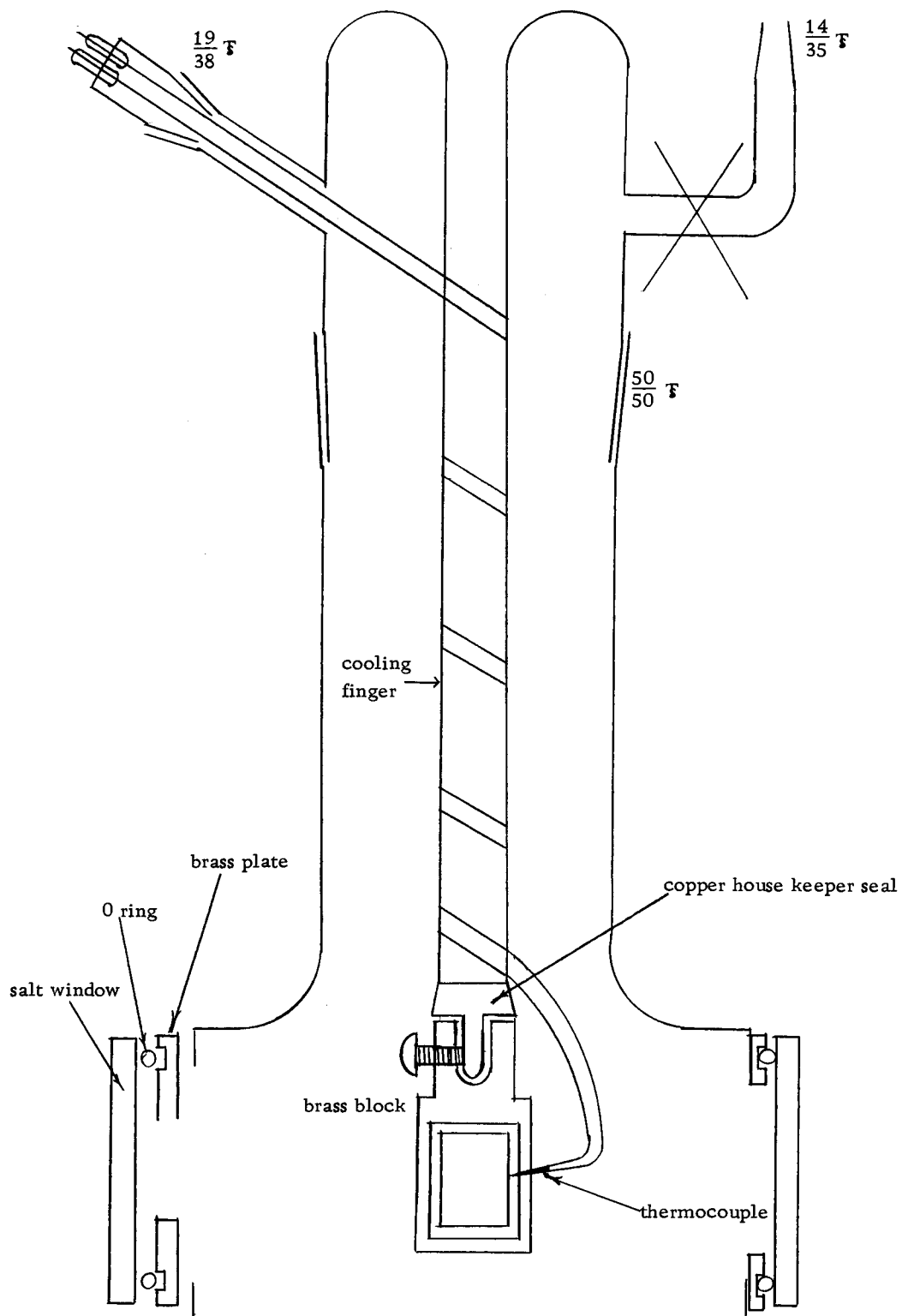


Figure 22. Low temperature cell: View I.

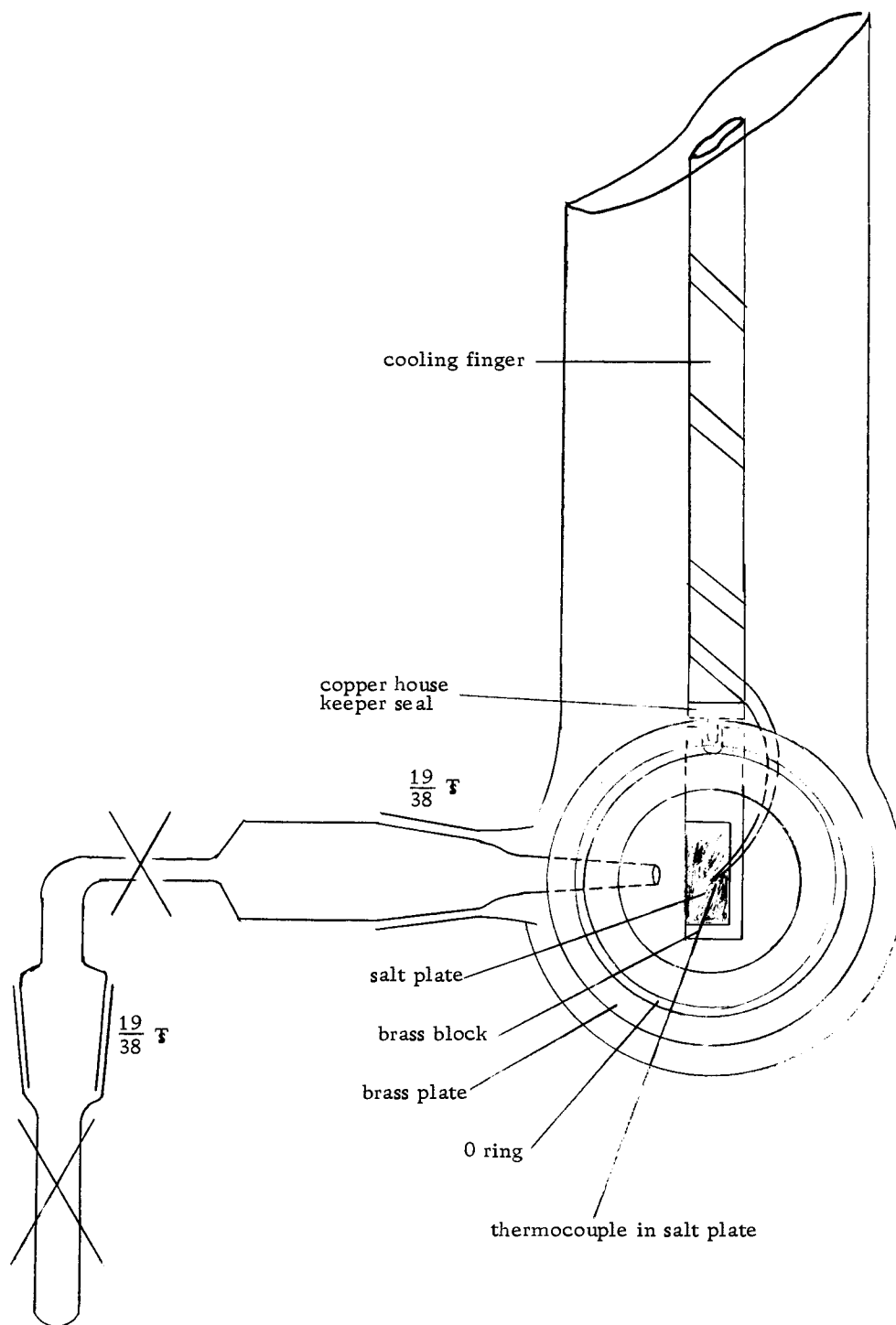


Figure 23. Low temperature cell: View II.

thermocouple was placed was filled with Dow Corning high vacuum grease.

In use, a sample of B_2F_4 was distilled into section A, Figure 23. Section A was then attached to the cell and the cell was evacuated. The salt plate was cooled by putting liquid nitrogen in the cooling finger.

To place a sample on the salt face a $-80^\circ C$ bath was placed around A. The stopcock on A was opened with the stopcock on B closed. In this way a sample was trapped between the stopcocks on A and B once A was closed. The sample was then deposited on the salt plate by opening B. This operation was repeated as many times as necessary to obtain a sample layer of the desired thickness. The spectrum was determined using a Beckman IR-7 with NaCl and CsI interchanges.

Mass spectrum data of B_2F_4 are given in Table 1. The mass spectrum included several peaks that could not be attributed to the molecule or any reasonable impurity. This indicates the possibility of free radical formation in the mass spectrograph after the particle was accelerated, as shown in Table 1. Evidence for the formation of free radicals during the preparation of B_2Cl_4 has been reported (81). The large BF_3 level is attributed to the fact that the pumping system of the mass spectrograph was not efficient enough to remove all of the oxygen leading to accelerated decomposition of B_2F_4 .

Table 1. Mass Spectrum of B₂F₄.

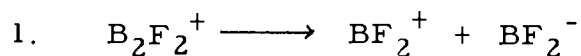
m/e	I	$\frac{I}{I}$ max.	Fragment	Ratios From Natural Abundance	
				Obs.	Calc.
10	11	.0073	B ¹⁰	.19	18.45-18.98
11	47	.0313	B ¹¹	.81	81.02-81.55
19	4	.0026	F		
20	6	.0040	HF		
28	14	.0093	N ₂ , CO, Si		
29	156	.1040	B ¹⁰ F	B ₂ F ₂ ⁺⁺ .21	.19
30	570	.3800	B ¹¹ F	.79	.81
32	4	.0026	O ₂		
38	2	.0013	B ₂ ^{10, 11} F ₃ ⁺⁺	.12	.31
39	14	.0093	B ₂ ^{11, 11} F ₃ ⁺⁺	.87	.66
40	4	.0026	B ₂ ^{10, 11} F	.11	.31
41	36	.0240	B ₂ ¹¹ F	.89	.66
44	5	.0033	CO ₂		
47	48	.0320	SiF		
48	350	.2330	B ¹⁰ F ₂	.19	.19
49	1500	1	B ¹¹ F ₂	.81	.81
54	4	.0026	SF ₄ ⁺⁺		
58	2	.0013	B ₂ ^{10, 10} F ₂	.11	.03
59	4	.0026	B ₂ ^{10, 11} F ₂	.23	.31
60	11	.0073	B ₂ ^{11, 11} F ₂	.64	.66
63	6	.0040	FB ¹⁰ (OH) ₂	.3	.19
64	14	.0093	FB ¹¹ (OH) ₂	.7	.81
66	8	.0053	SiF ₂		
67	12	.0080	B ¹⁰ F ₃	.25	.19
68	36	.0234	B ¹¹ F ₃	.75	.81
77	198	.1320	B ₂ ^{10, 10} F ₃	.13	.03
78	410	.273	B ₂ ^{10, 11} F ₃	.28	.31
79	840	.560	B ₂ ^{11, 11} F ₃	.58	.66
96	6	.004	B ₂ ^{10, 10} F ₄	.038	.036
97	48	.032	B ₂ ^{10, 11} F ₄	.312	.310
98	99	.066	B ₂ ^{11, 11} F ₄	.65	.66

Table 1. Continued.

m^* = observed mass

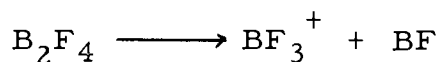
m_o = original mass of ion

m = mass of ion formed

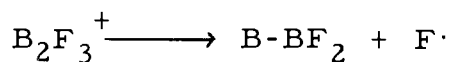


$$m^* = \frac{m^2}{m_o} = \frac{(49)^2}{60} = m^* = \frac{40.85}{38.3 \quad 39.7}$$

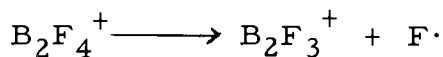
peaks appear at approximately these points.



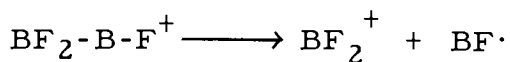
$$m^* = 47.2, 45.8, 46.1$$



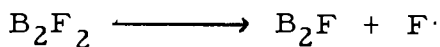
$$m^* = 45.5, 44.7$$



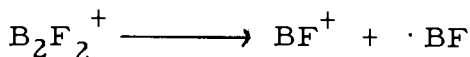
$$m^* = 63.7, 62.8 \quad \text{Correct isotopic abundance}$$



$$m^* = 30.4, 30.8, 29.4 \quad \text{Correct isotopic abundance}$$

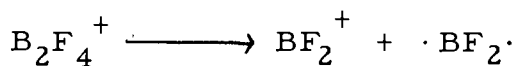


$$m^* = 28, 27$$



$$m^* = 15$$

Very weak



$$m^* = 24.5$$

Very weak

Figure 24 gives the IR spectrum of gaseous B_2F_4 and Figure 25 gives the IR spectrum of solid films of B_2F_4 . The assignment of the frequencies and the force constant calculation was carried out by J. N. Gayles (57). The results of this calculation are given in Tables in the Appendix.

On the basis of the observed spectral data for B_2F_4 it is believed that the molecule is very likely staggered in its gaseous state. Solid film assignments are made for the planar configuration of B_2F_4 .

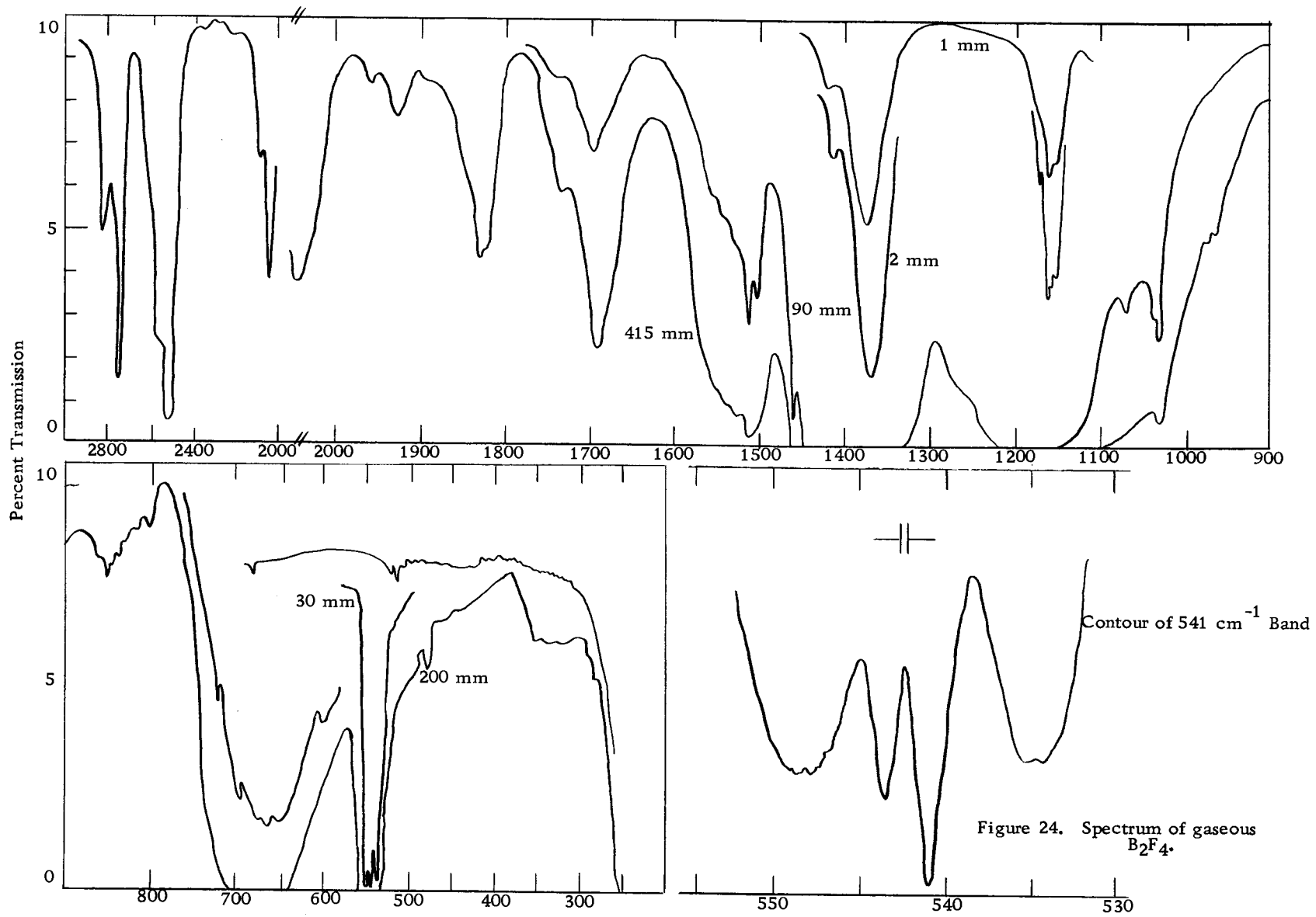
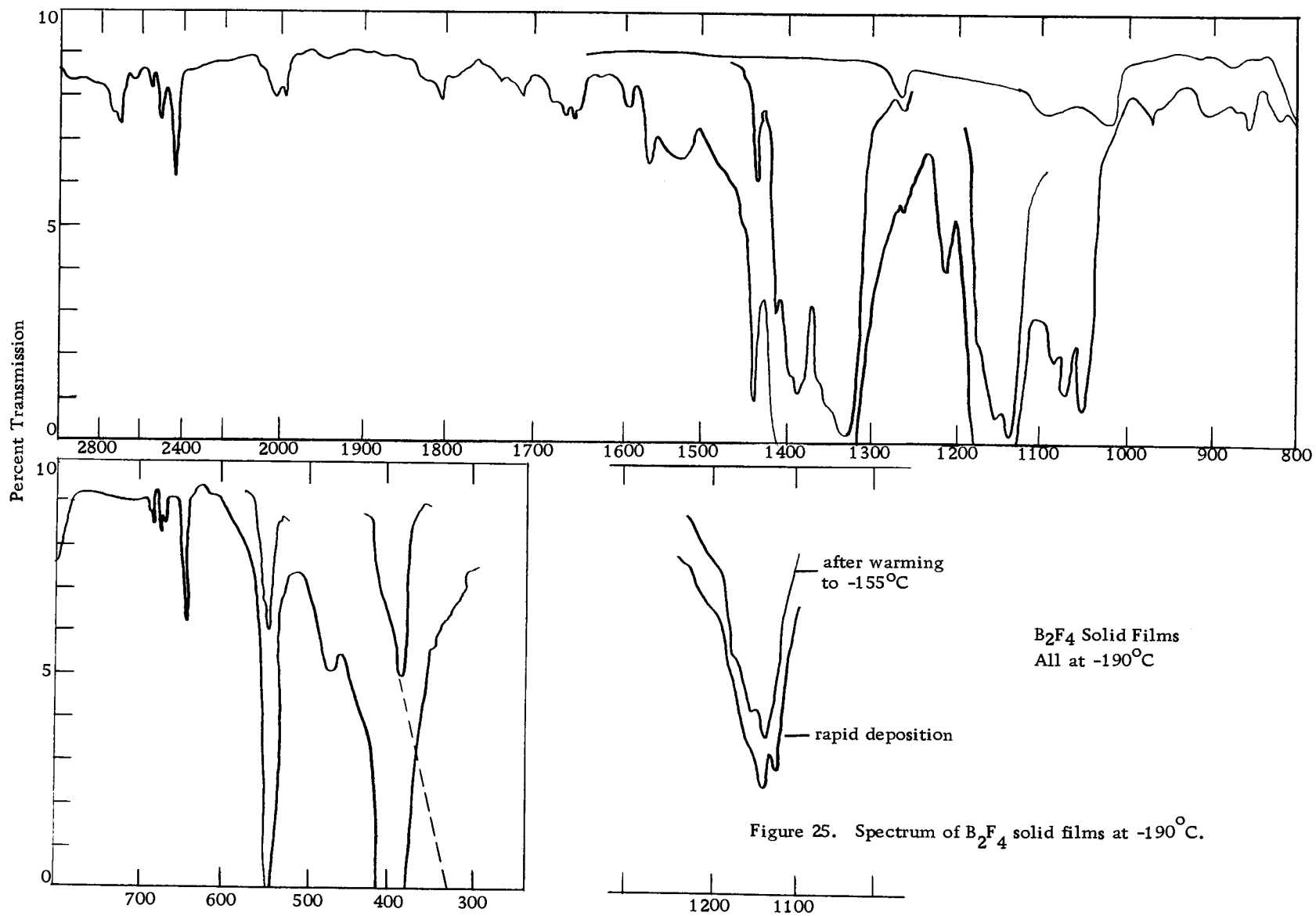


Figure 24. Spectrum of gaseous B_2F_4 .



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APPENDIX

Table 2. Correlation Diagram.

Molecular Group	Site Group	Factor Group
V_h	C_i	C_{2h}^5
A_g B_{1g} B_{2g} B_{3g}	A_g	A_g B_g
A_u B_{1u} B_{2u} B_{3u}	A_u	A_u B_u

Table 3. Symmetry Species-Active Modes.

		V_d	V_h
r_s	symmetric BF stretching	B_2	B_{1u}
B_s	symmetric FBF bending	B_2	B_{1u}
r_a	antisymmetric B-F stretching	E	B_{3u}
B_a	antisymmetric FBF bending	E	B_{3u}
r	out of plane FBF wagging	E	B_{2u}

Table 4. Estimates of Force Constants (millidynes / \AA)

<u>Parallel</u>		<u>Perpendicular</u>	
Constant	$\text{mD}/\text{\AA}$	Constant	$\text{mD}/\text{\AA}$
$K_r + F_r$	6.4707	$K_r - F_r$	4.5731
$H_a + H_\beta + F_\beta$	1.6866	$H_\beta - F_\beta$	0.6645
K_R	(2.50)	H_γ	0.3016
		$F'_{r\beta} - F_{r\beta}$	0.0619
		$f_{r\gamma}^g - f_{r\gamma}^t$	-0.0828
		$f_{\beta\gamma}^t - f_{\beta\gamma}^g$	0.0449

Table 5. Moments of Inertia ($\text{Amu} \cdot \text{\AA}^2$).

	V_d		V_h		
	I_a	I_b	I_a	I_b	I_c
$F_2B^{11}-B^{11}F_2$	99.338	234.924	99.338	185.255	284.592
$F_2B^{10}-B^{11}F_2$	99.338	234.235	99.338	184.567	283.904

$$r(\text{B-F}) = 1.32 \overset{\circ}{\text{\AA}}$$

$$R(\text{B-B}) = 1.67 \overset{\circ}{\text{\AA}}$$

$$\angle(\text{R}_2\text{B}) = 2 \pi/3$$

$$\tau = 0. \text{ or } \pi/2$$

Table 6. Valence Potential.

\overline{F}	r_1	r_2	β_1	B_2	γ_6	γ_5	a_5	R
r_1	K_r	F_r	$F_{r\beta}$	$F'_{r\beta}$	$f_{r\gamma}^t$	$f_{r\gamma}^g$		
β_1			H_β	F_β	$f_{\beta\gamma}^t$	$f_{\beta\gamma}^g$		
a_5							H_a	
γ_6					H_γ			
R								K_R

Table 7. Parallel vibrations.

No.	des.	V_d		C_{2v}		Obs.	Calc.	% dev.	Obs.	Obs.	Obs.		
		$B^{11}-B^{11}$	$B^{10}-B^{11}$	$B^{11}-B^{11}$ (cm^{-1})	$B^{10}-B^{11}$ (cm^{-1})							BF_3	CH_3BF_2
1	r_s	$\left. \begin{array}{l} A_1 \\ B_2 \end{array} \right\}$	$\left. \begin{array}{l} A_1 \end{array} \right\}$		(1382)	1377	1399	1.6		1250	1244		
2	R				(624)	--	650	--					
3	β_s				A_1	(301)	(315)	306	-2.9				
4						1151.2	1151.2	1163.7	1167	+0.3	888		
5	β_s					541.0	541.0	543.5	542.3	-0.4			
Perpendicular Vibrations													
6	r_a	$\left. \begin{array}{l} E \end{array} \right\}$	$\left. \begin{array}{l} B_1 \\ B_2 \end{array} \right\}$	1375	1377	1416.5	1428	+0.8	1505	1363	1410		
7	γ				B_1	657	657	657	657	--	482	607	541
8	β_s					325	322	325	324	-0.3	719	479	440
9								1385	1381	-0.3			
10					B_2			675	681	+0.9			
11						325	323	-0.6					

Table 8. Constants From Related Molecules.

Molecule	K_r	F_r	H_a	$H_a - F_a$	H_γ	(mD/Å)
BF_3	7.22	0.80	----	0.525	0.866	
CH_3BF_2	6.30	1.40	0.60	-----		
B_2F_4	5.52	0.95	----	-----	.302	

Table 9. Modes of gerade origin - solid.

No.	Sym	Des	$^{11}\text{B}-^{11}\text{B}$ Freq.	Sym	$^{10}\text{B}-^{11}\text{B}$ Freq.
1	A_g		1408	A_1	1413
2	A_g	R	513	A_1	523
3	A_g		323	A_1	323
4	B_{2g}		1340	B_1	1384
5	B_{2g}		395	B_1	395
6	B_{3g}		666	B_2	675

Table 10. Combination and Overtones - gas only.

i	j	Obs ₁ (cm ⁻¹)	Calc _f (cm ⁻¹)	Sym	B ^x -B ^y	
					x	y
9	9		2750	B ₂	11	11
1	9	2758	2762	A ₁	10	11
9	9		2770	A ₁	10	11
1	6	2831	2794	B ₁	10	11
6	6	2821	2834	A ₁	10	11
4	6	2519	2526	E	11	11
4	9	2519	2549	B ₂	10	11
4	6	2510	2581	B ₁	10	11
1	7	2043	2039	E	11	11
1	7	2089	2034	B ₁	10	11
1	10	2099	2052	B ₂	10	11
5	6	1927	1916	E	11	11
5	9	(1927)	1929	B ₂	10	11
5	6	1956	1961	B ₁	10	11
4	7	1811	1808	E	11	11
4	7	1829	1821	B ₁	10	11
4	10	1845	1839	B ₂	10	11
6	7	1691	1700	B ₂	11	11
9	11	1701	1710	A ₁	10	11
6	8	1736	1742	A ₁	10	11
	6	1505	1525	E	11	11
	9	1554	1535	B ₁	10	11
	6	1554	1567	B ₂	10	11
		1219	1225	E	11	11
		1275	1267	B ₁	10	11
		857	850	B ₂	11	11
3	5	836	842	B ₂	11	11
		836	834	E	11	11
		807	807	E	11	11

Table 11. Combination bands in the solid.

i	j	(cm ⁻¹)	(cm ⁻¹)	Sym	B ^x -B ^y	
					x	y
1	11	2740	2740	B _{3u}	11	
1	11	2775	2795	B _{3u}	10	
4	8	2468	2478	B _{2u}	11	
4	8	2545	2539	B ₂	10	
1	8	2583	2546	B ₂	11	
1	10	2000	2054	B _{2u}	11	
1	10	2025	2101	B ₂	10	
1	6	2032	2091	B ₂	10	
6	8	1806	1804	B _{2u}	11	
6	8	1830	1830	B ₂	10	
2	10	1830	1845	B _{2u}	11	
6	10	1840	1843	B ₂	10	
5	11	1713	1727	B _{1u}	11	
5	11	1736	1748	B ₁	10	
3	11	1650	1655	B _{3u}	11	
3	11	1672	1676	B ₂	10	
5	8	1533	1533	B _{1u}	11	
5	8	1560	1550	B ₁	10	
	?	1586				
3	8	1435	1461	B _{1u}	11	
3	8	1439	1478	B ₁	10	
	?	1212				
2	10	1175	1159	B ₁	10	
2	9	1050	1050	B _{1u}	11	
2	9	1070	1070	B ₁	10	
	?	1083				
3	10	973	969	B _{2u}	11	11
5	9	908	932	B _{3u}	11	11
3	9	860	860	B _{1u}	11	11
5	12	762	779	B _{1u}	11	11

Table 12. Solid film data--observed frequencies--gas to solid shifts.

ν	des.	$B^{11}-B^{11}$			$B^{10}-B^{11}$							FCH_2BF_2 (b)	
		sym.	cm^{-1}	shift	cm^{-1}	shift	sym.	(a) cm^{-1}	shift	cm^{-1}	shift		
8	r_s	B_{1u}	1138	-13.2	1155	- 8.7	A_1	1413	(-36)	1244	+ 4		
9	β_s	B_{1u}	536.9	- 4.1	541.8	- 1.7	A_1	---	--				
10	γ	B_{2u}	646	-11.0	688	--	B_2	675	--				
11	r_a	B_{3u}	1332	-43	1353	-32	B_1	1384	-32	1367	-43		
12	β_{3a}	B_{3u}	383.7	+58.7	383.7	--	B_1	395	--				

(a) Gerade originating modes

(b) Gobeau, et al. Ann. d. Chemie 604, 170 (1957).