MASTER

DISSOCIATION PRESSURES AND PHASE EQUILIBRIA OF
THE PENTAFLUOROANISOLE-BORON TRIFLUORIDE
COMPLEX SYSTEM

AUTHOR:

C. G. Jones

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DISSOCIATION PRESSURES AND PHASE EQUILIBRIA OF THE
PENTAFLUOROANISOLE-BORON TRIFLUORIDE
COMPLEX SYSTEM

C. G. Jones

Chemical Development Department
Technical Division

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A B S T R A C T

Using pentafluoroanisole (methoxypentafluorobenzene) as the donor molecule the effect on the strength of the addition complex of boron trifluoride and anisole produced by the substitution of fluorine atoms for hydrogen atoms on the benzene ring has been evaluated. The exothermic reaction of boron trifluoride gas with liquid pentafluoroanisole was readily carried out at temperatures below 0°C. The heat of dissociation of the reaction

was 8.7 kcal. mole⁻¹ as determined from dissociation pressure versus temperature curves for several different solution concentrations between 0:1 and 1:1 mole ratio of boron trifluoride to pentafluoroanisole. This value may be compared to the value of 12.3 kcal. mole⁻¹ reported for the boron trifluoride-anisole complex. Equations were fitted to the dissociation pressure-temperature data for the temperature range of -60 to 20°C. for pressures up to 279 cm. Hg. The pressure-composition relationship at constant temperature obeyed Henry's law up to about 0.6 mole ratio of

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boron trifluoride to pentafluoroanisole. Dissociation pressures at comparable temperatures are approximately two orders of magnitude higher for the pentafluoroanisole-boron trifluoride complex than for the anisole-boron trifluoride complex.

The solid-liquid phase equilibria were also determined under the orthobaric pressure of boron trifluoride. The melting point of pentafluoroanisole is -34.4°C . and the best estimate of the melting point of the 1:1 mole ratio complex was -30.0°C . The eutectic point between pentafluoroanisole and the 1:1 mole ratio complex was observed at -45.5°C . at an estimated composition of 0.31 mole ratio of boron trifluoride to pentafluoroanisole. The orthobaric pressure of boron trifluoride at the eutectic was 21 cm. Hg.

There was no evidence of any corrosion of the equipment and the solvent was not degraded. The isotopic separation factor for boron is apparently close to the value expected at the same temperature with anisole as the exchange agent. Despite these advantages, the process using pentafluoroanisole as the exchange agent is not attractive commercially because of the high cost of this solvent and the refrigeration requirements.

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analyses performed on the Dupont Thermal Analyzer.

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CHAPTER I

INTRODUCTION AND SURVEY OF PREVIOUS WORK

A. INTRODUCTION

Since the publication by Landolph¹ in 1878 of the reaction of boron trifluoride in a 1:1 mole ratio with aldehydes, ketones, and other carbonyl compounds, the preparation and properties of numerous organic boron trifluoride complex compounds have been reported and comprehensive reviews by Booth and Martin² and Greenwood and Martin,³ as well as a general review by Stone⁴ have been published. Many organic boron trifluoride complex compounds are successfully used in industrial applications and are produced commercially. Others have been investigated because of their relations to theoretical problems in chemical bonding and structure or only because of their uniqueness.

With the advent of the atomic energy program in the early 1940's, the importance of boron trifluoride complex systems was demonstrated for the separation of boron isotopes by a chemical exchange-distillation process employing the dimethyl ether-boron trifluoride complex. This process is still being used, but research in this country and Russia, among others, on the physical and chemical properties and isotopic exchange characteristics of numerous boron trifluoride complex systems continues.

The recent development of preparative methods for and the availability of highly fluorinated aromatic and alicyclic compounds has opened a new area of chemical interest. This interest includes the

potential industrial applications which, because of the present high cost of these chemicals, must now be in the speciality field, as well as research in the basic chemistry of fluoroaromatic systems.

The present investigation of the properties of the pentafluoro-anisole-boron trifluoride system was undertaken to provide information of use in several areas. First, it should add to the general knowledge of the chemical properties of aromatic fluorine compounds, particularly with regard to their reactivity towards and their ability to form addition compounds with Lewis acids, of which boron trifluoride is but one typical example. Second, the possible chemical utility of such compounds in chemical exchange processes for isotope separation can be evaluated. Possible benefits arise from an anticipated marked reduction in complex degradation and system corrosion with a resulting improved product yield. Third, such addition complexes may be useful as catalysts or intermediates for expanding research in the preparation and chemistry of aromatic fluorine compounds including high temperature lubricants, more thermally stable plastics, exotic pharmaceuticals, and perhaps many others.

B. NATURE OF THE BORON TRIFLUORIDE ADDITION COMPLEX

1. Introduction

Boron, unlike oxygen, nitrogen, carbon and other elements, appears to violate the octet rule and be satisfied with a sextet of valence electrons in compounds such as the halides. However, because of this lack of a completed octet, the boron atom in these compounds has a strong tendency to act as an electron acceptor or Lewis acid. Thus, compounds

such as boron trifluoride tend to combine with atoms having unshared electron pairs to achieve the stable octet of valence electrons. Atoms which are capable of acting as electron donors are those in the upper right corner of the Periodic Table in groups V, VI, and VII. Of these, nitrogen, oxygen, fluorine, and sulfur are found to be the more common donors and form the more stable complexes.

While the donor-acceptor principle is a criterion for the formation of an addition complex, it must be realized that the presence of an electron donor molecule in conjunction with an acceptor, such as boron trifluoride, does not predict the formation of an addition compound. Many factors are involved, but first it must be pointed out that while an addition complex might be expected, the reaction through the donor-acceptor mechanism may lead to the formation of an irreversible addition compound in which molecular rearrangement occurs with the elimination of molecules such as hydrogen, methane, and hydrogen fluoride.

2. Factors Governing Complex Stability

When the true molecular addition complex is formed, several factors govern its stability or formation; (1) the electronic configuration of the donor atom, (2) the presence of polar substituents on the donor molecule, and (3) the steric hindrance imposed by the donor molecule. The reorganization energy of the boron trifluoride molecule and perhaps that of the donor molecule also is important. These factors have been considered by several authors and will be briefly discussed.

a. Boron trifluoride reorganization. The accepted configuration

of boron trifluoride is trigonal planar with the boron in the center of the equilateral triangle formed by the three fluorine atoms. This configuration is dictated by the hybrid sp^2 bonding where the bond angles are 120° and the boron-fluorine bond distances are 1.30 Å.⁵

The reorganization of this structure and the energy involved for the boron trifluoride to form an addition complex has been treated by several investigators. Bauer, Finlay, and Laubengayer⁶ were among the first to show that the formation of the molecular addition complex of dimethyl ether and boron trifluoride resulted in the rearrangement of the boron trifluoride to a tetrahedral configuration with a B-F bond length of 1.41 Å. and a B-O distance of 1.52 Å., but left the organic molecule essentially unaffected. An estimate of 21 to 80 kcal. was made for the rearrangement energy of boron trifluoride, so that by adding the observed heat of reaction of the etherate complexes, $\sim 13 \text{ kcal. mole}^{-1}$, the total energy required to break the B-O bond would be 34 to 93 kcal. Thus, the B-O bond is comparable in strength to a normal covalent bond. At the same time Laubengayer and Finlay⁷ observed a decrease in the molar volume of the dimethyl, diethyl, and mixed ether complexes with boron trifluoride and showed that the contribution of the donor-acceptor bond on the dipole moments of these complexes was small, which suggested that the donor-acceptor bond character was covalent rather than due to dipole-dipole interaction.

Cotton and Leto⁸ have since applied molecular orbital theory to estimate the strength of π -bonding in boron halides and have used these to determine the reorganization of the planar molecule to the pyramidal

configuration existing in molecular addition complexes. A reorganization energy of $\sim 48 \text{ kcal. mole}^{-1}$ was calculated for boron trifluoride which is the sum of the π -bond energy and the energy change in the σ -bonds when boron changes its hybridization from sp^2 to sp^3 . When these conditions have been satisfied, then the formation of a σ -bond with the donor completes the formation of the addition complex, assuming the adjustments to the donor are minimal.

While the reorganization energy of boron trifluoride should be constant for all complex formations of this type, it has been discussed here because of its interrelation with the other factors governing stability. It should be apparent that if the total energy released in the donor-acceptor bond formation is not of sufficient magnitude to overcome the reorganization energy the stability of the complex will be negligible, if it exists at all. Thus, the heat of dissociation or formation of this type complex is a relative measure of the donor-acceptor bond energy and should reflect some of the other factors governing stability. A brief discussion of the energetics of addition-compound formation has been given by Stone.⁴

b. Electronic configuration of the donor atom. If oxygen is taken as a specific example from the more common donor atoms listed previously, the effect of the electronic configuration of a donor atom on the complex stability may be shown. In organic compounds, oxygen is found in a number of functional groups; namely, the alkoxy, hydroxy, oxo, and carboxy groups. In the first two groups the oxygen atom bonds through sp^3 hybrid orbitals and has two of these orbitals filled and available

for σ -bonding with the acceptor. In the case of the oxo and carboxy groups the carbonyl oxygen is double bonded to the carbon atom with the result that the nucleophilic character of the oxygen is decreased. The general order of stability has been observed to be ethers > alcohols > carbonyl compounds.³

c. Polar substituents on the donor molecule. Whereas the electronic configuration of the donor atom affects the stability of addition complexes, the basic strength of the donor is also affected by the substituent groups of the donor molecule. Thus, the more electronegative these substituents are the greater is the influence exerted on the electronic character of the donor atom. A specific example of this may be cited from the work of Brown, Schlesinger, and Burg.⁹ The reaction of boron trifluoride with the carbonyl group in acetone, acetaldehyde, and trimethylacetaldehyde results in complex compounds of much greater stability than the corresponding reactions with acetyl chloride and chloral. Similar reaction with carbonyl chloride (phosgene) was not observed even at temperatures as low as -120°C . Many other examples of the substituent influence may be found, but in some cases the steric hindrance may also be involved.

The present investigation allows such comparison to be made since pentafluoroanisole is a compound with complete fluorine substitution on the benzene nucleus and with physical properties close to those of anisole. Thus, the effect of the fluorinated benzene nucleus on the properties of the pentafluoroanisole-boron trifluoride complex can be compared with those of the well characterized anisole-boron trifluoride complex.

The recent production of halogenated acetones by the Allied Chemical Company would provide an interesting series of compounds for similar investigations.

d. Steric hindrance in the donor molecule. The importance of steric effects on the stability of addition complexes can be readily shown from investigations by Brown and his colleagues. Brown and Adams¹⁰ demonstrated the order of stability of etherate-boron trifluoride complexes to be tetrahydrofuran > methyl ether > ethyl ether > isopropyl ether, which they attributed to the steric effects. Similar effects were also observed by Brown, Schlesinger, and Cardon¹¹ in the pyridine system where methyl substitution in the alpha positions resulted in decreased stability in the complexes with boron trifluoride, but in the benzonitrile system methyl substitution did not show steric effects.¹²

C. EXPERIMENTAL TECHNIQUE

1. Introduction

The most frequently employed techniques for investigating the stability of complex* compounds are pressure measurements of the thermal dissociation of the compound into its component parts or calorimetric methods. Each of these methods has advantages depending on the volatility of the component molecules. Where both have been used in the same investigation, the heat of formation of the complex in solution

*Complex will be used throughout this thesis to designate the donor-acceptor compound. In much of the literature this is referred to as an addition or molecular addition compound or coordination compound or bond.

agrees well with the heat of dissociation in the vapor phase.^{7,13} Other methods that have been employed to show the existence or structure, and in some cases the relative strengths, of complex compounds, are ultra-violet, infrared, and visible spectroscopy, electrical conductivity, thermal analysis of the phase diagram, X-ray diffraction, and nuclear magnetic resonance spectroscopy.

Since the measurement of the dissociation pressure is the most satisfactory method for studying liquid boron trifluoride complexes and is the method chosen for this investigation, it will be discussed below.

2. Dissociation Pressure Measurement Method

This method involves the measurement of the pressure over a complex compound as a function of temperature. In application to this investigation the complex equilibrium will be

so that the variation of the boron trifluoride pressure above the liquid with temperature will be related to the dissociation pressure of the complex. The total pressure will be equal to the dissociation pressure if there is no complex in the gas phase and if the partial pressure of pentafluoroanisole is negligible. It will be shown in the next section that the vapor pressure of pentafluoroanisole is indeed negligible (it is estimated to be 0.5 mm. Hg at -30°C.) and especially so when considering the magnitude of the boron trifluoride pressure over the complex. Since the partial pressure of pentafluoroanisole is negligible and the complex is not exceptionally stable, it can be safely assumed

that the complex does not exist in the gas phase.

From dissociation pressure measurements the enthalpy or heat of dissociation can be calculated which should be equivalent to the heat of formation of the donor-acceptor bond and, consequently, a measure of the bond strength. The free energy and entropy changes may, in some cases, also be calculated employing classical concepts.

The experimental techniques employed in studying the dissociation pressure of complex compounds are basic, but vary in principle with the investigators. Brown and Adams,¹⁰ Brown, Taylor, and Gerstein,^{14,15} and McLaughlin and Tamres¹⁶ have developed techniques to obtain very precise measurements at low pressures. Palko and his colleagues^{17,18} have used a technique which is more applicable to this investigation.

The general principle of the dissociation pressure measurement is similar to that of the standard vapor pressure measurement; the measurements are made on the complex contained in a thermostated vessel attached to a manometer or mechanical pressure measuring device. A major exception to this analogy is that the quantity of complex should be large and the gas space small to prevent excessive variation in the complex composition due to the boron trifluoride escaping into the gas phase.

D. PROPERTIES OF MATERIALS

1. Physical and Chemical Properties of Boron Trifluoride

a. Physical properties. A complete presentation of the physical and chemical properties of boron trifluoride may be found in references

2, 17, 19, and 20. Relevant values of the physical properties of boron trifluoride are presented in Table I. The values presented are those used in all calculations in this thesis.

The heat of vaporization, 4.057 kcal. mole⁻¹, was obtained by Booth and Carter²¹ from the vapor pressure equation:

$$\log P_{\text{atm}} = 5.1009 - \frac{889.6^*}{T},$$

which holds over the pressure range of 10 to 50 atmospheres.

Rumold's²² determination of the gas density of boron trifluoride at 0°C. and 0 to 1 atmosphere pressure has been used to calculate, as shown in Appendix I, the coefficient of compressibility as 0.01674 atm.⁻¹ and an equation of state as

$$PV = nRT(1 - 0.01674P). \quad (1)$$

b. Chemical properties. Boron trifluoride is a colorless gas which readily reacts with atmospheric moisture producing white, pungent fumes. It does not burn or support combustion. Under anhydrous conditions it does not react with mercury, glass, or chromium plate at room temperature or below, even at high pressures.²¹ At low pressures and up to 200°C. nickel, Monel, copper, mild steel, stainless steel, zinc, cadmium, aluminum, brass, silver solder, and soft solder are not attacked, and many halogenated plastics are unattacked up to 80°C.²³

Boron trifluoride reacts with the alkali and alkaline earth metals to produce free elemental boron or the metal boride and metal

*Throughout this thesis the common logarithm will be designated as $\log$ and the natural logarithm as $\ln$.

TABLE I
PHYSICAL PROPERTIES OF BORON TRIFLUORIDE

Property	Value
Molecular Weight ^a	67.806
Melting Point ²	-127°C.
Boiling Point ²	-101°C.
Critical Temperature ²¹	-12.25°C.
Critical Pressure ²¹	49.2 atm.
Gas Density at 0°C. ²²	3.07666 g./l.
Heat of Vaporization ²¹	4.057 kcal./mole

^aAll molecular weights in this thesis are on the carbon-12 atomic weight scale.

fluoride. It reacts with many metallic oxides and oxygen containing salts giving a boron oxyfluoride and the corresponding metallic fluoride or tetrafluoroborate.² Tetrafluoroborates are also produced from the reaction with the fluorides of the alkali and alkaline earth metals and some other monovalent metal fluorides.¹⁹ It also reacts with many organic compounds where hydrogen fluoride is split out as a reaction product and many organoboron compounds are synthesized through the reaction of boron trifluoride with organometallic compounds.²

The solubility of boron trifluoride in most polar solvents is very great, primarily because of its strong electron pair acceptor properties. Thus, it dissolves in and forms coordination compounds with a large number of chemicals such as water, anhydrous ammonia, mineral acids, and organic compounds containing oxygen, nitrogen, sulfur, and phosphorus. Many of these addition or coordination compounds of boron trifluoride were discussed above.

More complete discussion of these compounds and the reactions of boron trifluoride are given by Booth and Martin,² Greenwood and Martin,³ Ryss,²⁰ and The Harshaw Chemical Company Data Sheets.²⁴

c. Toxic properties. The toxicity of boron trifluoride is due to the ease of hydrolysis by atmospheric moisture producing hydrogen fluoride and other products such as hydroxyfluoroboric acid, fluoroboric acid and boric oxide. Inhalation irritates the respiratory tract and contact with the skin can cause burns. The strong, pungent odor and white fumes characteristic of a boron trifluoride release are ample warning to prevent acute exposure under most circumstances.

2. Properties of Pentafluoroanisole

Since pentafluoroanisole (methoxypentafluorobenzene) is a relatively new compound, and relatively expensive at the present time, the available information on the physical and chemical properties is meager.

a. Physical properties. The reported physical properties²⁵⁻²⁷ of pentafluoroanisole are given in Table II. The melting point is believed to be in error as will be shown in Chapter III.

The heat of vaporization at a boiling point of 138°C. is calculated to be 8.6 kcal. mole⁻¹ assuming an entropy of vaporization of 21 cal. deg.⁻¹ mole⁻¹. The use of this value for Trouton's constant seems justified since values of 22.1 and 21.3 cal. deg.⁻¹ mole⁻¹ have been experimentally obtained for hexafluorobenzene and pentafluorobenzene, respectively, by Patrick and Prosser,²⁸ and a value of 21.4 cal. deg.⁻¹ mole⁻¹ can be calculated for hexafluorobenzene from the data of Counsell, Green, Hales, and Martin.²⁹ Using the heat of vaporization, the vapor pressure equation for pentafluoroanisole was calculated as

$$\log P_{\text{mm}} = 7.4698 - \frac{1886.8}{T^{\circ}\text{K.}} \quad (2)$$

Observation of the vapor pressure of pentafluoroanisole during distillation and mass spectrometer analyses indicates that this equation is a very close approximation of the pressure-temperature relationship.

b. Chemical properties. The chemical properties of pentafluoroanisole have not been widely investigated, but the available data suggest that it reacts in some ways like anisole.

TABLE II
PHYSICAL PROPERTIES OF PENTAFLUOROANISOLE

Property	Value
Formula	$C_6F_5OCH_3$
Formula Weight	198.093
Melting Point ²⁵	-37.0°C.
Boiling Point ^{25,26}	138-139°C.
Density, 25°C. ²⁵	1.493 g./cc.
Refractive Index, n_D^{25} ²⁵	1.4085
n_D^{20} ²⁶	1.4090
n_D^{18} ²⁷	1.417

Pentafluoroanisole, prepared by the reaction of sodium methoxide with hexafluorobenzene in methanol^{26,27} or pyridine,³⁰ is a clear, colorless, mobile liquid having an odor characteristic of many fluorinated compounds. It is miscible with ethyl alcohol, acetone, and benzene, but immiscible with water. Pentafluoroanisole is relatively stable to heat; pyrolysis products obtained at 525°C. and atmospheric pressure have been about 95 per cent pentafluoroanisole.³¹

Anhydrous aluminum chloride reacts with pentafluoroanisole at 120°C. giving a 58 per cent yield of pentafluorophenol when the mixture is poured onto ice.²⁶ Demethylation also occurs by action of hydrogen halide acids, but with more difficulty. Refluxing pentafluoroanisole with 47 per cent hydriodic acid for 48 hours yields only 20 per cent pentafluorophenol³⁰ while the use of 47 per cent hydrobromic acid and 17 hours reflux gives only 9 per cent yield.²⁶

Hydrazine hydrate in ethanol reacts with pentafluoroanisole under reflux conditions giving the hydrazine salt of pentafluorophenol, hydrazinium pentafluorophenoxide, $(C_6F_5O, ^- + H_3N \cdot NH_2)$.²⁶ Similarly, reaction with aqueous ammonia results in cleavage of the alkoxy bond producing ammonium pentafluorophenoxide.³² Water appears to be required for these reactions since they do not occur in nonaqueous solvents, but distilled water does not by itself give reaction.³²

Sodamide in liquid ammonia does not split the ether link, but does replace a fluorine atom with the amide group giving 14 per cent yield of tetrafluoro-p-anisidine.³²

Recent investigations^{26,27,30,32,33,34} on completely fluorinated

aromatic compounds, especially hexafluorobenzene, have shown that complete fluorine substitution on the benzene nucleus imparts unusual properties to this class of compounds. The small size of the fluorine atom and its strong inductive and mesomeric character influence the reactivity of the aromatic nucleus by decreasing its activity toward electrophilic attack, while increasing the susceptibility to nucleophilic attack. In general, pentafluoroanisole is relatively stable to nucleophilic attack in the nucleus because of the presence of the electron-releasing alkoxy group. Cleavage of the ether bonds by hydrolysis giving the phenoxide and demethylation producing the phenol do occur, but with difficulty. The reaction with aluminum chloride, a Lewis acid, indicates that pentafluoroanisole is a Lewis base of fair strength despite the powerful electron-withdrawing effect of the pentafluorophenyl group. The sodamide reaction as well as the formation of some tetrafluorodimethoxybenzene during preparation of pentafluoroanisole²⁷ shows that additional nucleophilic substitution can occur.

For a general review of the preparation, properties, reactions, and applications of fluorinated organic compounds reference should be made to the monograph by Pavlath and Leffler.³⁴

c. Toxic properties. The toxicity of pentafluoroanisole is not known. Consequently, necessary precautions should be observed when working with this or any other fluoroaromatic. There is evidence that hexafluorobenzene and other halogenofluorobenzenes have potential uses as anesthetics and analgesics.³⁵

E. PROPERTIES OF THE ANISOLE-BORON TRIFLUORIDE COMPLEX

As previously mentioned, the effect of complete substitution of fluorine atoms in the benzene nucleus on the donor properties of the ethereal oxygen atom may be shown by the relative properties of the pentafluoroanisole and the anisole complexes with boron trifluoride. The pertinent properties of the latter complex will be briefly reviewed.

The reaction of boron trifluoride with anisole, mole per mole, to give a clear, viscous liquid which could not be distilled was reported by Bowlus and Nieuwland³⁶ in 1931. In 1932 Meerwein and Maier-Hüser³⁷ reported the melting point of this new molecular compound to be -12° to -13°C .

More recently Paiko and his colleagues^{17,38,39} have investigated this system and found the formation of the complex to occur readily at 0°C . The freezing point of the complex was reported to be approximately 2°C , and the heat of reaction of boron trifluoride gas with liquid anisole was determined from dissociation pressure measurements on four compositions of boron trifluoride in anisole to be $12.3 \text{ kcal. mole.}^{-1}$. Vapor pressure equations for the dissociation data were not presented, but their curves show the pressure of boron trifluoride over a 0.92 mole ratio complex to be approximately 139 cm. Hg at 35°C . and 31.2 cm. Hg at 10°C .³⁹

Madix and Barber⁴⁰ have determined the freezing point of the anisole-boron trifluoride complex to be 3.0°C . and have measured the dissociation pressures for several compositions of boron trifluoride in anisole. The heat of dissociation calculated from the slopes of the

pressure curves were in agreement with the values which can be calculated from the pressures curves reported by Palko.³⁹ Henry's Law behavior was observed up to about 0.4 mole ratio of boron trifluoride to anisole. The density, viscosity, and volume relationships for the liquid complex were also determined. The density relationship with temperature and composition is shown in Appendix II of this thesis.

CHAPTER II

EXPERIMENTAL APPARATUS

A. GENERAL DESCRIPTION

The vapor-liquid equilibrium of the pentafluoroanisole-boron trifluoride complex was determined at pressures ranging from approximately 10 to 275 cm. Hg and temperatures ranging from approximately 20° to -60°C. The apparatus was designed to obtain these extreme conditions, especially the high pressure and low temperatures, and to maintain them for long periods of observation. Briefly, the apparatus consisted of the equilibrium tube in which the complex was prepared and studied, pressure and temperature measuring devices, a constant temperature bath and control system, and the gas manifold and vacuum system. These components are described in detail in the following sections.

B. EQUILIBRIUM TUBE FOR PREPARATION AND STUDY OF COMPLEX SOLUTIONS

The design of the all metal equilibrium tube was based on one previously used by McGill, Wendolkowski, and Barber⁴¹ in determining the phase diagram of the hydrogen fluoride-chlorine trifluoride system. The tube was of welded Monel and nickel construction and contained a totally enclosed, magnetically coupled, externally driven stirrer. The sample chamber could be immersed in a constant temperature bath. The valve and the magnet coupling housing for the stirrer were kept at ambient temperature. A cross section drawing of the tube is shown in Figure 1. Standard Monel tubing with 0.035-inch wall thickness was

Figure 1. Cross section of equilibrium tube for preparation and study of complex solutions.

used whenever possible and the Monel end caps were also machined to this thickness. The completed assembly was helium leak-tested under vacuum and hydrostatically pressure tested at 300 psig. Construction details of the equilibrium tube are given below.

1. Construction Details

a. Sample chamber. The sample chamber was 1 inch in diameter and 3-5/16 inches in length. With end caps in place, the inside length was 2.99 inches. A thermowell made from 1/8-inch diameter nickel capillary tubing with an inside diameter of 0.090 inch was welded closed at one end and extended through the bottom end cap into the sample chamber approximately 1-1/2 inches. The top end cap was welded to the 1/4-inch diameter tube of the plunger shaft housing.

b. Plunger shaft housing. The plunger shaft housing connected the sample chamber to the plunger housing. The total length was 9 inches, but consisted of two pieces of tubing and a Monel tee machined from a 1/2-inch diameter rod 3/4-inch long. The center of this tee was located 7 inches above the sample chamber and 2 inches below the plunger housing. A 1/4-inch Hoke model 1479 valve was welded to the tee. The equilibrium tube was attached to the manifold by a 1/4-inch Dalton fitting silver soldered to the valve tube. The design of this section of the equilibrium tube minimized the free volume above the sample chamber and the heat transfer between the plunger housing at ambient temperature and the sample chamber at the bath temperature, which was normally below 0°C. The valve permitted the tube to be

closed off when desired, especially when removed from the manifold for weighing or when the pressure transducer was being zeroed.

c. Plunger housing. The plunger housing was made of 3/4-inch diameter Monel tubing 2-5/8 inches long. The inside length was 2-11/32 inches, sufficient to permit maximum travel of the nickel plunger and, consequently, the stirrer basket in the sample chamber. The bottom end cap welded to the shaft housing was machined as were those for the sample chamber. The top cap was a Dalton fitting welded in place.

This fitting was sealed with a blank gland which was soldered to a 3/8-inch male flare coupling which provided a convenient and rigid connection for mounting the equilibrium tube in a given position in the constant temperature bath. An L-shaped 3/8-inch Monel tube with a flare nut on the short leg and the long leg clamped to the vacuum rack served as the mounting fixture and allowed clearance for the vertical movement of the magnet stirrup. The flare fitting connection also facilitated the attachment of a hanger when weighing the equilibrium tube below the Mettler balance.

2. Stirrer Construction and Operation

The totally enclosed, magnetically coupled stirrer permitted rapid attainment of liquid-vapor equilibrium. Another important consideration was that the system could be safely operated at high pressures without fear of a shaft seal failure and was leak tight under vacuum. The stirrer and drive mechanism are shown schematically in Figure 2.

Figure 2. Schematic diagram of enclosed magnetic stirrer and drive mechanism.

a. Construction. The stirrer basket was 1-3/4 inches in overall length and was fabricated from 1/16-inch diameter Monel welding rod. It consisted of three vertical supports at 120° intervals welded to the inside of three 11/16-inch rings spaced 1/2-inch apart. The stirrer shaft was an 11-inch long by 1/8-inch diameter Monel rod welded to the basket. One inch of this shaft was threaded and was screwed into a tapped hole in the bottom of the 0.5937-inch diameter by 1-inch long nickel plunger. The top of this plunger was slotted so that a screw-driver could be used to tighten it against a stainless steel nut previously screwed onto the shaft. This arrangement allowed the stroke of the plunger and basket to be adjusted before the end caps were welded to the bottom of the sample chamber and the top of the plunger housing. The diameter of the plunger was 0.0813 inch less than the inside diameter of the housing.

b. Motor and drive mechanism. The drive mechanism for the stirrer was a Brown Instrument Company motor with an internal gear reducer operating at 16-2/3 rpm. and a torque of 5 oz.-ft. This motor was mounted in the vacuum rack above the equilibrium tube. A brass drive wheel 4 inches in diameter was attached to the motor shaft. This wheel was drilled and tapped at various distances from the center so that the proper stroke could be chosen. A machine screw in the hole 1 inch from the center of this drive wheel served as a shaft for a small ball bearing instrument pulley wheel. The end loop of a 1/32-inch diameter stainless steel instrument cable was placed on this pulley, passed up and over another pulley, mounted to an aluminum bar directly

over the center of the drive wheel, then out along this bar and over another pulley positioned above the equilibrium tube, and down to the stirrup holding the magnets. The cable was secured at each end with screw lugs removed from electrical connectors. These lugs were found to be ideal connectors since the cable was very difficult to solder or tie. Also the length of the cable could be easily adjusted by loosening the lugs and moving the cable.

c. Magnets. The magnetic coupling of the stirrer plunger to the drive motor was through two, thin circular ceramic magnets. The poles were directed into the center hole of each magnet. The dimensions were 2-7/8-inches in diameter, 3/8-inch thick with a 1-inch diameter hole in the center. A stirrup which held the magnets was constructed as described below.

The magnets were placed one on top of the other and sandwiched between 1/16-inch thick aluminum plates with center holes cut to match those in the magnets. A 1/8-inch diameter brass rod bent into a V at the center and with parallel sides was threaded on both ends. The ends were passed through small holes in the aluminum plate on either side of the magnets and were secured on each side of the plates with screw nuts. The cable connecting the motor drive wheel to this stirrup was looped around the V portion of the brass rod. The magnet stirrup was placed on the plunger housing before the equilibrium tube was mounted.

d. Performance. Operation of this stirrer was very satisfactory. However, there were occasions when more rapid agitation of the liquid

complex was desired. On these occasions the magnets were lifted and dropped by hand at a faster rate than the 16-2/3-rpm. motor speed.

The flux produced by these two magnets was not known, but tests indicated that the coupling between the magnets and the nickel plunger in the housing required 1011 g. to effect separation. About 690 g. of this was required for stirrer movement.

One undesirable result of the stirrer operation was a small fluctuation in the pressure measurements. This was due in part to the change in liquid volume as the stirrer basket moved in and out of the liquid and to the compressive action of the plunger. This fluctuation was proportional to the pressure and was more serious at the higher pressures.

3. Calibrations

a. Volume. Since the true solution composition in the equilibrium tube depended on the accuracy with which the number of moles of boron trifluoride added to the system could be calculated from PVT. data, it was imperative that the system volume be known. Furthermore, the volume of the equilibrium tube had to be known when loading the pentafluoroanisole, and an approximation of the gas volume during the experiments was desirable.

One of the usual methods of calibrating volumes is to determine the weight of water contained by the vessel. However, with the construction of the equilibrium tube, the sharp corners, areas of small clearance, moving parts, and the double ends, the possibility of

difficulties and errors was obvious with this method. Consequently, the equilibrium tube and a larger nickel cylinder, to be used as the boron trifluoride charging volume, were submitted to the Powder Analysis Group of the Works Laboratory for the volume determination.

The volumes were then obtained by gas measurements using the precise equipment and techniques this group processes for the measurement of solid surface areas. The average values for three determinations with an error of approximately ± 0.2 per cent were 43.98 and 929.8 cc. for the volume of the equilibrium tube and storage cylinder number 1, respectively. The calculated volume of the equilibrium tube was 43.72 cc., in excellent agreement with the experimental value.

b. Temperature. Because temperature differences would normally exist between the sample chamber and plunger housing and these differences would directly affect the calculated number of moles of boron trifluoride in the gas phase at various pressures, an arithmetical analysis of the volume and temperature data was performed. With the equilibrium tube in the standard position (the top of the sample chamber 2-1/8 inches below the bath surface) the bath was controlled at three temperature levels. During these periods, the bath thermocouple was taped to the wall of the shaft and plunger housing at three locations. These were: position 1, top of shaft housing immediately below plunger housing, 2, shaft housing immediately below the tee, and 3, outside diameter at bottom of plunger housing. The temperature at each of these positions with respect to the sample chamber temperature was obtained. The volume for five sections of the equilibrium tube was calculated and

the average of the temperature differential for each section was determined from the temperature measurements. The arithmetic mean of the system temperature at each bath temperature was then calculated by the following equation

$$t_m = \frac{\Sigma [(\text{midpoint of temp. range}) (\text{volume in this range})]}{\Sigma (\text{volume})} .$$

As an illustration, at a bath temperature of -26.0°C . the temperature at thermocouple position 2 was 18.17°C . This temperature differential was along a 4-inch length of the shaft housing between the bath surface and position 2. The mid-point of the temperature differential was -3.91° and the volume was calculated to be 0.861 cc. giving a product of -3.36 . A similar treatment was carried out on the other sections and the mean temperature of the gas volume above the liquid complex at a bath temperature of -26.0°C . was calculated to be 7.76°C .

A plot of the mean temperature, t_m , as a function of the bath temperature, t_b , gave a straight line expressed by the equation

$$t_m = 0.3582 t_b + 17.15, \quad (3)$$

when the room temperature was 26.6°C . Since the room temperature would vary, it was assumed that a series of parallel lines around this line would be valid. Consequently, the value of the constant, 17.15, was changed in direct proportion to the difference between 26.6°C . and room temperature at the time of observation. This equation was then used for calculating the mean temperature of the gas phase as a function of the bath temperature and room temperature.

c. Thermal contraction. Another consideration was that contraction of the equilibrium tube would occur on cooling to low temperatures. Thus, a decrease in volume would result in a decrease in the gas volume. The linear thermal expansion coefficient, α , for Monel is 14×10^{-6} cm.cm. $^{-1}$ °C. $^{-1}$, and taking the calculated volume of the sample chamber as 33.303 cc., the volume change due to a change in temperature from 25° to -40°C. was calculated from the equation

$$V_t = V_{25} [1 + 3\alpha(t - 25)].$$

The volume, V_t , at -40°C. was calculated to be 33.212 cc. Thus, the 65° decrease in temperature results in a decrease in volume of approximately 0.091 cc. or 0.1 cc. maximum. This change was within the accuracy of the volume determination and well within the ability to calculate the solution density. Since this volume change was a minor source of error, it was neglected.

C. PRESSURE MEASUREMENTS

Due to the high pressure of the boron trifluoride over the pentafluoroanisole-boron trifluoride complex, the potential corrosive nature of boron trifluoride on exposure to moisture, and the necessity of minimizing the gas volume over the complex, special equipment for the pressure measurements was necessary. These requirements were satisfied by the pressure measuring system described below and schematically shown in Figure 3. Briefly, the system was built around a Statham pressure transducer which was the primary sensing element attached to the system. This transducer required an inert gas supply as a reference pressure to

Figure 3. Schematic diagram of reference pressure system.

maintain the differential pressure across its diaphragm within prescribed limits. Since the pressure transducer was a differential measuring device with a maximum differential pressure of 5 psig., the pressure of the reference system gives the absolute system pressure. The reference side of the transducer was connected to a manifold which could be evacuated, or pressured to 100 psig. with the building compressed air supply. The pressure in this system was measured with a Wallace and Tiernan Dial Manometer having a pressure range of 0 to 300 cm. Hg. A 125-cm. mercury manometer was also included in the reference system for calibrating the Wallace and Tiernan Dial Manometer and for continuously monitoring the performance of the reference system. Except for the pressure transducer, all of this system was mounted on the instrument rack with the recorder.

1. Transducer

A Statham Laboratories pressure transducer, model number P189a-5D-350, was used to measure the boron trifluoride pressure over the complex. It required a 10 volt DC excitation potential and had an output of 0 to 5 volts maximum for 0 to 5 psig.

The operating principle of the transducer is based on that of the unbonded strain gage transducer. The element is an electromechanical device which transduces minute changes of displacement to sensible resistance changes proportional to the displacement. It is simply described as a Wheatstone bridge comprised of four strain sensitive resistance wires. Displacement of the sensing diaphragm by pressure changes moves an armature which changes the resistance of the wire

filaments. This resistance change alters the electrical balance of the bridge to produce an electrical signal in the output circuit.

The transducer control unit was connected to the transducer through shielded cable with Cannon 6-pin connectors. This unit supplied the 10 volt DC input voltage to the transducer from two 6-volt dry cell batteries contained in the shielded metal box. It also contained the on-off switch, zero-adjustment and standardization controls, and connections for the output measuring device.

The transducer was custom fabricated, containing a Monel diaphragm for use with corrosive systems, and was supplied with a 1/4-inch Dalton gland for connecting it to the system. The volume of the transducer exposed to the system was small and was minimized even more by the use of a specially drilled Dalton gland which has a 1/32-inch diameter passage.

The transducer was connected to the system by means of the Dalton connection at a point just past the Hoke valve on the equilibrium tube. Immediately on the other side of this connection was another valve. The volume of this section of the manifold including the transducer was 3.61 cc. The connection of the transducer to this part of the system permitted it to be used for measuring either the manifold pressure by closing the valve to the equilibrium tube or the system pressure by closing the manifold valve. The equilibrium tube could also be closed off and removed from the manifold without moving the transducer and the transducer could be zeroed with an inert gas admitted through the manifold valve when the valve on the equilibrium tube was closed.

2. Recorder

A 0 to 10 millivolt Leeds and Northrup Speedomax strip chart recorder was connected to the control unit to measure and record the electrical output of the transducer bridge circuit. The signal to the recorder was adjusted by means of the zero control on the transducer control unit so that when the transducer was calibrated with the same pressure on either side, the zero or null position was at midscale, or 5.00 mv. Thus, at a given reference pressure, an increase in the recorder reading corresponded to an increase in the system pressure, and a decrease in the recorder reading represented a decrease in system pressure.

With this read-out a continuous record of pressure changes at a given reference pressure was obtained as a function of time. This was valuable due to the large pressure excursions which rapidly occurred when the complex froze or melted. It also permitted the recording of fewer data points during the pressure-temperature equilibrium studies since the equilibrium conditions were represented by the recorded pressure changes. As mentioned previously, the stirrer operation caused fluctuations in the pressure measurements. These were recorded as a rapid oscillation in the recorder trace which resulted in a continuous broad line, the width of which varied with the pressure levels. At low pressures this curve was approximately 0.02 mv. in width and increased to as much as 1.0 mv. at the highest pressures. Since the recorded curve was essentially a solid line, the midpoint was taken as the millivolt reading corresponding to the actual pressure.

3. Reference Pressure Manifold

The reference pressure manifold was fabricated with 1/4 and 3/8-inch diameter copper tubing. Connections within the system were silver soldered or made with standard compression or flare tubing fittings. The schematic diagram of this manifold was presented in Figure 3, page 30.

Pressures below atmospheric were obtained with a Welch Duo-Seal vacuum pump. This pump was also used to evacuate the absolute side of the mercury manometer and the Wallace and Tiernan Dial Manometer. These instruments were always evacuated for periods of at least 10 to 12 hours and then the valve was closed just prior to their use.

Reference pressures above atmospheric were obtained by using dry compressed air from the building service. A Taylor air-set regulator was used to adjust the pressure in the manifold up to about 30 psig. Above this pressure the high pressure air was slowly admitted directly into the manifold. A valve opening to the atmosphere was used to bleed the manifold pressure down when necessary. When the manifold pressure reached the upper range of the mercury manometer it was isolated to prevent blowing out the mercury.

The pressure transducer was located some distance from this manifold and was connected to it by 1/4-inch diameter, high pressure, polyethylene instrument tubing. This tubing was also used for connecting the system manifold to the reference pressure manifold. This connection was necessary for supplying the same pressure condition to both sides of the transducer when it was zeroed.

4. Wallace and Tiernan Dial Manometer

The Wallace and Tiernan manometer is a precision dial manometer having a range of 0 to 300 cm. Hg. It has a precision constructed mechanism and a hand drawn scale to match the calibration against a precision-bore liquid column at 100 or more points. The dial is 8-1/2 inches in diameter with an effective scale length of 45 inches in two revolutions. The scale has 600 graduations and is expanded at the low pressure-end. The smallest graduation is 0.5 cm. This instrument is said to respond to pressure changes with a sensitivity of 1 part in 10,000 of the scale range, or 0.3 mm. The accuracy is 1 part in 1,000 of the scale range and the hysteresis effect is 1 part in 1,000 for a full-range change in pressure. This is an accuracy and hysteresis effect of 0.3 cm. or 3 mm. This dial manometer was factory calibrated at 25°C., and the temperature correction was 0.375 per cent per 10°C. change in temperature above or below 25°C.

The case was constructed so that it could be completely evacuated for measuring absolute pressures or it could be pressured up to 35 psig. for extending the range or making differential measurements. A check valve between the reference and system sides of the mechanism opened when the pressure went above the maximum scale range. In this instrument the valve opened at about 285 cm.; consequently, the upper range of pressure measurements was limited to about 275 cm.

In this work the case was always evacuated for making absolute measurements. A mirrored band around the dial and a fine black pointer contributed to accurate readings. While the smallest scale division

was 0.5 cm. and the overall accuracy was only 0.3 cm. the spacing between graduations easily allowed the reading to be estimated to 0.1 cm., and in some cases this could be extended to 0.05 cm.

5. Calibration

a. Pressure transducer. Calibration of the pressure transducer consisted of the evaluation of the electrical output in terms of pressure and the hysteresis of the zero at different pressure levels. The output versus pressure calibration was obtained by using a loop system, one end of which was connected to the system side and the other to the reference side of the transducer. In each side was a mercury manometer and necessary valves to permit vacuum and pressure manipulation of nitrogen gas. Both sides of this loop could be opened to form a common system, or each side could be closed off and operated independently of the other. With this setup the transducer output recorded on the 0-10 millivolt recorder was checked at several different pressure levels. The recorder was zeroed at 5.00 mv. for zero pressure differential; the output was then checked over the ± 5.00 mv. range in units of one millivolt or less as the reference or system pressures were changed and measured on the manometers. Straight lines drawn through the points so obtained gave values of $1.045 \text{ mv.cm.}^{-1}$ or $0.961 \text{ cm.mv.}^{-1}$. Periodically during the course of the experimental work on the complex system a similar check, using only the reference manifold and its connection to the gas manifold, was made. These checks showed that this value was shifting upwards to an ultimate value of about 1.05 cm.mv.^{-1} . This change was believed to

have resulted from strain on the transducer caused by overranging which frequently occurred when the sample solidified or melted or when the equilibrium tube was opened too rapidly to the transducer at the start of each work period.

The value of $0.961 \text{ cm.mv.}^{-1}$ was used throughout this work. The reason the later values were not used was that the recorder readings were maintained within $\pm 0.5 \text{ mv.}$ or less of the midscale null point so that the difference in the pressure could be as much as $\pm 0.045 \text{ cm.}$ Since the accuracy of the reference pressure measured on the Wallace and Tiernan Dial Manometer was 0.3 cm. , this was considered to be a minor source of error.

The transducer hysteresis or zero shift was checked out in detail from vacuum to slightly above atmospheric pressure. The technique used was to put the same pressure on both sides of the transducer using the loop system described above and then varying the pressure level. Changes in the recorder null position could be established. It was found that the null position did not change except from about 3 mm. Hg to vacuum, where the output changed rapidly giving a maximum of about $+ 0.4 \text{ mv.}$ at zero pressure. Similar checks up to the highest pressure measured, 275 cm. Hg , showed that a hysteresis of only about 0.05 to 0.10 mv. existed over the whole range of pressures checked. In actual practice this effect was eliminated since the transducer was zeroed before each series of measurements by applying a null pressure to each side from the reference manifold. This pressure corresponded to the expected range of the experimental measurements; and if a large range was anticipated,

then two or more null pressure points were obtained and appropriate corrections made to the measurements.

b. Dial manometer. Calibration of the Wallace and Tiernan Dial Manometer was accomplished by checking it against the 125-cm. mercury manometer at various pressure levels. The pointer on the dial manometer was off zero by + 0.1 cm. A screwdriver adjustment was provided for setting the pointer, but efforts to remove a plug in the vacuum case for making this adjustment were not successful so it was used with this setting. Below pressures of about 60 cm. Hg, the difference in the dial and mercury manometer readings clearly reflected the error in the pointer setting. Above this pressure and up to 200 cm. Hg the difference in the readings was between + 0.16 and - 0.10 cm. These were considered as reading errors and within the 0.3 cm. accuracy of the dial manometer. Consequently, dial manometer readings below 60 cm. Hg were corrected by subtracting 0.1 cm. No corrections were applied for other readings except for a temperature correction of ± 0.0375 per cent per degree applied to all readings when ambient temperature differed from 25.0°C.

D. TEMPERATURE MEASUREMENTS

1. Potentiometer and Thermocouples

The temperature of the sample in the equilibrium tube and of the bath was measured with copper-constantan thermocouples. The e.m.f. of the thermocouples referenced to ice was measured with a Leeds and Northrup Portable Precision Potentiometer. The e.m.f. was converted to temperature reading using the National Bureau of Standards table for copper-

constantan thermocouples, 1948 calibration,⁴² and a specially prepared interpolation table for fractions of degrees. Negative e.m.f. values for temperatures below 0°C. were obtained by reversing the thermocouple connections to the potentiometer.

The copper-constantan thermocouples were made from the same roll of insulated, duplex 30-gauge wire. The wires for the measuring and reference junctions were stripped, twisted together, and fused with a torch. The bath thermocouple was passed through a nickel capillary tube supported by the bath cover and exposed bare to the alcohol in the bath. The sample thermocouple was wrapped around the shaft housing of the equilibrium tube, extended down this tube, and up into the small thermowell located in the bottom of the sample chamber.

Both thermocouples were referenced to ice by placing the junctions in a 10-mm. diameter glass tube sealed at the bottom and partially filled with Octoil S oil. This tube extended through a cork stopper into the ice bath contained in a 665-cc. silvered Dewar flask. The ice was made in the building ice machine from sanitary water and was washed approximately three times with distilled water to reduce surface contamination and to decrease the cube size. Both thermocouples were connected to a two-position Leeds and Northrup switch which was connected to the potentiometer with a short length of insulated copper wire. With this switch either of the thermocouples could be read without having to change the connections to the potentiometer.

2. Thermocouple Calibration

The sample thermocouple was calibrated at three fixed points:

the transition of sodium sulfate at $32.38^{\circ}\text{C}.$, the ice point at $0.00^{\circ}\text{C}.$, and the freezing point of mercury, $-38.87^{\circ}\text{C}.$ In all cases the reference junction was referenced to $0^{\circ}\text{C}.$

For calibration at the ice point the bare thermocouple junction was placed in a $3/32$ -inch diameter hole drilled about $1/4$ inch into the end of a $1/2$ -inch diameter copper rod 2-inches long. The wire close to the junction was wound around this rod several times and placed in a 265-cc. Dewar flask containing ice and water. The ice in this flask had been washed several times to remove surface contaminants and to reduce the cube size. This flask was then placed in a larger Dewar flask also containing ice and water. Readings were made with the thermocouple polarity in the positive and negative directions and in each case 0.000 mv. equaled $0.00^{\circ}\text{C}.$

The freezing point of mercury was determined by immersing the bare thermocouple in triple-distilled mercury contained to a depth of approximately 3 cm. in a nominal 15 x 130 -mm. Pyrex test tube. This tube was then immersed in an unsilvered Dewar flask containing ethyl alcohol cooled below the freezing point of mercury. The cooling and warming curves were followed visually and by thermal changes giving average values of -39.08° , -39.00° , and $-39.08^{\circ}\text{C}.$ An average value of $-39.05^{\circ}\text{C}.$ was taken as the freezing point which was $0.18^{\circ}\text{C}.$ lower than the actual value of $-38.87^{\circ}\text{C}.$

Between $0^{\circ}\text{C}.$ and this temperature an equation

$$t(\text{obs}) = bt(\text{real}) \quad (4)$$

was used to describe the relation of the observed, $t(\text{obs})$, to the true

or real, $t(\text{real})$, temperatures. Assuming a linear deviation using the data obtained with the mercury, the constant b has the value, 1.0046. Thus, the observed temperature was corrected by dividing by 1.0046. This may not be strictly correct, but was an approximation deemed to give sufficient accuracy to the temperature measurements considering the accuracy of the pressure measurements.

For the third calibration temperature, Baker and Adamson reagent grade sodium sulfate (sodium sulfate decahydrate) crystals, minimum purity of 99.987 per cent, was placed in a test tube. The bare thermocouple was inserted into these crystals and the tube placed in warm water. While stirring, the solid-liquid equilibrium was followed for 25 minutes at an average temperature of 32.49°C . The solid-liquid mixture was then cooled, crystallizing around the thermocouple. It was warmed again and the transition was obtained at 32.49°C . Thus, the observed value of 32.49°C . for the sodium sulfate decahydrate transition was 0.11°C . greater than the real value of 32.38°C . Since the thermocouple polarity was reversed from that used in taking the mercury point, this positive deviation was in the right direction, and the constant, b , in equation (4) becomes 1.0034. However, the b value of 1.0046 was used throughout this work for correcting the temperature readings since only a few measurements above 0°C . were made. At the maximum experimental temperature of 20.38°C ., the corrected temperature using this constant was 20.29°C . as compared to 20.31°C . if the actual value was used. Here again, the 0.02 degree maximum difference was well within the reading accuracy of the potentiometer and the use of only one constant simplified

the writing of the IBM program for correcting and calculating data points.

While temperature readings are reported to $0.03^{\circ}\text{C}.$, the accuracy of the temperature measurements was probably on the order of $\pm 0.05^{\circ}\text{C}.$, considering the ability to read the light galvanometer and the assumption of a linear calibration for the thermocouple.

E. CONSTANT TEMPERATURE BATH AND CONTROL SYSTEM

A sub-zero, constant temperature bath was necessary for obtaining liquid-vapor equilibrium data on the complex system. The bath, cooling system, and controls are described below and shown schematically in Figure 4.

1. Constant Temperature Bath

The bath employed was set up using a 4300-cc. silvered Dewar flask. The bath fluid was denatured ethyl alcohol of which approximately one gallon was required to give the desired liquid depth. This depth was such that the surface was maintained approximately $2\text{-}1/8$ inches above the top of the sample chamber of the equilibrium tube. The Dewar flask was fitted with a cover consisting of two layers of 1-inch thick Styrofoam. The top layer was 8 inches in diameter and the bottom layer was 6 inches in diameter. The top layer, glued to the bottom layer, rested on the flask while the bottom layer was a snug fit to the inside diameter of the flask and served to keep the cover in place. Holes of appropriate size were cut in this cover for inserting the equilibrium tube and the bath accessories. This bath was placed on a support stand

Figure 4. Schematic diagram of constant temperature bath and control system.

connected to the vacuum rack and could easily be removed leaving the equilibrium tube, cover, and the accessories in their fixed positions.

The principal components were the stirrer, bath, thermocouple support tube, thermometer, heater, sensing element for the control system, and the suction and discharge tubes from the cooling system. The latter two will be discussed with the principal part of their respective systems. The molded polyethylene stirrer was a 1-3/4-inch diameter, 3-blade propeller with a 1/4-inch diameter shaft 18-inches long. The shaft contained a metal insert for rigidity. It extended almost to the bottom of the bath and was powered by a Fultork Laboratory stirrer motor operating on 115 volts and turning counterclockwise.

The thermocouple support tube was described previously, but was simply a 1/8-inch diameter nickel capillary tube through which the thermocouple wire was extended into the bath. A low-temperature Weston dial thermometer also extended into the bath in order to monitor the temperature. A 115 volt, 250 watt knifeblade heater was employed to raise the bath temperature when desired. It was connected through a Variac to the auxiliary circuit on the control unit, but was not controlled by this unit.

2. Temperature Control Unit

a. Controller. The controller for the thermostatically controlled low temperature bath was a proportional temperature regulator designed and fabricated by the Instrument Development Department of the Oak Ridge Gaseous Diffusion Plant. It was similar to those used by

Ritter,⁴³ but was modified to accept a resistance type sensing element and to control temperatures from above the set point rather than below. Simply described, this unit contains an AC operated measuring and amplifying circuit which measures the difference in the resistance of the sensing element and that of the selected set point and proportions the AC output to the cooling system in relation to the deviations from the set point. Additional control was obtained since the output passed through a manually operated variable transformer in the unit. Very fine control was maintained by adjusting this transformer with respect to the desired temperature levels.

The reference resistances corresponding to the desired temperatures were manually set on a 25 ohm, ten-turn helipot which was calibrated in terms of temperature with the bath and sensing element used in these experiments. The 25 ohm variable resistance gave a temperature range of 64.5°C. with a sensitivity of 0.39 ohms per degree, and was connected with sufficient resistance to cover the temperature range between 25.6° and -38.9°C. To obtain lower temperatures an additional 20 ohm resistance connected through a switch could be put in series with the helipot. With this resistance added, the new range of temperatures covered by the 25 ohm helipot extended from -26.0° to -90.5°C. making possible continuous control from 25.6° to -90.5°C.

b. Sensing element. A Leeds and Northrup Thermohm, number 8195-A10, was the bath sensing element. This element was a copper resistance thermometer enclosed in a copper case 4-3/8-inches long and 15/32 inch in diameter and attached to a 10-foot long, 3-wire

conductor in a lead sheath. The element was valued at 100 ohms at 77°F. with a range of -198° to 121°C., a response time of 40 seconds, and a limit of error of $\pm 0.3^\circ\text{C}$. from -73° to 121°C.

3. Cooling Systems

a. Primary system. This system consisted of a centrifugal pump withdrawing alcohol from the bath and circulating it through a coil immersed in a Dewar flask containing a Dry Ice-trichloroethylene slush. As the control unit measured changes in the bath sensing element, an AC current in proportion to the measured resistance differential actuated the Eastern Model E-1 centrifugal pump. The suction and discharge lines to this pump were 1/4-inch diameter copper tubing. The suction line extended almost to the bottom of the constant temperature bath and was insulated with asbestos sleeving. The discharge line contained a 3.5-inch diameter, 11-turn coil of 1/4-inch diameter copper tubing. This coil was immersed in a Dry Ice-trichloroethylene slush bath contained in a 4300-cc. glass Dewar flask. The discharge line from the coil was insulated with 1-inch square rods of Styrofoam which were bored through, cut into halves, and taped around the copper tubing. This line went into the bath on the side opposite the discharge line and extended about 2 inches below the bath surface. Thus, as the pump was energized by the control unit output, it slowly began to pump alcohol from the bath through the coolant coil and back into the bath. As the differential between the bath and set point increased, the output current increased and the pump operated at a faster rate. Conversely, as the temperature

decreased, the controller output current decreased and the pumping rate decreased; this prevented overshooting the set point.

The operation of these components was very satisfactory and gave excellent temperature control. The smooth operation of the cooling unit, especially at very slow rates, and the response time were important factors in achieving this control. The heat conduction into the bath through the metallic accessories did not cause any difficulties. Overall, the temperature control of the bath was such that the temperature fluctuations were not usually detectable and when variations were detected they were on the order of $\pm 0.03^\circ$ to $\pm 0.06^\circ\text{C}$. One disadvantage of this unit was that the Dry Ice consumption was fairly great and the unit could not be operated without attention for periods longer than about 12 to 13 hours at temperatures as low as -25°C .

b. Secondary cooling system. After the experimental work was underway a Lauda Ultra Kryostat, Model UK-60DW, was received. This unit contained two 3/4-HP compressors, a 6-gallon bath, a duplex internal and external circulating pump, and a control system, and was specified to maintain temperatures to $\pm 0.03^\circ\text{C}$. at -60°C . Since the primary cooling system and controls were performing equally as well, this unit was used only as a secondary system. When the solution compositions contained in the equilibrium tube were greater than 0.5 mole ratio of boron trifluoride to pentafluoroanisole, the temperature had to be maintained at -25°C . or less to prevent complex dissociation which produced a very high pressure of boron trifluoride in the gas phase. Consequently, when these conditions might exist for excessive periods of time, the Lauda

Ultra Kryostat was used to maintain the required bath temperature. In this case a closed loop system was used wherein the methyl alcohol from the internal bath in the Ultra Kryostat was pumped through insulated silicone tubing to a U-shaped, copper heat exchanger immersed in the system bath. This arrangement allowed the solution composition to be kept at high concentrations of boron trifluoride for long periods of time under safe conditions.

F. GAS MANIFOLD AND VACUUM SYSTEM

An all metal gas manifold and vacuum system previously used for experiments with boron trifluoride was employed in this work with minor modifications. This manifold was used for purifying and charging the boron trifluoride to the equilibrium tube, distilling the pentafluoroanisole into the equilibrium tube, and drawing boron trifluoride samples for analysis. A schematic diagram of this system is presented in Figure 5.

1. Gas Manifolds

a. Main manifold. This was fabricated with 3/8-inch diameter nickel tubing and nickel plated copper fittings, and was silver soldered throughout. All valves in this part of the manifold were Hoke model 413 valves silver soldered to the manifold and fitted with Dalton connectors. This manifold was made in two parts which could be used independently. Ashcroft compound bourdon tube gauges were included in each of these sections for rough pressure measurements. A thermocouple

Figure 5. Schematic diagram of gas manifold and vacuum system.

vacuum gage tube was used to measure low pressures in the main manifold. This manifold contained the connections to the vacuum system, nitrogen, and compressed air.

b. Boron trifluoride charging manifold. Attached to the main manifold at two of the valve positions was a U-shaped manifold made of 1/4-inch diameter nickel tubing with silver soldered connections. A 2.5-inch compound Ashcroft bourdon tube gauge was used to measure pressures. Three other connections were available to this manifold. A Hoke model 432 valve silvered soldered to the manifold and to a special Dalton fitting was the connection to which the pressure transducer and equilibrium tube were attached. An identical valve also connected this manifold with the boron trifluoride cylinder and primary purification system. The third was an open connection to the valved storage volume for the purified boron trifluoride. This was a welded nickel cylinder 3 inches in diameter and 9-inches long with a Hoke model 411 valve welded to the top. It is labelled as cylinder no. 1. in Figure 5, page 49. Its volume was calibrated to be 929.8 cc., as previously stated.

Since this small manifold was used in conjunction with the storage volume and pressure transducer for charging boron trifluoride into the complex by PVT. measurements, the volume had to be determined. This was accomplished by using the storage volume and the equilibrium tube as standard volumes and calculating the manifold volume from PVT. measurements. As previously mentioned, the volume of the storage cylinder and the equilibrium tube were accurately determined by PVT. methods.

The volume of the manifold was determined to be 25.59 cc. and that of the pressure transducer section to be 3.61 cc. The total volume of the storage volume, manifold, and pressure transducer connection used in calculating the moles of boron trifluoride added to the complex system was 958.74 cc.

c. Boron trifluoride supply manifold. This manifold was connected to the Hoke model 432 valve on the boron trifluoride charging manifold. It was also of 1/4-inch diameter nickel tubing with silver soldered and compression fitting connections. The other end of this manifold was connected to the standard pressure regulator attached to the 60-pound high pressure cylinder containing boron trifluoride gas. Between the cylinder regulator and the charging manifold was a tee type Hoke model 415 valve. The through ports were soldered to the manifold and the tee soldered to a Dalton fitting. To this valve a nickel cylinder identical to the storage volume on the charging manifold was attached. This is labelled as cylinder no. 2 in Figure 5, page 49. This cylinder was used for the primary purification of boron trifluoride and for taking samples of the boron trifluoride for mass spectrometer analysis. A smaller nickel cylinder containing fluorine at about 5 psig. was attached at this point for treating the manifolds from time to time.

2. Vacuum Systems

There were two vacuum systems, the primary one being used most of the time. The other was the high vacuum system used only at the startup to ensure a dry, leak-tight system. It was a glass mercury

diffusion pump backed with a Welch Duo-Seal mechanical pump, and it was connected to the main manifold through 1/2-inch diameter copper tubing.

The primary system was connected to the main manifold in two places as shown in Figure 5, page 49. These connections were with 1/2-inch copper tubing. One of these lines contained the chemical trap for disposing of boron trifluoride and fluorine. This was a 4-inch diameter by 24-inch long flanged trap containing a mixture of soda lime and activated alumina. The exit line from this trap was connected to a Hoke valve which in turn teed into the vacuum line. The other line came from the manifold to this tee, thence to a glass trap cooled with a Dry Ice-trichloroethylene slush, and then to a Welch Duo-Seal vacuum pump. With the chemical trap valves closed, a vacuum in the manifold of approximately 5 microns could be obtained.

CHAPTER III

EXPERIMENTAL PROCEDURES

A. INTRODUCTION

The experimental procedures and techniques employed in this investigation will be outlined in detail in this chapter. Included will be the source, purification, and analysis of the reagents, preparation of the complex, and a general description of the procedures employed in obtaining the dissociation pressure and freezing point data. Frequent reference will be made to apparatus described in the foregoing chapter and other apparatus will be described in this chapter as necessary.

B. REAGENTS

1. Boron Trifluoride

The boron trifluoride used in these experiments was obtained from The Matheson Company in a 60-pound high pressure gas cylinder. This cylinder was connected to the system as described in Chapter II.

a. Purification. While the boron trifluoride in the high pressure cylinder was found to be of high-purity, it was further purified by the following procedure. Gas from the high pressure cylinder was admitted to the evacuated, 1-liter nickel cylinder (No. 2 in Figure 5, page 49) in the purification manifold to a pressure of about 40 psig. A Dewar flask containing liquid nitrogen was then placed around this vessel condensing the gas to solid boron trifluoride. The

vessel was opened to the vacuum system and evacuated to approximately 10 microns while being maintained at -198°C . The valve was closed, the liquid nitrogen bath removed, and replaced immediately by another bath at a temperature between -110° and -120°C . This bath was cooled to the desired temperature by slowly adding liquid nitrogen to the surrounding ethyl alcohol and stirring. The temperature of this bath was such that it was above the freezing point, but below the boiling point, of liquid boron trifluoride. Thus, the solid melted and a pressure of approximately one-half atmosphere of boron trifluoride gas was maintained over the liquid.

The first gas fraction from this cylinder was evacuated through the chemical trap. The remaining gas was distilled from the liquid into the boron trifluoride storage volume (cylinder no. 1, Figure 5, page 49) where it was condensed with liquid nitrogen. When the liquid boron trifluoride began to be depleted, as evidenced by a decreased pressure, the transfer was terminated. The solid boron trifluoride in the storage vessel was again pumped, the cylinder closed, and the liquid nitrogen removed. The tails in the purification vessel were evacuated through the chemical trap after the vessel had warmed up. The storage vessel containing the purified boron trifluoride was allowed to equilibrate with ambient temperature, usually over a period of 12 hours or more, before making a transfer to prepare solutions of the complex.

b. Analysis. A typical analysis of the boron trifluoride gas before and after purification is given in Table III. The hydrogen fluoride content was determined by infrared absorption; all other

TABLE III
ANALYSIS OF BORON TRIFLUORIDE GAS

Impurity	Mole Per Cent	
	Cylinder	Purified
N_2	0.13	0.00
O_2	0.06	0.00
SiF_4	0.11	0.11
HF^a	~ 0.003	--
BF_3 (by difference)	99.70	99.89

^aInfrared analysis; all other values by mass spectrometric measurements.

impurities were determined by mass spectrometric measurements. The hydrogen fluoride content of the purified sample was not determined since its level in the original sample was lower than that of the calibrations used in the infrared analysis. While the silicon tetrafluoride content is shown as having been unaffected by purification, there is a possibility that this was due to spectrometer background since some analyses gave lower values.

2. Pentafluoroanisole

The pentafluoroanisole (methoxypentafluorobenzene) used in this work was obtained from Imperial Smelting Corporation (Sales) Limited, London, England. At the time of purchase only Imperial Smelting Corporation was producing this compound. One pound (304 ml.) was obtained having a quoted minimum purity of 97 per cent pentafluoroanisole.

a. Purification. While the purity of the "as received" pentafluoroanisole was approximately 99.4 per cent, as will be discussed in the next section, it was further purified by distillation and contacted with molecular sieves to remove water.

An 8-mm. diameter Podbielniak Hyper-Cal Distillation Column was used. This column, of glass construction, contained approximately 12 inches of special Monel Heli-Grid packing, was vacuum jacketed, and had an automatic reflux ratio and vacuum control system. Three runs were made with the same nominal conditions; two were on 100-ml. samples of "as received" pentafluoroanisole while the third was on the first fractions from the previous runs plus 50 ml. of "as received" material.

In all cases, the product was the second fraction, representing about 72 per cent of the charge. This was collected over 2-1/2 to 4-hour periods at a reflux ratio of 20 to 1. The average boiling point was $122.6 \pm 1.0^{\circ}\text{C}$. at 200.6 ± 1.0 mm. Hg. The first sample was used in preliminary design experiments while the second and third were combined after analysis and used in the final experimental work.

Before the pentafluoroanisole was loaded into a tube for transfer into the equilibrium tube, it was contacted with molecular sieves to reduce the water content. While the presence of water was not definitely established, assumption of its presence is logical since Karl Fisher moisture analysis on normal anisole after distillation shows a water level of approximately 190 ppm. Similar analyses on the pentafluoroanisole were not made because of the small quantity of this expensive material available and the necessarily large samples required for accurate analytical results.

Linde Type 4A Molecular Sieves were used as the water removal agent. These were 1/16-inch pellets removed from a newly opened 5-pound can in which the sieves were stored under vacuum. A 125-ml. pear-shaped separatory funnel fitted with a Teflon valve was used to hold 11.5 g. of sieves. The pentafluoroanisole was poured into the funnel and drained out, giving a contact time of about 90 seconds. This was repeated twice, once with 90-seconds contact time and then with 15 minutes. To regenerate the sieves and remove absorbed pentafluoroanisole the separatory funnel was connected to a glass cold trap, heated with electrical heating tape, and evacuated.

Water analysis was not made on the pentafluoroanisole sample, for the previously stated reason, but previous work by the author had shown that the water content of normal anisole could be reduced to about 10 to 15 ppm. by a similar technique.

b. Analysis. Several methods were explored in determining the purity of the pentafluoroanisole; these were refractive index, melting point, infrared and mass spectrometric measurements, and gas-phase chromatography. The latter proved to be the most sensitive, giving results which were easily interpreted even though the identity of the impurities was not known.

The refractive index of the "as received" and distilled pentafluoroanisole was measured with an Abbé refractometer at 25.0°C. using a sodium vapor lamp. Identical values were obtained, n_D^{25} 1.4079, for these two samples while the reported²⁵ value is n_D^{25} 1.4085.

Imperial Smelting Corporation²⁵ reports a melting point of -37.0°C. for pentafluoroanisole. Determinations of the melting point of the "as received" and distilled material, however, gave values which differed but were higher than this. The technique employed was similar to that previously described for calibrating the thermocouple at the freezing point of mercury. The bare copper-constantan thermocouple was immersed in 1 ml. of liquid in the test tube. It was continuously stirred with a loop stirrer, made from 1/16-inch diameter silver solder wire, which went through a hole in the rubber stopper closing the test tube. This test tube was placed in a larger tube acting as a thermal shield and then into the pre-cooled ethyl alcohol bath contained in an

unsilvered, glass Dewar flask. Visual observations as well as thermal measurements could be made as the cooling and warming curves were run.

A large degree of supercooling occurred in all but one of the cooling curves, being on the order of 3.5°C . or greater. Because of this and the low heat of fusion, the cooling curves were of little use. The supercooling may account for the lower value of -37.0°C . reported.²⁵ The warming curves gave fairly long periods of constant temperature with time and were easily interpreted. The melting points so obtained for the "as received" and distilled pentafluoroanisole were -35.00° and -34.44°C ., respectively. The melting point of the distilled pentafluoroanisole, -34.44°C ., was thus found to be 2.56° higher than the previously reported value of -37.0°C .

As an independent check, samples of "as received" and distilled pentafluoroanisole were submitted for thermal analysis on a Dupont 900 Differential Thermal Analyzer. Again supercooling was observed, but to a greater degree, to as low as -76.35°C . The melting point for the "as received" sample was identical in two runs at -34.28°C . Three runs on the distilled sample gave two values at -34.26°C . and one at -33.83°C . Similar analyses on mercury and normal anisole gave melting points of -38.62°C ., which was 0.25°C . high, and -37.20°C ., which was 0.18°C . high, respectively. These data suggest that the melting points for the pentafluoroanisole samples may be slightly high. Nevertheless, considering the differences in the methods, the values are in good agreement.

Infrared absorption spectra were not useful for determining the purity of pentafluoroanisole because a standard was not available and the

absorption spectrum for this compound has not been reported in the literature. However, a spectrum was obtained on the "as received" liquid in a 0.1-mm. cell with silver chloride windows and was very complex. At this thickness, the liquid is essentially opaque at a frequency of 3000 cm.^{-1} and in the frequency range of 1500 to 1000 cm.^{-1} . The use of a 0.025-mm. cell thickness gave a sharper spectrum, but the spectrum was equally complex. Interpretation of these spectra is complicated by the large frequency shifts in the spectral bands normally associated with the phenyl group induced by the fluorine atoms on the benzene ring. A spectrum of the pentafluoroanisole vapor was less complex and was later useful in identifying pentafluoroanisole in boron trifluoride gas removed from the complex system.

Mass spectrometric measurements on the "as received" and distilled pentafluoroanisole gave a parent peak at mass 198, as expected, for pentafluoroanisole. A small peak at mass 186 corresponding to the parent peak of hexafluorobenzene was the only other constituent positively identified in the "as received" spectrum. This peak was not present in the spectrum on the distilled sample. Interpretation of these spectra was not carried further since the fragmentation routes of the pentafluoroanisole and hexafluorobenzene are not known. The parent peak at mass 198 was the highest mass observed in either sample. However, the lower masses were, in a few cases, less intense in the spectrum on the distilled sample. The purity of the "as received" pentafluoroanisole was estimated from the peak intensities of the 198 and 186 masses to be approximately 99.3 per cent. The distilled sample then was almost all

pentafluoroanisole since the 186 peak was eliminated.

As mentioned above, gas-phase chromatographic analyses gave the most sensitive and easily interpreted results. A more important factor was that the impurities were resolved and their concentrations determined even though they were not identified. These analyses were made on a Burrell Kromo-Tog Model KD Gas Chromatograph equipped with a 2-m. by 2-mm. column containing 15 per cent diisodecylphthalate on Gas Chrom P 80/100 and a flame ionization detector. The best results were obtained on the 1- μ l. samples with the temperature programmed between 50° and 150°C. at a rate of 5° min.⁻¹, the flash vaporizer operating at 175°C., and the helium carrier flowing at a rate of 25 cc. min.⁻¹

On the "as received" pentafluoroanisole a total of seventeen constituents were resolved; seven of these below and nine above the boiling point of pentafluoroanisole at 138°C. The minimum purity of this material calculated from the areas of the elution peaks was 99.4 per cent. Analyses on the distilled samples showed that the high boiling impurities were eliminated, except for the one located adjacent to the pentafluoroanisole peak, and four of the seven low boiling impurities were eliminated. In all cases these impurities were reduced in concentration by the distillation. The minimum purity of the two samples of distilled pentafluoroanisole used in this work was calculated to be 99.79 and 99.82 per cent.

C. PREPARATION OF COMPLEX

1. Loading Pentafluoroanisole into the Equilibrium Tube

a. Transfer tube. Approximately 28 ml. of liquid pentafluoroanisole was transferred with a pipette from the glass storage bottle into the copper transfer tube. This tube was $3/4$ inch in diameter, 6-inches long and reduced to a $3/8$ -inch brass flare connection. The other part of the flare connection was silver soldered to a Fulton HAP valve which had a Dalton connector soldered to its other port. The liquid was drained into this tube through the disconnected flare connection. The connection was then made and the tube attached to the manifold. The pentafluoroanisole was frozen with a Dry Ice-trichloroethylene slush and the air evacuated. The tube was allowed to warm to ambient temperature, weighed, as it was before the transfer, and replaced on the manifold in preparation for the transfer of the pentafluoroanisole to the equilibrium tube.

b. Loading the equilibrium tube. Pentafluoroanisole was loaded into the equilibrium tube by distilling the liquid from the transfer tube under vacuum. A small loading manifold which consisted of two Dalton fittings and a 2-inch compound Ashcroft bourdon tube gauge was connected to the vacuum manifold for this transfer. The transfer tube was connected to one of the Dalton fittings while the equilibrium tube was connected to the other. After evacuation, this manifold was isolated and the lines and transfer tube heated with insulated nichrome wire. When the pentafluoroanisole pressure approached atmospheric

pressure, the equilibrium tube was opened, and the vapor was condensed to a solid in the sample chamber with a Dry Ice-trichloroethylene slush bath. The transfer was periodically interrupted for weighing the transfer tube in order to determine the weight transferred. At the conclusion of this operation the transfer tube was closed off, the equilibrium tube containing the solid pentafluoroanisole evacuated, closed off, and allowed to equilibrate with ambient conditions for weighing.

c. Weighing. All weighings were made on a Mettler analytical balance, Type B5-C1000 GD, having a capacity of 1000 g. with ± 0.1 -mg. precision. This balance was provided with two apertures in the base plate for attaching a suspension stirrup to the pan for weighing objects suspended below the balance. Due to the physical size of the equilibrium tube this feature of the balance was utilized while other weighings were made in the normal manner. To facilitate weighing below the balance a special chamber was fabricated from a 7-inch diameter Lucite tube cut through lengthwise and fitted with hinges and handles. It was of sufficient length to give a snug fit between the bottom of the table and the floor.

The equilibrium tube was suspended from the suspension stirrup by a specially fabricated hanger. This hanger was made from 1/16-inch Monel welding rod and was 8-inches long with a hook on one end and a 3/8-inch brass flare cap on the other. Attachment of the flare cap was accomplished by drilling an oversized hole through its center, slipping it onto the rod, and then making a bead on the rod by melting it with a

torch. The hanger was attached to the equilibrium tube by means of this flare cap which screwed onto the flare plug mounted on top of the latter. This flexible connection allowed the bulky equilibrium tube to swing without adversely affecting the balance.

In all cases, the weights reported are the differences in the average of three weighings made on the hanger and the hanger and object, wherein the average was always within ± 0.2 mg. of an individual weight. Due to the large weights and small volumes of the equilibrium tube and the transfer tube, bouyancy corrections were not made. The tare weights of the evacuated equilibrium tube and transfer tube were 401.2907 and 412.3353 g., respectively.

2. Reaction of Boron Trifluoride and Pentafluoroanisole

a. Initial reaction. After the equilibrium tube was weighed, it was attached to the boron trifluoride charging manifold, the magnets were placed over the plunger housing, and the mounting rod was secured to the tube and vacuum rack. The stirrer was started, the low temperature bath and components were placed in their proper positions, the controls were set, and cooling was initiated. During the cooling, the pressure transducer was zeroed; and the manifold was evacuated, treated with fluorine, and again evacuated. When the sample in the equilibrium tube had equilibrated with the bath at the control temperature, purified boron trifluoride was expanded into the charging manifold by opening the valve on the storage vessel. The boron trifluoride was then slowly admitted to the transducer until the pressure of the storage

vessel was reached. Care was taken to maintain the reference pressure on the transducer within the prescribed differential limits.

The calculations required in preparing the desired complex solution compositions will be given in a following section. For the present it suffices to state that using the known weight of pentafluoroanisole in the equilibrium tube and the desired solution composition, the number of moles of boron trifluoride and the required pressure drop were calculated.

The initial pressure and ambient temperature readings were recorded and the valve on the equilibrium tube was partially opened allowing boron trifluoride to contact the cold, liquid pentafluoroanisole. The boron trifluoride pressure dropped as the complex formed. When the calculated pressure drop was attained, the valve on the equilibrium tube was closed. The final pressure and ambient temperature readings were then recorded, the valve on the storage vessel was closed, and the transfer manifold was evacuated. Next the valve between the transfer manifold and the pressure transducer was closed and the valve on the equilibrium tube was opened, bringing the gaseous boron trifluoride over the complex solution in contact with the pressure transducer. In this condition the system was ready for making pressure measurements on pentafluoroanisole solutions of the complex.

b. Subsequent reactions. When the measurements on a given composition were completed another charge of boron trifluoride was added to give the next composition to be studied. In all cases the initial charge of pentafluoroanisole was used, the only change in the initial

conditions being the addition of boron trifluoride to increase the concentration of the complex in solution. The procedure outlined above was followed in the subsequent additions of boron trifluoride. However, it must be emphasized that the experimental conditions were not identical; as the concentration of boron trifluoride was increased, the initial pressure was greater and the pressure drop of the boron trifluoride source differed in proportion to the desired change in composition. Also, the time required to attain the higher concentrations of boron trifluoride increased even though the additions were made with the complex solution at lower temperatures. Sometimes the bath temperature had to be changed during the addition in order to increase the rate of formation of complex.

The reaction of boron trifluoride gas with liquid pentafluoroanisole to give the boron trifluoride-pentafluoroanisole complex was exothermic. During periods of rapid addition of boron trifluoride, or when the stirring rate was increased by raising and lowering the magnets by hand, the heat evolved in the reaction would raise and maintain the sample temperature several degrees above the bath temperature despite the continuous operation of the cooling system at full capacity.

c. Calculations of complex solution compositions. The nomenclature used in this thesis with regard to the boron trifluoride-pentafluoroanisole complex solution concentrations will refer to the fraction of the total moles of pentafluoroanisole which may be reacted on a mole per mole basis with the available boron trifluoride. The composition is further defined as being the ratio of the moles of boron

trifluoride to the moles of pentafluoroanisole. As an illustration, consider the first solution of the complex prepared. The number of moles of boron trifluoride added to the pentafluoroanisole was approximately 0.1 of the number of moles of pentafluoroanisole. Thus, the moles of boron trifluoride divided by the moles of pentafluoroanisole gives a mole ratio of 0.1, and in the nomenclature of this report, the concentration of the complex is 0.1 mole ratio.

While the terminology of mole fractions is not being used, it must be realized that the mole fraction of boron trifluoride in pentafluoroanisole for a complex of 1:1 mole ratio will be 0.5. Likewise, for a complex solution composition of 0.5 mole ratio the mole fraction of boron trifluoride in pentafluoroanisole will be 0.333 and at a complex solution composition of 0.1 mole ratio, it will be 0.0909. On the other hand, if the system is considered to consist of the complex and free pentafluoroanisole as the two components, then the mole fraction of the complex is identical to the mole ratio as defined above.

The weight of pentafluoroanisole in the equilibrium tube was 36.9019 g. which represented 0.18628 moles based on a molecular weight of 198.0931 g. for pentafluoroanisole. The nominal complex solution compositions made up by addition of boron trifluoride were 0.10, 0.25, 0.50, 0.69, 1.00, and 1.08 mole ratios of boron trifluoride to pentafluoroanisole. Some other compositions were studied, but these were obtained by removing boron trifluoride from the highest complex solution composition.

The 0.1 mole ratio composition was the first to be studied. If

C is the complex solution composition and if n_1 is the moles of pentafluoroanisole, then the moles of boron trifluoride, n_2 , is calculated from the equation

$$Cn_1 = n_2 \quad (5)$$

For this composition 0.018628 moles of boron trifluoride gas had to be measured into the pentafluoroanisole. As mentioned above, in order to admit this quantity of boron trifluoride the pressure drop in the storage vessel and charging manifold had to be calculated. As a first approximation, the ideal gas equation,

$$PV = nRT, \quad (6)$$

was used for this calculation, where except for P and R the usual units are used. The pressure was expressed in centimeters of mercury and the gas constant R was converted to liters-centimeters per degree-mole by multiplying 0.08205 by 76 cm.atm.⁻¹ to give a value of 6.2358. Using the volume of the boron trifluoride storage vessel and charging manifold, 0.95874 l., the above equation simplifies to

$$P = 6.50416 nT. \quad (7)$$

With this equation the pressure drop required was readily calculated for a given number of moles of boron trifluoride, n, at the measured temperature of the gas volume expressed in degrees Kelvin. As previously described, boron trifluoride was then admitted to the equilibrium tube and the addition was stopped when the required pressure drop had been attained. If the pressure drop was not exactly as calculated, the calculations were repeated for the actual conditions.

For the next composition, 0.25 mole ratio, the total moles

of boron trifluoride required was calculated from equation (7) as before. The difference in this value and the number of moles already present in the complex solution was the moles of boron trifluoride necessary to reach the required composition. The addition of the boron trifluoride was then made on the basis of the pressure drop calculated for the experimental conditions as before.

As a check on the amount of boron trifluoride added, the equilibrium tube was weighed after the 0.10 and 0.25 mole ratio compositions were made up. In both cases, the weight changes showed that more boron trifluoride had been added than accounted for in the calculations. This was not unexpected since boron trifluoride is not a perfect gas.

D. DISSOCIATION PRESSURE MEASUREMENTS

The experimental procedures employed in the measurement of the complex dissociation pressures were identical in every point taken on all of the complex solution compositions. The procedure outlined below is thus common to all of the work periods.

1. Procedure and Collection of Raw Data

a. Preparation of apparatus. The status of the apparatus following the preparation of a given complex solution composition, as previously described, would be as follows: the valve on the equilibrium tube was closed, the pressure transducer and charging manifold were evacuated, the low temperature bath was cooled to and was being controlled at the desired temperature, and the reference pressure system

was evacuated. The pressure transducer was then reset to zero for the desired pressure range. This was accomplished by opening the valve between the reference and the main manifold and admitting dry air to the total system to reach the required pressure. If the pressure transducer output was not exactly midscale on the recorder, the necessary adjustments were made on the transducer control unit. The reference and system manifolds were then evacuated and returned to their normal status. The charging manifold and pressure transducer were then treated with fluorine at a low pressure for a few minutes. These lines were then evacuated to between 7 and 10 microns and the valve between the pressure transducer and the charging manifold closed. The valve on the equilibrium tube was slowly opened allowing boron trifluoride to expand into the pressure transducer connection while the reference pressure was being maintained within a ± 5 -cm. pressure differential.

b. Pressure measurements. After expanding the boron trifluoride into the pressure transducer connection, about 5 minutes was required for the complex solution to reach equilibrium with the gas phase. When the system pressure ceased to change, the reference pressure was adjusted to the null point and the timing started for this datum point.

The data recorded at this time were: time, sample temperature, reference pressure from Wallace and Tiernan Dial Manometer, pressure transducer output in millivolts, room temperature, the bath control setting, and in some cases the bath temperature which was the same as that of the sample. Readings of these values were then made at time intervals of 5 to 10 minutes. If successive readings were identical

after 10 minutes, this point was considered to be established. If the readings differed, the time intervals were extended until constant values were obtained. In a few cases the differences in the readings were of little consequence and an average was taken. In these cases, the temperature generally remained constant while the pressure changes corresponded to recorder shifts of 0.1 to 0.2 mv. or less. It should also be pointed out that while 10 minutes was the minimum time used for establishing the validity of a pressure point this was usually of longer duration, 15 to 20 minutes; and, in a few cases, periods of up to 60 minutes or more were experienced without changes in readings. Furthermore, 5 to 10 minutes usually elapsed after the equilibrium conditions were established before the initial readings were made.

Having obtained this point, the bath was cooled to a lower temperature and, after time for equilibration, the next point was obtained. Approximately 20 minutes was usually required between the onset of cooling and equilibrium at the lower temperature, the greater part of this period being required to establish the pressure equilibrium due to the slow stirrer speed. At higher pressures this time was generally greater while at the lower pressures it was less. It also depended on the magnitude of the temperature change and the cooling rate. The required data were then recorded and the bath cooled for the next temperature-pressure point.

This procedure was continued to the end of the work period. The Dewar flask containing the bath was then removed and a smaller Dewar flask containing liquid nitrogen was raised around the equilibrium tube,

freezing the complex, pentafluoroanisole, and the boron trifluoride. The liquid nitrogen remained around the equilibrium tube for about 10 minutes to ensure complete condensation of all materials in the system and the valve was then closed. The liquid nitrogen bath was replaced by the alcohol bath and the controls set for a temperature around -20° to -25°C . if the complex solution composition was 0.5 mole ratio or higher; otherwise the bath was allowed to warm to room temperature.

The residual pressure in the pressure transducer connection was checked with the thermocouple vacuum gage and always found to be around 10 microns or less. As a general precaution, the pressure transducer zero was checked in the same manner as described above. The system manifold and the vacuum sides of the Wallace and Tiernan Dial Manometer and mercury manometer were then evacuated until the next work period.

The foregoing procedure was followed for each set of data points. However, rather than continue the measurements from the last point, the initial points were taken within the range covered by the preceding set. This use of overlapping measurements was significant in that the internal consistency of the data was continually checked. Thus, if the composition changed or the instruments malfunctioned the data points would be out of line. Approximately 179 data points on the six primary compositions were obtained in this manner, while about 200 more were obtained on the secondary compositions and during determination of the phase diagram.

2. Correction of Pressure Data

Each data point represents the average of several readings over a given time period. Furthermore, each of the individual measurements

necessary for defining the temperature-pressure relationship required corrections and/or conversions to obtain the correct values of the parameters. The data reductions required were: converting the thermocouple millivolt reading to temperature in degrees Centigrade and computing the corrected temperature with the temperature calibration equation; correcting the Wallace and Tiernan pressure readings to 25°C.; converting the pressure transducer output in millivolts into centimeters of mercury, and summing this with the gage reading. In addition, the temperature had to be converted to degrees Kelvin and reciprocated, the mean temperature of the gas volume computed, and an estimation made of the concentration of boron trifluoride in the gas phase and in the solution.

The amount of time and effort required for processing this immense quantity of data was considerable; so a data reduction program was written for an IBM 7090 computer. The input for this program required only the sample temperature and room temperature in degrees Centigrade, the Wallace and Tiernan manometer reading in centimeters of mercury, the transducer output in millivolts, and the composition and other identification for each set of data submitted. The output consisted of the corrected temperature in degrees Centigrade, degrees Kelvin, and reciprocal degrees Kelvin, the corrected pressure in centimeters of mercury, the mean temperature of the gas volume in degrees Centigrade, an estimate of the moles of boron trifluoride in the gas phase, and the complex solution composition. The experimental results are presented in the next chapter.

E. FREEZING POINT DETERMINATIONS

1. Introduction

The determination of the solid-liquid equilibria for the boron trifluoride-pentafluoroanisole complex system was a rather difficult task. As previously mentioned, pentafluoroanisole exhibited a large degree of supercooling which was enhanced by the presence of boron trifluoride. The difficulties wrought by this phenomenon were compounded when freezing did occur. The heat liberated in the fusion of either the pentafluoroanisole or the complex or both when in the supercooled state was relatively large and was rapidly evolved. Consequently, a large increase in the sample temperature resulted in an instantaneous decomposition of the complex as manifested by a pressure increase. This pressure increase was usually quite large and was more sensitive to the actual onset of freezing since the response time, sensitivity, and recorded output of the transducer were sufficient to show the initial pressure increase several seconds before thermal changes were observed. Because of the decomposition of the complex during the fusion process, the composition of the solid phase was not known.

While the phenomenon of supercooling presented difficulties in the determination of the solid-liquid equilibrium, it was fortunate from the standpoint that it allowed the liquid-vapor equilibrium to be studied in more detail. In fact, more than half of the pressure data could not have been obtained if supercooling had not occurred.

2. Procedures for Determining Freezing Points

Two procedures were employed in determining the phase diagram of the boron trifluoride-pentafluoroanisole complex system. The first was the method of thermal analysis of the pentafluoroanisole and of the various complex solution compositions, while the second method was based on the pressure measurements of the solid-liquid-vapor equilibrium under thaw-melt conditions. The method of thermal analysis was abandoned after sufficient data had been obtained to show the general relation of the phase diagram because of the problems which prohibited the collection of better data. Sufficient data were obtained with the latter method to construct the phase diagram for this system with confidence. The procedures used in both of these methods are given below.

a. Thermal analysis. As previously mentioned, cooling and warming curves were run to obtain the freezing point of pentafluoroanisole. The apparatus consisted of Pyrex test tubes and an unsilvered glass Dewar flask which permitted visual observation. Thermal analysis measurements on the complex system were carried out in the equilibrium tube used for the measurement of the dissociation pressures.

Initially the alcohol bath was used as the heat exchange medium for running the cooling and warming curves. This was unsatisfactory due to the supercooling phenomenon and heat transfer problem. In order to have better control during the cooling and warming cycles, a thermal shield was placed around the sample chamber. Liquid nitrogen was used to cool the sample while it was allowed to warm by removing the liquid nitrogen and exposing the thermal shield to ambient temperature.

The thermal shield was a Styrofoam cylinder 2 inches in diameter and 5-inches long with a 3-3/4-inch well 1 inch in diameter. The sample chamber of the equilibrium tube fitted snugly into this well and was covered with a 1/2-inch thick Styrofoam top.

To run a thermal analysis on a given liquid composition the alcohol bath was removed and the thermal shield placed on the sample chamber. The thermocouple in the thermowell of the sample chamber was used to follow the temperature changes. A Dewar flask containing liquid nitrogen was then raised around the thermal shield until the liquid surface was just below the top of the shield. A timer was started and the initial thermocouple reading recorded. As the cooling progressed the time in seconds and the thermocouple voltages were recorded at convenient intervals, usually, 25, 50 or 100 seconds, until the temperature was well below the freezing point. The temperature range for the cooling curves was normally from about -25° to between -50° and -60°C . The observation time was between 1000 and 1700 seconds, depending on the degree of supercooling. The liquid nitrogen was removed, allowing the thermal shield and sample chamber to warm. When the sample temperature had reached about -55°C ., the timer was started and the thermocouple voltage recorded. The warming cycle was followed with appropriate time-thermocouple voltage readings. The temperature range covered by the warming cycle was about the same as that for the cooling cycle, but the observation time was usually about 2700 seconds or greater. Two and sometimes more complete cycles were run on a given solution composition.

After obtaining the thermal analysis data the thermocouple readings in millivolts were converted to temperature in degrees Centigrade and corrected. The temperature-time data were then plotted. As previously stated, almost all of the cooling curves exhibited supercooling and the usual method of extrapolating to obtain the freezing point was not practical due to the shape of the hump. On the other hand, the warming curves exhibited a very long halt and in only a few instances were constant temperatures obtained for any length of time. The halt was usually terminated by a period of temperature fluctuations caused by the stirrer breaking free of the solid mass. The usual method of extrapolating the initiation and termination of melting gave a fairly large temperature range which was not too definitive.

The problem of heat transfer and a continuously varying composition probably were the reasons for the failure of this method to give more useful results. A slower rate of cooling and warming could have improved the thermal equilibrium; but not the uncertainty due to the composition changes.

b. Pressure-temperature and thaw-melt measurements. Due to the failure of the thermal analysis method, the use of pressure-temperature measurements to obtain the phase diagram was considered. During the pressure-temperature measurements on the various solution compositions, about half of the data points obtained were on the supercooled liquid. This was beneficial in that the vapor pressure measurements did not show

a discontinuity when the liquid was supercooled,* so the pressure-temperature relation could be obtained for a much greater range. However, as expected, freezing would eventually occur resulting in pressure excursions and rapidly increasing temperatures. After very long periods of time equilibrium conditions would appear to have been established, but further attempts to measure the pressure of the solid were unsuccessful. The non-equilibrium conditions within the sample were apparent and the data points so obtained were scattered.

While taken separately neither the thermal analyses nor the pressure measurements on the solid defined the phase diagram, but the application of both methods under carefully controlled conditions was used to obtain information defining the phase boundaries of the system.

After defining the pressure-temperature curve for a given complex solution composition the bath was removed and the sample frozen with liquid nitrogen. The bath was then replaced and controlled at a temperature below the suspected eutectic temperature. The pressure changes were recorded as the sample slowly warmed to this temperature. The temperature was then slowly raised until the stirrer broke loose and the recorder trace began to oscillate. The system was allowed to equilibrate at these conditions and the pressure compared to the pressure observed at the same temperature on the liquid curve. The temperature was again slowly raised until the pressure was just below

*The vapor pressure is one of the physical properties along with the density, surface tension, and specific heat, which show no discontinuity when liquids are supercooled. Greenwood and Martin⁴⁴ have studied some of these in several boron trifluoride-organic complex systems as well as other properties having discontinuities.

or above the pressure curve on the liquid, depending on the composition and its relation to the eutectic. At this point the liquid was in equilibrium with solid at a complex solution composition very close to that which the dissociation pressure curve represented. Thus, when the sample had been frozen the composition was unknown, but by this technique the conditions were controlled so that the sample was in solid-liquid equilibrium very near the original composition. To ensure this condition, the temperature was raised and lowered to get the pressure reading as close as possible to the dissociation pressure curve while still maintaining a few crystals in the melt. The pressure and temperature were recorded and the bath temperature was then slowly lowered. If crystals were still present the pressure changed at a rate different from that for the liquid; if they had melted the pressure curve followed the one for the supercooled liquid. As the temperature was lowered, the phase represented by the crystals, i.e., solid complex above the eutectic or solid pentafluoroanisole below the eutectic, would freeze out. The system was allowed to come to equilibrium at various temperatures and the pressure and temperature recorded. When the eutectic temperature was reached, freezing caused pressure excursions and measurable temperature changes.

With this procedure the pressure-temperature data representing the solid-liquid-vapor equilibria at the various compositions were obtained and plotted with the dissociation pressure data. The intersection of the pressure-temperature curve for the three phases with the pressure-temperature curves for the gas-liquid equilibrium at the

various complex solution compositions was then the freezing point for that solution. The compositions on each side of the eutectic gave solid-liquid pressure versus temperature curves which represent the intersecting solid-liquid curves on the phase diagram. The eutectic point was defined by the intersection of these two solid-liquid curves.

Observation of the stirrer performance was also of value in defining many of these points. When the sample was mostly liquid the stirrer operated properly, but as the solid phase increased the operation became sluggish, and finally, immovable when mostly solid was present. By using the procedure described above for obtaining the equilibrium at known compositions, the sample conditions could be adjusted to a point where a temperature halt and the stirrer operation suggested the boundary of a phase transition. By varying the bath temperature around this point, the temperature halt could be used to define the transition. Thus, after abandoning the normal procedure involved in the method of thermal analysis, the techniques just outlined were used to obtain the phase diagram for the boron trifluoride-pentafluoroanisole complex system. The experimental results are presented in the next chapter.

CHAPTER IV

PRESENTATION OF EXPERIMENTAL RESULTS:
DISSOCIATION PRESSURES AND PHASE DIAGRAM

A. INTRODUCTION

The dissociation pressures of six primary compositions of boron trifluoride in pentafluoroanisole have been measured, and the pressure-temperature-composition relationships have been developed. During the determination of the phase diagram, dissociation pressure measurements also were made on other compositions, and these have been used to confirm the validity of the relationships developed. The chapter opens with a presentation and discussion of the primary compositions employed, the pressure ranges covered, the corrected experimental dissociation pressures for the several compositions studied, and the equations developed to correlate these data with temperature at each composition. The data points for all of the compositions are presented graphically and the equations fitted to these data are summarized. Subsequently, the composition dependence is developed and the experimental studies of the phase equilibria are presented. The experimental data presented in this chapter have been corrected as described in Chapter III.

B. DISSOCIATION PRESSURE DATA

1. Composition of the Primary Boron Trifluoride-Pentafluoroanisole Solutions

The primary dissociation pressure measurements were made at six

different mole ratios of boron trifluoride to pentafluoroanisole. These compositions are shown in Table IV along with the pressure-temperature data from which they were calculated.

a. Nominal composition. The nominal solution compositions listed in the first column in Table IV are the approximate compositions calculated by the ideal gas equation in the form of equation (7), page 68. The nominal composition will be used in the text for simplicity.

b. Actual compositions. As stated in Chapter III the weight of boron trifluoride added to the pentafluoroanisole in the equilibrium tube to form the 0.10 and 0.25 mole ratio solutions was greater than that calculated by equation (7), as was expected since boron trifluoride is not a perfect gas. The actual compositions shown in the second column of Table IV were then calculated by the derived equation of state for boron trifluoride, equation (1), page 11, or equation (42) in Appendix I. This is

$$PV = nRT(1 - 0.01674 P), \quad (1)$$

for which the units of atmospheres, liters, moles, and degrees Kelvin apply. The constant $0.01674 \text{ atm.}^{-1}$ is the compressibility coefficient for boron trifluoride calculated from Rumold's²² data, as shown in Appendix I. At standard conditions, denoted by the subscript, this equation may be written as

$$P_o V_o = RT_o (1 - 0.01674 P_o), \quad (8)$$

where V_o for one mole of boron trifluoride was calculated from Rumold's data to be $22.039 \text{ l. mole}^{-1}$.

TABLE IV
CONDITIONS EMPLOYED FOR ADDITION OF BORON TRIFLUORIDE TO PENTAFLUOROANISOLE

Calculated Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$		Boron Trifluoride Pressure, cm. Hg ^a		Boron Trifluoride Temperature, °C.		Time for Addition, minutes	Bath Temp., °C.	Calculated Boron Trifluoride Added, moles
Nominal	Actual	Initial	Final	Initial	Final			
0.10	0.1023	{ 180.64 ^b 144.24 ^b	{ 144.24 0.0	{ 27.3 27.3	{ 27.3 27.3	10	-13	0.01906
0.25	0.2526	138.90	85.11	26.0 ^c	25.7	12	-26	0.02799
0.50	0.5075	247.98	157.67	25.1	25.1	23	-36	0.04750
0.69	0.7020	153.49	84.01	26.1 ^c	26.3 ^c	85	-52 to -41	0.03624
1.00	1.0188	274.60	162.88	25.3	25.3	103	-39 to -41	0.05900
1.08	1.0928	241.89	245.20	26.1	26.1	23	-39	0.01379

^aThe ΔP in atmospheres was used for the calculations in equation (11).

^bVolume was 3.61 cc., in all other cases the total volume was 0.95874 l.

^cWhen the temperature changed during the addition, the average was used in the calculation.

The experimental conditions were reduced to the standard conditions in the usual manner to obtain the moles of boron trifluoride where the following ratio applies

$$\frac{P V T_o (1 - 0.01674 P_o)}{P_o V_o T (1 - 0.01674 P)} = n. \quad (9)$$

Substituting the values for the standard conditions gives

$$\frac{12.18690}{(1 - 0.01674 P)} \frac{PV}{T} = n. \quad (10)$$

This expression was further simplified to

$$\frac{11.68407 P}{(1 - 0.01674 P) T} = n. \quad (11)$$

on substituting 0.95874 l. for V, the volume of the boron trifluoride storage vessel and charging manifold. This equation was used to calculate the moles of boron trifluoride added to the pentafluoroanisole from which the actual compositions were calculated by equation (5), page 68.

The weight of the solutions of 0.10 and 0.25 mole ratio composition calculated from the data in Table IV by these equations was in excellent agreement with the observed weights as shown in Table V. The weight of the solutions with higher mole ratios of boron trifluoride to pentafluoroanisole were not obtained because the system could not be permitted to warm to room temperature where the decomposition of the complex could produce high pressures.

2. Experimental Dissociation Pressure Data

The ranges over which the dissociation pressures were measured

TABLE V
COMPARISON OF CALCULATED AND OBSERVED WEIGHTS
FOR TWO DIFFERENT SOLUTION COMPOSITIONS

Solution Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$	Total Weight of Solution, g.	
	Calculated	Observed
0.1023	38.1932	38.1960
0.2526	40.0904	40.1036

on the six primary solutions of the complex are summarized in Table VI. The nominal and actual compositions, as previously defined, are shown in the first and second columns of this table. The third column gives the variation of the liquid composition, due to the amount of boron trifluoride in the gas phase, for the temperature and pressure ranges indicated in the fourth and fifth columns. The temperature and pressure ranges for each composition were limited by the absolute range of the Wallace and Tiernan Dial Manometer at the high end and by the solidification of the supercooled liquid at the low end of the ranges. The last column gives the number of data points obtained on each of the six compositions.

The experimental data points for the temperature-pressure equilibria of the six compositions are shown in Figure 6. The data shown have been corrected for experimental conditions as described in Chapter III and represent all of the 179 points except nine. These nine points were for pressures less than 10 cm. Hg; seven of these were on the 0.25 mole ratio solution between 10 and 8.29 cm. Hg, and two were on the 0.50 mole ratio solution between 10 and 8.31 cm. Hg.

a. Discussion. The curves drawn through the data points for the 0.10, 0.25, 0.50, and 0.69 mole ratio compositions in Figure 6 are approximately parallel. Those for the two compositions above 1.0 mole ratio of boron trifluoride to pentafluoroanisole are almost identical in slope, but have less slope than the curves representing the compositions below this mole ratio. The interpretation for these differences is that up to 1.0 mole ratio the pressure of boron trifluoride in equilibrium

TABLE VI
EXPERIMENTAL CONDITIONS FOR DISSOCIATION PRESSURE MEASUREMENTS

Solution Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$			Temperature Range, °C.		Pressure Range, cm. Hg		Number of Data Points
Nominal	Actual	Liquid Composition ^a Range for Measurements	High	Low	High	Low	
0.10	0.1023	0.0858 to 0.1016	20.29	-41.69	262.00	10.55	39
0.25	0.2526	0.2351 to 0.2520	- 3.07	-53.54	273.86	8.29	54
0.50	0.5075	0.4904 to 0.5070	-16.43	-60.25	279.44	8.31	38
0.69	0.7020	0.6859 to 0.7009	-22.86	-57.19	276.26	18.42	24
1.00	1.0188	1.0044 to 1.0161	-32.28	-57.07	268.68	45.92	19
1.08	1.0928	1.0786 to 1.0876	-34.30	-50.56	270.62	94.22	5

^aLiquid composition range refers to actual solution composition corrected for boron trifluoride in gas phase. The values represent this calculated composition at the highest and the lowest pressure and temperature range.

Figure 6. Dissociation pressures of pentafluoroanisole-boron trifluoride complex solutions.

with the liquid complex should be proportional to the composition. However, the change in slope of the pressure-temperature curves above the 1.0 mole ratio composition indicates that one mole of boron trifluoride combines with one mole of pentafluoroanisole to form the complex and the remaining boron trifluoride must then be dissolved in the liquid complex. On addition of more boron trifluoride to the 1.08 mole ratio composition, the pressure-temperature curve should have a smaller slope than that of the 1.08 composition. This trend should continue until the vapor pressure curve for boron trifluoride is approximated. At this point, the solution would consist of liquid boron trifluoride and liquid complex. It may be that the 1:1 complex is not the only one that could be formed, especially as the pressure of boron trifluoride is increased to these very large values.

While the temperature and pressure ranges covered are fairly large, the curvature exhibited by the lines for solutions with mole ratios below 1.0 is greater than normally expected. The reason for this is that the complex concentration in the solution is a function of the boron trifluoride pressure over the solution at constant volume. However, it must be realized that in a system having a different gas volume, or even in this system if the quantity of solution were changed, the curvature would be different. It will also be noted that as the concentration of the complex was increased, the curvature decreased, implying, as expected, that at essentially constant volume the moles of boron trifluoride in the gas phase under given conditions of temperature and pressure will be the same. Since this is true, this loss of boron

trifluoride from solutions of lower complex concentration would result in larger decreases in the complex concentration in the liquid.

b. Calculation of the variation in the composition of the liquid.

In order to calculate the number of moles of boron trifluoride in the gas phase, and the resulting composition of the liquid phase, the temperature, the pressure, and the volume of the gas space must be known. The mean temperature of the gas volume could be estimated reasonably well from the calibration equation previously described, equation (3), page 28, and the pressure was measured. The gas volume was not accurately known because of the anticipated volume change due to complex formation and the volume change of the liquid due to temperature changes. Since the volume of the equilibrium tube and transducer connection was known, the gas volume could be calculated if the volume occupied by the liquid and its variation with temperature could be estimated. For this the liquid density and its variation with temperature would be the most useful, but these data were not available and are not easily determined. The application of an empirically estimated molar volume for the complex and the calculation of the complex density as a function of temperature was deemed to be a satisfactory approach.

Greenwood and Martin⁴⁵ have postulated an empirical rule for estimating the density of boron trifluoride coordination compounds when experimental values are not known. In Appendix II this method is discussed and modified for application where other than 1:1 complexes are involved and where the donor molecule contains aromatic groups.

To calculate an approximate liquid density as a function of

temperature for the solutions studied, the following values and equations from Appendix II are employed. For a more complete discussion, reference should be made to this appendix. The density, ρ , of the solution at 20°C. is

$$\rho^{20}_{(C)} = M_{(C)} / V_{m(C)}, \quad (12)$$

where M is the effective molecular weight and V_m is the effective molar volume of the complex solution denoted by (C) . The effective molecular weight of the solution is obtained as

$$M_{(C)} = M_{(D)} + M_{BF_3} C, \quad (13)$$

where (D) is the donor molecule, pentafluoroanisole in this case with a molecular weight of 198.093 g. mole⁻¹, M_{BF_3} is the molecular weight of boron trifluoride, 67.81 g. mole⁻¹, and C is the mole ratio of boron trifluoride to pentafluoroanisole in the solution. Similarly, the effective molar volume of the solution is

$$V_{m(C)} = V_{m(D)} + 33.6 C, \quad (14)$$

where $V_{m(D)}$ is the molar volume of pentafluoroanisole, 132.68 cc. mole⁻¹, 33.6 is the apparent molar volume for complexed boron trifluoride, and C the mole ratio as before. The relationships expressed by equations (13) and (14) permitted the solution density to be obtained by equation (12). This density at 20°C. was then used to calculate the density at 0°C. by

$$\rho_t = \rho_o - \alpha t, \quad (15)$$

where the subscripts refer to the temperatures and α is the density-

temperature coefficient taken as $1.32 \times 10^{-3} \text{ g.cc.}^{-1}\text{C.}^{-1}$. This relationship was used to calculate the density of the solutions at the temperature, t , at which the dissociation pressure was measured.

With the liquid densities calculated by this method and the calculated weights of the liquid mixture, assuming all weight to be in the liquid phase, the liquid volume was readily estimated. The volume occupied by boron trifluoride gas was then the difference in the liquid volume and the total volume. The number of moles of boron trifluoride in the gas phase at the experimental conditions was calculated by the ideal gas equation and corrected to standard conditions. The ideal gas equation was used since the calculation did not warrant the use of the more complex equation of state.

The actual liquid composition for a given datum point was adjusted for the moles of uncomplexed boron trifluoride in the gas phase at the experimental conditions. While this procedure was used to estimate the variation of the liquid composition with temperature and pressure, calculations indicated that if the volume changed 1 cc. from that originally calculated at 25°C.^* , an error of about 0.5 per cent would be introduced in the liquid composition at the highest pressures. Thus, while neither the actual molar volume of boron trifluoride in the pentafluoroanisole solutions of the complex nor the variation of density with temperature was known, the error introduced by using the above relations must be small.

*This volume was 22.87 cc. and was the volume of the equilibrium tube minus the volume of pentafluoroanisole.

In Table VI, page 87, the third column shows the liquid composition ranges calculated for the indicated temperature and pressure ranges. For 0.10 mole ratio the liquid composition at the lowest pressure and temperature was about 99.3 per cent of the actual composition, while at the highest pressure and temperature it was 83.9 per cent. The corresponding values for the 0.69 mole ratio composition were 99.8 and 97.8 per cent for the low and high extremes in pressure and temperature, respectively. At 1.00 and 1.08 mole ratios the respective liquid compositions at the lowest pressures were calculated to be 99.7 and 99.5 per cent of the actual compositions. The corresponding values at the higher pressures were 98.6 and 98.7 per cent. The boron trifluoride pressure versus the calculated variation of the solution composition is shown for each of the six nominal compositions in Figures 7 to 12. These curves show a positive deviation from linearity which is pronounced at the higher pressures for all of the compositions, but which decreases with increasing concentration of the complex in the solution. The variation of the liquid volume with increasing nominal complex concentration and the density changes with temperature are primarily responsible for the deviations.

C. MATHEMATICAL RELATIONS FOR DISSOCIATION PRESSURE DATA

1. Introduction

Generally, the equation used to relate the dissociation or vapor pressure and temperature of boron trifluoride coordination complexes has been the classical Clausius-Clapeyron equation. In most studies on

Figure 7. Boron trifluoride pressure versus the calculated variation of the nominal 0.10 mole ratio solution composition.

Figure 8. Boron trifluoride pressure versus the calculated variation of the nominal 0.25 mole ratio solution composition.

Figure 9. Boron trifluoride pressure versus the calculated variation of the nominal 0.50 mole ratio solution composition.

Figure 10. Boron trifluoride pressure versus the calculated variation of the nominal 0.69 mole ratio solution composition.

Figure 11. Boron trifluoride pressure versus the calculated variation of the nominal 1.00 mole ratio solution composition.

Figure 12. Boron trifluoride pressure versus the calculated variation of the nominal 1.08 mole ratio solution composition.

solutions of boron trifluoride complexes, the pressure or temperature range has not been as extensive as in this work and the pressure-temperature relations have been, or were assumed to be, linear.

In this investigation the conventional presentation in Figure 6, page 88, of the logarithm of the pressure versus the reciprocal of the absolute temperature for the complete experimental ranges shows considerable deviation from the linear relationship. However, the curves are almost linear over much of the low pressure region and are considered to be so within experimental error. Consequently, equations have been fitted for the linear region as well as for the complete range. Expressions relating the pressure and temperature to the composition have also been obtained.

2. Equation for Linear Regions

a. Linear regions. For each of the six solution compositions the linear region was chosen so that the maximum variation in the solution composition was approximately 0.8 per cent of that at the lowest pressure measured. The maximum variation from the actual composition was 1.5 per cent for the 0.10 mole ratio solution and decreased to less than 1 per cent for the higher mole ratio compositions. In Figures 7 through 12 the linear regions extend from the lowest pressure to the horizontal line across the pressure versus composition curve. Reference to Figure 6, page 88, will also show that the vapor pressure curves are linear in the chosen ranges.

b. Application of Clausius-Clapeyron equation over linear regions.

The Clausius-Clapeyron equation is the classical expression for vapor pressure data over a limited range of temperature and for which the latent heat of vaporization is assumed to be constant, the liquid volume negligible as compared to the vapor volume, and the vapor ideal. The differential and integrated forms of this equation may be found in any physical chemistry text or treatise and will not be presented here. The indefinite integral form of the Clausius-Clapeyron equation is

$$\ln P = - \frac{\Delta H}{RT} + C', \quad (16)$$

where $\ln P$ is the natural logarithm of pressure, ΔH is the latent heat of vaporization or dissociation in calories per mole and is assumed to be constant over the range of the equation, R is the gas constant, $1.987 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$, T is the temperature in degrees Kelvin, and C' is the integration constant. This equation is readily converted to the more usual form involving the common logarithm of the pressure by dividing by 2.303 giving

$$\log P = \frac{-\Delta H}{4.576T} + C. \quad (17)$$

The constant 4.576 is $2.303R$ and C is $C'/2.303$. It is apparent that these equations represent a straight line when the logarithm of the pressure is plotted against the reciprocal of the absolute temperature,

$$\log P = A - \frac{B}{T}. \quad (18)$$

In this equation the A constant is the intercept and is equivalent to the C constant in equation (17). The negative of the slope is the

B constant which is related to the heat of vaporization or dissociation as

$$B = \frac{\Delta H}{2.303 R} = \frac{\Delta H}{4.576} , \quad (19)$$

for the common logarithm form where 2.303 is the conversion factor for natural to common logarithms. Equation (18) was fitted, by the method of least squares, to the experimental dissociation pressure data over the linear region for the six primary solution compositions. The constants and heats of dissociation are presented in Table VII. Also included in this table are the constants for the equation calculated for the vapor pressure of pentafluoroanisole. As previously mentioned, the boiling point of 138°C. and a Trouton constant of 21 cal. deg.⁻¹ mole⁻¹ were used to estimate the heat of vaporization from which the vapor pressure equation was calculated.

The heats of dissociation were calculated from the slopes by equation (19). The average heat of dissociation for the range of complex compositions from 0.01 to 0.69 mole ratio was 8.773 ± 0.460 kcal. mole.⁻¹ The entropy of dissociation, at atmospheric pressure calculated from the equations given in Table VII, are tabulated along with the heats of dissociation in Table VIII.

In Tables IX to XIV the experimental and calculated dissociation pressures are shown for each of the six solution compositions. The pressures calculated from the applicable equations in Table VII are in good agreement with the experimental data. The consistency was within the a priori estimate of precision imposed on the pressure measurements, ± 0.3 cm. Hg. The average of the six standard deviations about the line

TABLE VII
CONSTANTS FOR DISSOCIATION PRESSURE EQUATION

$$\log P_{\text{cm}} = A - \frac{B}{T^{\circ}\text{K.}}$$

Nominal Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$	Constants,		ΔH^b kcal./mole
	A ^a	B, °K.	
0.00	6.4698 ^c	1886.8 ^c	8.634 ^c
0.10	8.6524	1765.94	8.080 ± 0.116
0.25	9.7514	1939.00	8.871 ± 0.058
0.50	10.3310	2001.84	9.159 ± 0.071
0.69	10.1992	1928.46	8.823 ± 0.106
1.00	9.1268	1611.73	7.374 ± 0.089
1.08	8.7114	1499.34	6.861 ± 0.030

^aPressure in cm. Hg.

^bAverage ΔH for compositions from 0.10 to 0.69 mole ratio equals 8.733 ± 0.460 kcal. mole⁻¹ at 95% confidence level given as

$$\sigma_{\text{avg}} = \pm (\sigma_a^2 + \sigma_i^2)^{1/2},$$

where

$$\sigma_a = \pm 1.9600 \left[\frac{\sum (\bar{x} - x)^2}{n(n-1)} \right]^{1/2}$$

for the average and $\sigma_i = \Sigma \sigma_{ci}/n$, where σ_{ci} is the 95% confidence level for each value presented.

^cConstants for pentafluoroanisole calculated using Trouton' rule, $\Delta H/T_b = 21$, and the experimental normal boiling point, $T_b = 138^{\circ}\text{C}$.

TABLE VIII
HEAT AND ENTROPY OF DISSOCIATION AT ATMOSPHERIC PRESSURE

Nominal Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$	ΔH , cal./mole	Normal Dissociation Temperature, °K. ^a	ΔS , cal./deg.mole
0.10	8080	260.8	31.0
0.25	8871	247.4	35.9
0.50	9159	236.9	38.7
0.69	8823	231.8	38.1
1.00	7374	222.4	33.2
1.08	6861	219.5	31.3

^aCalculated at 76.0 cm. Hg from equations given by Table VII.

TABLE IX

EXPERIMENTAL AND CALCULATED PRESSURES FOR 0.10 MOLE RATIO
SOLUTION OVER LINEAR REGION

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs. - Calc.)
	Observed	Calculated	
241.57	22.07	21.99	0.08
241.17	21.54	21.38	0.16
241.00	20.98	21.13	-0.15
240.74	20.68	20.75	-0.07
237.95	17.12	17.02	0.10
237.50	16.35	16.48	-0.13
235.11	13.84	13.84	0.00
234.97	13.71	13.70	0.01
234.80	13.51	13.53	-0.02
234.77	13.42	13.50	-0.08
234.71	13.52	13.44	0.08
234.10	12.85	12.85	0.00
233.63	12.46	12.41	0.05
233.49	12.27	12.28	-0.01
231.47	10.55	10.55	0.00

TABLE X

EXPERIMENTAL AND CALCULATED PRESSURES FOR 0.25 MOLE RATIO
SOLUTION OVER LINEAR REGION

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs.-Calc.)
	Observed	Calculated	
237.66	39.18	39.15	0.03
237.52	38.49	38.72	-0.23
237.52	38.47	38.72	-0.25
235.93	33.90	34.11	-0.21
234.68	30.78	30.84	-0.06
234.63	30.71	30.71	0.00
234.63	30.62	30.71	-0.09
234.60	30.58	30.64	-0.06
234.43	30.16	30.22	-0.06
234.37	29.96	30.07	-0.11
232.78	26.47	26.40	0.07
232.64	25.93	26.10	-0.17
232.17	25.11	25.11	0.00
231.18	23.10	23.12	-0.02
231.12	23.22	23.01	0.21
231.04	22.84	22.85	-0.01
229.95	21.04	20.85	0.19
227.90	17.64	17.51	0.13
227.87	17.78	17.47	0.31

TABLE X (CONTINUED)

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs.-Calc.)
	Observed	Calculated	
227.81	17.43	17.38	0.05
224.64	13.37	13.18	0.19
224.56	13.12	13.08	0.04
224.47	13.09	12.98	0.11
222.98	11.52	11.36	0.16
222.92	11.30	11.30	0.00
221.37	9.77	9.82	-0.05
221.28	9.69	9.74	-0.05
221.25	9.65	9.72	-0.07
221.22	9.62	9.69	-0.07
220.66	9.13	9.21	-0.08
219.71	8.38	8.44	-0.06
219.62	8.29	8.37	-0.08

TABLE XI

EXPERIMENTAL AND CALCULATED PRESSURES FOR 0.50 MOLE RATIO
SOLUTION OVER LINEAR REGION

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs. - Calc.)
	Observed	Calculated	
234.63	62.13	62.97	-0.84
234.28	60.62	61.15	-0.53
234.25	60.60	61.00	-0.40
234.19	60.48	60.69	-0.21
234.19	60.44	60.69	-0.25
232.55	52.15	52.82	-0.67
231.01	46.25	46.29	-0.04
230.98	46.38	46.17	0.21
229.39	40.41	40.20	0.21
229.30	39.70	39.89	-0.19
228.89	38.44	38.48	-0.04
227.75	35.14	34.79	0.35
227.40	33.89	33.72	0.17
227.34	33.73	33.54	0.19
225.97	29.90	29.66	0.24
224.50	26.32	25.95	0.37
224.21	25.29	25.27	0.02
224.18	25.20	25.20	0.00
222.68	22.15	21.94	0.21

TABLE XI (CONTINUED)

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs. - Calc.)
	Observed	Calculated	
222.54	21.83	21.66	0.17
221.19	19.42	19.09	0.33
221.11	19.00	18.94	0.06
220.93	18.76	18.62	0.14
220.87	18.56	18.52	0.04
219.44	16.18	16.16	0.02
217.69	13.67	13.65	0.02
216.27	11.88	11.88	0.00
216.15	11.66	11.74	-0.08
214.55	9.83	10.01	-0.18
212.91	8.31	8.49	-0.18

TABLE XII

EXPERIMENTAL AND CALCULATED PRESSURES FOR 0.69 MOLE RATIO
SOLUTION OVER LINEAR REGION

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs.-Calc.)
	Observed	Calculated	
232.23	77.78	78.54	-0.76
230.89	69.84	70.29	-0.45
230.82	70.03	69.88	0.15
229.01	59.57	60.02	-0.45
227.63	53.49	53.37	0.12
227.31	51.99	51.92	0.07
225.64	45.21	44.93	0.28
224.32	40.65	40.02	0.63
224.09	39.33	39.21	0.12
222.39	33.96	33.70	0.26
220.81	29.35	29.22	0.13
219.17	25.15	25.13	0.02
217.57	21.46	21.65	-0.19
215.97	18.42	18.62	-0.20

TABLE XIII
EXPERIMENTAL AND CALCULATED PRESSURES FOR 1.00 MOLE RATIO
SOLUTION OVER LINEAR REGION

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs. - Calc.)
	Observed	Calculated	
232.26	153.28	153.97	-0.69
230.62	137.15	137.43	-0.28
228.98	122.45	122.47	-0.02
227.34	109.44	108.96	0.48
225.70	97.00	96.77	0.23
224.09	86.18	85.99	0.19
224.09	86.09	85.99	0.10
222.42	76.02	75.93	0.09
220.81	67.13	67.24	-0.11
220.79	67.30	67.13	0.17
219.17	59.39	59.29	0.10
217.57	51.98	52.35	-0.37

TABLE XIV

EXPERIMENTAL AND CALCULATED PRESSURES FOR 1.08 MOLE RATIO
SOLUTION OVER LINEAR REGION

Temperature, °K.	Pressure, cm. Hg,		ΔP , cm. Hg, (Obs.-Calc.)
	Observed	Calculated	
238.86	270.62	271.21	-0.59
234.31	205.36	204.83	0.53
230.76	163.27	163.28	-0.01
227.52	132.08	131.95	0.13
222.60	94.22	94.34	-0.12

for the logarithm of the pressure was 3.14×10^{-3} in the logarithm.

The number of significant figures in the values of the constants for the equations as given in Table VII, and later on for other equations, should not be confused with the experimental accuracy and precision. These values are reported because knowledge of the values of the constants, relative to each other, to the significance given is required in order that the calculated result reflect the true precision of the experimental data. Likewise, the number of significant figures in the observed and calculated values for the pressure presented in Tables IX to XIV and in Appendix III should not be interpreted in terms of experimental precision, but only as an indication of the fit of the mathematical expressions. The estimates of precision in the experimental pressure and temperature measurements are ± 0.3 cm. Hg and $\pm 0.05^\circ\text{C.}$, respectively.

3. Equations for Complete Range of Pressure Data

The dissociation pressure data obtained over the total ranges were fitted, by the method of least squares, to four equations on the chance that one would yield a better fit than the others. An equation was also desirable which could be solved explicitly for temperature or pressure. The equations were the Antoine equation, (20), the Kirchhoff equation, (21), and two polynomial equations involving the powers of the absolute temperature and reciprocal absolute temperature, (22) and (23), respectively. These equations in the common logarithm form are:

$$\log P = A + \frac{B}{(t + c)}, \quad (20)$$

$$\log P = A + \frac{B}{T} + C \log T, \quad (21)$$

$$\log P = A + BT + CT^2, \quad (22)$$

and

$$\log P = A + \frac{B}{T} + \frac{C}{T^2}. \quad (23)$$

In all of these equations the pressure is in centimeters of mercury and the temperature is in degrees Kelvin, except for the Antoine equation where the temperature is in degrees Centigrade. All of these equations except the Antoine fitted the data very well, but all showed deviations at high pressures. Equation (22) gave the best fit, while equation (20) gave the poorest. The constants in the Kirchhoff equation have theoretical significance regarding the heat of vaporization or dissociation and heat capacity, but those obtained in this investigation can not be completely interpreted as such because of the excessive curvature due to the variation of the liquid composition with pressure. The use of powers higher than 2 generally gives a better fit with polynomials, but statistical analysis of a cubic equation of the form of equation (22) fitted to the four compositions below 1.0 mole ratio indicated that the cubic term was not significant for two of the curves and it was just barely significant for the others. Thus, use of the second degree equation in the absolute temperature was found to be justified statistically.

The constants, obtained by methods of least squares, for each nominal composition are presented in Tables XV and XVI for equations (21) and (22), respectively. The constants obtained for equations (20) and (23) are not presented since their use was not further considered. The average of the standard deviations of the fit of each equation to the pressure data on the six compositions was ± 0.00195 in the logarithm of pressure for equation (21) and ± 0.00184 for equation (22). Pressures calculated

TABLE XV
CONSTANTS FOR DISSOCIATION PRESSURE EQUATION

$$\log P_{\text{cm}} = A - \frac{B}{T} - C \log T$$

Nominal Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$	Constants,		
	A	B, °K.	C
0.10	89.45900	4779.64	28.6720
0.25	78.59201	4394.56	24.6260
0.50	76.95481	4334.47	23.9150
0.69	72.54650	4111.62	22.3800
1.00	37.96209	2630.22	10.3341
1.08	22.01472	1975.68	4.7562

TABLE XVI
CONSTANTS FOR DISSOCIATION PRESSURE EQUATION

$$\log P_{\text{cm}} = A + BT + CT^2$$

Nominal Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$	Constants,		
	A	B, $^{\circ}\text{K.}^{-1}$	C, $^{\circ}\text{K.}^{-2}$
0.10	-16.36998	116.69×10^{-3}	-17.95×10^{-5}
0.25	-18.67249	137.35×10^{-3}	-21.92×10^{-5}
0.50	-19.90192	150.13×10^{-3}	-24.57×10^{-5}
0.69	-18.98271	145.18×10^{-3}	-23.81×10^{-5}
1.00	-14.24124	111.98×10^{-3}	-17.76×10^{-5}
1.08	-11.84591	93.66×10^{-3}	-14.19×10^{-5}

by equation (22) were within ± 0.5 per cent of the experimental pressures in most cases and always within ± 1.0 per cent. The lines drawn through the data points shown in Figure 6 are a good approximation of the fit of the Kirchhoff equation. The complete experimental data for the pressure measurements and the values calculated by equations (21) and (22) will be found in Appendix III.

D. PRESSURE-TEMPERATURE-COMPOSITION RELATIONS

1. Introduction

As shown in the preceding sections, the pressure of boron trifluoride at constant temperature and essentially constant volume is dependent on the solution composition. Likewise, at a constant pressure the system temperature is a function of the solution composition. Since there are two components, boron trifluoride and pentafluoroanisole, and two phases, gas and liquid, the system is in accord with the phase rule which predicts two degrees of freedom; i.e., at a defined temperature and pressure the solution composition will be fixed. The gas-liquid phase equilibria in this system appears to be similar to that found for solutions of gases in liquids. If this is the case, Henry's Law and the van't Hoff equation should be applicable for determining the influence of pressure and temperature, respectively, on the composition, at least over part of the composition range.

2. Application of Henry's Law

The influence of pressure on the composition of a gas dissolved in a liquid at constant temperature is expressed by Henry's Law as

$$m = kp. \quad (24)$$

This states that at constant temperature the mass, m , of a gas dissolved by a given volume of solvent is proportional to the pressure, p , of the gas. The constant, k , is the distribution ratio.

The Henry's Law plots for the boron trifluoride-pentafluoroanisole complex solutions are shown in Figure 13. The concentration of boron trifluoride in the solvent is given in terms of mole ratio of boron trifluoride to pentafluoroanisole while that in the gas phase is given as the pressure in centimeters of mercury. The points indicated were obtained by calculating the pressure for each composition at 5° intervals between -20 and -45°C . The equations used for these calculations were those given in Table VII, page 103, for the linear region and were assumed to hold for the entire range shown in the Henry's Law plot. Linear relationships are observed for the data up to compositions of about 0.6 mole ratio which is indicative of Henry's Law behavior. The distribution ratios for each temperature, calculated by methods of least squares, are shown in Table XVII. While the intercept should be zero, the calculated intercept, i , shows minor deviations from the zero intercept as shown in the table.

A similar plot is presented in Figure 14. In this case the equations given in Table XVI, page 116, for the complete pressure-temperature range were solved for the pressure at each composition in 5° intervals between -20 and -45°C . The compositions have also been corrected for the boron trifluoride in the gas phase, employing the relationships presented in Figures 7 to 12, pages 94 to 99. The least squares solutions

Figure 13. Henry's Law plots for pentafluoroanisole-boron trifluoride complex solutions, uncorrected for boron trifluoride in gas phase.

TABLE XVII

DISTRIBUTION RATIOS OF PENTAFLUOROANISOLE-BORON TRIFLUORIDE
COMPLEX SOLUTION BETWEEN -20° and -45°C.

Temperature, °C.	Distribution Ratio, k, mole ratio/cm.Hg	Intercept, i, mole ratio
-20.0	1.85×10^{-3}	1.75×10^{-2}
-25.0	2.70×10^{-3}	1.26×10^{-2}
-30.0	4.00×10^{-3}	0.73×10^{-2}
-35.0	6.02×10^{-3}	0.14×10^{-2}
-40.0	9.24×10^{-3}	0.51×10^{-2}
-45.0	14.46×10^{-3}	-1.26×10^{-2}

Figure 14. Henry's Law plots for pentafluoroanisole-boron trifluoride complex solutions, corrected for boron trifluoride in gas phase.

for the constants are presented in Table XVIII.

For the two sets of data the same trends are observed, but the distribution ratio increased slightly when corrections were applied for deviations from the nominal composition. More significant is the value of the intercepts, i , which are smaller when the corrections were made in the composition. The relative behavior of the corrected and uncorrected data can be easily seen in Figure 15 where the distribution ratio is plotted as a function of the reciprocal of the absolute temperature.

Since the distribution ratio is in terms of concentration per unit pressure, Figure 15 shows the variation of the solution composition with temperature. While the pressure at each point is the orthobaric pressure of boron trifluoride over the solution, the slope of the lines should be related to the heat of solution (or heat of reaction in this case) as expressed by a van't Hoff type equation to be discussed in the next section. The equations for the uncorrected and corrected data in Figure 15 are

$$\log k = \frac{2062.49}{T} - 10.87998$$

and

$$\log k = \frac{1883.90}{T} - 10.11200,$$

respectively. From the slopes the heats of reaction are calculated to be 9.436 ± 0.067 kcal. mole⁻¹ for the uncorrected compositions and 8.619 ± 0.337 kcal. mole⁻¹ when the compositions were corrected for uncomplexed boron trifluoride in the gas phase. The latter value is in excellent agreement with the heat of dissociation calculated from the dissociation pressure data.

TABLE XVIII

DISTRIBUTION RATIOS OF PENTAFLUOROANISOLE-BORON TRIFLUORIDE
COMPLEX SOLUTION BETWEEN -20° and -45°C. CORRECTED
FOR VARIATION IN SOLUTION COMPOSITION

Temperature, °C.	Distribution Ratio, k, mole ratio/cm.Hg	Intercept, i, mole ratio
-20.0	2.19×10^{-3}	-0.17×10^{-2}
-25.0	3.00×10^{-3}	-0.11×10^{-2}
-30.0	4.24×10^{-3}	-0.17×10^{-2}
-35.0	6.17×10^{-3}	-0.34×10^{-2}
-40.0	9.24×10^{-3}	-0.61×10^{-2}
-45.0	14.28×10^{-3}	-1.07×10^{-2}

Figure 15. Effect of temperature on the distribution ratios for boron trifluoride in the gas phase and pentafluoroanisole-boron trifluoride solutions.

3. Application of the van't Hoff equation

The influence of temperature on the composition of a gas dissolved in a liquid at constant pressure is expressed by the definite integral form of the van't Hoff equation as

$$\ln \frac{c_2}{c_1} = - \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (25)$$

where c_2 and c_1 are the concentrations of the solution at temperatures T_2 and T_1 , respectively. The differential heat of solution in calories per mole is denoted by ΔH , and R is the gas constant in calories per degree per mole. The indefinite integral form of this equation stated in terms of the common logarithm is

$$\log C = \frac{-\Delta H}{2.303RT} + I, \quad (26)$$

where I is the integration constant. A plot of the logarithm of the concentration against the reciprocal of the absolute temperature should give a straight line, and the negative of the slope will be $\Delta H/2.303R$.

As previously stated, the reaction

is exothermic. While the heat of dissociation calculated from dissociation pressure data is a good approximation of the heat of dissociation for the reverse reaction, the heat of solution (in this case the heat of reaction or formation of the complex for the above reaction) may be evaluated by using equation (26).

The logarithm of the solution compositions are plotted against the reciprocal temperature at selected pressures in Figure 16. The

Figure 16. Variation of solution composition with temperature at constant pressures, uncorrected for boron trifluoride in gas phase.

points shown were obtained by solution of the equations given in Table VII, page 103, for temperature at the indicated pressures. As with the Henry's Law plots, a linear relationship appears to hold up to solution compositions of 0.50 to 0.70 mole ratio. The constants evaluated for equation (26), by the methods of least squares, and heats of reaction are given in Table XIX. The values of the heats of reaction are in good agreement with the values of the heats of dissociation obtained from the pressure data; the average of the values for pressures at 20, 40, and 60 cm. Hg are in agreement with that for the average of the dissociation data, 8.729 kcal. mole⁻¹ versus 8.733 kcal. mole⁻¹, respectively. It is not unexpected that the heats of reaction calculated at the higher pressures are less than this since the solution compositions were not corrected for the boron trifluoride in the gas phase.

A similar plot is presented in Figure 17. The equations given in Table XVI, page 116, for the complete pressure-temperature range were solved for the temperature at each composition at the indicated pressures. The solution compositions have been corrected for the boron trifluoride in the gas phase since the equations fitted over the total pressure range were employed. The constants for equation (26), page 125, and the heats of reaction are given in Table XX. The heats of reaction calculated from the slopes have increased slightly when the solution compositions are corrected for the boron trifluoride in the gas phase. The average value of the heat of reaction for pressures of 20, 40, and 60 cm. Hg are in agreement with the value of the heat of

TABLE XIX

CONSTANTS FOR VAN'T HOFF EQUATION AND HEATS OF REACTION
FOR CONSTANT PRESSURES BETWEEN 20 and 300 cm. Hg^a

Pressure, cm. Hg	Constants,		$-\Delta H$, kcal./mole
	Slope, °K.	I	
20	2001.97	-9.3247	9.159 ± 0.224
40	1890.00	-8.5385	8.647 ± 1.043
60	1831.63	-8.1240	8.380 ± 1.634
100	1741.93	-7.5550	7.970 ± 0.537
140	1714.74	-7.3134	7.845 ± 0.522
200	1684.45	-7.0563	7.707 ± 0.616
260	1663.66	-6.8759	7.612 ± 0.740
300	1651.99	-6.7774	7.558 ± 0.807

^aUncorrected for variation in solution composition due to boron trifluoride in gas phase.

Figure 17. Variation of solution composition with temperature at constant pressures, corrected for boron trifluoride in gas phase.

TABLE XX
 CONSTANTS FOR VAN'T HOFF EQUATION AND HEATS OF REACTION
 FOR CONSTANT PRESSURES BETWEEN 20 and 300 cm. Hg^a

Pressure, cm. Hg	Constants,		-ΔH, kcal./mole
	Slope, °K.	I	
20	2010.66	-9.3665	9.199 ± 1.490
40	1982.16	-8.5498	8.657 ± 0.467
60	1822.70	-8.0841	8.339 ± 1.030
100	1704.53	-7.3902	7.798 ± 0.517
140	1649.59	-7.0287	7.547 ± 0.425
200	1576.72	-6.5911	7.214 ± 0.406
260	1548.98	-6.3971	7.087 ± 1.164
300	1450.33	-5.9335	6.636 ± 0.757

^aCorrected for variation in solution composition due to boron trifluoride in gas phase.

dissociation obtained from the dissociation pressure data; 8.732 versus 8.733 kcal. mole⁻¹, respectively.

E. DISSOCIATION PRESSURE MEASUREMENTS DURING STUDY OF SOLID-LIQUID-VAPOR PHASE EQUILIBRIA

1. Introduction

After the completion of the dissociation pressure measurements on the six solution compositions just discussed, boron trifluoride was removed from the system to obtain compositions below 1:1 mole ratio so that the freezing points could be better established. The boron trifluoride was expanded from the equilibrium tube into the evacuated charging manifold and storage vessel. An approximation of the composition resulting from each expansion was made by the procedure previously described.

The calculated compositions were only useful for performing the expansion because the gas collected was not pure boron trifluoride. Mass spectrometer analysis on the first sample of boron trifluoride withdrawn indicated a purity of about 98 per cent. The impurities were 1.0 to 1.5 mole per cent of fluorocarbon fragments possibly from mass spectrometer decomposition of pentafluoroanisole, about 0.3 mole per cent silicon tetrafluoride, and 0.2 mole per cent nitrogen. An infrared spectrum of this same gas sample showed only the presence of pentafluoroanisole. This would be expected since the vapor pressure of pentafluoroanisole at the bath temperature of approximately -30°C. should be about 0.5 mm. Hg and the concentration of silicon tetrafluoride is probably

too low for detection.

Since an undetermined amount of pentafluoroanisole was removed with the boron trifluoride, the mole ratios of the residual solutions could not be accurately calculated. While this was a disadvantage, the solution compositions could be closely approximated by making pressure measurements and using the pressure-temperature-composition relationships developed in the preceding section. Thus, prior to or during the determination of the freezing points on these solutions, dissociation pressure measurements were made over ranges in the proximity of the freezing points.

2. Dissociation Pressure Data

The dissociation pressure data for seven solution compositions obtained by removing boron trifluoride in successive steps from the higher solution composition are shown in Figure 18. The dissociation pressure curves for the six primary compositions are indicated by the broken lines which are labeled with their nominal mole ratios. The pressure-temperature expression given by equation (17), page 101, was fitted to each curve. The constants for the equation at each composition and the calculated heats of dissociation are shown in Table XXI. The solution compositions shown in this table and in Figure 18 were obtained by relating the solution of the equations for either pressure or temperature with the Henry's Law or van't Hoff plots given in Figure 13, page 119, or 16, page 126.

The heats of dissociation calculated from this series of pressure measurements are in very good agreement with those obtained on the

Figure 18. Dissociation pressures for complex solutions obtained on removal of boron trifluoride from 1.08 mole ratio composition compared to dissociation pressures given in Figure 6.

TABLE XXI
CONSTANTS FOR DISSOCIATION PRESSURE EQUATION

$$\log P_{\text{cm}} = A - \frac{B}{T}$$

Solution Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$	Constants,		ΔH , kcal./mole
	A ^a	B, °K.	
0.959	9.1645	1633.49	7.474 ± 0.073
0.650	9.7273	1824.55	8.349 ^b
0.520	10.5201	2042.78	9.346 ± 0.183
0.386	10.2619	2013.51	9.212 ± 0.329
0.292	9.8570	1948.14	8.913 ± 0.175
0.213	9.4855	1892.76	8.660 ± 0.125
0.109	9.1970	1889.20	8.646 ± 0.208
Average			= 8.657 ± 0.504

^aPressure in cm. Hg.

^bOnly two points, no limits of error can be calculated.

initial series of solution compositions and presented in Table VII, page 103. For this series the average value of the heat of dissociation is 8.657 ± 0.504 kcal. mole⁻¹ and in the initial series the average value obtained for the compositions below 1:1 mole ratio was 8.733 ± 0.460 kcal. mole⁻¹. This is particularly gratifying since the amount of pentafluoroanisole was slightly changed with each withdrawal of boron trifluoride and the pressure ranges over which the equations were fitted differed in some cases. This second series of measurements also followed the general trend showing the highest heat of dissociation around the 0.5 mole ratio composition.

F. SOLID-LIQUID-VAPOR PHASE EQUILIBRIA

1. Introduction

The liquid-vapor equilibria for the pentafluoroanisole-boron trifluoride complex system have been considered in the preceding sections of this chapter. As previously discussed, the determination of the solid-liquid-vapor equilibria was a rather difficult and demanding task because the pentafluoroanisole exhibited a large degree of supercooling which was enhanced by the presence of boron trifluoride. Because of supercooling and the resulting changes in the solution composition when freezing did occur, a combination of techniques described in Chapter III were employed for determining the freezing points.

2. Solid-Liquid-Vapor Equilibria

a. Solid-liquid equilibrium. The freezing points of the seven

compositions obtained by the removal of boron trifluoride, as described in the preceding section, were determined by a combination of pressure measurements and thermal analysis by the thaw-melt method. The melting point for each composition was defined by the intersection of the pressure-temperature curves for the solid-liquid equilibrium and the liquid-vapor equilibrium. While supercooling was a hindrance to this part of the experimental study by normal techniques, it did permit a more thorough study of the liquid-vapor equilibria, which was necessary for success of the methods finally employed in the freezing point determinations.

The experimental data for the solid-liquid equilibria are presented in Table XXII and diagramed in Figure 19. The transition temperatures for each composition studied were determined under the orthobaric pressure of boron trifluoride for that solution and are given in Table XXII. Included in the table and diagram are the freezing points of the six primary solution compositions. Those for the nominal 0.10, 0.25, and 1.00 mole ratio compositions were experimentally obtained while the others were estimated from the intersection of the solid-liquid and liquid-vapor dissociation pressure curves.

b. Pressure-temperature-composition diagram for the solid. In Figure 20 the solid-liquid curve is shown in relation to the dissociation pressure curves for all of the compositions. On the low temperature side of the solid-liquid curve is the region in which the dissociation pressure measurements were made on supercooled liquid. As previously mentioned, pressure measurements made in this region when

TABLE XXII

EXPERIMENTAL DATA FOR THE SOLID-LIQUID
EQUILIBRIUM AT ORTHOBARIC PRESSURE

Solution Composition, mole ratio $\text{BF}_3/\text{C}_6\text{F}_5\text{OCH}_3$	Temperature, °C.		Orthobaric Press. at Freezing Temp., cm. Hg
	Freezing	Eutectic ^a	
0.00	-34.4		0.0 ^b
0.101	-38.6		13.3
0.109	-38.8	-45.5	13.8
0.213	-42.2	-45.9 to -45.4	19.4
0.251	-43.6		20.4
0.292	-45.1	-45.9 to -45.4	20.9
Eutectic ^c		-45.4	21.0
0.386	-40.6	-45.6	40.0
0.503	-36.4 ^d		73
0.520	-35.9	-45.5	79
0.650	-33.0		143
0.693	-32.0 ^d		157
0.959	-30.1		279
1.002	-30.0		308
1.075	-30.2 ^d		350

^aTemperature indicated where second transition could be defined.

^bActually at atmospheric pressure since this point was obtained in open tube.

^cEstimated from intersection of solid-liquid dissociation pressure curves.

^dEstimated - see text.

Figure 19. Solid-liquid equilibrium of the pentafluoroanisole-boron trifluoride complex system.

Figure 20. Boron trifluoride pressure as a function of temperature over liquid and solid phases at indicated mole ratios.

freezing had occurred were very erratic. However, when solids were present pressure measurements within the shaded area, labeled A in Figure 20, approximated either one or the other of the boundaries outlined by the broken lines. On either warming or cooling the system when a solid phase was present, a sudden temperature and pressure change was observed when the eutectic point was reached. Within the designated area below the eutectic temperature pressure measurements on solids frozen from liquids with mole ratios less than the mole ratio at the eutectic composition appeared to attain levels indicated by the upper dashed curve. The lower dashed curve was usually followed during pressure measurements when the solids were frozen from liquids having higher mole ratios than the mole ratios of the eutectic, but when the pressure over these solids was initially greater than the pressure observed in this area, the trend was for the pressure to increase with increasing temperature until near the eutectic temperature where the pressure would abruptly drop to about 20 to 21 cm. Hg. After the eutectic transition, the pressure followed the appropriate branch of the solid-liquid curve as the temperature was increased.

c. Solid-vapor equilibrium. The orthobaric pressure of boron trifluoride for each solid-liquid transition was given in Table XXII, page 137, and the relationship of the boron trifluoride pressure to the solid-liquid curve was shown in Figure 20. A more explicit presentation of the solid-liquid-vapor equilibria is given in Figure 21. It must be remembered that the temperature at any point on the curves in Figure 21 will be characteristic of the freezing point of the system at

Figure 21. Orthobaric pressure as a function of composition for the solid-liquid-vapor equilibria.

that particular composition.

d. Eutectic point. Observed eutectic temperatures were given in Table XXII, page 137, and shown in Figure 19, page 138. The average of these values gives a eutectic temperature of -45.5°C . The orthobaric pressure of boron trifluoride at the eutectic was observed to be approximately 21.0 cm. Hg. The eutectic composition was estimated, from the intersection of the two branches of the solid-liquid curve presented in Figures 19 and 21, to be 0.31 mole ratio boron trifluoride to pentafluoroanisole.

CHAPTER V

SUMMARY AND DISCUSSION

A. PROPERTIES OF THE PENTAFLUOROANISOLE-BORON TRIFLUORIDE COMPLEX

The reaction of boron trifluoride gas with liquid pentafluoroanisole was investigated at temperatures below 0°C. The addition of boron trifluoride to pentafluoroanisole was found to occur readily at temperatures from -13° to -52°C. with the evolution of heat. Existence of the molecular addition complex was established by measurements of the dissociation pressures and the presence of a maximum in the freezing points of the mixture at a 1:1 mole ratio.

The dissociation pressures of several nominal solution compositions between 0.10 and 1.08 mole ratio of boron trifluoride to pentafluoroanisole were measured over the temperature range of -60° to 20°C. and a pressure range of 8 to 279 cm. Hg. The pressure data for each nominal composition did not show a linear relationship with the reciprocal of the absolute temperature over the complete experimental range. The deviations from linearity are attributed primarily to the changes in liquid composition resulting from the decomposition of the complex to yield the boron trifluoride required to fill the gas space over the liquid to equilibrium pressures at the higher temperatures. In agreement with this deduction, within the experimental ranges of temperature and pressure for each composition, the deviations were greater at the lower compositions and higher pressures. At lower pressures these curves were considered to be linear within the accuracy of the experimental

measurements.

The Clausius-Clapeyron equation was fitted to the linear regions of each pressure-temperature curve. The heat of dissociation of the complex was then calculated to be 8.773 ± 0.460 kcal. mole⁻¹ since the dissociation pressure was assumed to represent the overall reaction

The assumption that only boron trifluoride exerts pressure at the temperature studied was considered valid because the boiling point of pentafluoroanisole is 138°C. and the vapor pressures below 0°C. were estimated to be less than 4 mm. Hg.

The heat of dissociation of the complex at each solution composition studied was not constant. Reference to Table VII, page 103, or VIII, page 104, illustrates the range covered and the fact that the heat of dissociation increased to a maximum at a mole ratio of about 0.5. While the reason for this is not established, the deviations at higher concentrations may reflect the presence of uncomplexed boron trifluoride gas in the liquid phase.

The Kirchhoff equation and an empirical power series equation were fitted to the pressure data over the complete experimental range. The latter equation fitted the data very well and was used to show the temperature-pressure-composition relationships. The reader is cautioned not to use these equations for extrapolating the data beyond the experimental ranges because of the mathematical functions involved and because of the limited ranges over which they were employed.

Henry's Law was found to hold up to solution compositions of

about 0.6 mole ratio boron trifluoride to pentafluoroanisole. When the solution compositions were corrected for uncomplexed boron trifluoride in the gas phase, a heat of reaction of 8.619 ± 0.337 kcal. mole⁻¹ was calculated from the slopes of the plot of the logarithm of the distribution ratio (Henry's Law constant) versus the reciprocal of the absolute temperature. This value was in good agreement with the heat of dissociation calculated from the dissociation pressure measurements.

From plots of the logarithm of the solution composition as a function of the reciprocal temperature at constant pressures, the van't Hoff equation was employed to calculate the heat of reaction. The average value of the heat of reaction for pressures of 20, 40, and 60 cm. Hg was in excellent agreement with the heat of dissociation obtained from the dissociation pressure measurements over the same pressure range; 8.732 versus 8.733 kcal. mole⁻¹, respectively.

Pressure measurements were also made on various solution compositions resulting from the removal of boron trifluoride from the nominal 1.08 mole ratio composition. The dissociation pressure measurements showed excellent agreement with the prior data with regard to the slopes of the pressure-temperature curves and the calculated heats of dissociation; the average for seven different compositions was 8.657 ± 0.504 kcal. mole⁻¹.

The solid-liquid equilibria were determined under the orthobaric pressure of boron trifluoride over the nominal composition range of 0.10 to 1.08 mole ratio. The melting point of pentafluoroanisole was determined by thermal analyses to be -34.4°C. rather than -37°C. as

reported.²⁵ A maximum was observed in the melting point of the mixture at the 1:1 mole ratio composition indicating the existence of the 1:1 addition complex of boron trifluoride and pentafluoroanisole. The eutectic point was observed at -45.5°C . with an orthobaric pressure of boron trifluoride of 21 cm. Hg. The eutectic composition was estimated from the intersection of the solid-liquid and pressure-composition curves for the solid-vapor equilibria to be about 0.31 mole ratio of boron trifluoride to pentafluoroanisole.

While the solid-vapor curve shown in Figure 20, page 139, is not linear from the eutectic to the 1:1 complex, it is almost linear from the eutectic to about the 0.5 mole ratio composition. From the slope of this portion of the curve the heat of dissociation of the solid complex was calculated to be about 15 kcal. mole.⁻¹ The difference between this value and the heat of dissociation of the liquid complex, 8.733 kcal. mole.⁻¹ is 6.3 kcal. which should be a reasonable estimate of the heat of fusion of the complex. The increasing slope of the solid-vapor curve is probably due to the effects of unassociated boron trifluoride gas dissolved in liquid pentafluoroanisole or complex at the higher compositions. The broad maximum shown in the freezing points in the vicinity of the 1:1 complex in Figure 19, page 138, probably reflects depression of the freezing points of these compositions due to the presence of uncomplexed boron trifluoride dissolved in the solution.

Examination of the solid-liquid equilibrium in Figure 19, page 138, shows that the depression of the freezing point of pentafluoroanisole is almost a linear function from the pure solvent to the eutectic

composition. Assuming this to be the case, the heat of fusion of pentafluoroanisole was estimated as 2.65 kcal. mole⁻¹ or 13.4 cal. g.⁻¹ This value is reasonable and the fact that it is small ties in with the large degree of supercooling observed for this compound. This value agrees well with the heat of fusion of hexafluorobenzene reported as 2.77 kcal. mole⁻¹²⁹ or 14.89 cal. g.⁻¹

B. MISCELLANEOUS PROPERTIES

1. Physical Stability

Comparison of the data on the physical properties of this complex system with those of the anisole-boron trifluoride complex system indicate marked differences due to the presence of the fluorine atoms on the benzene nucleus. The properties showing this effect are the heat of formation or dissociation and the dissociation pressures. The fact that this system had to be studied at temperatures 70° to 100°C. lower than those for the anisole complex is a relative measure of the instability of the pentafluoroanisole complex. The heat of dissociation of the pentafluoroanisole complex measured at temperatures between -35° and -50°C. is 8.7 kcal. mole⁻¹ while that of the anisole complex is about 12.3 kcal. mole⁻¹ determined at room temperature and above.^{17,38,39} Extrapolating dissociation pressures of the pentafluoroanisole-boron trifluoride complex to a temperature range where they may be compared with the anisole-boron trifluoride complex, shows that the former complex system has dissociation pressures about two orders of magnitude greater than the latter.

2. Chemical Stability

While no attempt was made to determine the chemical stability of pentafluoroanisole to attack by boron trifluoride or traces of hydrogen fluoride, which could possibly be present in the system, there was little evidence of instability. As previously mentioned, a mass spectrum of the first sample of boron trifluoride removed from the complex system showed about 1.0 to 1.5 per cent fluorocarbon fragments. Infrared analysis of the same gas sample showed only the presence of pentafluoroanisole. Thus, after approximately 5 months of exposure to boron trifluoride little, if any, reaction with pentafluoroanisole had occurred.

The reactant producing these fluorocarbon fragments may have been one of the minor impurities not removed during the distillation of the pentafluoroanisole. A sample of pentafluoroanisole, which had been used in a preliminary experiment, removed from a copper reaction tube after being in contact with boron trifluoride for approximately one year was still a clear, colorless liquid. Gas chromatographic analysis on this sample showed that an impurity present in the distilled material had been eliminated, but the concentration of a trace impurity of lesser volatility than pentafluoroanisole had increased. The sum of the estimated concentrations of both of these impurities in the distilled sample was about the same as the concentration of the one in the sample after being contacted with boron trifluoride. All other peaks in this sample were practically identical with the distilled sample and the calculated purity of the pentafluoroanisole was unchanged.

As additional evidence for the stability of pentafluoroanisole

to boron trifluoride, a sample of "as received" pentafluoroanisole in a glass bulb has been in contact with a low concentration of boron trifluoride for over a year at room temperature with no visual evidence of reaction.

These data indicate that under the conditions of this investigation, i.e., pressures up to about 4 atmospheres and temperatures ranging from about 28°C. to -195°C., except for complexing, pentafluoroanisole does not undergo reaction with boron trifluoride or its hydrolysis products, even over long periods of time.

3. Isotopic Separation

While it would have been desirable to determine the gas-liquid isotopic exchange of boron isotopes between boron trifluoride and the pentafluoroanisole-boron trifluoride complex, it was not practical at the present time. However, evidence of isotopic chemical exchange was obtained. In one case, 3.61 cc. of boron trifluoride at a pressure of 100 cm. Hg was removed from the complex system and condensed in a small nickel sample tube. The solution composition at the time of withdrawal was about 0.77 mole ratio and the temperature was -34.6°C. Mass spectrometer isotopic ratio analyses were made on this sample and a sample of the purified, tank boron trifluoride gas. The ratio of the ratios of the boron-11 to boron-10 in the tank sample and the sample from the complex was 1.0376 indicating that boron-10 trifluoride was concentrating in the gas phase. While attempts were not made to determine accurately separation factors for the chemical exchange of boron trifluoride with the complex, this determination and others on larger samples showing

less separation indicate that this system should have isotopic separation factors at least comparable to those of the anisole-boron trifluoride system.³⁹

APPENDIXES

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APPENDIX I

EQUATION OF STATE FOR BORON TRIFLUORIDE

A. INTRODUCTION

It is surprising, in view of the tremendous amount of research involving boron trifluoride, that an empirical equation of state is not available for the low pressure region. Perhaps this is due to the fact that boron trifluoride is usually employed in high pressure processes. Equations for the high pressure region have been reported; Kilpatrick and Luborsky⁴⁶ published in 1954 a pressure-volume relationship for boron trifluoride at 19.2°C. for pressures from 15 to 800 psi. and, in 1960, Smith⁴⁷ fitted a generalized equation of state to experimental data over the pressure range of 30 to 240 atmospheres. While an empirical equation of state is not available, an equation can be derived from density data using the ideal gas equation.

The density of boron trifluoride at 0°C. between 0 and 1 atmosphere pressure is known from the precise measurements of Rumold.²² From these data the coefficient of compressibility was calculated by Booth and Martin^{2*} to be 0.01631 atm.⁻¹ Recently, Barber¹⁹ has used Rumold's data to obtain the equation of state,

* Booth and Martin² frequently refer to Rumold's²² data for the calculated coefficient of compressibility and the limiting density. These values must have been calculated at a later date since they are not shown in Rumold's thesis. Rumold's limiting density, 3.02636 g.l.⁻¹, was obtained by extrapolation while the value reported by Booth and Martin, 3.02662 g.l.⁻¹, was calculated by the method of least squares and has been verified by the author who obtained the value of 3.026636 g.l.⁻¹ by the same method.

$$PV(1 + 0.01657P) = RT, \quad (27)$$

for boron trifluoride at temperatures near room temperature and pressures from 0 to above atmospheric. In this equation P is the pressure in atmospheres, V is the molar volume in liters, R is the gas constant in liter-atmosphere per degree-mole, and T is the temperature in degrees Kelvin. The constant, 0.01657, is the coefficient of compressibility, obtained by using the accepted values of physiochemical constants and the oxygen -16 atomic weight scale. This may be compared with the value of 0.01631 calculated in 1931.

B. DERIVATION OF EQUATION OF STATE

1. Equation of State Based on Coefficient of Compressibility

The deviation of a real gas from ideal behavior may be determined from accurate density determinations at standard conditions as presented in Glasstone.⁴⁸ The outline given below is thus applicable to the derivation of an equation of state for boron trifluoride gas using available density data.

The equation of state of an ideal gas is given by the well known equation

$$PV = nRT. \quad (28)$$

Since the number of moles, n , is

$$\frac{w}{M} = n, \quad (29)$$

and the density, ρ , is

$$\frac{w}{V} = \rho, \quad (30)$$

equation (28) may be written as

$$P = \frac{\rho}{M} RT. \quad (31)$$

Inasmuch as most gases deviate from ideal behavior, corrections must be made for equation (31) to apply. If V_1 is the volume of one mole of gas at standard conditions, P_1 equals 1 atm., T equals $0^\circ\text{C}.$, and V_0 is the volume at an infinitely small pressure, P_0 , where the ideal gas laws apply; then a quantity γ may be defined by

$$\frac{P_0 V_0}{P_1 V_1} = 1 + \gamma, \quad (32)$$

Defining the normal density, ρ_n , of the gas as the weight of 1 liter at $0^\circ\text{C}.$ and 1-atm. pressure, the volume, V_1 , of 1 mole at STP is equal to M/ρ_n , where M is the molecular weight of the gas. Substitution in equation (32) gives

$$M = \frac{P_0 V_0}{P_1} \frac{\rho_n}{1 + \gamma}. \quad (33)$$

Since P_0 and V_0 have been defined as the conditions, i.e., very low pressure and large volume, where 1 mole of gas, n , obeys the ideal gas laws, the product $P_0 V_0$ may be replaced by RT in equation (28) which is 22.414 l.-atm. at $0^\circ\text{C}.$ whereby equation (33) becomes

$$M = \frac{RT}{P_1} \frac{\rho_n}{1 + \gamma} = \frac{22.414}{P_1} \frac{\rho_n}{1 + \gamma}. \quad (34)$$

Since P_1 is 1 atm., equation (34) may be written

$$M = 22.414 \frac{\rho_n}{1 + \gamma}. \quad (34a)$$

The limiting density, ρ_0 , is defined as the density of a gas at the conditions defined above where Avogadro's law is applicable and should be

equivalent to the normal density, ρ_n , of an ideal gas,

$$\rho_o = \frac{M}{22.414} \text{ or } M = 22.414 \rho_o \quad (35)$$

Examination of equations (34) and (35) will show that for a real gas, $\rho_n/1 + \gamma$ is equal to ρ_o , the limiting density of an ideal gas in g.l.⁻¹, and the correction to the ideal gas law is $1/1 + \gamma$. The concept of limiting density is utilized in the more common relation based on equation (31)

$$M = \left(\frac{\rho}{P} \right)_o RT, \quad (36)$$

which should apply to any gas, where $(\rho/P)_o$ is the extrapolated value at zero pressure obtained from a plot of ρ/P versus P .

It can be shown that

$$\frac{1}{1 + \gamma} = (1 - \zeta P) \quad (37)$$

where ζ is the compressibility coefficient. Since experimentally PV is a linear function of P in the low pressure region, one notes

$$PV = PoVo(1 - \zeta P), \quad (38)$$

which provides for the correction of a real gas to ideal behavior. This is the case for all gases except the most compressible, thus equation (38) represents an equation of state for real gases in the low pressure region. When the pressure is 1 atm., the P terms in equation (38) are set to unity and, as before, $PoVo$ is equal to RT so that for 1 mole of gas the volume is

$$V = RT(1 - \zeta). \quad (39)$$

Again, since $V = M/\rho_n$, equation (39) may be written

$$M = 22.414 \rho_n (1 - \zeta). \quad (40)$$

2. Calculation of Compressibility Coefficient

As shown in the preceding discussion, a simple equation of state for boron trifluoride may be obtained if the compressibility coefficient can be evaluated. While there are methods based on the use of critical data, the most accurate and direct approach for evaluating the compressibility coefficient involves the use of experimental density data as presented above.

Very precise determinations of the density of boron trifluoride were made by Rumold²² at 1.0, 0.66657, and 0.33315 atm. and 0°C. The results were 3.07666, 3.05958, and 3.04340 g.l.⁻¹-atm.⁻¹, respectively.

With these data, the equations presented above may be employed to calculate the compressibility coefficient. The following values are used in these calculations: RT equals 22.414 l.-atm. mole⁻¹ at 0°C., M, is the molecular weight of boron trifluoride, 67.806. g. mole⁻¹, and ρ_n , the normal density of boron trifluoride, the weight of 1 liter at 0°C. and 1 atm., equals 3.07666 g.l.⁻¹

The volume occupied by 1 mole of boron trifluoride at standard conditions is

$$\frac{M}{\rho_n} = \frac{67.806 \text{ g. mole}^{-1}}{3.07666 \text{ g. l.}^{-1}} = 22.039 \text{ l. mole}^{-1}.$$

Using the values defined above equation (34a) gives

$$\frac{1}{1 + \gamma} = 0.98326,$$

which by equation (37) is

$$0.98326 = (1 - \zeta)$$

at 1 atm., so ζ equals 0.01674 atm.⁻¹ The same result was obtained by equation (40).

3. General Equation of State

With the evaluation of the compressibility coefficient, equation (38) expresses the equation of state for boron trifluoride between 0 and slightly above atmospheric pressure at 0°C. as

$$PV = 22.414(1 - 0.01674 P), \quad (41)$$

when n equals 1 mole. The generalized equation of state may be written as

$$PV = nRT(1 - 0.01674 P). \quad (42)$$

At standard conditions P is 1 atm., V is 22.039 l. mole⁻¹, n is the number of moles of boron trifluoride, R is the gas constant, 0.08205 l.-atm. mole⁻¹-deg.⁻¹, and T is 273.16°K. This equation is presented as equation (1) on pages 11 and 82.

APPENDIX II

MOLAR VOLUME AND DENSITY RELATIONS FOR
BORON TRIFLUORIDE COMPLEXES

A. EMPIRICAL RULE

Laubengayer and Finlay⁷ were among the first to show that the molar volume and other constitutive properties deviated from ideal behavior due to the formation of the boron trifluoride coordination or complex compounds of methyl and ethyl ether. More recently Greenwood and Martin⁴⁵ have postulated an empirical rule for estimating the density of boron trifluoride coordination compounds when experimental values are not available. This rule based on a calculation of the molar volume of the complex is

$$\rho_{20}^{20}(\text{complex}) = M(\text{complex}) / [V_m(\text{donor}) + 28], \quad (43)$$

where ρ_{20}^{20} is the density of the complex at 20°C., and M is the molecular weight of the complex. V_m is the molar volume of the donor molecule and may be obtained by dividing the molecular weight by the density, as

$$V_m = M/\rho. \quad (44)$$

The constant 28 is the apparent molar volume in cubic centimeters per mole of coordinated boron trifluoride and is an average value derived from the examination of 26 liquid complexes. This value is simply the difference in the molar volumes of the complex and donor as calculated from the density relationships on these complexes. The relation is

$$\Delta V_m = V_m(\text{complex}) - V_m(\text{donor}) = \text{constant} = 28. \quad (45)$$

Greenwood and Martin³ have also shown that for 14 boron trifluoride complexes, the variation of density with temperature could be represented by the simple equation

$$\rho_4^t = \rho_4^o - \alpha t, \quad (46)$$

where ρ is the density, α the density-temperature coefficient, and t the temperature in °C. The value of α varied between 0.934×10^{-3} and 1.32×10^{-3} , but the averaged value was $1.17 \times 10^{-3} \text{ g.cc.}^{-1}\text{.}^{\circ}\text{C.}^{-1}$

The use of these relationships should be suitable for estimation of the molar volumes and densities of the boron trifluoride-pentafluoro-anisole complex system. However, while the correlations of Greenwood and Martin⁴⁵ show good agreement, the compounds they examined were primarily simple aliphatic ethers, alcohols, and carboxylic compounds. Two complexes they included contained aromatic groups for which the apparent molar volume of boron trifluoride was 33.6 and 32.1 cc. This suggests that the apparent molar volume of coordinated boron trifluoride in more complex molecules and especially in complexes containing aromatic donors, i.e., anisole and phenol, may be greater than 28 cc.

1. Tests of Empirical Rule

To determine if this might be the case, the accurate density data on the boron trifluoride-anisole system obtained by Madix and Barber⁴⁰ was analyzed. The relationship of the density as a function of the complex composition and the temperature was expressed by the equation

$$\rho = \left[A_1 + A_2 X + A_3 X^2 \right] \left[1 + \alpha'(t - t_1) + \beta'(t - t_1)^2 \right]. \quad (47)$$

In this equation ρ is the density in g.cc.^{-1} , X is the mole ratio of

boron trifluoride to anisole, α' and β' are the negative of the coefficients of thermal expansion, and t and t_1 the temperature in degrees Centigrade, with t_1 being the reference temperature for the density of pure anisole. The A constants give the relationship of density to composition. In the temperature range of 20° to 40°C. and the composition range of 0 to 1.0 mole ratio boron trifluoride to anisole, this equation is stated to fit the data with a standard deviation of 5 parts in 10,000 or 0.05 per cent.

Using a table of density values as a function of composition and temperature, calculated by the above equation, the simple density relationship

$$\rho_t = \rho_0 - \alpha t \quad (48)$$

was fitted to the 1:1 complex composition over the temperature range of 0° to 25°C. This equation was cited as equation (15), page 91. From these data the best value of the density-temperature coefficient, α , was approximated to be $1.32 \times 10^{-3} \text{ g.cc.}^{-1}\text{°C.}^{-1}$. Taking the density of the complex, ρ , at 20°C. as a standard, the density at 0°C, ρ_0 , was calculated to be $1.2614 \text{ g.cc.}^{-1}$. The density, ρ_t , at various temperatures from 3° to 25°C. was then calculated and found to agree with the values calculated by equation (47) to within ± 0.05 per cent. Considering the approximations and the differences in the equations, the agreement over this temperature range was excellent.

Since this estimate of the variation of density with temperature was very good, the next step was to determine if equation (43) could be satisfactorily employed. The molar volume of the donor, $V_{m(D)}$, anisole, at 20°C. was calculated from equation (44) as

$$V_m = 108.13 \text{ g.mole}^{-1} / 0.9947 \text{ g.cc.}^{-1} = 108.7 \text{ cc.mole.}^{-1}$$

The sum of the molecular weight of anisole, 108.13 g., and boron trifluoride, 67.81 g., gives the molecular weight of the complex, 175.94 g. Thus, $M_{(C)}$ and $V_{m(D)}$, where (C) and (D) stand for complex and donor, respectively, in equation (43), are known and the complex density at 20°C. was calculated to be 1.287 g.cc.⁻¹. This value was 4.2 per cent high, suggesting again that the value of 28 cc. for the apparent molar volume of boron trifluoride coordinated with a donor containing an aromatic structure was too low.

2. Modification of Empirical Rule

In order to calculate the densities for solution compositions less than 1:1 mole ratio, the equations had to be modified for the concentration. If C is the complex solution composition expressed in moles of boron trifluoride per mole of donor, then the effective molecular weight of the complex solution at this composition can be calculated as

$$M_{(C)} = M_{(D)} + M_{(BF_3)}C, \quad (49)$$

which is equation (13), page 91.

Likewise, an effective molar volume for the complex applies as

$$V_{m(C)} = V_{m(D)} + V_{m(BF_3)}C. \quad (50)$$

Equation (50) is, except for the C term, identical to equation (45) and $V_{m(C)}$ should be recognized as equivalent to the denominator in equation (43).

The densities at 20°C. were calculated at three solution compositions, 0.8, 0.5, and 0.25 mole ratio, for the boron trifluoride-anisole system and found to be high as with the calculation on the 1:1 complex. The actual densities at 20°C. were then used to calculate an apparent molar volume for boron trifluoride in this system. The values so obtained for the above compositions ranged between 33.44 and 33.77 cc. with an average of 33.61 cc. Substituting this value for the apparent molar volume of boron trifluoride in equation (50), and obtaining the necessary complex solution molecular weights by equation (49), complex solution densities at 0°C. were calculated by equation (43). With these values for ρ_0 and the previously selected value of $1.32 \times 10^{-3} \text{ g.cc.}^{-1}\text{C}^{-1}$ for α , the densities of three compositions, 1.0, 0.5, and 0.1 mole ratio were calculated for temperatures between 3° and 25°C. The agreement with the tabulated values was excellent, the maximum deviations varying between 0.048 and 0.40 per cent from the 1.0 and 0.1 complex solution compositions, respectively.

B. DISCUSSION

The suggestion of a larger apparent molar volume for boron trifluoride coordinated with a donor containing an aromatic group appears to be valid. The value of 33.6 cc. agrees with the two previously given values listed by Greenwood and Martin,⁴⁵ but which were averaged with the others to yield the value of 28 cc. Since the molar volume of liquid boron trifluoride is approximately 39 cc. at the melting point and approximately 43 cc. at the boiling point and that of solid boron

trifluoride is approximately 35 cc., Greenwood and Martin⁴⁵ state that the formation of a donor-acceptor bond seems to reduce the volume by about 10 cc., which is due to the decrease in the distance of closest approach of the unlike molecules in the formation of the chemical bond. For the anisole-boron trifluoride system the calculated molar volume of boron trifluoride suggests that the decrease in the volume is only about 6 cc., indicating the volume requirements of boron trifluoride to be greater and the distance of closest approach greater.

While the donor-acceptor bond formation appears to result in a decrease in the molar volume of boron trifluoride, does the donor molecule also change? Bauer, Finlay, and Laubengayer⁶ determined from an X-ray diffraction study on the dimethyl ether-boron trifluoride complex that the dimethyl ether structure was essentially unaffected while the boron valence angles were tetrahedral and the boron-fluorine bond distances increased. On the other hand, there must also be a limit to the magnitude of change in the molar volume of boron trifluoride.

In the present investigation there is no clear guide as to what the molar volume of boron trifluoride will be when complexed with the fluoroaromatic donor, or for that matter, even fluoroaliphatic donors. However, the fluorine atoms on the benzene ring and those on boron will, due to their high electronegativity, cause a greater separation between the molecules in their closest approach on complex formation. The distortion of the boron trifluoride molecule from a planar trigonal to a tetrahedral configuration with complex formation may be more severe in the fluorinated system, since the fluorine atoms in the two molecules

will try to maintain maximum separation. On the other hand, the inductive and mesomeric effects of the fluorine atoms on the benzene nucleus will have an effect on the lone pair of electrons on the ethereal oxygen, the consequence being to pull these electrons in more tightly where they will not be as available for donation to the boron atom. These effects would tend to give a weaker complex as observed.

Without additional information for guidance, the apparent molar volume of boron trifluoride complexed with pentafluoroanisole was assumed to be $33.6 \text{ cc.mole.}^{-1}$. The molar volume of pentafluoroanisole calculated by equation (44), using a molecular weight of 198.093 g. and a density of 1.493 g.cc.^{-1} at 25°C. , was $132.68 \text{ cc.mole.}^{-1}$. The effective molar volume of the pentafluoroanisole-boron trifluoride complex solution can be estimated by substituting these values into equation (50). The density can then be calculated by equation (43), on substituting the effective molar volume and the effective molecular weight given by equation (49).

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APPENDIX III

EXPERIMENTAL AND CALCULATED DISSOCIATION PRESSURES

The experimental dissociation pressures for the six primary solution compositions are presented in Tables XXIII to XXVIII. The experimental temperatures and pressures have been corrected as described in Chapters II and III. The pressures are reported to more significant figures than the experimental precision warrants, but because only the uncorrected experimental data were used as input to the computer, the number of significant figures in the corrected and calculated values presented in the tables serve only as an indication of the mathematical precision with which the equations fitted the data. They should not be interpreted in terms of the experimental precision.

In each table the calculated pressures were obtained by using the appropriate constants for the indicated compositions from Table XV, page 115, and Table XVI, page 116, in equation (21), page 113, and equation (22), page 114, respectively. These equations were

$$\log P = A + \frac{B}{T} + C \log T \quad (21)$$

and
$$\log P = A + BT + CT^2. \quad (22)$$

As can be seen, both of these equations fitted the data well, but the latter was more satisfactory since it could be solved explicitly for temperature and pressure.

TABLE XXIII

EXPERIMENTAL AND CALCULATED PRESSURES FOR
THE NOMINAL 0.10 MOLE RATIO SOLUTION

Temperature, °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
293.45	262.00	264.38	259.73
293.25	260.43	262.79	258.38
290.03	236.71	237.76	236.40
286.71	213.06	213.14	213.77
286.34	210.13	210.48	211.27
280.41	171.10	170.13	172.24
280.18	169.63	168.66	170.79
273.87	131.71	131.10	132.95
273.55	130.70	129.35	131.16
267.16	98.19	97.31	98.26
267.11	98.22	97.08	98.02
267.03	97.65	96.72	97.65
260.62	70.89	70.44	70.60
260.50	70.29	70.00	70.15
260.24	68.80	69.06	69.18
254.12	49.19	49.34	49.08
253.92	48.88	48.78	48.51
253.76	47.99	48.33	48.05
250.62	40.20	40.11	39.77
247.53	32.82	33.09	32.76
247.28	32.56	32.56	32.24
247.19	32.06	32.38	32.05
244.40	26.78	26.97	26.70
244.07	26.22	26.38	26.12
241.57	22.07	22.22	22.04

TABLE XXIII (CONTINUED)

Temperature, °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
241.17	21.54	21.61	21.43
241.00	20.98	21.35	21.18
240.75	20.68	20.98	20.82
237.95	17.12	17.13	17.07
237.49	16.35	16.56	16.52
235.11	13.84	13.82	13.87
234.97	13.71	13.68	13.73
234.80	13.51	13.50	13.55
234.77	13.42	13.46	13.52
234.71	13.52	13.40	13.46
234.10	12.85	12.78	12.86
233.63	12.46	12.32	12.41
233.49	12.27	12.18	12.28
231.47	10.55	10.36	10.52

TABLE XXIV

EXPERIMENTAL AND CALCULATED PRESSURES FOR
THE NOMINAL 0.25 MOLE RATIO SOLUTION

Temperature, °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
270.09	273.86	277.40	272.26
266.90	236.43	237.52	235.67
266.85	235.33	236.93	235.12
263.79	201.54	202.74	202.72
260.38	169.81	169.01	169.94
260.36	169.39	168.82	169.76
260.27	168.54	168.00	168.95
257.23	142.21	141.71	142.90
253.95	117.05	116.95	118.04
253.85	117.48	116.18	117.26
250.59	96.26	95.15	95.96
247.31	78.10	77.04	77.54
247.31	77.67	77.04	77.54
247.19	76.89	76.44	76.92
247.14	76.88	76.18	76.69
244.07	62.59	61.93	62.16
244.07	61.78	61.93	62.16
240.85	49.26	49.34	49.37
240.82	49.72	49.23	49.26
240.77	49.01	49.06	49.08
240.77	48.83	49.06	49.08
240.71	48.98	48.84	48.87
237.66	39.18	38.98	38.89
237.52	38.49	38.57	38.48
237.52	38.47	38.57	38.48

TABLE XXIV (CONTINUED)

Temperature , °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
235.93	33.90	34.15	34.03
234.68	30.78	30.98	30.84
234.63	30.71	30.86	30.72
234.63	30.62	30.86	30.72
234.60	30.58	30.78	30.64
234.43	30.16	30.37	30.23
234.37	29.96	30.23	30.09
232.78	26.47	26.62	26.47
232.64	25.93	26.32	26.17
232.17	25.11	25.33	25.19
231.18	23.10	23.35	23.21
231.12	23.22	23.23	23.10
231.04	22.84	23.08	22.95
229.95	21.04	21.07	20.95
227.90	17.64	17.68	17.59
227.87	17.78	17.63	17.55
227.81	17.43	17.54	17.46
224.64	13.37	13.24	13.21
224.56	13.12	13.14	13.12
224.47	13.09	13.03	13.01
222.98	11.52	11.36	11.37
222.92	11.30	11.30	11.31
221.37	9.77	9.76	9.80
221.28	9.69	9.68	9.72
221.25	9.65	9.65	9.70
221.22	9.62	9.62	9.67
220.66	9.13	9.12	9.18

TABLE XXIV (CONTINUED)

Temperature , °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
219.71	8.38	8.32	8.39
219.62	8.29	8.25	8.32

TABLE XXV

EXPERIMENTAL AND CALCULATED PRESSURES FOR
THE NOMINAL 0.50 MOLE RATIO SOLUTION

Temperature , °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
256.73	279.44	282.33	278.03
253.71	233.82	235.69	234.16
250.44	192.22	192.16	192.18
247.19	155.96	155.40	156.03
243.98	125.43	124.81	125.53
240.77	99.46	99.25	99.82
237.61	78.12	78.40	78.75
237.55	78.29	78.05	78.39
234.63	62.13	62.17	62.33
234.28	60.62	60.46	60.60
234.25	60.60	60.32	60.46
234.19	60.48	60.03	60.16
234.19	60.44	60.03	60.16
232.55	52.15	52.58	52.63
231.01	46.25	46.29	46.29
230.98	46.38	46.18	46.17
229.39	40.41	40.37	40.32
229.30	39.70	40.06	40.01
228.89	38.44	38.68	38.62
227.75	35.18	35.04	34.96
227.40	33.89	33.98	33.90
227.34	33.73	33.80	33.72
225.97	29.90	29.93	29.84
224.50	26.32	26.20	26.11
224.21	25.29	25.51	25.42

TABLE XXV (CONTINUED)

Temperature, °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
224.18	25.20	25.44	25.35
222.68	22.15	22.13	22.06
222.54	21.83	21.84	21.77
221.19	19.42	19.22	19.16
221.11	19.00	19.07	19.02
220.93	18.76	18.74	18.69
220.87	18.56	18.64	18.58
219.44	16.18	16.22	16.19
217.69	13.67	13.63	13.63
216.27	11.88	11.80	11.82
216.15	11.66	11.65	11.68
214.55	9.83	9.87	9.92
212.91	8.31	8.29	8.37

TABLE XXVI

EXPERIMENTAL AND CALCULATED PRESSURES FOR
THE NOMINAL 0.69 MOLE RATIO SOLUTION

Temperature, °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
250.30	276.26	276.90	275.39
247.00	225.44	224.83	224.69
243.80	182.25	182.01	182.36
243.61	178.47	179.69	180.05
241.14	152.44	151.60	152.01
240.48	144.87	144.72	145.51
237.26	114.82	114.69	114.95
234.08	90.68	90.21	90.30
234.08	90.40	90.21	90.30
233.78	88.08	88.14	88.22
232.23	77.78	78.06	78.08
230.89	69.84	70.13	70.10
230.82	70.03	69.74	69.70
229.01	59.57	60.14	60.07
227.63	53.49	53.59	53.50
227.31	51.99	52.16	52.06
225.64	45.21	45.20	45.10
224.32	40.65	40.27	40.17
224.09	39.33	39.46	39.36
222.39	33.96	33.87	33.81
220.81	29.35	29.30	29.26
219.17	25.15	25.12	25.12
217.57	21.46	21.54	21.58
215.97	18.42	18.41	18.49

TABLE XXVII
 EXPERIMENTAL AND CALCULATED PRESSURES FOR
 THE NOMINAL 1.00 MOLE RATIO SOLUTION

Temperature, °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
240.88	268.68	268.64	268.37
240.22	257.53	257.92	257.76
238.58	233.06	232.79	232.82
236.99	210.79	210.38	210.50
234.13	174.60	174.55	174.70
234.10	174.94	174.20	174.35
232.26	153.28	153.98	154.09
230.62	137.15	137.64	137.70
228.98	122.45	122.77	122.79
227.34	109.44	109.26	109.24
225.70	97.00	97.03	96.98
224.09	86.18	86.16	86.10
224.09	86.09	86.16	86.10
222.42	76.02	75.99	75.93
220.81	67.13	67.16	67.12
220.79	67.30	67.06	67.02
219.17	59.39	59.08	59.07
217.57	51.98	52.01	52.04
216.09	45.92	46.12	46.19

TABLE XXVIII
EXPERIMENTAL AND CALCULATED PRESSURES FOR
THE NOMINAL 1.08 MOLE RATIO SOLUTION

Temperature, °K.	Pressure, cm. Hg,		
	Observed	Calc., Eq. (21)	Calc., Eq. (22)
238.86	270.62	270.78	270.75
234.31	205.36	204.98	205.04
230.76	163.27	163.51	163.51
227.52	132.08	132.08	132.05
222.60	94.22	94.20	94.21

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