

DOCTORAL DISSERTATION SERIES

Publication No. : 12,609

AUTHOR: Ray Derward Long, Ph. D., 1955
University of Michigan

TITLE: LIQUID-VAPOR EQUILIBRIA OF THE
SYSTEM BROMINE PENTAFLUORIDE-
BROMINE TRIFLUORIDE

University Microfilms, Ann Arbor, Michigan

LIQUID-VAPOR EQUILIBRIA OF THE SYSTEM BROMINE
PENTAFLUORIDE-BROMINE TRIFLUORIDE

by
Ray D. ^{BERWARD} Long

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
1955

Doctoral Committee:

Associate Professor J. J. Martin, Chairman
Associate Professor L. E. Brownell
Professor D. L. Katz
Doctor Stephen Lawroski, Argonne National Laboratory
Associate Professor M. J. Sinnott
Associate Professor E. F. Westrum

ABSTRACT

LIQUID-VAPOR EQUILIBRIA OF THE SYSTEM BROMINE PENTAFLUORIDE-BROMINE TRIFLUORIDE

by
Ray D. ^{DERWARD} Long

The liquid-vapor equilibria for the system bromine pentafluoride-bromine trifluoride have been measured and correlated. The measurements were made in a welded nickel Othmer still. Temperatures were measured with a calibrated platinum resistance thermometer. Pressures were measured with a metal steam ebulliometer in conjunction with the temperature measuring equipment and the known vapor pressure-temperature relation for water.

Isothermal diagrams at 50, 75, 100, 125 and 150°C and an isobaric diagram at 1 atmosphere have been measured. At higher temperatures, pressures become excessive and bromine trifluoride tends to decompose. It is felt that the smoothed data can be safely extrapolated to 25°C so that the complete 1 atmosphere diagram can be calculated and compared with the experimental isobar.

The five isotherms are each fitted with the two-constant, thermodynamically consistent van Laar equations,

$$\log_{10} \gamma_1 = A / (1 + Ax_1/Bx_2)^2, \text{ and}$$

$$\log_{10} \gamma_2 = B / (1 + Bx_2/Ax_1)^2.$$

Ideal behavior of the vapor phase is assumed for the purpose of calculating activity coefficients, and the subscripts 1 and 2 refer to bromine pentafluoride and bromine trifluoride, respectively. The constants A and B of the van Laar equations represent the logarithm of the activity coefficients at infinite dilution of bromine pentafluoride and bromine trifluoride,

respectively. They are fitted as a function of temperature by the following equations,

$$A = 0.1290 + 0.001076t, \text{ and}$$

$$B = 0.4000 + 0.001000t.$$

The vapor pressures of the pure components were also measured over the same temperature range and are represented by the equation,

$$\log_{10} P = 6.4545 + 0.001101t - 895/(t + 206),$$

for bromine pentafluoride and by the equation,

$$\log_{10} P = 7.65757 - 1627.5/(t + 215),$$

for bromine trifluoride, where P is in mm, and t is in °C. With the aid of the above correlation, isotherms and isobars are calculated at even temperatures and pressures.

The critical constants are estimated to be 486 and 612°K and 47 and 69 atmospheres pressure, respectively, for bromine pentafluoride and bromine trifluoride. These values are used in conjunction with the low-pressure form of the Berthelot equation of state to calculate saturated gas volumes. Entropies and enthalpies of vaporization are calculated from the Clausius-Clapeyron equation with the aid of the slopes of the vapor pressure equations and the calculated saturated gas volumes.

The entropies of vaporization for bromine pentafluoride and bromine trifluoride are compared with the value for "normal" liquids. Bromine pentafluoride is found to exhibit a slightly greater entropy of vaporization than is expected for a normal liquid and bromine trifluoride shows considerable excess entropy of vaporization.

The experimentally determined data on the liquid-vapor equilibria of the system bromine pentafluoride-bromine trifluoride were compared with the liquid-vapor equilibria behavior predicted by the "regular solution theory."

The theoretically predicted behavior was found to offer a very poor approximation and the reason for this is not completely clear. In the treatment of the regular solution theory that was used, no attempt was made to account for specific interactions. The excess entropy of vaporization that is found for bromine trifluoride suggests that there is considerable association in the condensed phase. This effect would be expected to carry over into solutions in which bromine trifluoride is a component. The regular solution theory predicts large positive deviations and consequently two immiscible liquid phases. The much smaller deviation from ideality that is actually observed and the failure of the system to exhibit immiscible liquid phases might be explained by a specific interaction of unlike molecules in the solution.

SUMMARY

The liquid-vapor equilibria for the system bromine pentafluoride-bromine trifluoride have been measured and correlated. Isothermal diagrams at 50, 75, 100, 125 and 150°C and an isobaric diagram at 1 atmosphere have been prepared. At higher temperatures, pressures become excessive and bromine trifluoride tends to decompose. It is felt that the smoothed data can be safely extrapolated to 25°C so that the complete 1 atmosphere diagram can be calculated and compared with the experimental isobar.

The five isotherms were each fitted with the two-constant, thermodynamically consistent van Laar equations,

$$\log_{10} \gamma_1 = A / (1 + Ax_1/Bx_2)^2 \quad , \text{ and}$$

$$\log_{10} \gamma_2 = B / (1 + Bx_2/Ax_1)^2 \quad .$$

Ideal behavior of the vapor phase is assumed for the purpose of calculating activity coefficients, and the subscripts 1 and 2 refer to bromine pentafluoride and bromine trifluoride, respectively. The constants A and B of the van Laar equations represent the logarithm of the activity coefficients at infinite dilution of bromine pentafluoride and bromine trifluoride, respectively. They are fitted as a function of temperature by the following equations,

$$A = 0.1290 + 0.001076t \quad , \text{ and}$$

$$B = 0.4000 + 0.001000t \quad .$$

The vapor pressures of the pure components were also measured over the same temperature range and are represented by the equation,

$$\log_{10} P = 6.4545 + 0.001101t - 895/(t + 206) \quad ,$$

for bromine pentafluoride and by the equation,

$$\log_{10} P = 7.65757 - 1627.5/(t + 215) \quad ,$$

for bromine trifluoride, where P is in mm, and t is in °C.

With the aid of the above correlation, isotherms and isobars are calculated at even temperatures and pressures.

ACKNOWLEDGMENTS

I would like to acknowledge here the aid of Dr. R. C. Vogel of Argonne National Laboratory who has supervised the experimental work. I am very appreciative of the help of Prof. J. J. Martin of the University of Michigan who suggested a thesis under the Participating Institution Program and who has served as chairman of the graduate committee. I am also indebted to many members of the Chemical Engineering Division of Argonne National Laboratory: to Dr. S. Lawroski for his kind interest and advice, to Dr. R. K. Steunenberg for frequent consultation, to Dr. L. Stein for the benefit of his analytical method which aided greatly in the investigation, and to the research group as a whole for assistance and cooperation. Prof. Scott Wood and Prof. J. H. Hildebrand have kindly given advice on the theoretical treatment of the liquid-vapor equilibria data.

TABLE OF CONTENTS

	<u>Page</u>
SUMMARY	i
ACKNOWLEDGMENTS	ii
LIST OF TABLES	v
LIST OF ILLUSTRATIONS.	vii
NOMENCLATURE	viii
 I. INTRODUCTION	 1
II. EXPERIMENTAL PROCEDURE	3
A. Purification and Dispensing Equipment, Construction and Operation	 3
B. Othmer Still and Auxiliary Equipment, Construction and Operation	 8
C. Method of Analysis.	24
III. EXPERIMENTAL DATA	27
IV. METHOD OF CALCULATION.	60
A. Vapor Pressure Equations.	60
B. Saturated Liquid and Vapor Volumes	62
C. Enthalpy and Entropy of Vaporization.	64
D. Liquid-Vapor Correlation	64
V. CALCULATED RESULTS	72
VI. EXPERIMENTAL ERRORS AND COMPARISON WITH OTHER WORK.	 96
A. Comparison with Previous Work.	96
B. Experimental Errors	99
C. Errors in Calculated Quantities	100

TABLE OF CONTENTS

	<u>Page</u>
VII. THEORY	102
A. Chemical Behavior of the Interhalogens	102
B. Comparison with "Normal" Liquids.	105
C. Comparison with Regular Solution Theory	106
VIII. CONCLUSIONS.	109
APPENDICES	111
A. Safety Precautions	111
B. Prediction of Critical Constants	114
C. Sample Data Sheets	117
REFERENCES.	119

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Ethanol-Water System (comparison with literature values)	23
II	N-Heptane-Toluene System (comparison with literature values).	24
III	Experimental Vapor Pressures of Bromine Pentafluoride	28
IV	Experimental Vapor Pressures of Bromine Trifluoride	29
V - X	Experimental Liquid-Vapor Equilibria Data	31-35
XI- XVI	Activity Coefficients	36-41
XVII- XXII	Experimental Liquid-Vapor Equilibria Data (adjusted to even temperature and pressure)	48-53
XXIII	Constant A of the van Laar Equation (comparison at 25°C intervals with smoothed values)	67
XXIV	Constant B of the van Laar Equation (comparison at 25°C intervals with smoothed values)	69
XXV	Temperature Derivative of Vapor Pressure for Bromine Pentafluoride	73
XXVI	Temperature Derivative of Vapor Pressure for Bromine Trifluoride	74
XXVII	Predicted Saturated Liquid Volume for Bromine Pentafluoride.	75
XXVIII	Predicted Saturated Liquid Volume for Bromine Trifluoride	76
XXIX	Predicted Saturated Vapor Volume for Bromine Pentafluoride.	77
XXX	Predicted Saturated Vapor Volume for Bromine Trifluoride	78

LIST OF TABLES

<u>Table</u>		<u>Page</u>
XXXI	Enthalpy of Vaporization of Bromine Pentafluoride. .	79
XXXII	Enthalpy of Vaporization of Bromine Trifluoride . . .	80
XXXIII	Entropy of Vaporization of Bromine Pentafluoride . .	81
XXXIV	Entropy of Vaporization of Bromine Trifluoride. . . .	82
XXXV - XL	Calculated Isothermal Liquid-Vapor Equilibria Diagrams	83-88
XLI - XLVII	Calculated Isobaric Liquid-Vapor Equilibria Diagrams	89-95
XLVIII	Comparison of Vapor Pressure Equation of Bromine Pentafluoride with Data of Ruff and Menzel	97
XLIX	Comparison of Vapor Pressure Equation of Bromine Trifluoride with Data of Ruff and Braida.	98
L	Comparison of Vapor Pressure Equation of Bromine Trifluoride with Data of Oliver and Grisard	99
LI	Cohesive Energy Densities.	107
LII	Activity Coefficients at Infinite Dilution	108

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Purification Still	4
2	Dispensing Apparatus	7
3	Equilibrium Still	9
4	Photograph of Equilibrium Still	10
5	Manifold System	17
6	Photograph of Manifold System	18
7	Ebulliometer.	21
8-13	Activity Coefficients.	42-47
14-19	Experimental Liquid-Vapor Equilibria Data	54-59
20	Liquid-Vapor Equilibria Correlation.	68

NOMENCLATURE

T	temperature in degrees Kelvin
t	temperature in degrees Centigrade
P	pressure in atmospheres (unless otherwise noted)
V	vapor volume in (liters)/(gram mole)
v	liquid volume in (liters)/(gram mole)
R	0.082057 (liter)(atmosphere)/(degrees Kelvin) (gram mole)
J	24.218 (calories)/(liter-atmospheres)
x	mole fraction in liquid phase
y	mole fraction in vapor phase
p	vapor pressure of pure component
H	enthalpy in (calories)/(gram mole)
S	entropy in (calories)/(gram mole)

Superscripts

'	refers to first differences
''	refers to second differences

Subscripts

1	refers to bromine pentafluoride
2	refers to bromine trifluoride
r	refers to reduced temperature or pressure
c	refers to critical temperature or pressure
v	refers to vapor phase
l	refers to liquid phase
f	refers to final composition
i	refers to initial composition

THE LIQUID-VAPOR EQUILIBRIA OF THE SYSTEM BROMINE PENTAFLUORIDE-BROMINE TRIFLUORIDE

by

Ray D. Long

I. INTRODUCTION

The purpose of the present investigation was the determination and correlation of the liquid-vapor equilibria data on the system bromine pentafluoride-bromine trifluoride. This work was carried out in the Chemical Engineering Division of Argonne National Laboratory, under the Participating Institution Program, in conjunction with the Chemical and Metallurgical Engineering Department of the University of Michigan. This work will be submitted to the University of Michigan as a thesis in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.

As an introduction to the present investigation, the pertinent information available prior to the present work will be reviewed very briefly. Bromine and fluorine combine to form at least two so-called interhalogen compounds. Bromine monofluoride has been reported but has never been satisfactorily isolated and may not exist in the pure state. Bromine trifluoride begins to show noticeable decomposition above 180°C . Steady vapor pressures have been measured at temperatures as high as 225°C and it appears that it rapidly reaches an equilibrium state with its decomposition products. Bromine pentafluoride shows no signs of instability within the temperature range studied and has been reported to be stable at several hundred $^{\circ}\text{C}$.

The preparation of bromine trifluoride by combination of the elements was first carried out by Lebeau⁽¹⁾ and later by Ruff and Menzel.⁽²⁾ Present practice calls for the use of a water-cooled, tubular copper reactor which is inclined at a slight angle from the horizontal. Bromine is brought into the upper end of the reactor, and fluorine is introduced near the lower end from which the bromine trifluoride is withdrawn.

When pure, bromine trifluoride is a pale yellow-green liquid which solidifies to prisms of the same color. Early values of the boiling point were several degrees too high. By interpolation with their vapor pressure equation, Grisard and Oliver⁽³⁾ found the boiling point to be 125.75°C . The early high values were probably due to the presence of impurities. The vapor pressure of liquid bromine trifluoride from the melting point to 150°C was found by Grisard and Oliver to be accurately represented by the equation,

$$\log_{10}P = 7.74853 - 1685.8/(t + 220.57) \quad ,$$

where P is in mm and t is in degrees C. Their data appear to be accurate and compare well with the vapor pressure measurements made during the present investigation. Bromine trifluoride may associate slightly in the vapor phase but vapor density measurements of sufficient accuracy have not been made to establish this point.

Ruff and Menzel⁽²⁾ were first to prepare bromine pentafluoride. The preparation was carried out by direct combination of bromine and fluorine to form bromine pentafluoride in copper apparatus at 200°C. This is essentially the same as present practice. Pure bromine pentafluoride is colorless when a liquid and crystallizes to form a colorless or whitish solid, melting at approximately - 61.3°C.

The vapor pressure of the liquid bromine pentafluoride was determined by Ruff and Menzel for temperatures below 20°C and is represented by the equation,

$$\log_{10}P = 8.0716 - 1627.8/T \quad ,$$

where P is in mm and T is in °K. The vapor pressure of bromine pentafluoride was not measured below 25°C in the present investigation, but the results check the above equation very well upon extrapolation.

A single measurement of the gas density of bromine pentafluoride was made by Ruff and Menzel from which they concluded that at 29°C and 330 mm, there was no association of the gas molecules. This conclusion has been borne out by recent work.⁽⁴⁾

No previous attempt has been made to measure the vapor-liquid equilibrium of the bromine pentafluoride-bromine trifluoride system.

II. EXPERIMENTAL PROCEDURE

This section will describe the design, construction and operation of the various pieces of apparatus. The main pieces of apparatus are the Othmer equilibrium still, manifold system, ebulliometers and manometer system. The purification still and pure material dispensing apparatus will be described for the sake of completeness. It should be understood, however, that the development of these two pieces of equipment was the result of the work of the group studying fluorine chemistry in the Chemical Engineering Division. The author cooperated in this work to approximately the same extent as the other members of the group.

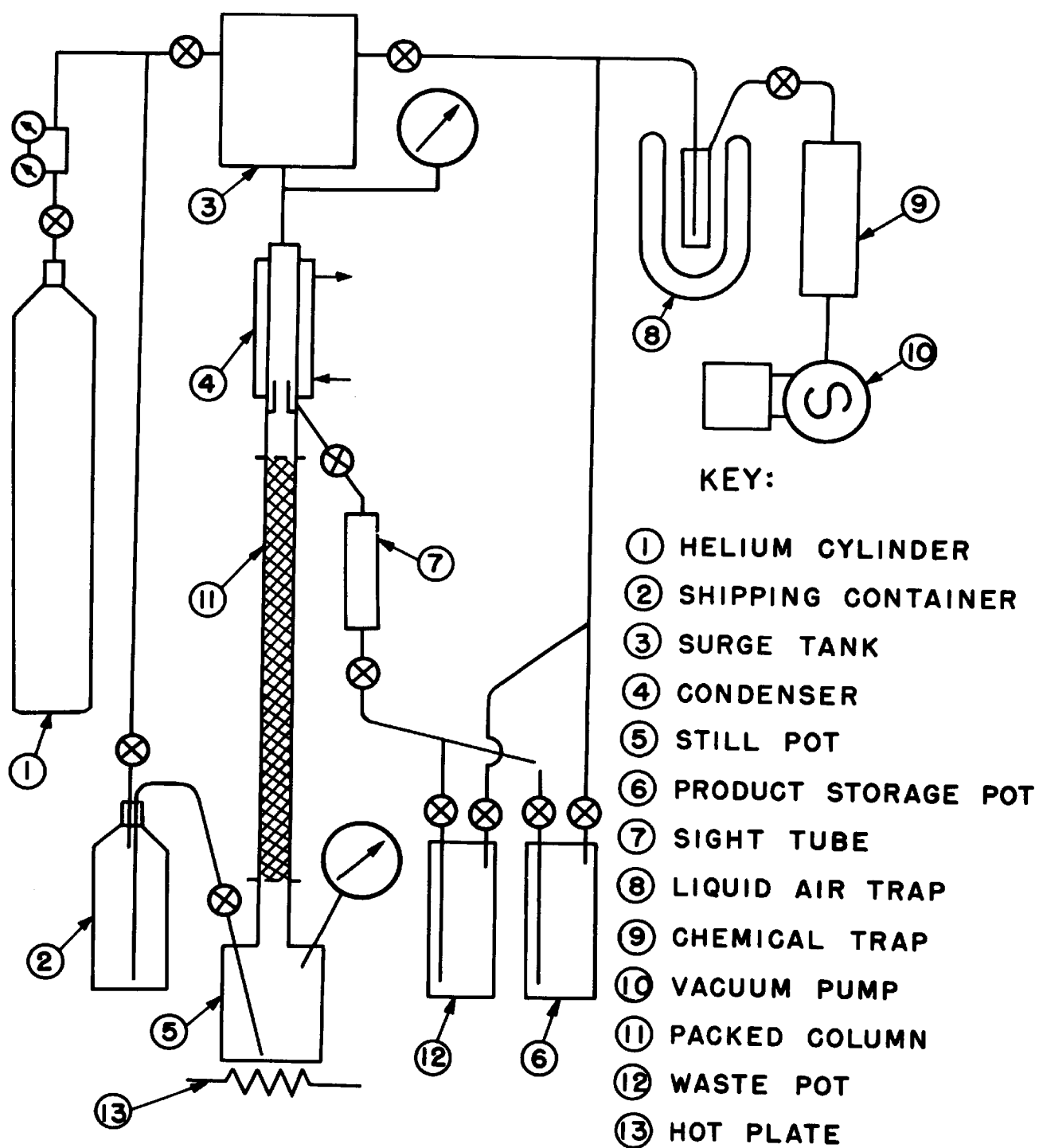
Certain safety precautions must be obeyed if interhalogen compounds are to be handled without injury. These precautions are discussed in Appendix A.

A. Purification and Dispensing Equipment, Construction and Operation

Bromine pentafluoride and bromine trifluoride as received from the manufacturer are labeled as either the pentafluoride or as the trifluoride. However, in the past, cylinders labeled as bromine pentafluoride might contain as much bromine trifluoride as the pentafluoride, and vice versa. This situation has markedly improved recently, but it is still necessary to have some method available to purify the materials before use. Other impurities usually present are hydrogen fluoride, free bromine and metal salts. Fractional distillation has been found to be a practicable method of purification. The extreme reactivity of the interhalogens requires the use of certain techniques. Contact with the moisture of the atmosphere will cause formation of hydrogen fluoride and the destruction of the protective metal fluoride film. Contact with a vessel that has not been prefluorinated will cause the formation of bromine. Failure to guard against either of these conditions will result in contamination of the interhalogen solution.

Purification Still. The still was constructed of welded nickel. A schematic diagram of the still and associated equipment is shown in Figure 1. The connections between the still pot and the column and also between the column and the still head were made by means of teflon-gasketed flanges. Teflon is extremely resistant to corrosion and has the proper mechanical properties to form a tight seal. The rest of the connections were made with nickel flare fittings. Hoke diaphragm valves were used with the lines welded into the valve body. Connecting lines were all of three-eighths inch nickel tubing. The column was made of nickel pipe, approximately five-eighths inch inside diameter, and was packed with one-sixteenth inch nickel helices.

FIGURE 1.
PURIFICATION STILL.



When not in use, a slight positive pressure of helium was kept on the still and accessory equipment. This procedure enabled a visual check for the presence of leaks when the still is to be put in service and furthermore ensured the protection of the fluoride film on the inside of the equipment from the moisture of the air.

The interhalogen was received from the manufacturer in steel cylinders with plug and valve cap. A special plug with two connections, one of them a downleg, was screwed into the cylinder in place of the manufacturer's plug. The still pot was charged by forcing the interhalogen out of the downleg of the cylinder and into the still pot.

The product valve between the column and the fluorothene sight tube was closed to isolate the column from the product system. The desired operating pressure was adjusted on the still by allowing helium to flow into or out of the surge tank. The hot plate was then turned on and the still operated at total reflux while coming to equilibrium. The sight tube and the previously fluorinated product storage receivers were evacuated and then sealed off from the vacuum pump. When the still had reached equilibrium conditions, the valve at the bottom of the sight tube was closed and the valve at the top cracked to allow product removal at the desired rate. The rate of removal of product will determine the reflux rate in the still. The rate of removal can be estimated by the rate at which the drops fall into the sight tube or by the rise in the liquid level in the sight tube. The fluorothene sight tube was calibrated by volume. By keeping a record of the amount of product collected, overfilling of the product storage pot can be prevented.

The procedure used in operating the still will depend somewhat on whether the major portion in the still pot and the desired product is bromine pentafluoride or bromine trifluoride. If the product is to be the pentafluoride, the forerun will be hydrogen fluoride. This is collected in the waste pot together with some bromine pentafluoride. This ensures that all the hydrogen fluoride is out of the still and flushed out of the sight tube and lines. The next cut will be bromine pentafluoride.

When most of the pentafluoride is out of the still pot, the trifluoride will start up the column. This can be detected by a sudden rise in temperature at the lower part of the column. When it is observed that most of the pentafluoride is over, the valves are adjusted to pass the remainder into the waste pot. It is not necessary to distill over all the bromine trifluoride since it will serve to push out the more volatile materials the next time the still is used. The procedure when bromine trifluoride is the desired product is the same except in this case the forerun will consist of hydrogen fluoride, free bromine and bromine pentafluoride.

After the product has been collected, a slight positive pressure of helium was put on the product storage pot and the valves on the two connections closed.

Dispensing Apparatus. The low solubility of nickel fluoride in bromine pentafluoride and bromine trifluoride prevents the contamination of the interhalogens with metal salts and contributes to the stability of the nickel fluoride film. A further requirement for this stability is the absence of moisture. This necessitates either handling the interhalogens in a closed system or in a very dry atmosphere. A dispensing apparatus which allows interhalogen to be drawn from the product storage pots without contamination was built.

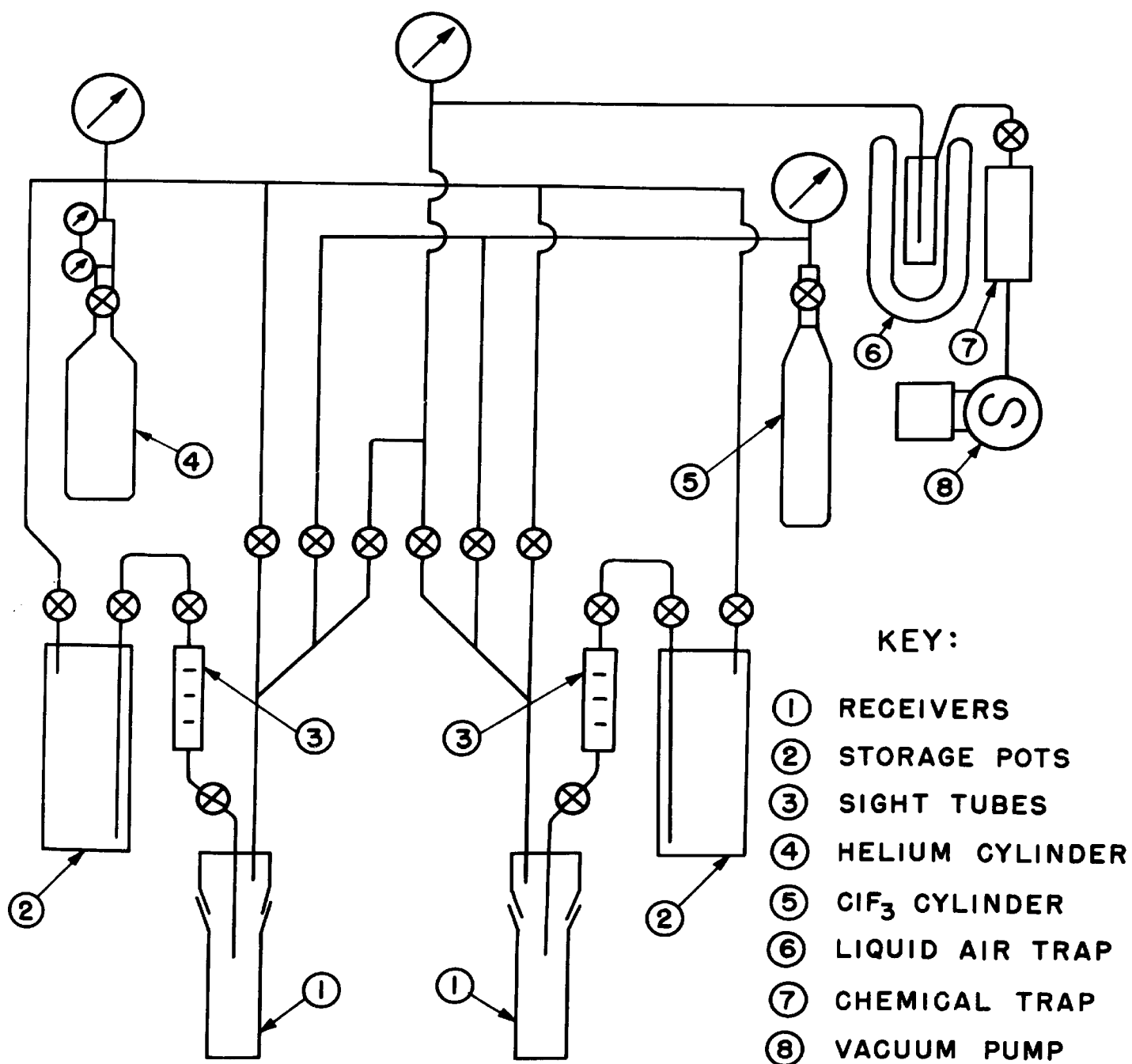
A schematic diagram of the dispensing apparatus is shown in Figure 2. The apparatus is of welded nickel construction with all connections made by means of nickel flare fittings. The valves that may contact either the interhalogen liquid or vapor are Hoke diaphragm valves with legs welded to the valve body. The diaphragms are constructed of Inconel, an alloy showing excellent corrosion resistance. The receivers which are to be filled are connected to the apparatus by means of three-quarter inch nickel flare fittings. These receivers are usually molded fluorothene tubes or welded nickel pots of 100, 250 or 500 ml volume.

The apparatus is designed so that the receiver can be prefluorinated with chlorine trifluoride before filling. The chlorine trifluoride is used for this purpose since it has a convenient vapor pressure at room temperature and can be completely removed after fluorination by drawing a vacuum on the receiver. The receiver fits on a flare plug through which pass two lines. The liquid inlet line allows a measured amount of interhalogen to be metered into the receiver by visual observation of the calibrated fluorothene sight tube. The other connection can be used to admit helium, chlorine trifluoride or to evacuate the receiver.

The procedure in filling a receiver would be somewhat as follows:

- (a) make the connection of the clean receiver to the plug,
- (b) evacuate the receiver,
- (c) fill the receiver with chlorine trifluoride vapor and let stand a few minutes,
- (d) evacuate the receiver once more,
- (e) admit helium into the vapor space of the product storage pot,
- (f) meter the desired amount of interhalogen into the receiver by visual observation of the calibrated fluorothene sight tube,

FIGURE 2.
DISPENSING APPARATUS.



- (g) allow helium to flow into the receiver to bring the pressure slightly above room pressure,
- (h) break the connection and seal the receiver with a plug and the apparatus with an empty receiver.

B. Othmer Still and Auxiliary Equipment, Construction and Operation

The extreme chemical reactivity of bromine pentafluoride and bromine trifluoride made it rather improbable that vapor-liquid equilibrium data of a very high order of precision could be determined. Therefore a design for an equilibrium still was chosen that would be simple to operate and of all metal construction. An Othmer still of the type used by Barber and Cady⁽⁵⁾ was selected. All welded nickel construction was used because of the excellent corrosion resistance of nickel in the presence of interhalogens.

As the most dependable method for measurement of temperature, a platinum resistance thermometer was used in conjunction with a Leeds and Northrup G-2 Mueller Bridge. A National Bureau of Standards certificate of calibration for the resistance thermometer assured sufficient accuracy for the temperature measurements.

The most convenient and accurate method for pressure measurement was found to be the use of a metal steam ebulliometer in conjunction with the apparatus for temperature measurement. The vapor pressure of water is very well known and the boiling temperature of the water was a very accurate measure of the pressure on the ebulliometer. As an added precaution, a series of mercury-in-glass manometers was used to check the operation of the ebulliometer.

In order to prevent the danger of allowing the interhalogen vapor from the still to contact the steam from the ebulliometer, a Taylor "Differential Blind Manometer" was used to equilibrate the pressure on the two pieces of apparatus. Thus the brass bellows of the "DBM" insures that the interhalogen and steam will not come into contact.

Design of Equilibrium Still. Welded nickel construction was used for the equilibrium still except in those places where a valve was inserted. This was necessary since no completely satisfactory valve was available and silver-soldered connections allowed a routine replacement of these valves. The still was built in three separate sections with connections made by teflon-gasketed flanges. The three separate sections were used so that it would be easier to clean the still or alter its design should this prove necessary. A schematic diagram of the still is shown in Figure 3, and a photograph in Figure 4.

FIGURE 3.
EQUILIBRIUM STILL

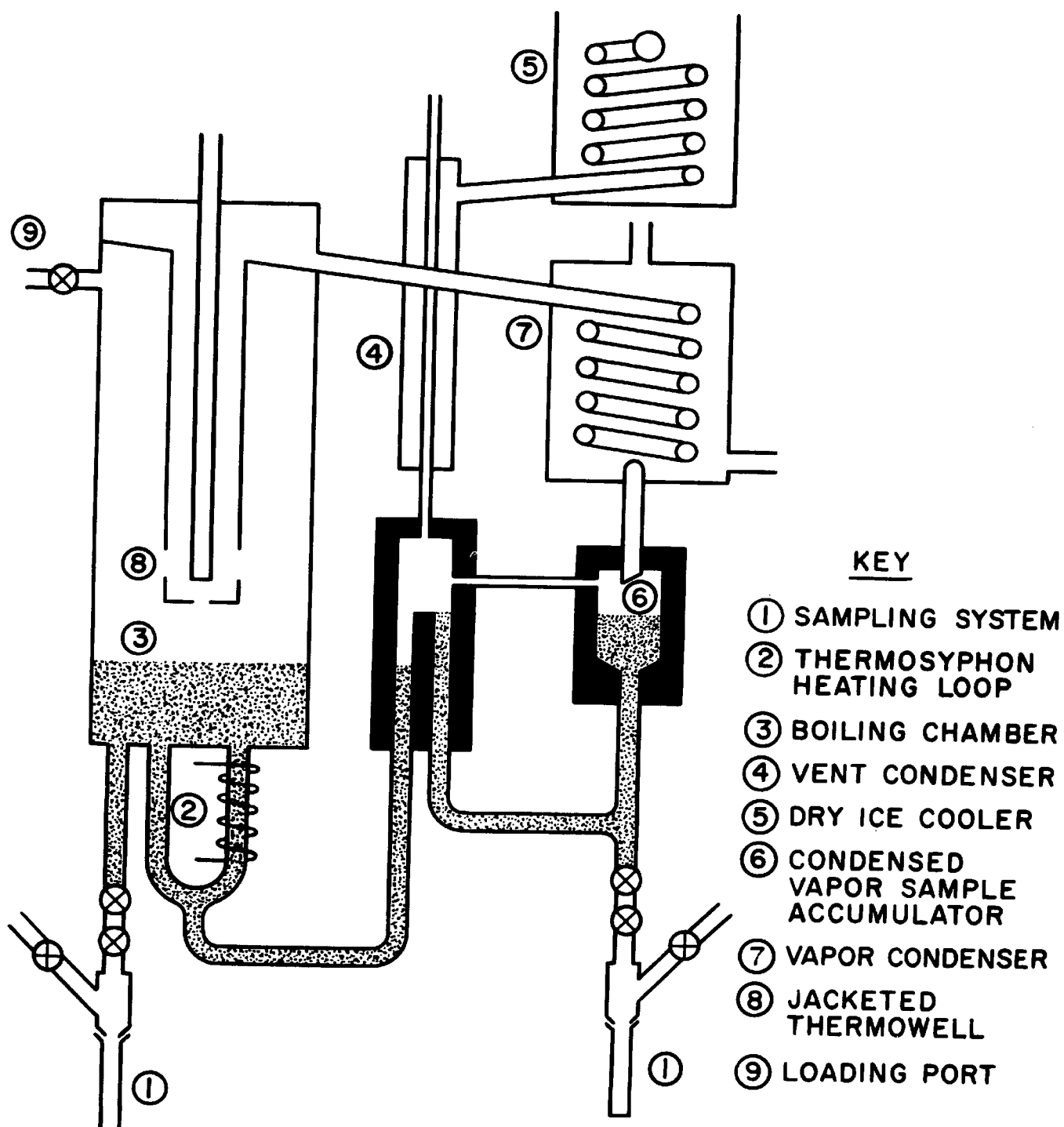
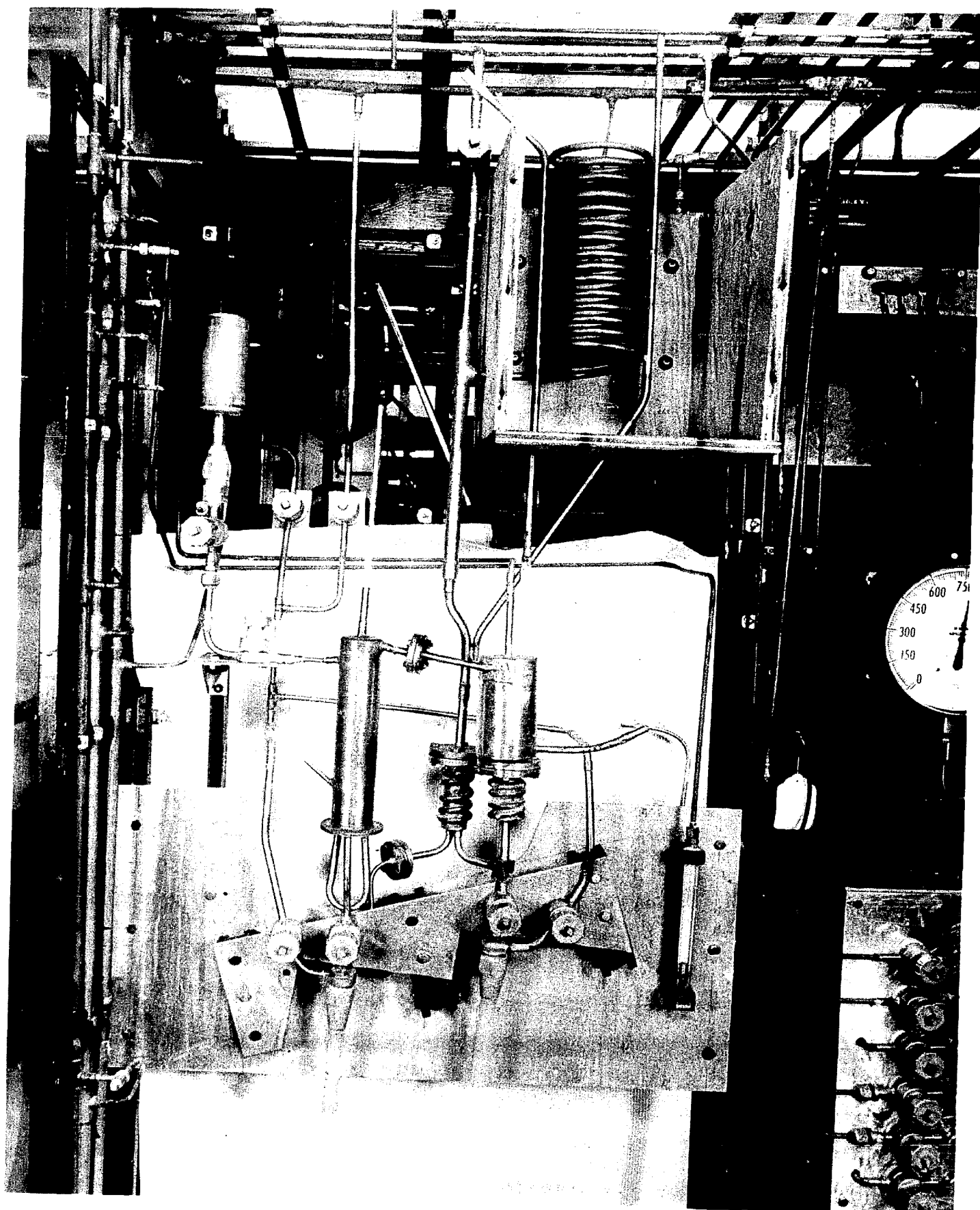


Figure 4
EQUILIBRIUM STILL



Heat was added to the boiling chamber of the Othmer still by means of a winding of asbestos-covered nichrome wire on one side of a loop of three-eighths inch nickel tubing. This generated a thermo-syphoning effect which served to mix the contents of the boiling chamber. Further mixing was secured by bringing the vapor condensate back to the center of the loop rather than directly to the boiling chamber. Mixing is always somewhat of a problem with an Othmer still and the very high relative volatility of the bromine pentafluoride-bromine trifluoride system aggravated the situation.

A loading port placed rather high up on the boiling chamber was used to charge the interhalogen into the still. The one-quarter inch line and attached valve also served as a mount to hold the still in position.

A three-eighth inch piece of nickel tubing with the bottom end plugged and welded served as a well for the resistance thermometer. The vapors generated in the boiling chamber passed up an annulus around the thermometer well and then to the condenser. The vapor entered holes on the sides of the annulus rather than at the bottom to minimize entrainment. A small hole was present in the bottom closure of the annulus for drainage.

From the annulus surrounding the thermometer well, the vapor passed to a total condenser consisting of several turns of three-eighth inch nickel tubing surrounded by a cooling water jacket. The cooling water gave a steady temperature which was cool enough to properly condense the interhalogen, yet not cool enough to freeze the bromine trifluoride (freezing point, 8.8°C).

The vapor condensate flowed over the weir in the condensate level device and back to the boiling chamber. The condensate receiver provided a reservoir of about fifteen to twenty ml of material for the vapor sample. The condensate level device served to maintain a constant holdup of condensate in part of the still and allowed the still to maintain a stable equilibrium. The pressure on the still was maintained by an inert buffer of helium in the vent condenser over the level device. A vent between the level device and the condensate receiver allowed the condensate receiver, the total condenser and the boiling chamber of the still to be at the same pressure as the inert helium buffer.

The condenser on the vent over the level device caused some difficulty. The condensate receiver and level device were kept at room temperature where bromine pentafluoride has a vapor pressure of about 400 mm. In order to prevent loss of the pentafluoride out the vent and into the manostat system, it was necessary to maintain the vent condenser at approximately -50°C . A condenser made of several loops of three-eighth inch copper tubing was connected to the vent condenser. The two condensers were partially filled with "Freon-12" and helium. The vent condenser now

became a boiler. If it became too warm the "Freon-12" boiled, the vapor being condensed with dry ice placed in contact with the loops of copper tubing. The amount of helium in this sealed system was adjusted so that the "Freon-12" boiled at -50°C . Thus, if the temperature of the vent attempted to rise above -50°C , the boiling "Freon-12" would remove heat just fast enough to hold that temperature.

Fluorothene tubes, molded with flares that fit the machined nickel plugs, were used to collect samples. The connection was made just like any standard three-quarter inch flare fitting. The vapor sample was drawn from the condensate receiver and the liquid sample from the boiling chamber. A second connection to the nickel plugs was used to evacuate the sample tubes prior to drawing the samples.

Difficulties in Operation of Still. An equilibrium still is designed to produce liquid and vapor of a two or more component system which are in equilibrium. The Othmer or liquid-recirculating type of still was used in this investigation. In this type of still, the liquid is boiled, condensed, and then recycled to the reboiler. Liquid samples are taken from the reboiler, and vapor samples are removed as liquid from the condensate recycle. This type of still suffers several drawbacks which will be discussed. However, the extremely corrosive nature of the interhalogens necessitated the use of all-metal construction, and only the liquid-recirculating type of still allows the simplicity of operation, minimum attention and ease of construction required.

The operating conditions of a liquid-recirculating type of equilibrium still are controlled by adjusting the pressure as the independent variable. When the still is operating properly, the temperature will automatically choose the equilibrium temperature corresponding to the controlled pressure. After enough heat is added to the reboiler to make up for losses to the surroundings, further heat will be expended as heat of vaporization. The evolution of the vapor will take place just fast enough to maintain the equilibrium temperature. This makes possible the ease of control which is responsible for the simplicity of operation.

Several precautions are necessary if proper operation is to be obtained. The vapor evolved in the reboiler will contain a slight amount of superheat. In a well-designed still, the superheat will not be more than 0.1 or 0.2°C and cannot be completely eliminated.

Except possibly for the slight amount of superheat, no heat may be subtracted from the vapor until it reaches the condenser. Any condensation of the vapor will change the composition of the remaining vapor and neither the boiling temperature nor the composition of the vapor will be the correct equilibrium value. The possibility of this occurrence can be minimized by thorough insulation. If difficulty is still encountered, this part of the

equilibrium still can be heated a fraction of a degree above the boiling temperature of the liquid. Care must be taken not to warm too much since the thermometer in the well would then tend to measure the temperature at the base of the thermometer well rather than the temperature of the vapor passing around the well. The conduction of heat from the base of the well through the metal well could easily more than equal the heat added to the well by the vapor. This would be anticipated since the film coefficient for heat transfer for a gas would be very low. In the present investigation both methods were tried and it was found that thorough insulation was sufficient precaution to insure proper operation. It is obvious that the equilibrium still should not be grasped for mounting purposes in an area where good insulation is important.

Another precaution which must be observed for proper operation pertains to the attainment of thorough mixing in the boiling chamber. If any portion of the recycling condensate vaporizes before it mixes intimately with the liquid in the reboiler, equilibrium will not be reached. This difficulty is further aggravated by operation with a mixture such as bromine pentafluoride-bromine trifluoride whose components differ greatly in volatility. The relative volatility varies from 10 to 30 for this system over the range of conditions investigated. The usual procedure is to return the recycled condensate directly to the boiling chamber. To minimize mixing difficulties in the present investigation, the vapor condensate was returned to the center of the heating loop. The heating loop was constructed of thin-wall, three-eighth inch tubing and the condensate returned through heavy-wall, one-quarter inch tubing. The small inside diameter of the condensate return line insured a more steady flow of the condensate at the point of juncture with the heating loop. The vapor evolving from the heating loop should be very close to the composition of the vapor leaving the reboiler and make the mixing problem in the reboiler less critical.

A mixture of pentafluoride and trifluoride was charged directly to the boiling chamber of the still. Until the still has had sufficient time to reach a steady state, the returning condensate will be different in composition from the vapor leaving the reboiler and the temperature of the evolved vapor will change slowly. A steady equilibrium temperature will result only when the condensate returning to the reboiler has the same composition as the vapor leaving. Any change in the vapor or vapor condensate holdup after equilibrium has been reached will cause a similar instability of operation. A change in temperature of the total condenser is sufficient to cause this. If precaution is taken to insure that the cooling water through the condenser is allowed to flow at a fairly high rate and is given sufficient time to approach a steady temperature, no trouble of this sort should occur.

A further difficulty that may be encountered is the problem of securing liquid and vapor samples for analysis that are truly representative of the liquid in the reboiler and the vapor condensate in the condensate receiver, respectively. The connecting line to the sampling valve may contain a portion of liquid which does not mix readily with the bulk of the liquid to be sampled. If this is the case, the sample drawn for analysis would not be truly representative of the bulk of liquid. The possibility of nonrepresentative sampling should be kept in mind during the design of the still and can be checked after the still is in operation. A charge of material is used for which vapor-liquid equilibrium data is available. Samples just large enough to empty the volume suspected of poor mixing are drawn. If such samples check the published data, the situation is not serious. This was the case with the still described in the present work.

When the still is operating properly, the equilibrium temperature should not be sensitive to small changes in the rate of heat input to the reboiler. A possible reason for a small change in boiling temperature with boiling rate is pressure buildup in the boiling chamber due to resistance to the flow of the vapor in the annulus around the thermometer well and in the line to the condenser. The result would be that the ebullition would take place at a pressure higher than the pressure measured and inaccurate data would result. This should not occur if reasonable dimensions are used in constructing the still. This point can be checked by charging the still with a compound such as water and demonstrating that the vapor pressure-temperature relationship is independent of the heat input to the reboiler. Another reason for a small change in boiling temperature with heat input for a mixture might be an increase in holdup of condensate in the condenser with higher heat input. The small amount of additional condensate flowing in the condenser will cause the boiling temperature to rise slightly, but the still will reach a new condition of equilibrium and no error will be involved. A major change in temperature with heat input may indicate entrainment of liquid particles in the vapor which would cause serious operating difficulties. As a precaution to minimize this difficulty, the lower end of the annulus around the thermometer well was closed except for a small drain hole. The vapor must make a right-angle turn when passing from the boiling liquid into the annulus, and it was believed that large droplets of liquid would not be able to negotiate the turn and would fall back into the liquid.

In the present investigation, all the difficulties mentioned were considered and the possible checks for proper operation were made. The equilibrium still was found to operate favorably in all cases.

Operating Procedure. The steps followed in the operation of the equilibrium still are the following:

- (a) The equilibrium still required a charge of about 100 to 120 ml. An all-welded nickel pot of 250 ml capacity was used for transferring the charge from the pure material dispenser to the still. It was equipped with a three-quarter inch female nickel flare fitting and was plugged with a three-quarter inch male plug. The outlet of the plug was welded to a Hoke diaphragm valve and one-quarter inch flare fitting.
- (b) The pot was prefluorinated and charged with the desired proportions of bromine pentafluoride and bromine trifluoride from the dispensing apparatus. The pot was disconnected from the dispensing apparatus and plugged with the nickel plug and valve. The pot was then connected to the charging port of the still in an inverted position.
- (c) The equilibrium still was prepared for charging by closing the valve connecting the still to the manostat system and evacuating the still through the sampling system. This allowed a more direct path to the vacuum pump used on the interhalogen side of the system and minimized the contamination of the system with interhalogen. It also prevented the necessity of evacuating the surge tank.
- (d) When the evacuation was complete, the sampling valves were closed and the material from the charging pot allowed to flow into the still. The entire charge was drained into the still in a few minutes, and the valve on the charging port was closed.
- (e) Dry ice was added to the "Freon-12" condenser which served to cool the vent and prevent losses from the still. About 15 to 20 minutes was allowed for the "Freon-12" system to come to equilibrium.
- (f) The desired operating pressure was adjusted on the manifold system, the valve between the still and the manifold system opened, and the heat to the reboiler of the still turned on. The water flow was started in the condenser at a sufficiently high rate so that the condenser would reach a steady temperature by the time the still was approaching equilibrium.
- (g) The progress of the still in approaching equilibrium was followed by the variation in the boiling temperature. At equilibrium, the temperature will be steady. After the temperature had become constant, at least an hour was allowed before sampling. While waiting for the still to warm up and come to equilibrium, the heat to the metal steam ebulliometer was turned on and the pressure in the inert and interhalogen systems equilibrated.

- (h) When the equipment was operating smoothly, the temperature constant and the pressure properly equilibrated, the temperature was read with the resistance thermometer at 15-minute intervals for one hour.
- (i) The sampling tubes were evacuated, and when the last measurement had been made, the valves used to evacuate the sample tubes were closed and the sampling valves opened to allow about 10 to 15 ml of sample to flow into the sample tubes.
- (j) After the samples have been drawn, the heat may be turned off on the equilibrium still and the metal steam ebulliometer. These pieces of equipment are then sealed off from the rest of the manifold system. The rest of the charge in the still can be removed if desired by taking samples and discarding them into the waste pot.

It was found that it was possible to carry out the complete series of operations in about 6 hours. This allowed a regular procedure of making a run on the equilibrium still each day while analyzing the two samples from the previous day.

Manifold system. The purpose of the manifold system is to regulate the pressure on the measuring apparatus and to serve to isolate the extremely reactive interhalogen vapors from the pressure-measuring apparatus. The manifold system was set up with two completely isolated parts. One side was used to adjust the pressure on the equilibrium still and the metal ebulliometer used for vapor pressure measurements on bromine trifluoride. This side of the system was filled with helium but contained a little interhalogen vapor that had diffused out of the equipment. The other side of the manifold system controlled the pressure on the metal steam ebulliometer, used for pressure measurement, and the manometer system. A schematic diagram of the manifold system is shown in Figure 5 and a photograph in Figure 6.

The only contact between the two systems was across the bellows of a Taylor "Differential Blind Manometer." This instrument is a pneumatically operated device which magnifies a difference in pressure across the bellows. The "DBM" is supplied with approximately 18 psig pressure and the output is read on a 0-1500 mm Bourdon tube gage. As the difference in pressure across the bellows varies from -1 to +1 mm, the output gage will read from 1000 to 1200 mm. By adjusting the pressure on the two sides of the system until the output gage reads 1100 mm, the pressure can be equilibrated between the interhalogen and inert sides of the system to within a few hundredths of a mm.

FIGURE 5.
MANIFOLD

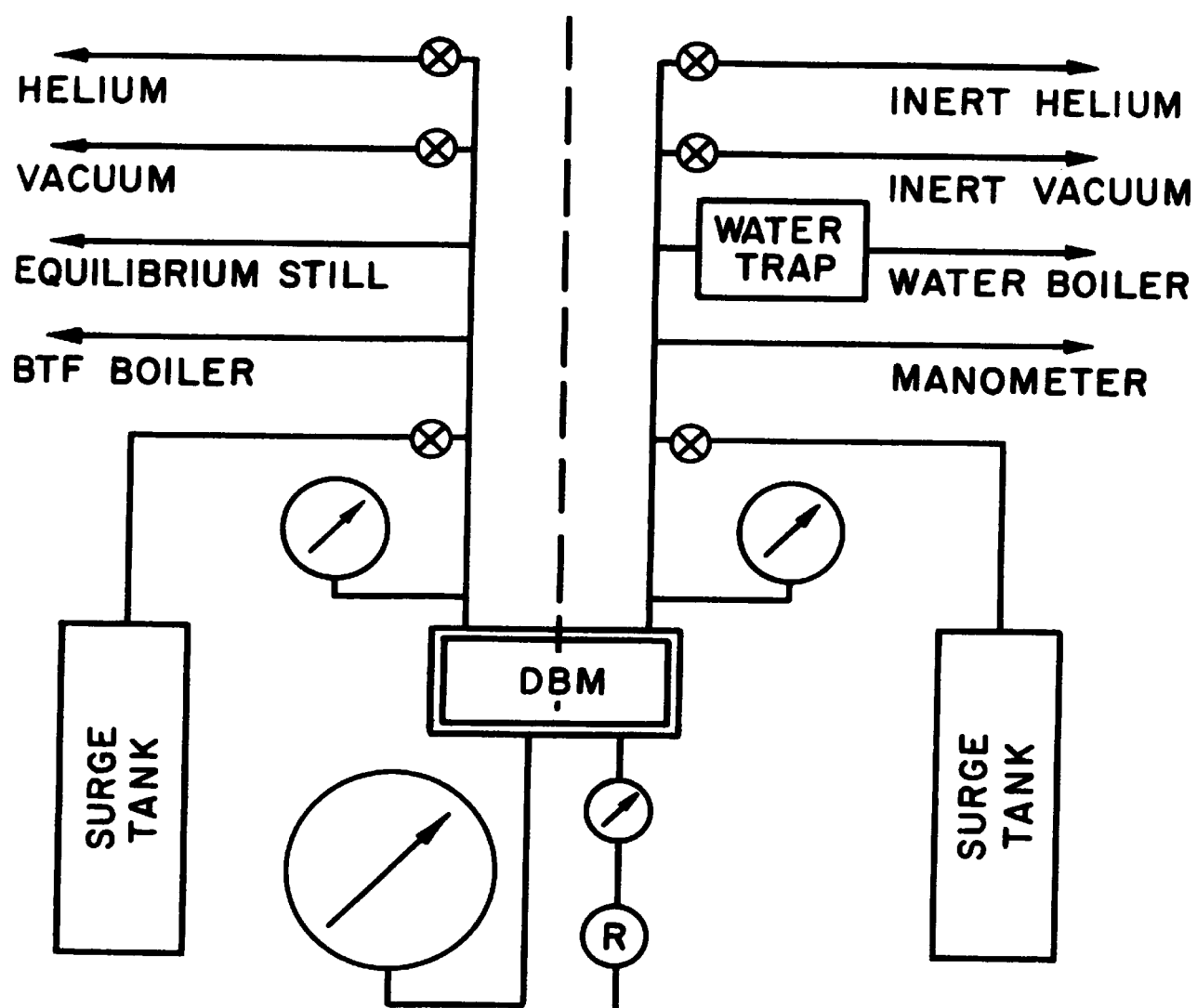


Figure 6
MANIFOLD SYSTEM



Both sides of the system contained a 0-6000 mm Bourdon tube gage for preliminary adjustment, a helium pressure supply cylinder and empty nitrogen cylinders for surge tanks. The nitrogen cylinders that were used for ballast were located outside the fume hood. They were covered with several layers of glass wool insulation to prevent pressure fluctuations due to variation in room temperature. There was a separate vacuum pump for each side of the system. On the interhalogen side, the vacuum pump was protected by fluorothene cold traps cooled in liquid air. After the liquid air cold traps, the gases passed through a chemical trap filled with limestone, before reaching the vacuum pump. On the inert side of the system, the manometers were protected by a liquid air cold trap from water vapor that may be present.

The pressure was adjusted manually and independently on each side of the system by either admitting or evacuating helium. The large ballast or surge tanks allowed the pressure to be accurately controlled and equilibrated.

Measurement of Temperature. Temperatures were measured with a platinum resistance thermometer and a Leeds and Northrup G-2 Mueller bridge. A certificate of calibration from the National Bureau of Standards was available for the resistance thermometer. Since a platinum resistance thermometer is used as an interpolation instrument to define the International Temperature Scale, this was the best equipment obtainable.

It is difficult to determine just how accurately an all-metal Othmer equilibrium still can measure the temperature corresponding to the liquid and vapor compositions. Due to errors existing in the data reported in the literature, operating the still on known mixtures is not a completely satisfactory solution. At any rate, it is doubtful if an Othmer still can give data over the complete range of composition with an accuracy of better than 0.1 to 0.2°C.

It is always desirable to have the vapor pressures of the pure components as accurately as possible when correlating vapor-liquid equilibrium data. The measurement of pressure by the ebulliometric method also requires the use of very accurate temperature measuring equipment. It is felt that in the present investigation the use of the very accurate temperature measuring equipment was justified.

Measurement of Pressure. When the investigation began, it was felt that the range of pressure involved would be a few atmospheres at most. An excellent Gaertner cathetometer was available and it was decided that mercury-in-glass manometers would be used in series. Three manometers, each with a useful length of 1000 mm and a bore diameter of 12 mm, were arranged in series. A valve manifold was connected to the manometers so that nitrogen could be admitted or evacuated from any part of the system.

The connections were made with glass sockets to metal ball joints. With the last manometer of the series open to the atmosphere, the system could be used with a barometer to measure pressures as high as 5 atm.

It was found during the investigation that bromine pentafluoride and bromine trifluoride were more stable toward decomposition at higher temperatures and pressures than was at first expected. It was possible to determine an isothermal diagram at 150°C and this involved pressures near 13,000 mm. In searching for a method of measuring accurately these higher pressures, it was recalled that an all-metal steam point apparatus functioned extremely well. The apparatus was adapted for pressures above one atm, and in conjunction with the well-known vapor pressure of water and the resistance thermometer, was found convenient for pressure measurement. The vapor pressure of water for this purpose was taken from Dorsey.⁽⁶⁾

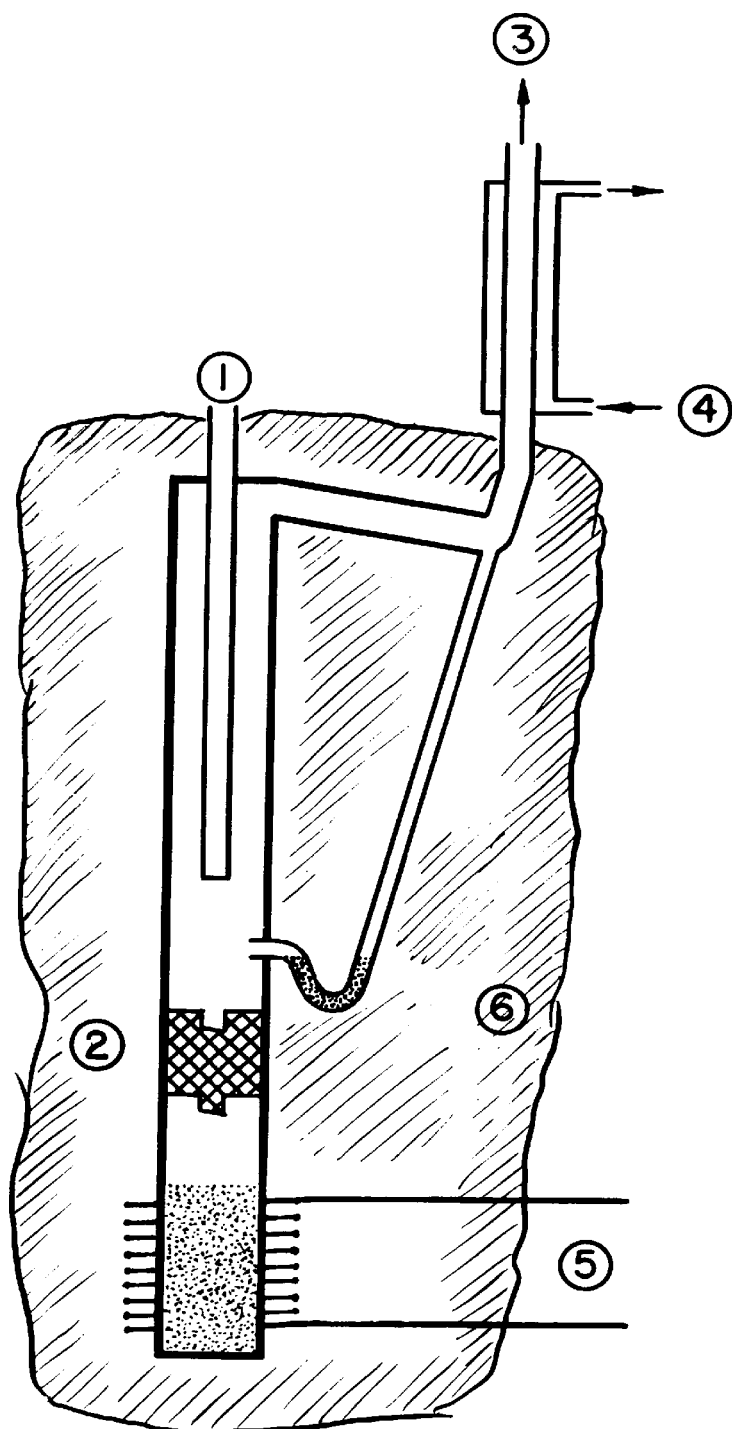
A schematic diagram of the metal steam ebulliometer is shown in Figure 7. The heat necessary for supplying the vapor was added to the liquid by a winding of asbestos-covered nichrome wire. The vapor passed through a packed section and then by the thermometer well to the total condenser. The condensate returned from the condenser and flowed over the packed section and back to the boiling liquid. A loop in the condensate return line prevented the vapor from traversing this route.

The unique feature of the design is the section packed with one-half inch nickel Raschig rings. Vapor leaving a vigorously boiling liquid will possess several tenths of a degree of superheat. The returning condensate will be approximately at the temperature of the cooling water used for the condenser. Enough of the rising vapor will be condensed to bring this down-flowing condensate to the boiling point. This will require the condensation of several percent of the vapor and ensure that no superheat is present when the vapor passes the thermometer well. Helium was used for the inert buffer since a gas with a molecular weight greater than steam would tend to displace the lighter water vapor in the condenser. This would result in loss of water from the ebulliometer and infiltration of the moisture throughout the pressure system.

The entire apparatus was well insulated to reduce unwanted heat losses. It was possible to properly operate the apparatus with as low as ten to thirty watts, depending on the pressure being measured. The usual test for proper operation of an ebulliometer is to determine if the condensation temperature measured is independent of the boiling rate. It was possible to add heat at a rate as high as three or four hundred watts without altering the condensation temperature. The operation of the apparatus was in every way satisfactory. The apparatus could reach operating conditions in a few minutes and give condensation temperatures with an accuracy of several thousandths of a degree.

FIGURE 7.

EBULLIOMETER



- ① THERMOMETER WELL
- ② PACKED SECTION
- ③ TO MANIFOLD
- ④ COOLING WATER INLET
- ⑤ HEATER
- ⑥ INSULATION

As a check between the two methods, four of the data points for the vapor pressure of bromine pentafluoride were measured with the manometer system. The rest of the vapor pressure data for bromine pentafluoride were obtained using the ebulliometer for pressure measurement. The agreement between the two methods was excellent. The manometer system was not used further since its operation was time consuming and rather tedious. The vapor pressure data points on bromine trifluoride were obtained in an ebulliometer constructed of nickel and of exactly the same design as the one used for pressure measurement.

The design of the ebulliometer is such that neither nonvolatile solutes nor noncondensable gases present in the liquid will cause any error in the measurement of the condensation temperature. The nonvolatile solute will cause greater superheat which is removed in the packed section and the noncondensable gases will be flushed to the condenser where they will remain and do no harm.

Calibration of Equilibrium Still. The foregoing precautions should all be observed even though the still will be later calibrated against a known mixture. The accuracy of vapor-liquid equilibrium data reported in the literature is always open to a certain amount of suspicion. There is no completely certain method of checking the accuracy of vapor-liquid equilibrium data. Although the thermodynamically consistent equations are a great convenience in correlating vapor-liquid equilibrium data, the ability of the data to be so fitted is neither a sufficient nor necessary criterion for accuracy. It is not a sufficient criterion since small consistent errors in temperature, pressure or composition would probably not be detected. It is not necessary since the derivation of these equations involves the assumption that the components measured are also the species present and this is not necessarily the case. Nonetheless, useful information can be gained by operation of a newly constructed equilibrium still on a known mixture.

The system ethanol-water was chosen for checking the operation of the equilibrium still for several reasons. It is a common system for which liquid-vapor equilibrium measurements have been made by several investigators. The ethanol-water system shows a relative volatility of approximately 10 in the water-rich end of the diagram. Since the bromine pentafluoride-bromine trifluoride system has a high relative volatility, it was desirable to check the operation of the still on a mixture which also shows a high relative volatility. The measurement of refractive index serves as an excellent method of analysis in the water-rich composition range. The refractive index values used for analysis were those of Leach and Lythgoe.⁽⁷⁾

The experimentally determined liquid-vapor equilibria on the system ethanol-water are compared with the published values of Ju Chin Chu⁽⁸⁾ taken originally from Carey and Lewis,⁽⁹⁾ Noyes and Warfle,⁽¹⁰⁾ and

Jones, et al. The data taken in the present investigation are listed in Table I together with deviations from the smoothed values given by Ju Chin Chu.

Table I
ETHANOL-WATER SYSTEM

1-Atmosphere Isobaric Data

<u>Temp. °C</u>	<u>Obs. x</u>	<u>Obs. x - Calc. x</u>	<u>Obs. y</u>	<u>Obs. y - Calc. y</u>
95.34	1.8	-0.1	17.1	-0.6
95.32	1.7	-0.2	17.5	-0.3
94.88	1.9	-0.3	18.9	-0.4
94.81	1.9	-0.3	18.7	-0.9
94.55	1.6	-0.7	20.2	-0.3

In Table I, x and y are the mole per cent ethanol in the liquid and vapor, respectively. Observed values are the experimental values taken in the equilibrium still and the calculated values are the smoothed values taken from the literature.

The average deviation was 0.4 mole per cent. It is felt that this is within the error of the published values.

It was felt that as a further check of proper operation the equilibrium still should be tested with a system showing a small relative volatility. Errors in temperature might be more apparent in a system with low relative volatility. The system chosen was n-heptane-toluene, for which the relative volatility varies from 1.1 to 1.8 over the range of composition. The best set of data available in the literature is considered to be that of Hipkin and Myers.⁽¹²⁾ The data on this system taken in this investigation are listed in Table II. The deviations are the differences between these values and the smoothed data of Hipkin and Myers. Here x and y are the mole per cent n-heptane in the liquid and vapor, respectively. Observed values are the experimental values taken in the equilibrium still and the calculated values are the smoothed values taken from the literature.

The average deviation is 0.8 mole per cent. This agreement is at least as good as is found between the data of Hipkin and Myers and the data of Steinhauser and White⁽¹³⁾ and Bromiley and Quiggle.⁽¹⁴⁾

Table II
N-HEPTANE-TOLUENE SYSTEM

1-Atmosphere Isobaric Data

<u>Temp. °C</u>	<u>Obs. x</u>	<u>Obs. x - Calc. x</u>	<u>Obs. y</u>	<u>Obs. y - Calc. y</u>
106.71	16.0	1.0	24.1	1.2
106.58	16.1	0.6	24.0	0.1
105.98	18.3	-0.1	27.4	0.0
104.02	32.3	2.3	41.2	1.4
100.14	66.8	-0.7	72.1	-0.6

Measurement of the refractive index was used as the method of analysis for the n-heptane-toluene system. Refractive index as a function of composition is given by Stein⁽¹⁵⁾ at 10 mole per cent intervals.

C. Method of Analysis

The measurement of refractive index was used as the method of analysis for the solutions of bromine pentafluoride and bromine trifluoride. Glass is attacked very rapidly by these compounds and commercially available instruments for measurement of refractive index would be quickly ruined. Stein, Vogel and Ludewig⁽¹⁶⁾ have developed a suitable apparatus for use with interhalogens and obtained the refractive index as a function of composition for solutions of bromine pentafluoride and bromine trifluoride. Essentially, the method involved the use of a Spencer spectrometer with a specially constructed prism. The prism was machined from solid nickel and fitted with replaceable, optically flat quartz windows.

The prism was maintained at 25°C by means of circulating water from a temperature-controlled bath through holes drilled in the solid nickel parts of the prism.

The operation of the equipment was somewhat tedious, but not difficult, and gave reliable results. The operations carried out to make an analysis will be described in some detail.

- (a) The samples were drawn from the still into fluorothene tubes which were molded to fit three-quarter inch male nickel flare fittings. The sample was frozen in liquid air to condense any of the sample in the vapor phase. Helium was admitted to prevent moisture from the air being drawn in when the connection was broken.

- (b) The sample tube was then removed from the still and plugged with molded fluorothene three-quarter inch plugs. The sample could then be stored until analyzed. While the still was operating, the samples taken the previous day were analyzed.
- (c) The prism assembly was always disassembled whenever left overnight, since it was not possible to eliminate all traces of the interhalogen and extreme corrosion of the windows would have resulted. The first operation was then the assembly of the prism, using new windows or gaskets if necessary.
- (d) The prism was then prefluorinated with chlorine trifluoride by connecting it to the pure material dispensing apparatus. The excess chlorine trifluoride was removed by purging with helium. Had the prism not been prefluorinated, reaction of the interhalogen with the metallic surface would have formed bromine and contaminated the sample.
- (e) The connection of the fluorothene sample tube with the prism was made by means of a three-quarter inch male nickel flare fitting which was welded to a one-quarter inch nickel line, flared at the end. The sample was again frozen in liquid air and the sample tube and prism attached to the special fitting.
- (f) When the sample of interhalogen melts, a slight positive pressure will develop and can be used to force the sample into the prism. The melted sample was shaken lightly so as to be homogeneous and the inlet valve of the prism opened. If sufficient sample were available, the outlet valve was cracked and some of the interhalogen sample allowed to flow completely through the prism and into a beaker. The connections were then broken and the flare fittings on the prism capped to prevent accidental leakage.
- (g) The water lines from the constant temperature bath were connected to the cooling labyrinth of the prism and the prism set on the spectrometer stand. While the prism was adjusting to the proper temperature, the angle of the prism windows was measured. This was necessary since the angle was slightly different each time the prism was assembled. Three screws supported the prism and were used to level it prior to the measurement.
- (h) When the prism was at the proper temperature, the refractive index was measured by determining the angle made by the light rays (sodium D line) in passing through the prism.

- (i) When the measurement had been completed the cooling water lines were disconnected, and the water blown out of the prism. This must not be forgotten because an explosion will result if water contacts the interhalogen while emptying the prism.
- (j) The sample was drained out of the prism and into a dry beaker reserved for this use. The dispensing apparatus was then used for blowing out interhalogen that remained in the form of a liquid film. The windows could then be removed, being careful of any interhalogen that may remain.

The refractive index is calculated from the prism angle and the angle of deviation of the light beam by substitution into the equation,

$$n = \frac{\sin [(\phi + \delta)/2]}{\sin (\phi/2)}$$

where ϕ = is the prism angle, and

δ = the angle of deviation of the light beam.

Stein, Vogel, and Ludewig⁽¹⁶⁾ obtained the refractive indices of the bromine pentafluoride-bromine trifluoride system at 25°C and fitted the refractive index as a function of composition with the equation,

$$n_D^{25} = 1.4536 - 0.1243x_1 + 0.0124x_1^2 + 0.0112x_1^3,$$

where x_1 is the mole fraction of bromine pentafluoride.

III. EXPERIMENTAL DATA

The experimental measurements made in this investigation consisted of the vapor pressures of bromine pentafluoride and bromine trifluoride, and the liquid-vapor equilibria of the system bromine pentafluoride-bromine trifluoride. The vapor pressure of bromine pentafluoride was measured in the range 25 to 146°C, and the vapor pressure of bromine trifluoride was measured in the range 63 to 181°C. The liquid-vapor equilibria of the system bromine pentafluoride-bromine trifluoride was measured at 50, 75, 100, 125 and 150°C and at 1 atm pressure.

This section will give a comparison of the experimental data with the smoothed values or correlation. The exact procedure used in making the calculations will be presented in a later section.

Vapor Pressure. The vapor pressure data for bromine pentafluoride were collected using the equilibrium still to measure the condensation temperatures. Pressures were measured by comparing the condensation temperature of water in the ebulliometer with the known vapor pressure of water. The pressure on the equilibrium still was equilibrated with the pressure on the ebulliometer by means of the Taylor "Differential Blind Manometer." The vapor pressure-temperature relation at saturation for water was taken from Table 242, page 561, of "Properties of Ordinary Water Substance," by N. E. Dorsey.⁽⁶⁾ In order to check the ebulliometric method of pressure measurement, four of the data points were secured using a mercury-in-glass manometer system. These points are distinguished by an asterisk in Table III. It is seen that excellent checks were obtained. The data were obtained from seven different fillings of the equilibrium still. A modified form of the Antoine equation was found to fit the data within experimental error.

The vapor pressure data for bromine trifluoride were measured by using a metal ebulliometer for measurement of condensation temperatures of bromine trifluoride and a similar metal steam ebulliometer for measurement of pressure. The metal steam ebulliometer was used in exactly the same manner as in the vapor pressure measurement of bromine pentafluoride. The ebulliometer used for the bromine trifluoride was connected to the inter-halogen side of the manifold system and the steam ebulliometer was connected to the inert side. The pressure on the two systems was equilibrated by means of the Taylor "Differential Blind Manometer."

The data presented in Table IV were secured from four different fillings of the ebulliometer. It was found that an Antoine equation fitted the data within experimental error. Three data points were taken at 201, 215 and 225°C which were not used in fitting the equation. The bromine trifluoride was not stable at these temperatures, but apparently had reached an equilibrium with its decomposition products since the temperatures measured were steady.

Table III

VAPOR PRESSURE OF BROMINE PENTAFLUORIDE

Data fitted to the equation

$$\log_{10}P = 6.4545 + 0.001101t - 895/(t + 206)$$

Data collected from seven different fillings of the equilibrium still

Temp., °C	Obs. Pres., mm	$100 \frac{(\text{Obs. } P - \text{Calc. } P)}{\text{Calc. } P}$
25.073	406.21	-0.03
26.164	425.04	0.04
27.755	453.19	0.00
29.149	479.32	0.03
29.808	491.75	-0.03
30.885	513.54	0.06
33.188	561.43	0.02
34.513	590.39	-0.03
34.518	590.09	-0.10
36.011	625.12	0.00
37.706	666.20	0.01
39.062	700.53	0.01
42.505	794.06	0.02
44.289	845.98	-0.01
44.391	848.67	-0.05
45.961	897.34	0.00
49.689	1020.4	-0.02
54.676	* 1205.8	-0.01
56.643	1285.9	0.00
62.271	* 1537.5	-0.02
64.134	1628.7	-0.02
68.222	1844.9	0.03
76.517	2348.2	-0.01
77.520	* 2416.5	0.02
80.346	2618.4	0.15
84.995	2968.2	0.02
89.020	* 3303.6	0.04
89.408	3334.6	-0.04
93.974	3759.0	0.16
99.658	4318.1	-0.19
104.910	4915.6	0.05
110.836	5655.6	0.17
117.842	6620.0	0.07
126.262	7939.7	-0.01
137.486	9991.7	-0.14
145.991	11815.0	-0.03

* Pressure measured with mercury-in-glass manometer system.

Table IV

VAPOR PRESSURE OF BROMINE TRIFLUORIDE

Data fitted to the equation

$$\log_{10}P = 7.65757 - 1627.5/(t + 215)$$

Data collected from four different fillings of the ebulliometer

<u>Temp., °C</u>	<u>Obs. Pres., mm</u>	<u>100 $\frac{(\text{Obs. } P - \text{Calc. } P)}{\text{Calc. } P}$</u>
63.475	65.010	-0.06
64.342	67.831	0.01
64.809	69.472	0.16
74.252	107.15	-0.23
75.049	111.26	-0.03
84.875	169.70	-0.14
85.020	171.33	0.21
94.428	250.28	0.13
94.693	252.28	-0.11
104.410	365.34	0.11
104.663	368.26	-0.03
104.690	368.78	0.02
114.026	514.57	0.07
114.264	518.96	0.09
114.354	520.14	0.01
124.965	741.74	-0.01
125.013	743.15	0.02
134.141	991.31	0.02
134.421	999.86	0.02
144.732	1359.9	0.03
144.916	1364.5	-0.16
154.429	1787.4	0.02
155.589	1844.7	0.01
164.580	2343.1	-0.03
165.223	2384.5	0.03
173.699	2954.9	0.00
180.730	3508.9	0.06
* 201.4	5839.	4.1
* 215.0	7786.	4.4
* 225.4	9660.	5.4

* These data were not fitted to the Antoine equation.

Experimental liquid-vapor data. The experimental data on the liquid-vapor equilibria of the system bromine pentafluoride-bromine trifluoride were determined at 50, 75, 100, 125 and 150°C and at a pressure of 1 atm. An equilibrium still of the type used in this investigation is controlled by adjusting the pressure over the boiling liquid. At least an hour must be allowed after the still has settled down to equilibrium conditions. Thus, it was desirable to determine liquid-vapor data that at times differed slightly from the desired temperature or pressure. This was considered a lesser evil than throwing the still out of equilibrium by attempting to approach the desired temperature more closely.

The temperatures and compositions listed in Tables V through X were obtained from the equilibrium still in conjunction with the resistance thermometer and analytical equipment. Pressures were measured by the use of a metal steam ebulliometer in exactly the same manner as described for the measurements of vapor pressure of bromine pentafluoride.

In a few cases, a sample was lost due to faulty technique or faulty operation of the equipment, and a blank inserted in place of the composition.

Table V

LIQUID-VAPOR EQUILIBRIA, 50°C ISOTHERM; SYSTEM: BrF₃ - BrF₅

Data not adjusted to exactly 50°C

Temperature, °C	Pressure, mm	Mole Fraction BrF ₅ in Liquid	Mole Fraction BrF ₅ in Vapor
49.67	330.6	0.206	0.924
53.04	385.1	0.225	0.910
49.82	445.5	0.297	0.961
49.98	546.5	0.393	0.960
49.50	597.8	0.449	0.963
49.87	711.1	0.560	0.976
49.96	769.1	0.623	0.983
50.02	927.0	0.859	0.990
50.00	961.9	0.913	0.995

Table VI

LIQUID-VAPOR EQUILIBRIA, 75°C ISOTHERM; SYSTEM: BrF₃ - BrF₅

Data not adjusted to exactly 75°C

Temperature, °C	Pressure, mm	Mole Fraction BrF ₅ in Liquid	Mole Fraction BrF ₅ in Vapor
74.97	351.8	0.067	0.705
74.93	522.1	0.120	0.820
75.27	680.4	0.180	0.829
74.91	748.3	0.194	0.884
75.11	752.8	0.209	0.895
74.11	888.8	0.270	-
74.57	902.1	0.246	0.909
75.53	1022.3	0.287	-
74.91	1171.9	0.359	0.949
75.27	1213.7	0.379	0.934
74.67	1257.5	0.410	0.950
74.79	1352.0	0.436	0.949
75.00	1476.0	0.520	0.944
75.34	1556.2	0.548	-
75.18	1571.5	0.574	0.952
74.71	1754.1	0.673	0.980
74.96	1786.0	0.693	0.985
74.71	1810.7	0.712	0.976
74.94	2016.7	0.849	0.990
74.97	2147.6	0.934	0.996

Table VII

LIQUID-VAPOR EQUILIBRIA, 100°C ISOTHERM; SYSTEM: BrF₃ - BrF₅

Data not adjusted to exactly 100°C

Temperature, °C	Pressure, mm	Mole Fraction BrF ₅ in Liquid	Mole Fraction BrF ₅ in Vapor
100.01	414.2	0.006	0.246
100.03	611.3	0.048	0.518
100.46	855.4	0.094	0.670
99.82	1108.6	0.131	0.759
100.22	1306.7	0.155	0.780
99.55	1341.5	0.169	0.814
99.70	1591.6	0.225	0.863
100.18	1853.0	0.245	0.868
100.42	2211.9	0.328	0.875
100.71	2364.0	0.352	0.911
100.32	2491.1	0.385	0.930
99.99	2834.2	0.481	0.931
99.80	3072.1	0.545	0.922
99.50	3312.2	0.632	0.964
100.29	3666.9	0.735	0.980
99.84	3680.2	0.774	0.989
100.09	4034.0	0.864	0.994
100.01	4176.2	0.932	0.996

Table VIII

LIQUID-VAPOR EQUILIBRIA, 125°C ISOTHERM; SYSTEM: BrF_3 - BrF_5

Data not adjusted to exactly 125°C

Temperature, °C	Pressure, mm	Mole Fraction BrF_5 in Liquid	Mole Fraction BrF_5 in Vapor
125.02	994.2	0.019	0.268
123.89	1548.9	0.072	0.551
125.32	1970.8	0.094	0.639
123.88	2417.8	0.136	0.731
123.55	2715.3	0.177	0.767
125.24	2997.4	0.181	0.772
123.60	3942.8	-	0.874
123.34	4252.4	0.342	0.903
124.89	4495.2	0.359	0.889
125.00	5289.	0.472	0.910
125.27	5601.	0.541	0.940
124.93	5629.	0.500	0.947
124.69	5747.	-	0.943
124.90	5996.	0.584	0.948
123.25	6192.	-	0.955
125.08	6704.	0.736	0.966
125.08	6971.	0.809	0.969
124.98	7058.	0.816	0.986
124.91	7358.	0.916	0.993
124.97	7394.	0.926	0.992

Table IX

LIQUID-VAPOR EQUILIBRIA, 150°C ISOTHERM; SYSTEM: BrF_3 - BrF_5

Data not adjusted to exactly 150°C

Temperature, °C	Pressure, mm	Mole Fraction BrF_5 in Liquid	Mole Fraction BrF_5 in Vapor
150.03	2564	0.035	0.384
149.92	2603	0.036	0.426
150.40	3250	0.070	0.549
149.97	4429	0.132	0.689
149.92	5904	0.211	0.785
149.95	6038	0.232	0.810
149.84	6079	0.247	0.797
149.87	7309	0.337	-
149.82	7460	0.345	0.845
150.70	9084	0.458	0.852
149.81	9500	0.523	0.910
150.21	10228	0.590	0.945
149.60	11312	0.764	0.969
150.01	12522	0.970	1.000

Table X

LIQUID-VAPOR EQUILIBRIA, 1 ATM. ISOBAR; SYSTEM: BrF_3 - BrF_5

Data not adjusted to exactly 1 atm.

Temperature, °C	Pressure, mm	Mole Fraction BrF_5 in Liquid	Mole Fraction BrF_5 in Vapor
43.56	762.8	0.898	0.987
45.56	761.4	0.811	1.000
45.88	760.8	0.806	0.968
48.24	760.2	0.686	0.997
52.58	758.8	0.548	0.984
56.23	761.3	0.471	0.975
62.79	736.5	0.346	0.949
64.44	760.2	0.322	0.941
69.04	759.8	0.264	0.932
72.66	743.1	0.229	-
78.92	760.0	0.177	0.865
82.43	759.3	0.144	-
85.14	760.4	0.144	0.794
89.78	758.3	0.095	0.742
95.14	760.0	0.087	0.679
96.14	758.1	0.079	0.650
103.46	759.5	0.074	0.565
110.39	741.4	0.033	0.426
114.42	742.0	0.020	0.302
120.54	749.3	0.004	0.156

Activity Coefficients. Activity coefficients were calculated directly from the experimental liquid-vapor equilibria data by the use of the following equations,

$$\gamma_1 = Py_1/p_1x_1 \text{ and } \gamma_2 = Py_2/p_2x_2 .$$

where P = total pressure

P_1, P_2 = vapor pressures of pure bromine pentafluoride and bromine trifluoride, respectively, at the observed temperature.

x_1, x_2 = mole per cent bromine pentafluoride and bromine trifluoride in the liquid phase, respectively.

y_1, y_2 = mole per cent bromine pentafluoride and bromine trifluoride in the vapor phase, respectively.

It was assumed that the vapor phase behaves ideally, i.e., the partial pressure of a component in the vapor is equal to the total pressure multiplied by the mole per cent of that component.

It is expected that the activity coefficient is independent of temperature and pressure for the very small deviation of these quantities from the desired temperature or pressure. Thus if a datum point is adjusted in composition for the small temperature deviation from the desired temperature of the isotherm, the quantities P , y , x and p will vary in such a way as to keep γ relatively constant.

The activity coefficients are listed in Tables XI through XVI and plotted in Figures 8 through 13. The activity coefficients are plotted separately to avoid confusion.

Table XI

LIQUID-VAPOR EQUILIBRIA, 50°C ISOTHERM; SYSTEM: $\text{BrF}_5 - \text{BrF}_3$

Data not adjusted to exactly 50°C

Activity Coefficients (assuming ideal gas behavior)

Pressure, mm.	Temperature, °C	γ_1	$\log_{10} \gamma_1$	γ_2	$\log_{10} \gamma_2$
330.6	49.67	1.476	0.169	0.977	-0.010
385.1	53.04	1.361	0.134	1.161	0.065
445.5	49.82	1.406	0.148	0.759	-0.120
546.5	49.98	1.294	0.112	1.099	0.041
597.8	49.50	1.265	0.102	1.253	0.098
711.1	49.87	1.208	0.082	1.189	0.075
769.1	49.96	1.178	0.071	1.057	0.024
927.0	50.02	1.035	0.015	2.004	0.302
961.9	50.00	1.014	0.006	1.683	0.226

Table XII

LIQUID-VAPOR EQUILIBRIA, 75°C ISOTHERM; SYSTEM: BrF₅ - BrF₃

Data not adjusted to exactly 75°C

Activity coefficients (assuming ideal gas behavior)

<u>Pressure, mm</u>	<u>Temperature, °C</u>	<u>γ_1</u>	<u>$\log_{10} \gamma_1$</u>	<u>γ_2</u>	<u>$\log_{10} \gamma_2$</u>
351.8	74.97	1.652	0.218	1.002	0.001
522.1	74.93	1.585	0.200	0.968	-0.014
680.4	75.27	1.380	0.140	1.262	0.101
748.3	74.91	1.517	0.181	0.977	-0.010
752.8	75.11	1.432	0.156	0.897	-0.047
888.8	74.11	1.500	0.176	1.000	0.000
902.1	74.57	-	-	-	-
1022.3	75.53	-	-	-	-
1171.9	74.91	1.380	0.140	0.836	-0.078
1213.7	75.27	1.321	0.121	1.140	0.057
1257.5	74.67	1.309	0.117	0.973	-0.012
1352.0	74.79	1.315	0.119	1.114	0.047
1476.0	75.00	1.191	0.076	1.560	0.193
1556.2	75.34	-	-	-	-
1571.5	75.18	1.153	0.062	1.578	0.198
1754.1	74.71	1.146	0.059	0.998	-0.001
1786.0	74.96	1.130	0.053	0.804	-0.095
1810.7	74.71	1.112	0.046	1.387	0.142
2016.7	74.94	1.047	0.020	1.167	0.067
2147.6	74.97	1.016	0.007	1.180	0.072

Table XIII

LIQUID-VAPOR EQUILIBRIA 100°C ISOTHERM, SYSTEM: $\text{BrF}_5 - \text{BrF}_3$

Data not adjusted to exactly 100°C

Activity coefficients (assuming ideal gas behavior)

Pressure, mm	Temperature, °C	γ_1	$\log_{10} \gamma_1$	γ_2	$\log_{10} \gamma_2$
414.2	100.01	3.954	0.597	1.014	0.006
611.3	100.03	1.517	0.181	0.998	-0.001
855.4	100.46	1.374	0.138	0.989	-0.005
1108.6	99.82	1.476	0.169	1.122	0.050
1306.7	100.22	1.493	0.174	1.089	0.037
1341.5	99.55	1.496	0.175	0.984	-0.007
1591.6	99.70	1.409	0.149	0.918	-0.037
1853.0	100.18	1.500	0.176	1.042	0.018
2211.9	100.42	1.340	0.127	1.306	0.116
2364.0	100.71	1.377	0.139	1.023	0.010
2491.1	100.32	1.368	0.136	0.906	-0.043
2834.2	99.99	1.259	0.100	1.225	0.088
3072.1	99.80	1.197	0.078	1.718	0.235
3312.2	99.50	1.172	0.069	1.069	0.029
3666.9	100.29	1.114	0.047	0.875	-0.058
3680.2	99.84	1.081	0.034	0.562	-0.250
4034.0	100.09	1.062	0.026	0.545	-0.264
4176.2	100.01	1.023	0.010	0.891	-0.050

Table XIV

LIQUID-VAPOR EQUILIBRIA, 125°C ISOTHERM; SYSTEM: $\text{BrF}_5 - \text{BrF}_3$

Data not adjusted to exactly 125°C

Activity coefficients (assuming ideal gas behavior)

Pressure, mm	Temperature, °C	γ_1	$\log_{10}\gamma_1$	γ_2	$\log_{10}\gamma_2$
994.2	125.02	1.774	0.249	1.000	0.000
1548.9	123.89	1.578	0.198	1.047	0.020
1970.8	125.32	1.726	0.237	1.050	0.021
2417.8	123.88	1.722	0.236	1.052	0.022
2715.3	123.55	1.570	0.196	1.086	0.036
2997.4	125.24	1.644	0.216	1.191	0.076
3942.8	123.60	-	-	-	-
4252.4	123.34	1.503	0.177	0.889	-0.051
4495.2	124.89	1.445	0.160	1.057	0.024
5289.	125.00	1.318	0.120	1.216	0.085
5601.	125.27	1.380	0.140	0.807	-0.093
5629.	124.93	1.250	0.097	1.038	0.016
5747.	124.69	-	-	-	-
5996.	124.90	1.261	0.101	1.023	0.010
6192.	123.25	-	-	-	-
6704.	125.08	1.138	0.056	0.337	-0.472
6971.	125.08	1.079	0.033	1.503	0.177
7058.	124.98	1.104	0.043	0.745	-0.128
7358.	124.91	1.033	0.014	0.845	-0.073
7394.	124.97	1.026	0.011	1.030	0.013

Table XV

LIQUID-VAPOR EQUILIBRIA 150°C ISOTHERM; SYSTEM: $\text{BrF}_5 - \text{BrF}_3$

Data not adjusted to exactly 150°C

Activity coefficients (assuming ideal gas behavior)

<u>Pressure, mm</u>	<u>Temperature, °C</u>	<u>γ_1</u>	<u>$\log_{10} \gamma_1$</u>	<u>γ_2</u>	<u>$\log_{10} \gamma_2$</u>
2564	150.03	2.178	0.338	1.035	0.015
2603	149.92	2.404	0.381	0.984	-0.007
3250	150.40	1.986	0.298	0.986	-0.006
4429	149.97	1.811	0.258	1.002	0.001
5904	149.92	1.726	0.237	1.021	0.009
6038	149.95	1.660	0.220	0.944	-0.025
6079	149.84	1.542	0.188	1.042	0.018
7309	149.87	-	-	-	-
7460	149.82	1.436	0.157	1.127	0.052
9084	150.70	1.897	0.278	0.938	-0.028
9500	149.81	1.300	0.114	1.140	0.057
10228	150.21	1.279	0.107	0.865	-0.063
11312	149.60	1.135	0.055	1.064	0.027
12522	150.01	1.012	0.005	-	-

Table XVI

LIQUID-VAPOR EQUILIBRIA, 1 ATM.; SYSTEM: BrF_5 - BrF_3

Data not adjusted to exactly 1 atm.

Activity Coefficients (assuming ideal gas behavior)

Temperature, °C	Pressure, mm.	γ_1	$\log_{10} \gamma_1$	γ_2	$\log_{10} \gamma_2$
43.56	762.8	1.016	0.007	4.305	0.634
45.56	761.4	1.062	0.026	-	-
45.88	760.8	1.021	0.009	4.742	0.676
48.24	760.2	1.138	0.056	0.234	-0.631
52.58	758.8	1.062	0.026	0.719	-0.143
56.23	761.3	1.242	0.094	0.791	-0.102
62.79	736.5	1.294	0.112	0.918	-0.037
64.44	760.2	1.352	0.131	0.966	-0.015
69.04	759.8	1.416	0.151	0.832	-0.080
72.66	743.1	-	-	-	-
78.92	760.0	1.479	0.170	0.948	-0.023
82.43	759.3	1.406	0.148	1.069	0.029
85.14	760.4	-	-	-	-
89.78	758.3	1.750	0.243	1.042	0.018
95.14	760.0	1.528	0.184	1.045	0.019
96.14	758.1	1.578	0.198	5.984	0.777
103.46	759.5	1.213	0.084	1.016	0.007
110.39	741.4	1.690	0.228	0.975	-0.011
114.42	742.0	1.875	0.273	1.016	0.007
120.54	749.3	4.046	0.607	0.991	-0.004

FIGURE 8.

LIQUID-VAPOR EQUILIBRIA, 50 °C
ISOTHERM SYSTEM BrF_5 - BrF_3 .

Activity Coefficients

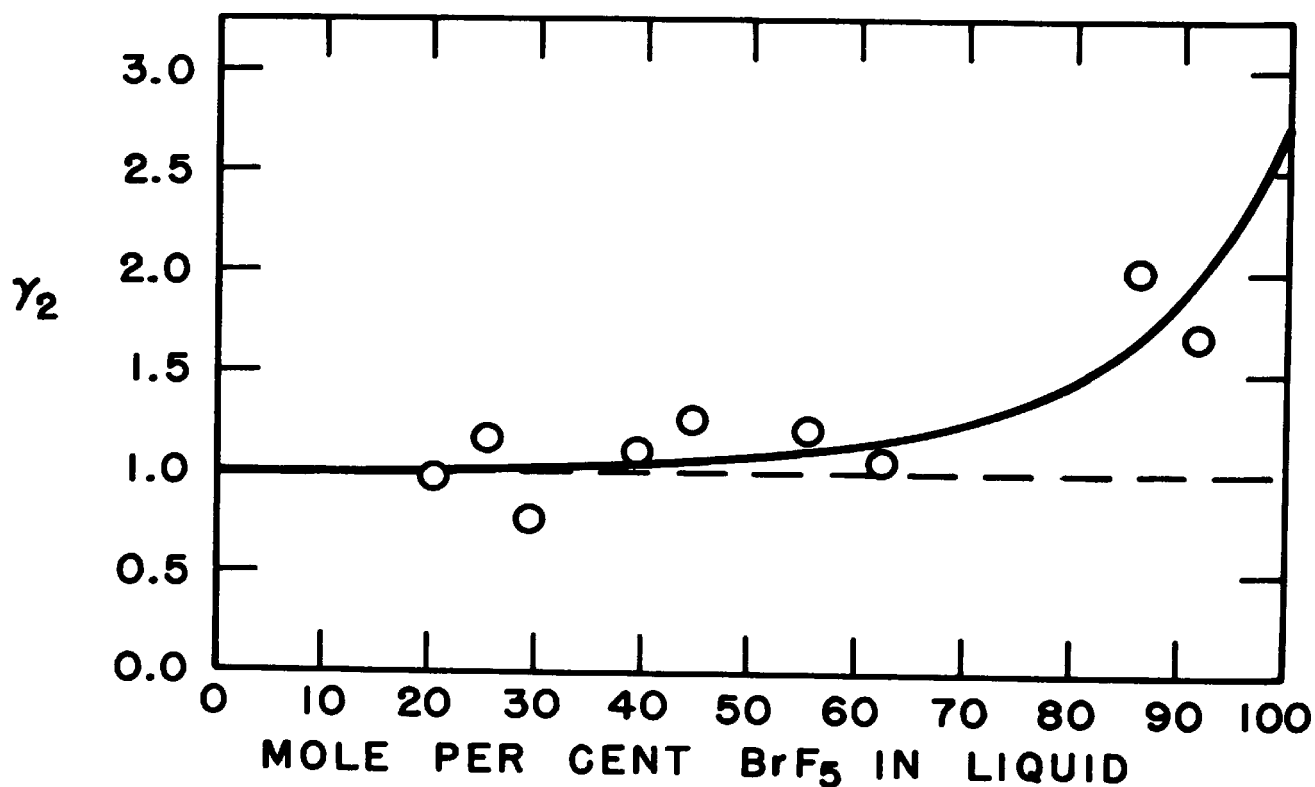
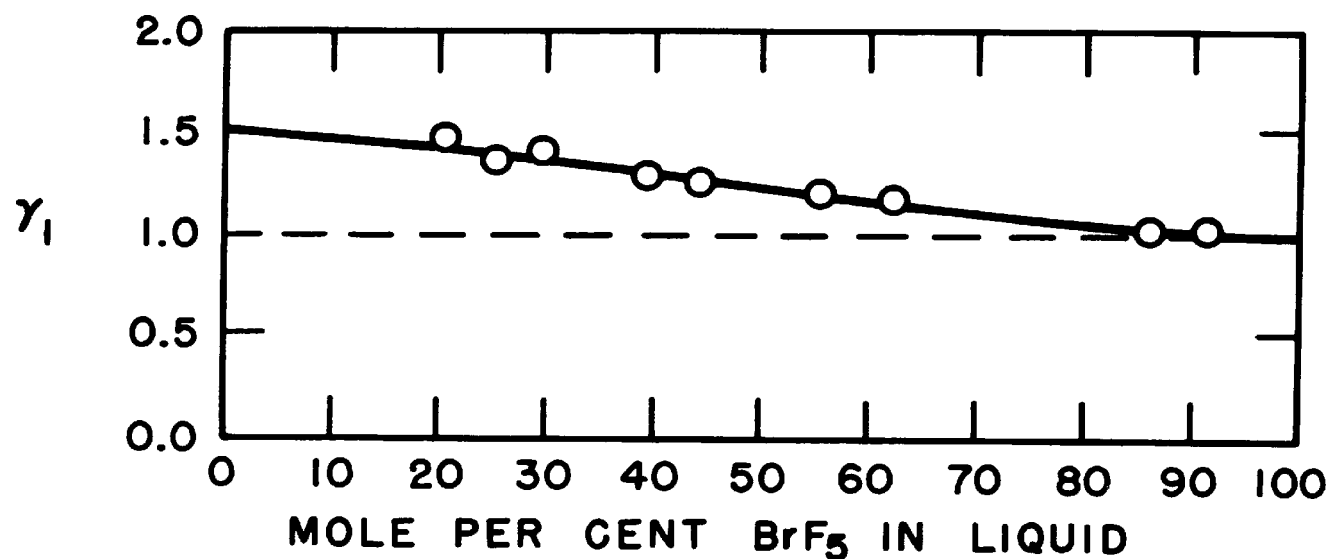


FIGURE 9.
LIQUID-VAPOR EQUILIBRIA, 75 °C
ISOTHERM SYSTEM BrF_5 - BrF_3 .
Activity Coefficients

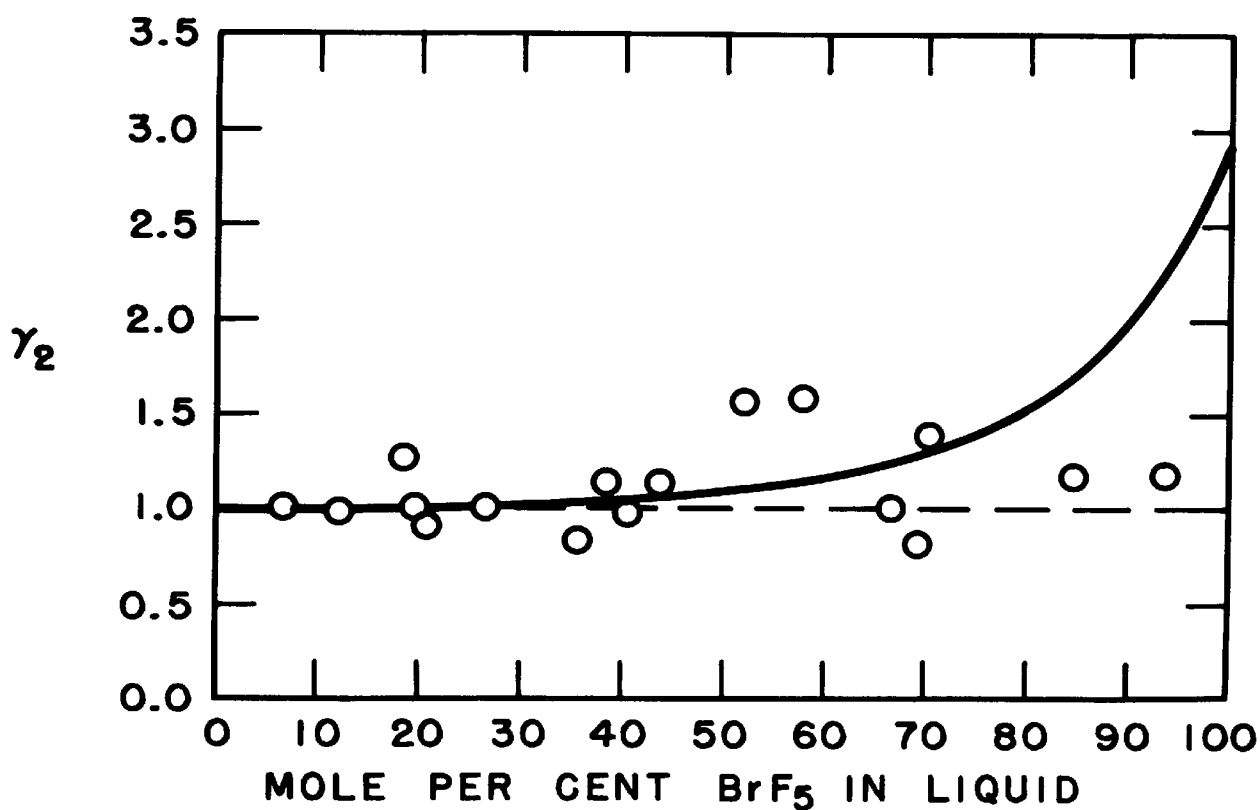
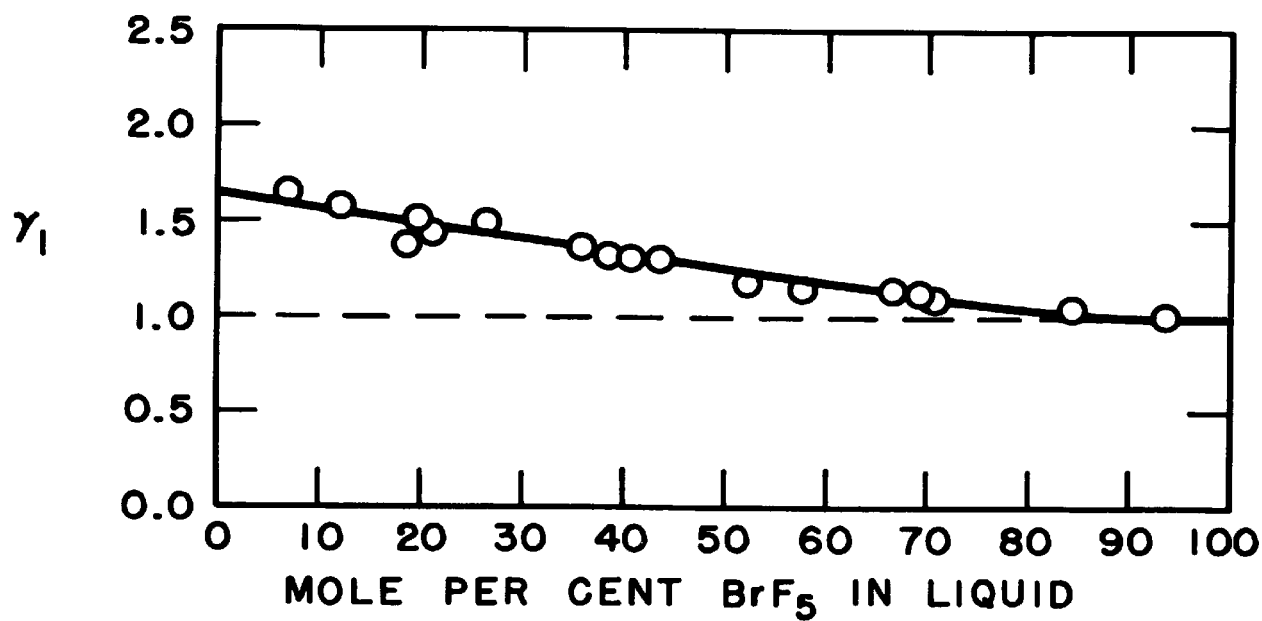


FIGURE 10.
LIQUID-VAPOR EQUILIBRIA, 100 °C
ISOTHERM SYSTEM BrF_5 - BrF_3
Activity Coefficients

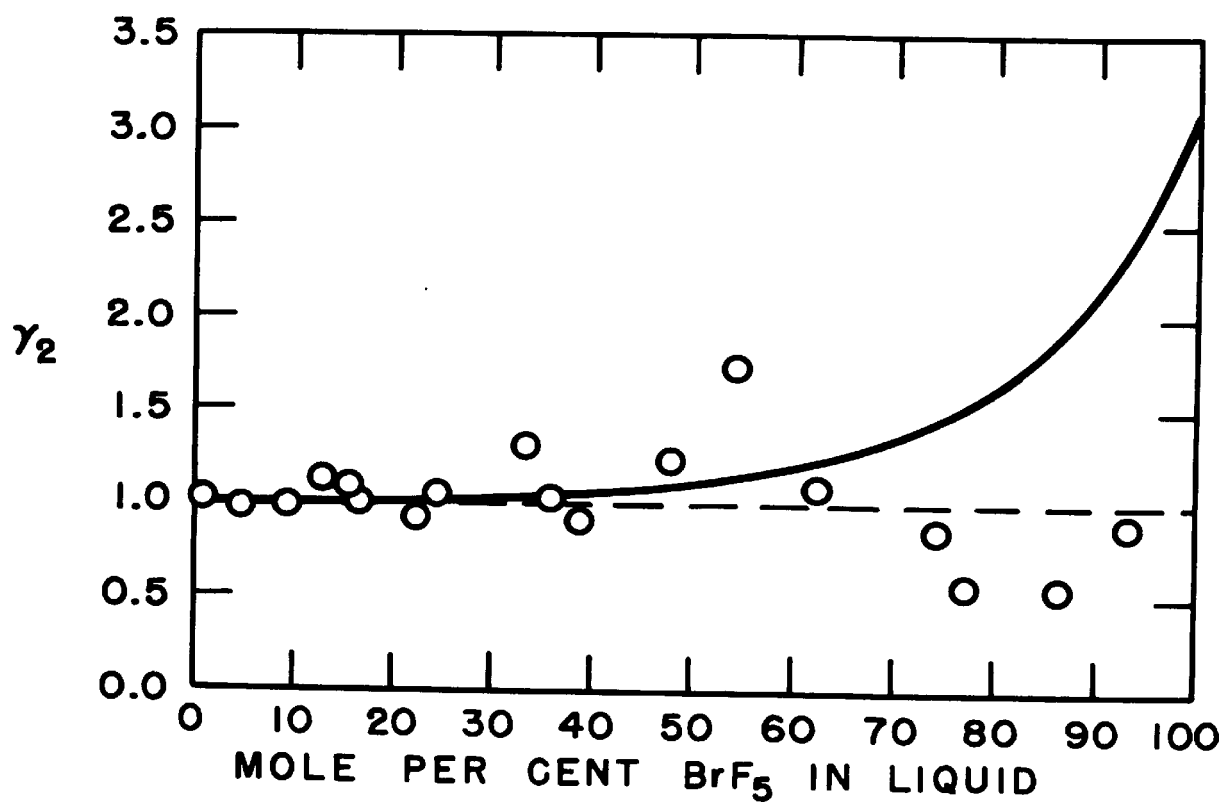
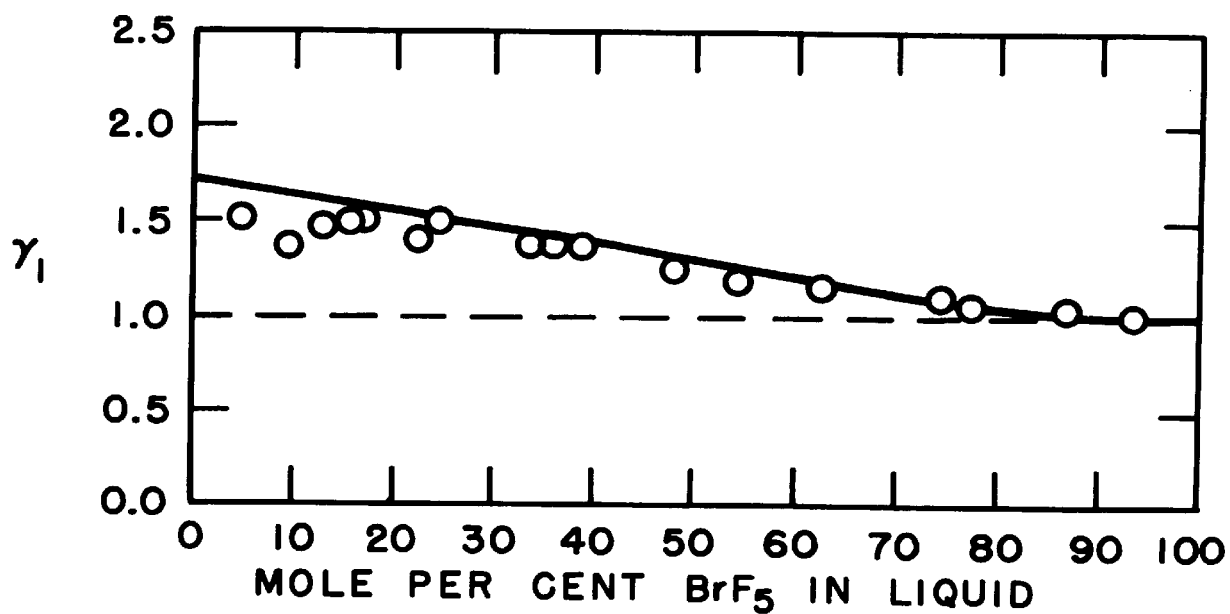


FIGURE II.
LIQUID-VAPOR EQUILIBRIA, 125 °C
ISOTHERM SYSTEM BrF_5 - BrF_3 .
Activity Coefficients

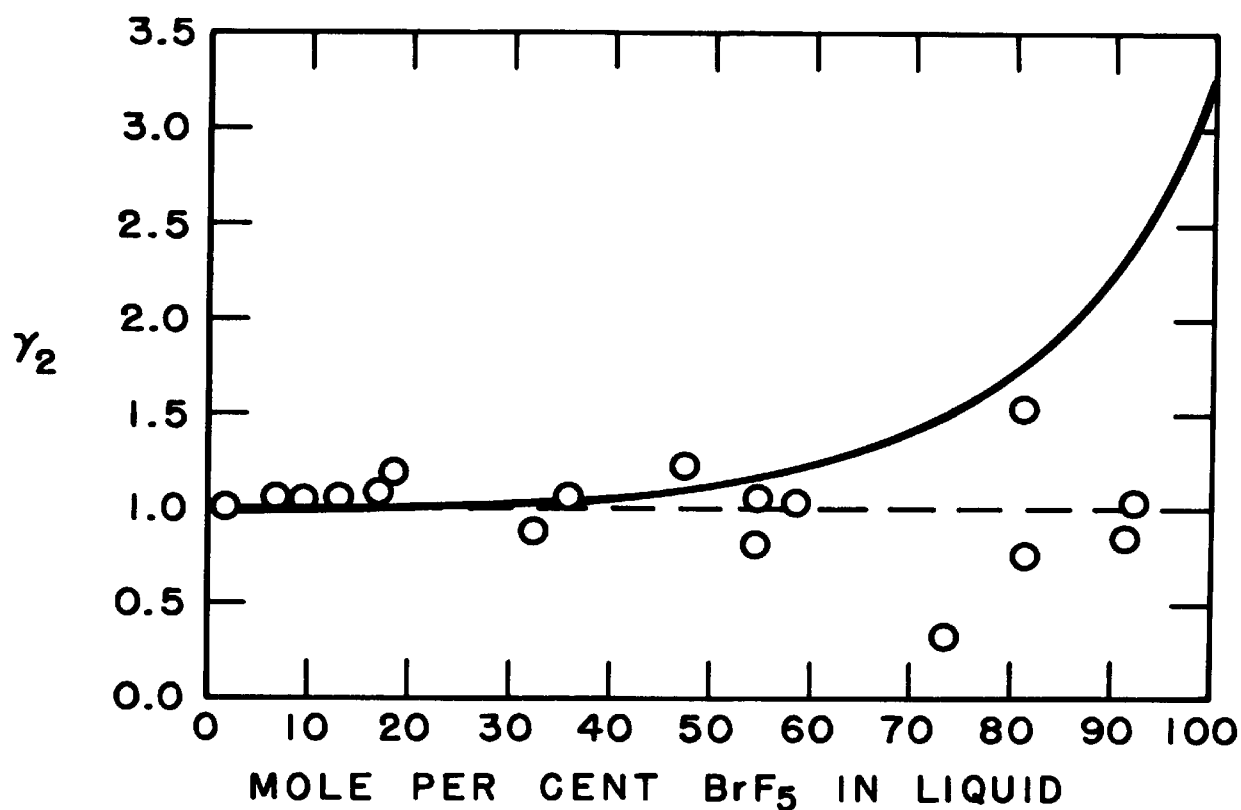
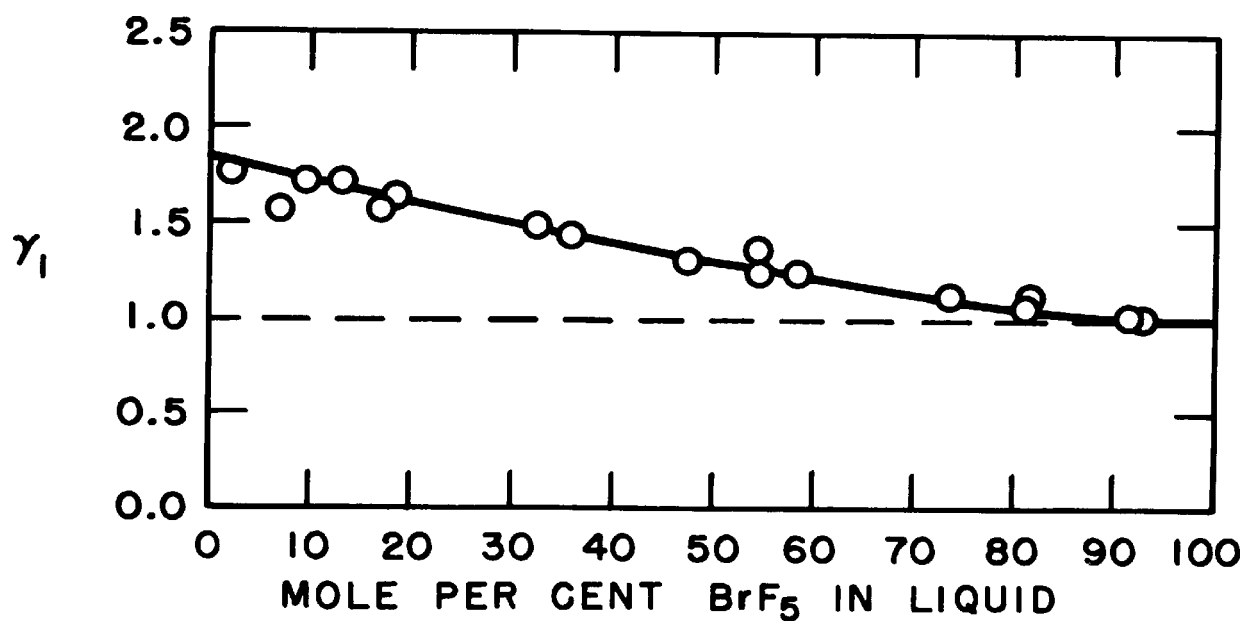


FIGURE 12.
LIQUID-VAPOR EQUILIBRIA, 150 °C
ISOTHERM SYSTEM $\text{BrF}_5 - \text{BrF}_3$.
Activity Coefficients

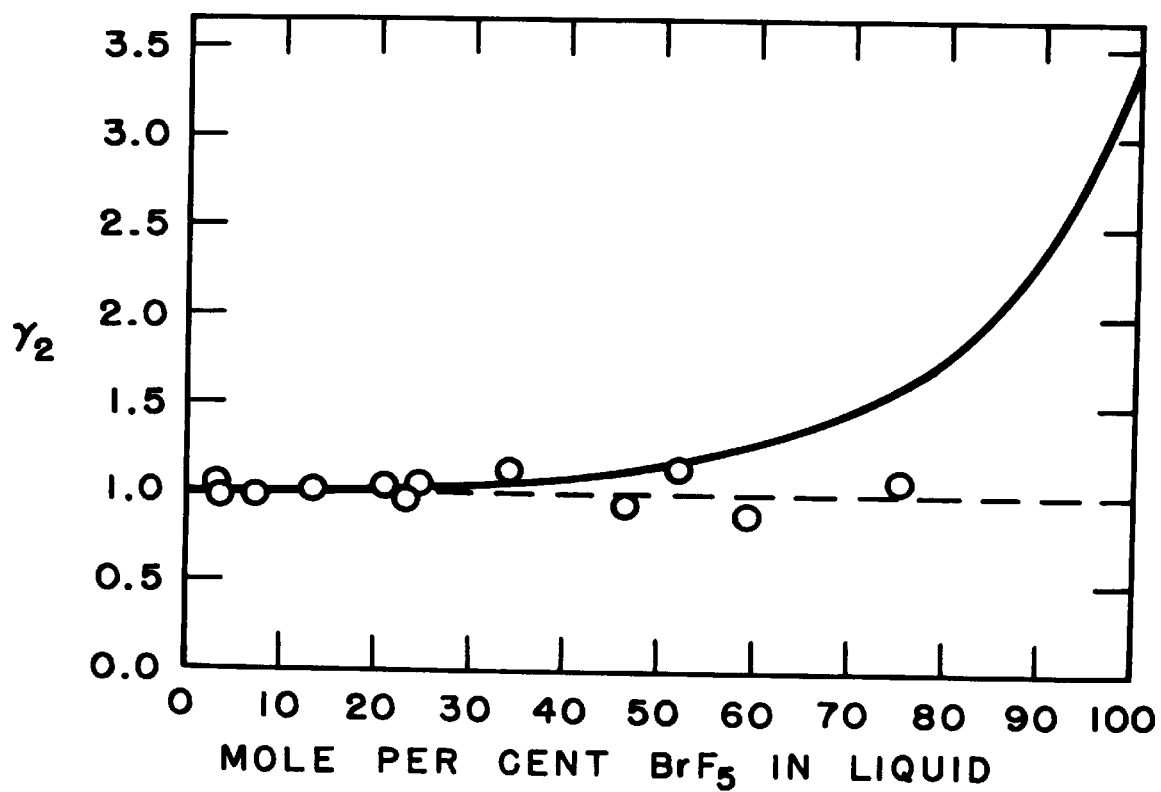
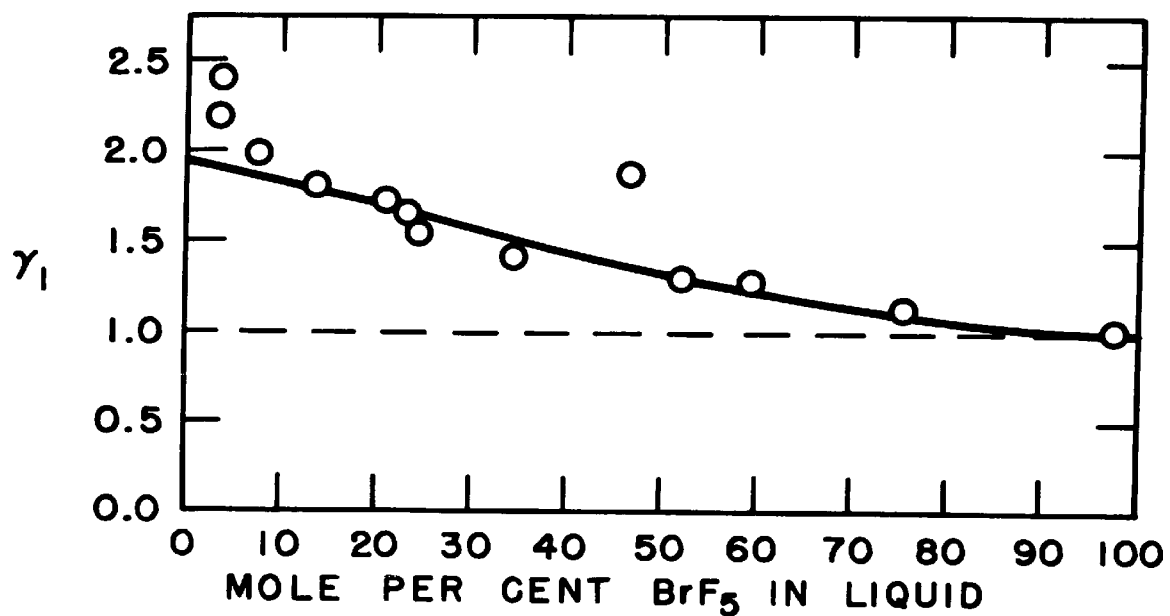
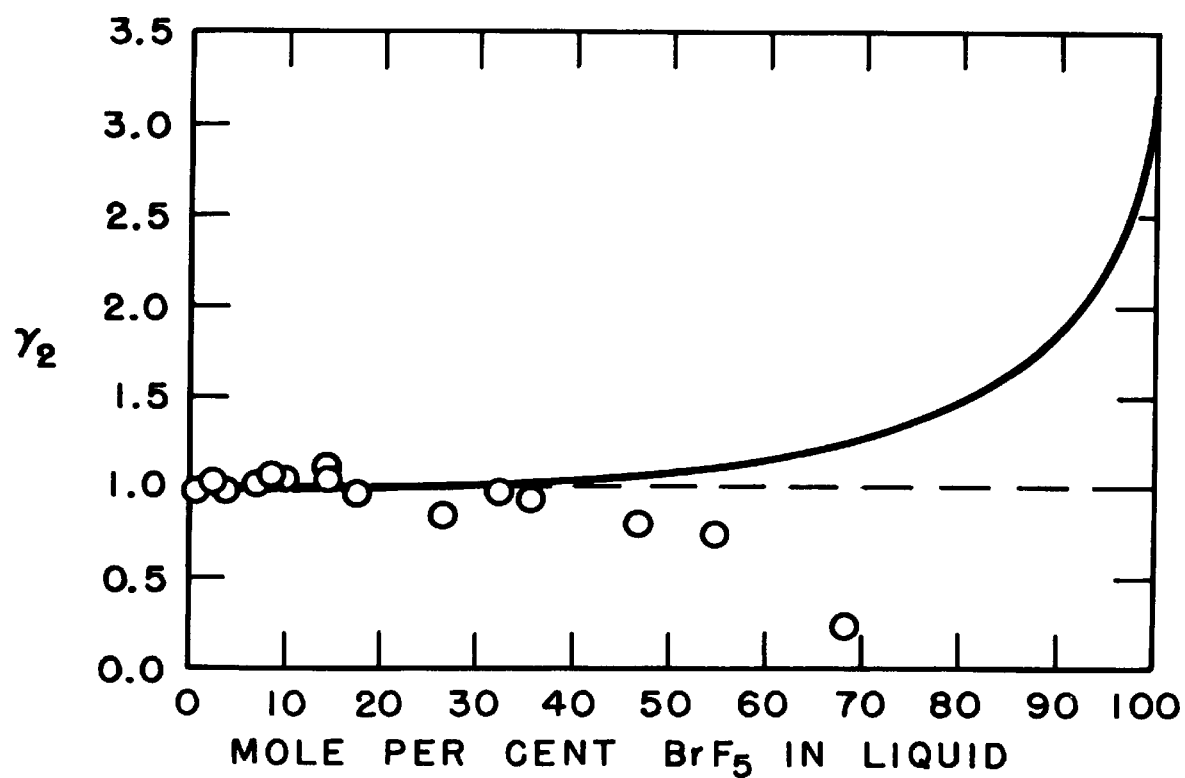
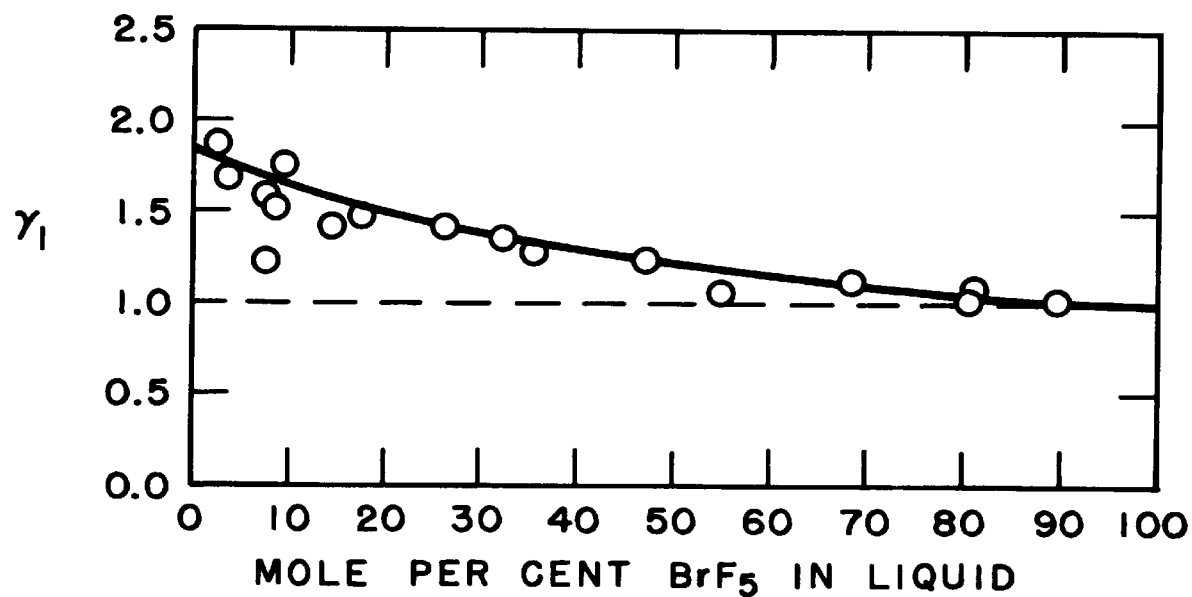


FIGURE 13.
LIQUID-VAPOR EQUILIBRIA, 1 Atm.
ISOBAR SYSTEM $\text{BrF}_5\text{-BrF}_3$.
Activity Coefficients



Comparison of liquid-vapor data with correlation. The liquid-vapor equilibria data were correlated by fitting a pair of van Laar equations

$$\log_{10} \gamma_1 = A / (1 + Ax_1/Bx_2)^2 ,$$

$$\log_{10} \gamma_2 = B / (1 + Bx_2/Ax_1)^2$$

to the experimental activity coefficients. The constants A and B of the van Laar equations represent the logarithm of the activity coefficients at infinite dilution of bromine pentafluoride and bromine trifluoride, respectively. These constants were fitted as functions of temperature by the following equations:

$$A = 0.1290 + 0.001076 t ,$$

$$B = 0.4000 + 0.001000 t .$$

These equations, in conjunction with the vapor pressure equations of bromine pentafluoride and bromine trifluoride, are intended to represent the liquid-vapor equilibria data. In Tables XVII through XXII, the data which have been corrected to the desired isothermal temperatures and to the desired isobaric pressure, are compared with the above equations. The same information is given in graphical form in Figures 14 through 19.

Table XVII

LIQUID-VAPOR EQUILIBRIA, 50°C ISOTHERM; SYSTEM: BrF₃ - BrF₅

Data adjusted to 50°C

Comparison of Observed and Calculated Compositions

<u>Pressure, mm.</u>	<u>Obs. x</u>	<u>Obs. x-Calc. x</u>	<u>Obs. y</u>	<u>Obs. y-Calc. y</u>
330.6	0.203	-0.005	0.923	0.002
385.1	0.252	0.000	0.927	-0.008
445.5	0.295	-0.007	0.961	0.013
546.5	0.393	0.003	0.960	-0.003
597.8	0.441	0.001	0.961	-0.007
711.1	0.557	-0.004	0.976	-0.002
769.1	0.622	-0.010	0.983	0.001
927.0	0.860	-0.002	0.990	-0.002
961.9	0.913	0.001	0.995	0.001

Table XVIII

LIQUID-VAPOR EQUILIBRIA, 75°C ISOTHERM; SYSTEM: BrF₃ - BrF₅

Data adjusted to 75°C

Comparison of Observed and Calculated Compositions

<u>Pressure, mm.</u>	<u>Obs. x</u>	<u>Obs. x-Calc. x</u>	<u>Obs. y</u>	<u>Obs. y-Calc. y</u>
351.8	0.067	0.010	0.705	0.053
522.1	0.120	-0.002	0.819	0.007
680.4	0.182	0.007	0.831	-0.032
748.3	0.194	-0.003	0.883	0.003
752.8	0.209	0.010	0.895	0.014
888.8	0.262	0.015	-	-
902.1	0.243	-0.008	0.907	0.001
1022.3	0.292	-0.004	-	-
1171.9	0.358	0.002	0.949	0.013
1213.7	0.382	0.008	0.936	-0.003
1257.5	0.406	0.012	0.949	0.006
1352.0	0.434	-0.003	0.948	-0.002
1476.0	0.520	0.022	0.944	-0.013
1556.2	0.553	0.015	-	-
1571.5	0.577	0.030	0.953	-0.009
1754.1	0.667	0.008	0.979	0.007
1786.0	0.692	0.011	0.985	0.011
1810.7	0.706	0.008	0.975	0.000
2016.7	0.847	-0.003	0.990	0.005
2147.6	0.934	-0.004	0.996	0.003

Table XIX

LIQUID-VAPOR EQUILIBRIA, 100°C ISOTHERM; SYSTEM: BrF₃ - BrF₅

Data adjusted to 100°C

Comparison of Observed and Calculated Compositions

<u>Pressure, mm.</u>	<u>Obs. x</u>	<u>Obs. x-Calc. x</u>	<u>Obs. y</u>	<u>Obs. y-Calc y</u>
414.2	0.006	-0.008	0.246	-0.018
611.3	0.048	0.005	0.519	0.001
855.4	0.096	0.017	0.677	0.011
1108.6	0.130	0.012	0.757	0.005
1306.7	0.156	0.006	0.782	-0.016
1341.5	0.166	0.010	0.811	0.006
1591.6	0.223	0.024	0.861	0.018
1853.0	0.246	0.000	0.869	-0.003
2211.9	0.332	0.014	0.878	-0.022
2364.0	0.360	0.009	0.914	0.004
2491.1	0.389	0.010	0.931	0.013
2834.2	0.480	0.019	0.931	-0.003
3072.1	0.542	0.015	0.921	-0.024
3312.2	0.623	0.020	0.962	0.008
3666.9	0.741	0.006	0.981	0.014
3680.2	0.771	0.031	0.989	0.021
4034.0	0.866	-0.021	0.995	0.013
4176.2	0.932	-0.006	0.996	0.006

Table XX

LIQUID-VAPOR EQUILIBRIA, 125°C ISOTHERM; SYSTEM: BrF₃ - BrF₅

Data adjusted to 125°C

Comparison of Observed and Calculated Compositions

<u>Pressure, mm.</u>	<u>Obs. x</u>	<u>Obs. x-Calc. x</u>	<u>Obs. y</u>	<u>Obs. y-Calc. y</u>
994.2	0.019	0.000	0.268	0.000
1548.9	0.068	0.007	0.533	-0.015
1970.8	0.095	-0.001	0.643	-0.016
2417.8	0.131	-0.005	0.720	-0.011
2715.3	0.169	0.005	0.754	-0.015
2997.4	0.182	-0.008	0.774	-0.022
3942.8	-	-	0.866	0.005
4252.4	0.327	0.002	0.895	0.019
4495.2	0.358	0.003	0.888	0.001
5289	0.472	0.003	0.910	-0.006
5601	0.545	0.025	0.942	0.016
5629	0.547	0.021	0.942	0.015
5747	-	-	0.947	0.017
5996	0.583	-0.011	0.947	0.009
6192	-	-	0.947	0.003
6704	0.738	-0.020	0.967	0.009
6971	0.811	-0.014	0.970	0.004
7058	0.815	-0.033	0.986	0.017
7358	0.914	-0.008	0.992	0.010
7394	0.925	-0.005	0.992	0.008

Table XXI

LIQUID-VAPOR EQUILIBRIA, 150°C ISOTHERM, SYSTEM: BrF₃ - BrF₅

Data adjusted to 150°C

Comparison of Observed and Calculated Compositions

<u>Pressure, mm.</u>	<u>Obs. x</u>	<u>Obs. x-Calc. x</u>	<u>Obs. y</u>	<u>Obs. y-Calc. y</u>
2564	0.036	-0.008	0.385	-0.023
2603	0.036	-0.010	0.424	0.004
3250	0.077	0.001	0.554	0.004
4429	0.132	-0.003	0.689	0.000
5904	0.210	-0.008	0.784	-0.003
6038	0.231	0.003	0.810	0.016
6079	0.246	0.016	0.796	0.000
7309	0.336	0.022	-	-
7460	0.343	0.018	0.844	-0.006
9084	0.466	0.000	0.856	-0.038
9500	0.521	0.012	0.909	0.005
10228	0.592	-0.007	0.946	0.025
11312	0.756	-0.011	0.966	0.020
12522	0.971	0.003	1.000	0.012

Table XXII

LIQUID-VAPOR EQUILIBRIA, 1 ATM. ISOBAR; SYSTEM: BrF_3 - BrF_5

Data adjusted to 1 Atm.

Comparison of Observed and Calculated Compositions

Temperature, °C	Obs. x	Obs. x-Calc. x	Obs. y	Obs. y-Calc. y
43.6	0.895	-0.006	0.986	-0.010
45.6	0.810	0.010	1.000	0.009
45.9	0.805	0.020	0.968	-0.022
48.2	0.686	0.000	0.997	0.011
52.6	0.549	0.009	0.984	0.009
56.2	0.470	0.013	0.975	0.009
62.8	0.355	0.018	0.950	0.006
64.4	0.322	0.006	0.941	0.004
69.0	0.264	0.005	0.932	0.016
72.7	0.237	0.014	-	-
78.9	0.177	0.005	0.865	0.010
82.4	0.144	-0.003	-	-
85.1	0.144	0.012	0.794	-0.008
89.8	0.095	-0.012	0.743	-0.011
95.1	0.087	0.003	0.679	-0.010
96.1	0.078	-0.002	0.652	-0.022
103.5	0.075	0.022	0.565	0.004
110.4	0.037	0.003	0.442	0.018
114.4	0.023	0.000	0.320	-0.010
120.5	0.006	-0.004	0.169	0.003

FIGURE 14.

LIQUID-VAPOR EQUILIBRIA, 50 °C
ISOTHERM SYSTEM $\text{BrF}_5 - \text{BrF}_3$.

Data adjusted to 50 °C

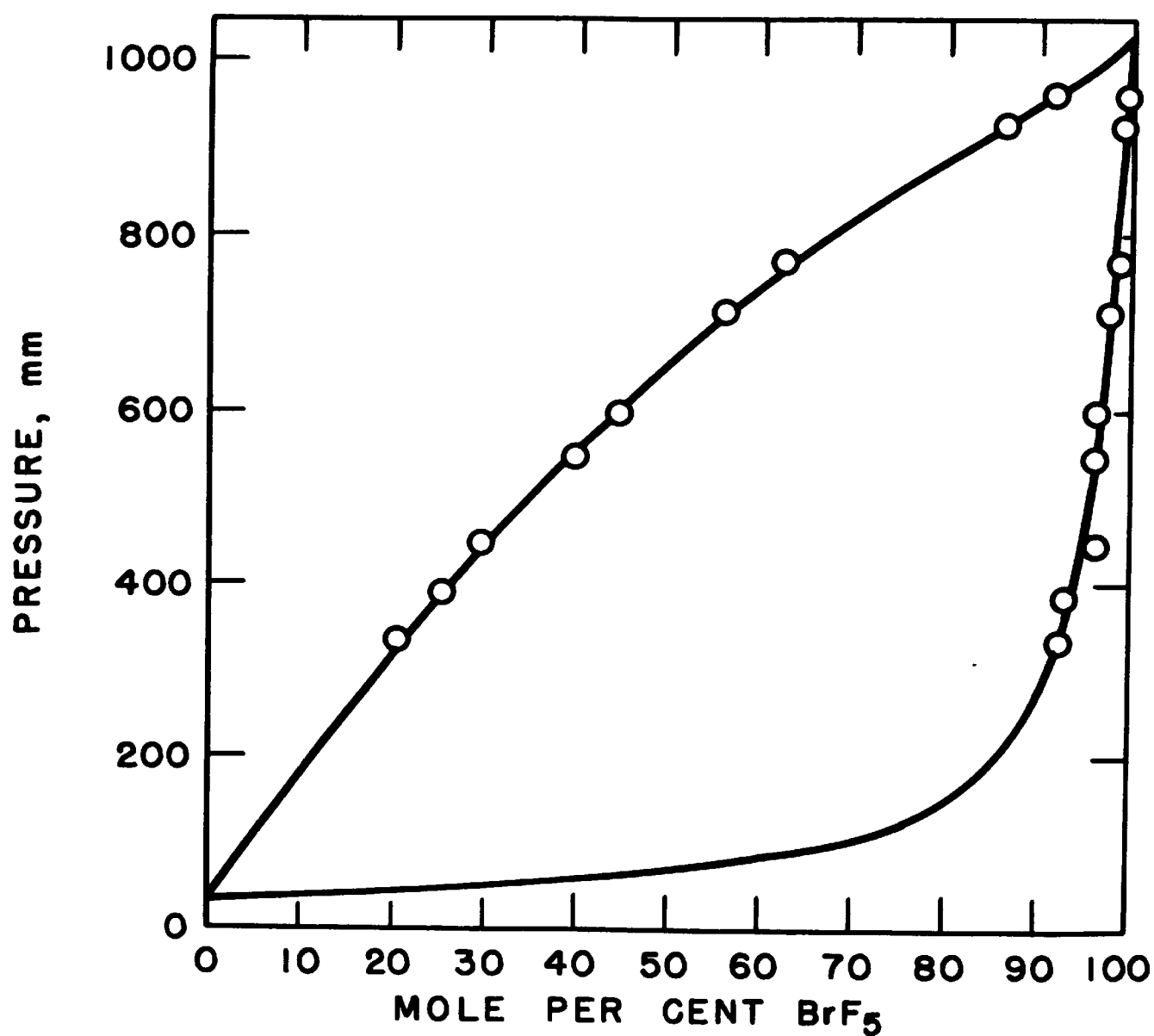


FIGURE 15.
LIQUID-VAPOR EQUILIBRIA, 75 °C
ISOTHERM SYSTEM BrF_5 - BrF_3 .
Data adjusted to 75 °C

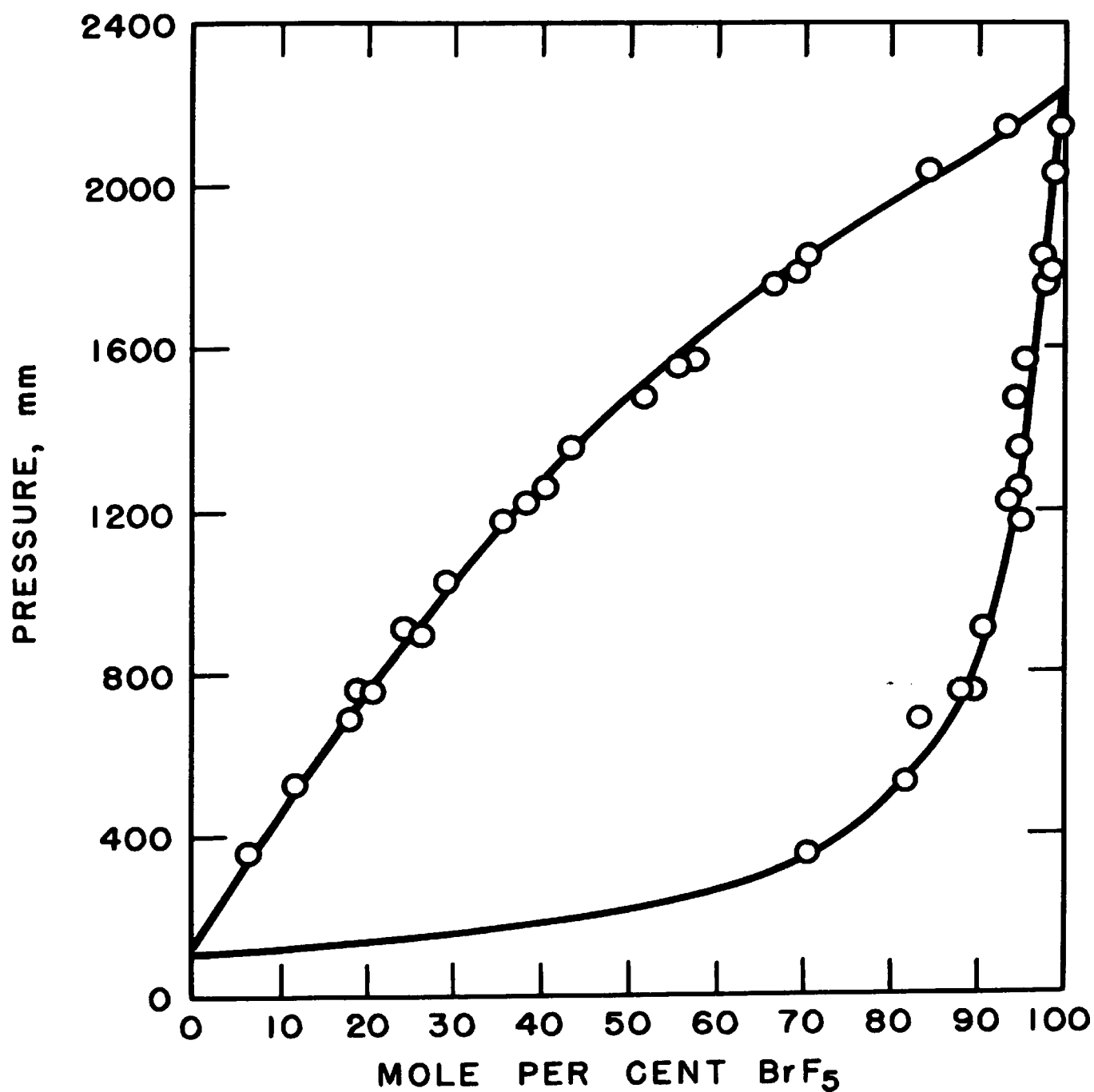


FIGURE 16.

LIQUID-VAPOR EQUILIBRIA, 100 °C
ISOTHERM SYSTEM BrF_5 - BrF_3 .

Data adjusted to 100 °C

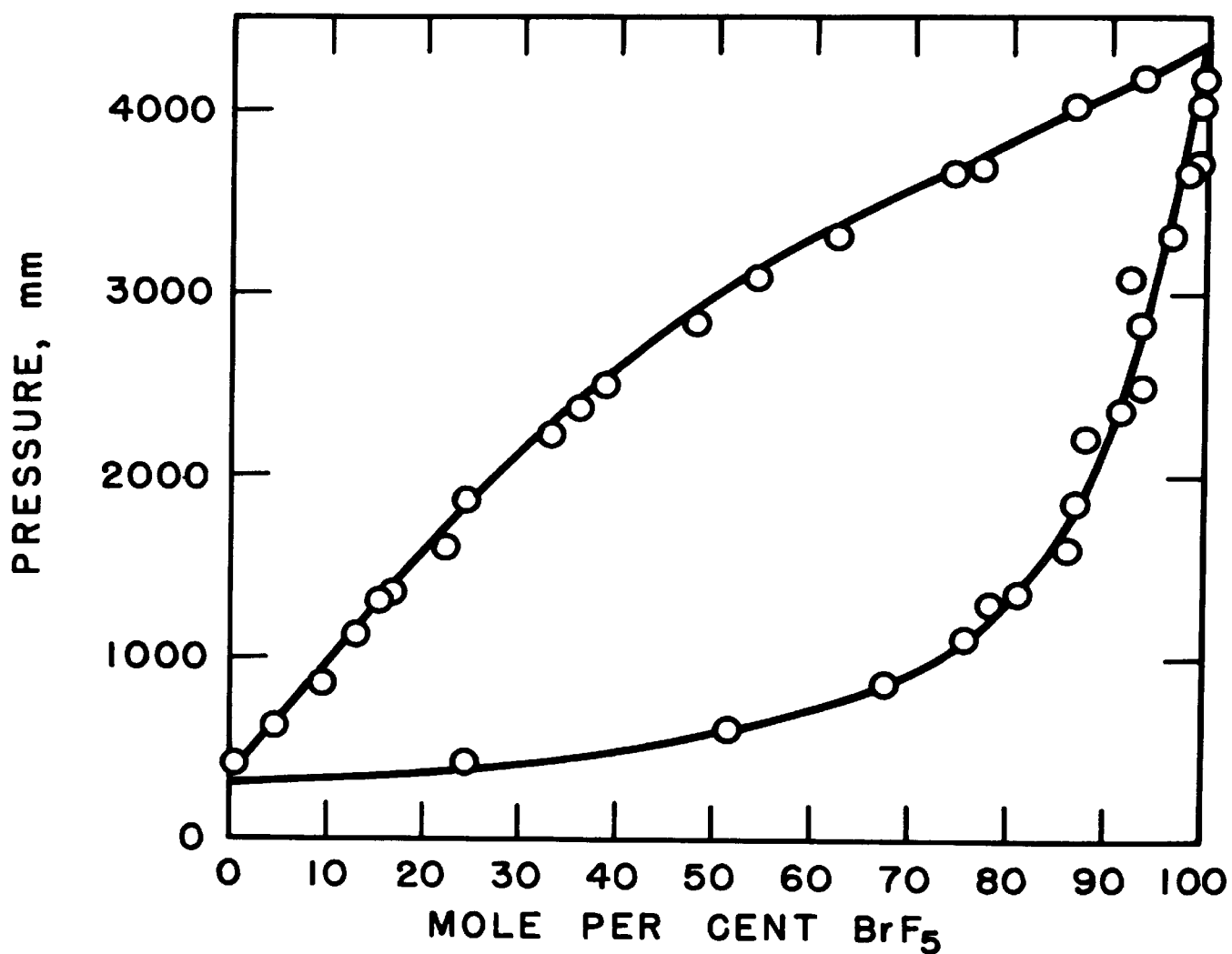


FIGURE 17.
LIQUID-VAPOR EQUILIBRIA, 125 °C
ISOTHERM SYSTEM BrF_5 - BrF_3 .
Data adjusted to 125 °C

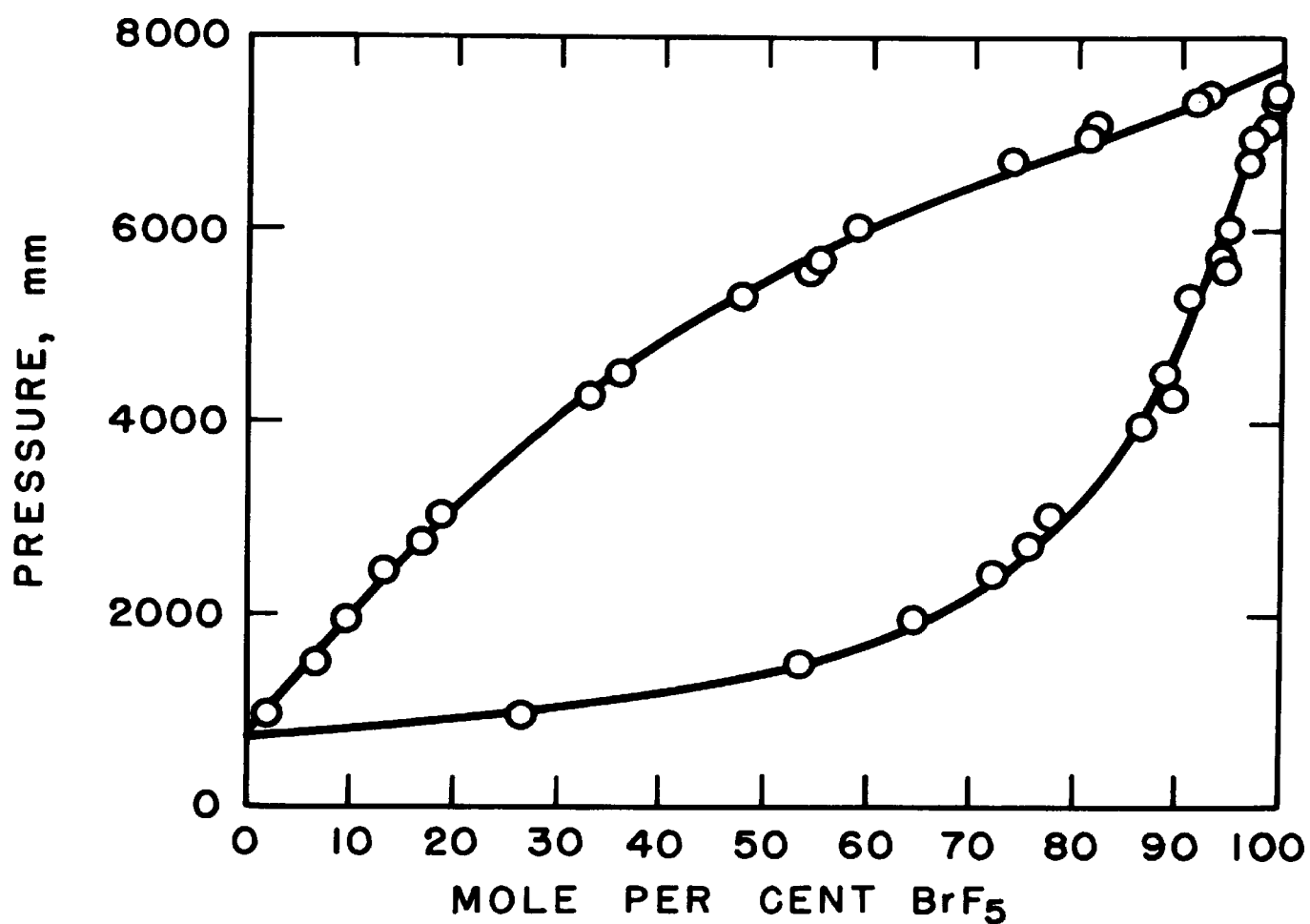


FIGURE 18.

LIQUID-VAPOR EQUILIBRIA, 150 °C
ISOTHERM SYSTEM $\text{BrF}_5 - \text{BrF}_3$.

Data adjusted to 150 °C

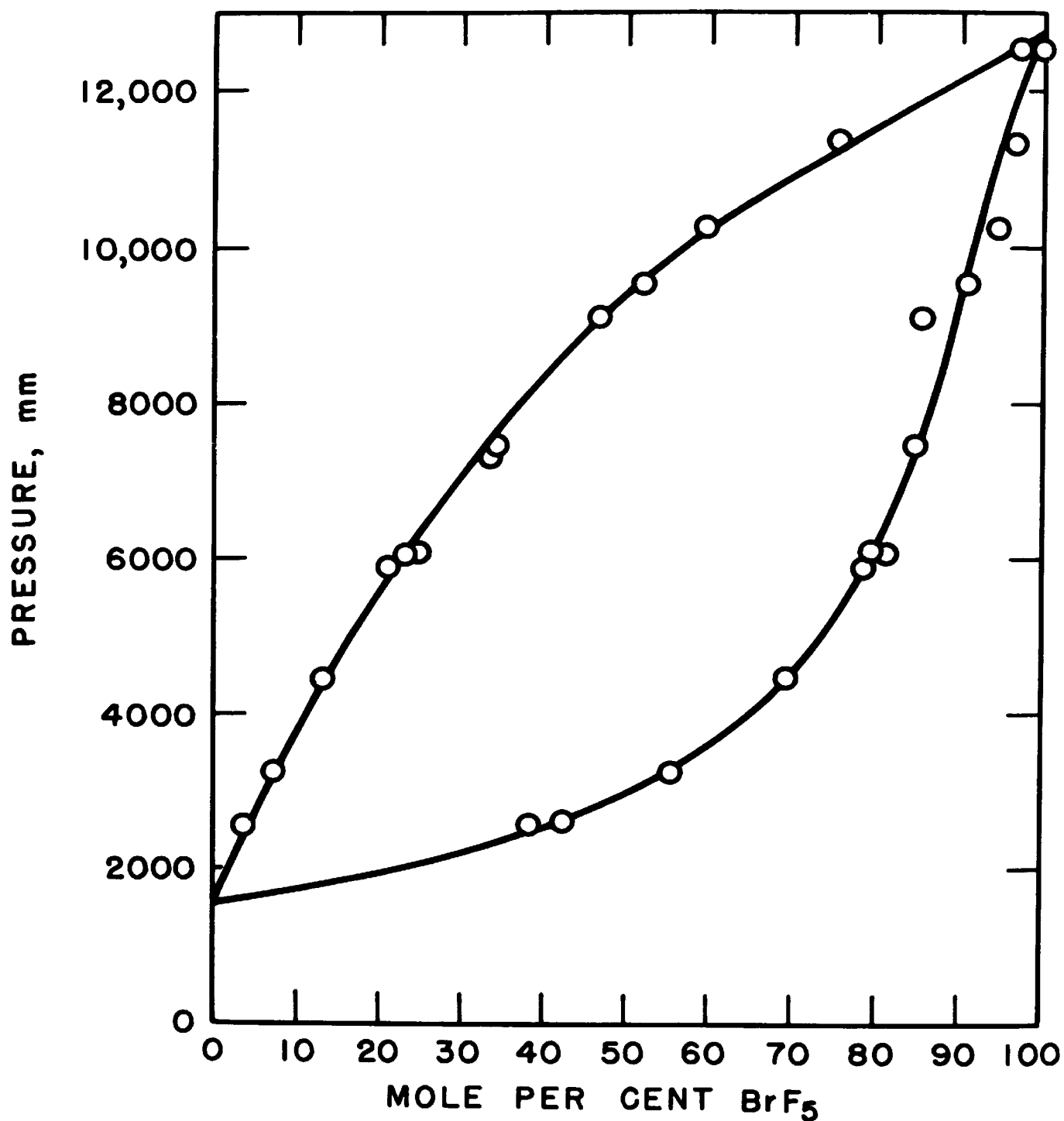
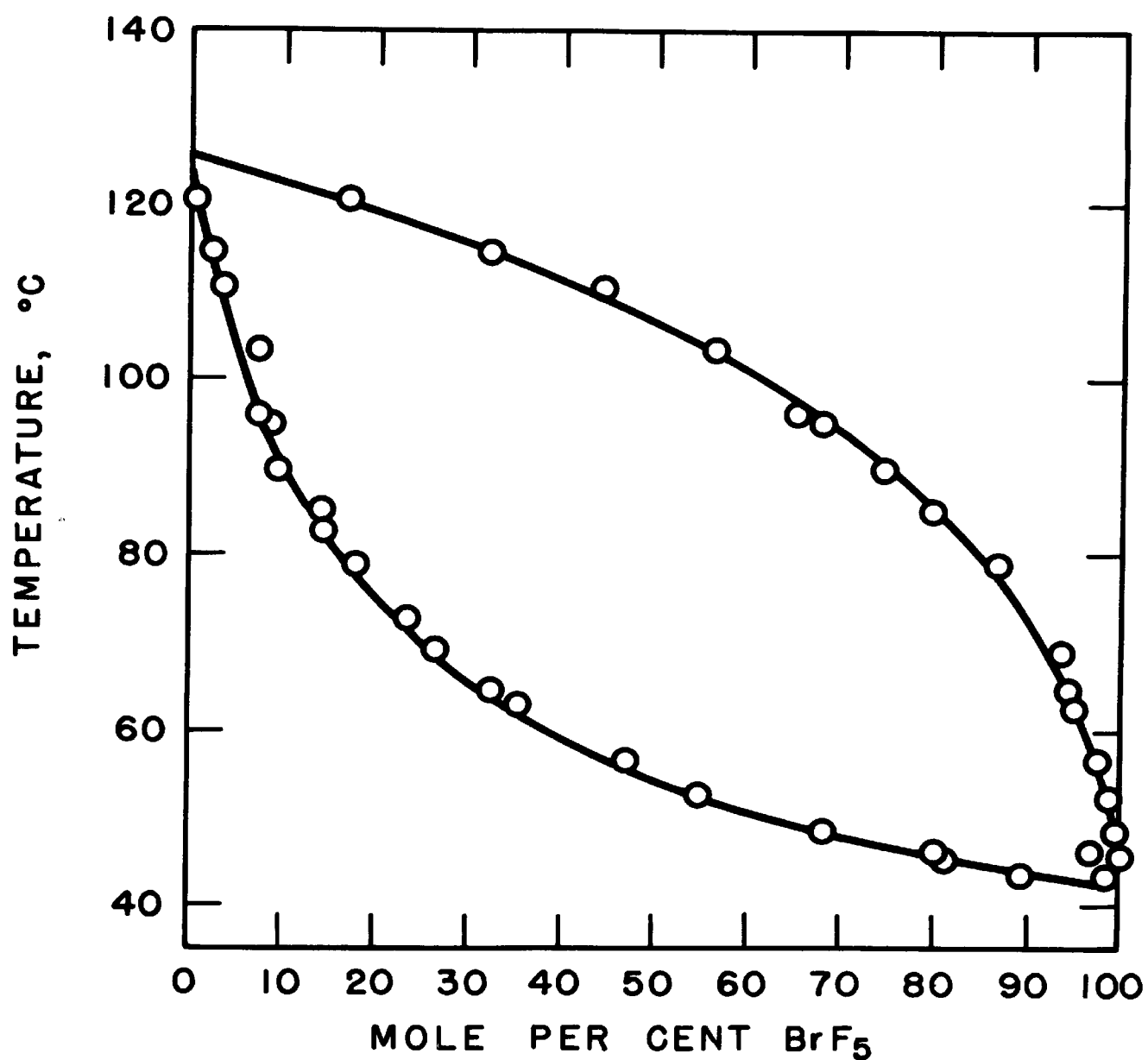


FIGURE 19.
LIQUID-VAPOR EQUILIBRIA, 1 Atm.
ISOBAR SYSTEM $\text{BrF}_5 - \text{BrF}_3$.
Data adjusted to 1 Atm.



IV. METHOD OF CALCULATION

This section will describe the method used to correlate the experimental data. The vapor pressure data for bromine pentafluoride was represented by a modified Antoine equation,

$$\log_{10} p_1 = A + Dt - B/(t + C),$$

and the data for bromine trifluoride was represented by an Antoine equation,

$$\log_{10} p_2 = A - B/(t + C).$$

The liquid-vapor equilibria data were fitted with a set of thermodynamically consistent (obeys Gibbs-Duhem relation) van Laar equations,

$$\log_{10} \gamma_1 = A/(1 + Ax_1/Bx_2)^2, \text{ and}$$

$$\log_{10} \gamma_2 = B/(1 + Bx_2/Ax_1)^2,$$

where A and B represent the logarithm of the activity coefficient in infinitely dilute solution for bromine pentafluoride and bromine trifluoride, respectively. A pair of constants, A and B, were found for each isotherm. These constants were then fitted as linear functions of temperature. This correlation assumed ideal behavior in the vapor phase and nonideal behavior in the liquid phase. This correlation was used in conjunction with the vapor pressure equations to calculate smoothed isotherms and isobars.

A. Vapor Pressure Equations

Fitting of Vapor Pressure Equations. The modified Antoine and Antoine equations were chosen to represent the vapor pressure data of bromine pentafluoride and bromine trifluoride. These equations will fit experimental vapor pressure data as well as any other empirical relationship, and in addition are superior to other equations for extrapolation beyond the range of the data. It was necessary to extrapolate the vapor pressure curve for bromine pentafluoride a few degrees above the range of the data, and the vapor pressure curve for bromine trifluoride was extrapolated approximately 40°C below the range of the experimental data.

The Antoine equations are not linear in the independent variable and cannot be made so by manipulation. This makes least squares a very tedious method of curve fitting to use. A method of differences, very similar to that given by Weissberger,⁽¹⁷⁾ was used. This method has the advantage that one constant at a time is determined and only significant figures need be retained. The method will be described in some detail below.

Since the Antoine equation is a special case of the modified Antoine equation, the modified Antoine equation is used for the illustration. One of the points was chosen as a base point, and from the general equation the base point is subtracted to give the first differences:

$$[(\log_{10}P) - (\log_{10}P)_1] / (t - t_1) = D + [B / (t_1 + C)(t + C)] = w_1' .$$

A base point among the first differences is selected and second differences are taken.

$$(w_1' - w_2') / (t_1 - t_2) = -B / (t_2 + C)(t_1 + C)(t + C) = w_2'' .$$

A second base point among the first differences is selected and the second differences are taken again.

$$(w_1' - w_3') / (t_1 - t_3) = -B / (t_3 + C)(t_1 + C)(t + C) = w_3'' .$$

Now, if the last equation is divided into the preceding equation, most of the terms will cancel out and leave,

$$w_2'' / w_3'' = (t_3 + C) / (t_2 + C) .$$

Rearranging, C is found as a function of the temperature of the last two base points and of the second differences:

$$C = (w_3'' t_3 - w_2'' t_2) / (w_2'' - w_3'') .$$

The number of values of C found in this way will be three less than the number of data points. The average of the values can be used for this constant and the distribution about the average value will determine how many places are significant. Three significant figures are usually found sufficient: for example, C = 206 for bromine pentafluoride.

Using this value for C, one of the previous equations can be solved for B,

$$B = -w_3'' (t_3 + C)(t_1 + C)(t + C) .$$

The number of values found in this manner for B will be two less than the number of data points. In the same manner as was used for C, the average of these values is used for B. The value of B was found to be 895 for bromine pentafluoride. This procedure is carried on until a value for D and then A are found, in each case carrying only as many figures as are significant.

The equation,

$$\log_{10}P = 6.4545 + 0.001101t - 895 / (t + 206) ,$$

where

p = pressure in mm. and

t = temperature, °C

was fitted to the vapor pressure data of bromine pentafluoride. The average deviation of the 36 data points was approximately 0.05 per cent in pressure. The equation,

$$\log_{10} p = 7.65757 - 1627.5/(t + 215) ,$$

where the symbols have the same meaning as above, was fitted to the vapor pressure data of bromine trifluoride. The average deviation of the 27 data points was approximately 0.06 to 0.07 per cent in pressure.

Slope of Vapor Pressure Curves. If we differentiate the vapor pressure equation for bromine pentafluoride with respect to temperature, we find that

$$(dp_1/dt)_v = p_1/0.4343 [0.001101 + 895/(t + 206)^2] ,$$

where

p_1 = vapor pressure of bromine pentafluoride in mm.,

t = temperature in °C, and

$(dp_1/dt)_v$ = rate of change of vapor pressure with temperature, mm./°C.

In exactly the same manner, the vapor pressure equation for bromine trifluoride is differentiated to give,

$$(dp_2/dt)_v = p_2/0.4343 (1627.5)/(t + 215)^2 ,$$

where the symbols have the same meaning as above.

The slopes of the vapor pressure equations are listed at 5°C intervals in Tables XXV and XXVI.

B. Saturated Liquid and Vapor Volumes

Saturated Liquid Volumes. The saturated liquid volume for bromine pentafluoride is calculated by substituting temperatures and pressures from the vapor pressure curve into the equation,

$$0.0088404/v = 0.1327 - (0.115 - 0.012p_1/47)[0.70711 - (1 - T/499)^{1/2}]$$

developed by G. W. Thomson, (18) where

v = saturated vapor volume, (liters)/(gram mole),

p_1 = pressure, atm.,

T = temperature, °K.

The constants 0.0088404 and 499 were chosen so that the equation will give the liquid volumes given by Stein, Vogel and Ludewig.⁽¹⁶⁾ These are 0.06866 liter/gram mole at 0°C, and 0.07109 liter/gram mole at 25°C.

The saturated liquid volume for bromine trifluoride is calculated by substituting temperatures into the equation,

$$0.15179/v = 2(1-T/643)^{-3} + 0.9(1-T/643) + 1$$

in the form given by Reilly and Rae,⁽¹⁹⁾ where the symbols have the same meaning as above. The constants 0.15179 and 643 were chosen so that the equation will give the liquid volumes reported by Stein, Vogel and Ludewig.⁽¹⁶⁾ These are 0.04885 liter/gram mole at 25°C and 0.05006 liter/gram mole at 50°C. The saturated liquid volumes for bromine pentafluoride and bromine trifluoride are listed at 5°C intervals in Tables XXVII and XXVIII.

Saturated Vapor Volumes. The saturated vapor volumes for bromine pentafluoride are found by substituting pressures and temperatures from the vapor pressure equation into the low pressure form of the Berthelot equation of state,

$$PV = RT [1 + (9/128)(T_c/T)(P/P_c)(1 - 6T_c^2/T^2)] ,$$

where P = pressure, atm.,

T = temperature, °K,

R = gas constant, 62,361 (mm) (liter)/(°K) ,

T_c = predicted critical temperature, 486°K,

P_c = predicted critical pressure, 47 atm., and

V = vapor volume in (liter)/(gram mole).

The saturated vapor volumes for bromine trifluoride are found in exactly the same manner. The predicted critical temperature for bromine trifluoride is 612°K and the predicted critical pressure is 69 atm. The method of predicting the critical constants is discussed in Appendix B. The saturated vapor volumes for bromine pentafluoride and bromine trifluoride are listed at 5°C intervals in Tables XXIX and XXX.

C. Enthalpy and Entropy of Vaporization

Heat of Vaporization. The enthalpies of vaporization of bromine pentafluoride and bromine trifluoride are calculated by means of the Clausius-Clapeyron equation,

$$H_v - H_l = J(dp/dt)_v T(V - v) ,$$

where,

- H_v = enthalpy of the saturated vapor, calories/gram mole,
- H_l = enthalpy of the saturated liquid, calories/gram mole,
- $(dp/dt)_v$ = slope of the vapor pressure curve, atm/°C,
- T = temperature, °K,
- V = volume of saturated vapor, liters/gram mole,
- v = volume of saturated liquid, liters/gram mole,
- J = energy equivalent, 24.218 calories/liter-atmosphere.

Entropy of Vaporization. The entropy of vaporization is calculated from the equation,

$$S_v - S_l = J(dp/dt)_v (V - v) = (H_v - H_l)/T ,$$

where,

- S_v = entropy of the saturated vapor, calories/gram mole(°K) ,
- S_l = entropy of the saturated liquid, calories/gram mole(°K) .

The quantities that are to be substituted into these equations have already been calculated. The enthalpies and entropies of vaporization for bromine pentafluoride and bromine trifluoride are listed at 5°C. intervals in Tables XXXI through XXXIV.

D. Liquid-Vapor Correlation

The liquid-vapor correlation was made for the purpose of smoothing the liquid-vapor equilibria data and calculating isotherms and isobars at even temperatures and pressures. It was assumed that the vapor phase behaves in ideal fashion. Although this assumption is not completely justified, the resulting correlation was used to calculate nearly the same information as given by the experimental data, and most of the error should cancel out. Very little would be gained in the accuracy of the calculated isotherms and isobars by assuming nonideal behavior of the vapor phase and such an assumption would add very greatly to the amount of labor involved.

van Laar Correlation. Activity coefficients have proven to be very useful in correlating liquid-vapor equilibria data. The activity coefficient is defined as the activity of a component in the solution divided by the mole fraction of the component. If the pure component at the same temperature as the solution is taken as the standard state, then the activity coefficient will equal unity for ideal solutions. For positive deviations from Raoult's law, the activity coefficient will be greater than unity, and for negative deviations the activity coefficients will be less than unity. If the vapors may be regarded as behaving ideally, the activity coefficients are given as,

$$\gamma_1 = P_{y1}/p_1x_1, \text{ and } \gamma_2 = P_{y2}/p_2x_2 .$$

The activity coefficient may be regarded as a deviation factor, by considering the numerator as the actual partial pressure of the component in the vapor divided by the amount of the component that would be in the vapor if the solution were ideal.

It has been shown by Carlson and Colburn⁽²⁰⁾ that for a binary system the following relation

$$x_1(d\log\gamma_1/dx_1)_{t,p} = x_2(d\log\gamma_2/dx_2) ,$$

exists between the logarithm of the activity coefficients and the mole fractions of the components. This relation can be utilized directly with the slopes of the logarithm of the activity function plotted against mole fraction. However, it is found more convenient to use a particular solution of this differential equation.

One of the most useful of the possible solutions is that of van Laar.⁽²¹⁾ In the form as rearranged by Carlson and Colburn,

$$\log_{10}\gamma_1 = A/(1 + Ax_1/Bx_2)^2 ,$$

and

$$\log_{10}\gamma_2 = B/(1 + Bx_2/Ax_1)^2 .$$

In this symmetrical form, constants A and B have the property of being equal to the terminal values of $\log \gamma$ of the two curves. It is also seen that as a component approaches the pure state, its activity coefficient approaches unity, and Raoult's law holds for a component whose concentration approaches 100 mole per cent.

In the method of correlation to be used values of the constants A and B will be found for each of the 5 isotherms. Each constant can then be fitted as a function of temperature. The pair of van Laar equations together with the constants fitted as functions of temperature will constitute a suitable correlation of the liquid-vapor equilibria data. This correlation can be used,

with the vapor pressure equations of the pure components, to predict the 1 atm isobaric diagram. It will be noticed that the differential equation relating the logarithm of the activity coefficients with the mole fractions is strictly true only at constant temperature and pressure. In the case of either an isobaric or isothermal diagram, one of the restrictions is violated. It is found in practice that the activity coefficients are stronger functions of temperature than pressure. Therefore it is preferable to use the integrated forms of this differential equation with isothermal data.

The system bromine pentafluoride-bromine trifluoride offers some particular difficulties in determining the values of the constants A and B. This is due to the high relative volatility and lack of a high degree of precision. The relative volatility varies from 10 to 30 over the range of conditions for which data are available. The relatively nonvolatile bromine trifluoride contributes so little to the total pressure over the solution that the total pressure in turn does not offer much information concerning the activity coefficients of bromine trifluoride. The result is that the scatter of the logarithm of the activity coefficients of bromine trifluoride is so great as to render them useless for correlation purposes. This is not true of activity coefficients for bromine pentafluoride.

If a method developed by Carlson and Colburn⁽²⁰⁾ for correlating total pressure data is used, the high relative volatility can be used to advantage. By this method from an isothermal measurement of total pressure versus liquid composition or from an isopiestic boiling point-composition curve, the van Laar equations can be used to estimate equilibrium liquid and vapor compositions. When used with isothermal measurements, the assumption is made that the activity coefficients do not vary with pressure and when used with isopiestic measurements, the assumption is made that the activity coefficients do not vary with temperature. As explained above, isothermal data are preferred.

From the definition of the activity coefficients, we may write,

$$\gamma_1 = (P - \gamma_2 p_2 x_2) / p_1 x_1 \quad ,$$

and

$$\gamma_2 = (P - \gamma_1 p_1 x_1) / p_2 x_2 \quad .$$

As x_2 approaches 1.0, γ_2 approaches 1.0 so that we may calculate an approximate activity coefficient for component 1 by assuming $\gamma_2 = 1$. By plotting the logarithm of the apparent activity coefficients versus concentration, we may extrapolate to find the terminal values of the activity coefficients, whose logarithms are the constants of the van Laar equations. These constants can be used with the equation

$$P = \gamma_1 p_1 x_1 + \gamma_2 p_2 x_2$$

to calculate the total pressure. If the calculated total pressure agrees well with the measured total pressure, accurate values of the constants have been found. If the calculated total pressures do not agree with the measured total pressures, the entire procedure can be carried out once more. This time, however, instead of using $\gamma_2 = 1$, we would use values of γ_2 calculated from the van Laar equations with the approximate constants already found.

It was mentioned above that the high relative volatility of the bromine pentafluoride-bromine trifluoride proved useful. This arises since in the equation

$$\gamma_1 = (P - \gamma_2 p_2 x_2) / p_1 x_1 ,$$

the vapor pressure of bromine trifluoride, p_2 , is so small that the term $\gamma_2 p_2 x_2$ is much smaller than P and almost no error is involved in assuming that $\gamma_2 = 1$. This method of apparent activity coefficients works very well for determining the constant A , the value of $\log \gamma_1$ at infinite dilution of component 1. It will not work at all, however, for component 2, that is, bromine trifluoride, and some other method must be found.

The constant B , the terminal value of $\log \gamma_2$ in infinitely dilute solution, was found by trial and error. A value of B was chosen such that when used with the value of A already found, the van Laar equations gave the best possible fit of the data. The comparison was made by using the van Laar equations and the vapor pressure equations of the pure compounds to calculate the isothermal compositions. Since both vapor and liquid compositions are available, the vapor and liquid compositions are calculated at the pressure of the data points. When only liquid composition and pressures are available, it must be assumed that the data are thermodynamically consistent. That is, there is no specific chemical interaction, dimerization, etc., in the vapor phase.

The constants of the van Laar equations, which were calculated in the above manner, are listed in Tables XXIII and XXIV and fitted as functions of temperature. The data are plotted in Figure 20.

Table XXIII

CONSTANT A OF VAN LAAR EQUATION

<u>t° C.</u>	<u>Obs. A</u>	<u>Obs. A-Calcd. A</u>
50	0.188	0.005
75	0.222	0.012
100	0.192	-0.045
125	0.274	0.010
150	0.313	0.023

FIGURE 20.

LIQUID-VAPOR EQUILIBRIA CORRELATION (Ideal Gases).

The van Laar equations:

$\log_{10} \gamma_1 = A / (1 + Ax_1/Bx_2)^2$ and $\log_{10} \gamma_2 = B / (1 + Bx_2/Ax_1)^2$
are fitted to the data by finding the constants A and B as
functions of temperature.

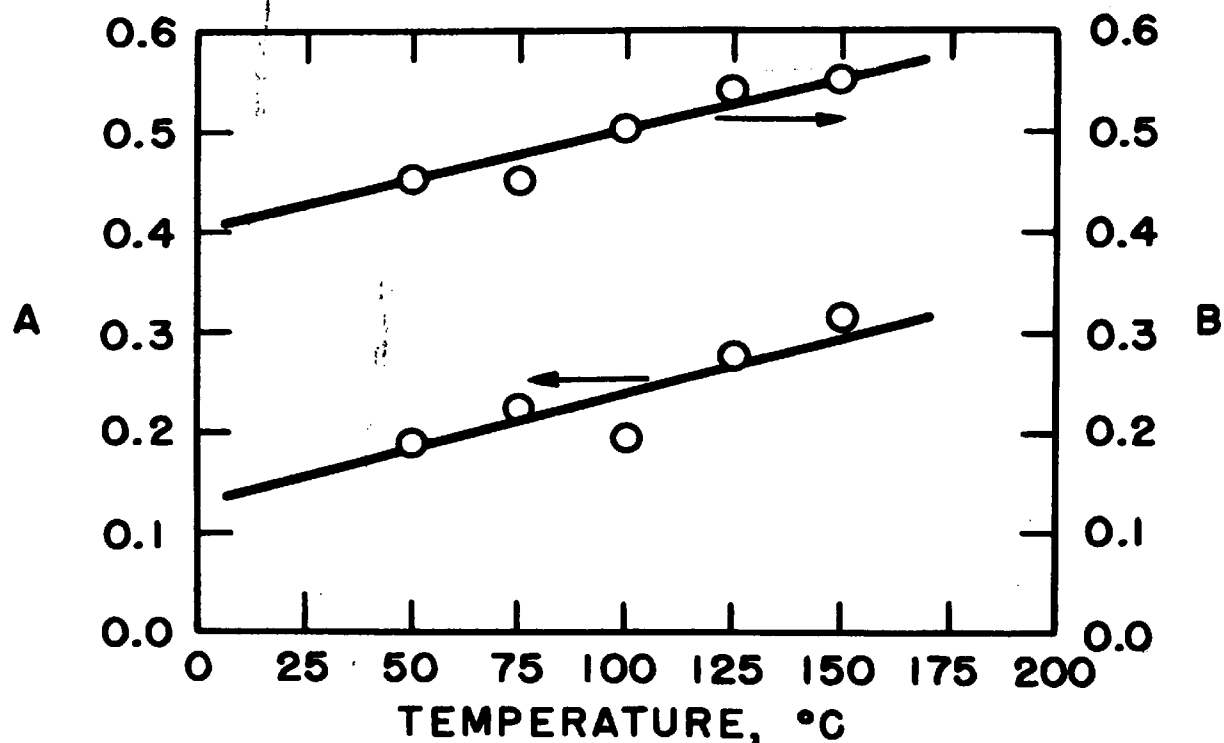
$$A = \lim_{x_1 \rightarrow 0} (\log_{10} \gamma_1) = 0.1290 + 0.001076t, \text{ and}$$

$$x_1 \rightarrow 0$$

$$B = \lim_{x_2 \rightarrow 0} (\log_{10} \gamma_2) = 0.4000 + 0.001000t, \text{ and}$$

$$x_2 \rightarrow 0$$

where t = temperature, °C



The observed values of A above were fitted with the equation,

$$A = 0.1290 + 0.001076 t ,$$

where t is in °C.

Table XXIV

CONSTANT B OF VAN LAAR EQUATION

<u>t°C.</u>	<u>Obs. B</u>	<u>Obs. B-Calc. B</u>
50	0.450	0.000
75	0.450	-0.025
100	0.500	0.000
125	0.540	0.015
150	0.550	0.000

The observed values of B above were fitted with the equation,

$$B = 0.4000 + 0.001000 t ,$$

where t is in °C.

If the functions of A and B with temperature are used in conjunction with the van Laar equations,

$$\log_{10} \gamma_1 = A / (1 + Ax_1/Bx_2)^2 ,$$

and

$$\log_{10} \gamma_2 = B / (1 + Bx_2/Ax_1)^2 ,$$

we have a correlation of activity coefficient with both temperature and composition. Smoothed isotherms and isobars are calculated from this correlation and the data are listed in Tables XXXV through XLVII.

Adjustment of Compositions. The calculated isotherms and isobar given in Tables XVII through XXII and shown in Figures 14 through 19 were compared with the experimental liquid-vapor equilibria data. The experimental data were adjusted to the even temperature of the isotherms and to one atmosphere.

The adjustment of the isobaric data will be discussed first, since the equations are more simple. For non-ideal solutions, Raoult's law may be given in the form

$$P = p_1 x_1 \gamma_1 + p_2 x_2 \gamma_2 .$$

We may write

$$dx = (dx/dp)_t dp ,$$

and

$$dy = (dy/dp)_t dp ,$$

where the subscript has been omitted. We shall use x and y to represent the mole fraction in the liquid and vapor, respectively, of bromine pentafluoride. It will be assumed that γ_1 , γ_2 , $(dx/dp)_t$, and $(dy/dp)_t$ do not change significantly in the small range of pressure considered and may be treated as constants. The derivatives may be evaluated by differentiating the generalized form of Raoult's law given above. The resultant equations are

$$x_f - x_i = (p_f - p_i)/(p_1 \gamma_1 - p_2 \gamma_2) ,$$

and

$$y_f - y_i = (p_f - p_i)(p_1 \gamma_1)/(p_1 \gamma_1 - p_2 \gamma_2) ,$$

where the subscripts f and i refer to final and initial values.

The adjustment of the isothermal data were made in exactly the same manner, the equations being somewhat more complicated. Once again we may write,

$$dx = (dx/dt)_P dt$$

and

$$dy = (dy/dt)_P dt .$$

In the same manner as before, the derivatives are evaluated by differentiating the generalized form of Raoult's law this time with respect to temperature. It will be assumed that γ_1 , γ_2 , $(dx/dt)_P$, and $(dy/dt)_P$ are independent of temperature for the small range of temperature involved and may be regarded as constants during the integration. From the differentiation, we have

$$(dx/dt)_P = \frac{(dp_2/dt)[\gamma_2(P - \gamma_1 p_1)] - (dp_1/dt)[\gamma_1(P - \gamma_2 p_2)]}{(\gamma_1 p_1 - \gamma_2 p_2)^2} ,$$

and

$$(dy/dt)_P = (dy/dx)_P (dx/dt)_P = (\gamma_1 p_1 / P) (dx/dt)_P .$$

Integrating, under the assumption mentioned above, we have

$$x_f - x_i = (dx/dt)_P (t_f - t_i) ,$$

and

$$y_f - y_i = (dy/dt)_P (t_f - t_i) = (\gamma_1 p_1 / P)(x_f - x_i) .$$

For use with a particular isotherm, the differential of x with respect to temperature is evaluated at several compositions, and the value plotted. The value of the differential is read off the curve at the composition of the point being adjusted. The differential of y with respect to t is easily calculated from the differential of x with respect to t , or a curve can be drawn in this case also.

V. CALCULATED RESULTS

The calculated results of this investigation have been collected in this section for ease of reference. The tables of vapor pressure, temperature derivative of vapor pressure, entropy and enthalpy of vaporization, and the isothermal and isobaric vapor-liquid equilibria were all calculated from correlations of experimental data. The saturated vapor volumes were calculated from predicted critical constants; liquid volumes were extrapolated from the low temperature experimental liquid densities of Stein, Vogel, and Ludewig.⁽¹⁶⁾

Table XXV

RATE OF CHANGE OF VAPOR PRESSURE WITH TEMPERATURE
BROMINE PENTAFLUORIDE

The rate of change of vapor pressure with temperature for bromine pentafluoride was found by analytically differentiating the vapor pressure equation. The slope of the vapor pressure curve is calculated from the equation

$$(dP/dt)_v = (P/0.4343) [0.001101 + 895/(t + 206)^2]$$

where P = pressure, mm,
 t = temperature °C.

Temperature °C	$dP/dt(\text{mm}/^\circ\text{C})$	$dP/dt(\text{Atm}/^\circ\text{C})$
20	14.081	0.018528
25	16.672	0.021937
30	19.595	0.025783
35	22.873	0.030096
40	26.526	0.034903
45	30.579	0.040236
50	35.051	0.046120
55	39.961	0.052580
60	45.335	0.059651
65	51.184	0.067347
70	57.535	0.075704
75	64.404	0.084742
80	71.806	0.094482
85	79.757	0.10494
90	88.278	0.11616
95	97.381	0.12813
100	107.08	0.14089
105	117.39	0.15446
110	128.33	0.16886
115	139.90	0.18408
120	152.12	0.20016
125	165.00	0.21711
130	178.56	0.23495
135	192.79	0.25367
140	207.72	0.27332
145	223.35	0.29388
150	239.70	0.31539
155	256.77	0.33786

Table XXVI

RATE OF CHANGE OF VAPOR PRESSURE WITH TEMPERATURE
BROMINE TRIFLUORIDE

The rate of change of vapor pressure with temperature for bromine trifluoride was found by analytically differentiating the vapor pressure equation for bromine trifluoride. The slope of the vapor pressure curve is calculated from the equation

$$(dP/dt)_v = P(1627.5)/0.4343(t + 215)^2$$

where P = pressure, mm,
 t = temperature °C.

<u>Temperature °C</u>	<u>dP/dt(mm/°C)</u>	<u>dP/dt(Atm/°C)</u>
20	0.36613	0.00048175
25	0.48937	0.00064391
30	0.64586	0.00084982
35	0.84225	0.0011082
40	1.0861	0.0014291
45	1.3859	0.0018236
50	1.7511	0.0023041
55	2.1918	0.0028839
60	2.7193	0.0035780
65	3.3457	0.0044022
70	4.0841	0.0053738
75	4.9662	0.0065345
80	5.9529	0.0078328
85	7.1131	0.0093593
90	8.4457	0.011113
95	9.9676	0.013115
100	11.695	0.015388
105	13.648	0.017958
110	15.843	0.020846
115	18.300	0.024079
120	21.038	0.027682
125	24.076	0.031679
130	27.433	0.036096
135	31.130	0.040961
140	35.183	0.046293
145	39.614	0.052124
150	44.443	0.058478
155	49.689	0.065380
160	55.365	0.072849
165	61.496	0.080916
170	68.095	0.089599
175	75.181	0.098922
180	82.767	0.10890

Table XXVII

PREDICTED SATURATED LIQUID VOLUME FOR
BROMINE PENTAFLUORIDE

The saturated liquid volumes for bromine pentafluoride were calculated by substituting temperatures and pressures from the vapor pressure curve into the equation

$$0.0088404/v = 0.1327 - (0.115 - 0.012P/47) [0.70711 - (1 - T/499)^{1/2}]$$

developed by G. W. Thomson,⁽¹⁸⁾ where

v = saturated liquid volume, liters/gm mol,
 P = pressure, atm
 T = temperature, °K.

The constants 0.0088404 and 499 were chosen so that the equation will give the liquid volumes given by Stein, Vogel and Ludewig,⁽¹⁶⁾

at 0°C, $v = 0.06866$ liter/gm mol, and
 25°C, $v = 0.07109$ liter/gm mol.

Temperature, °C	Sat'd Liquid Volume (liters/gm mol)	Temperature, °C	Sat'd Liquid Volume (liters/gm mol)
20	0.07058	95	0.08002
25	0.07109	100	0.08082
30	0.07162	105	0.08165
35	0.07216	110	0.08251
40	0.07271	115	0.08340
45	0.07328	120	0.08434
50	0.07387	125	0.08530
55	0.07447	130	0.08631
60	0.07509	135	0.08736
65	0.07573	140	0.08846
70	0.07639	145	0.08961
75	0.07707	150	0.09081
80	0.07777	155	0.09213
85	0.07850		
90	0.07924		

Table XXVIII

PREDICTED SATURATED LIQUID VOLUME FOR
BROMINE TRIFLUORIDE

The saturated liquid volumes for bromine trifluoride were calculated at 5°C intervals by substituting the corresponding temperatures into the equation

$$0.15179/v = 2(1 - T/643)^{-3} + 0.9(1 - T/643) + 1$$

in the form given by Reilly and Rae,⁽¹⁹⁾ where

v = saturated vapor volume, liters/gm mol,
 T = temperature, °K.

The constants 0.15179 and 643 were chosen so that the equation will give the liquid volumes reported by Stein, Vogel and Ludewig,⁽¹⁶⁾

at 25°C, $v = 0.04885$ liter/gm mol, and
50°C, $v = 0.05006$ liter/gm mol.

Temperature, °C	Sat'd Liquid Volume (liter/gm mol)	Temperature, °C	Sat'd Liquid Volume (liter/gm mol)
20	0.04862	110	0.05341
25	0.04885	115	0.05372
30	0.04908	120	0.05404
35	0.04932	125	0.05436
40	0.04956	130	0.05469
45	0.04981	135	0.05503
50	0.05006	140	0.05538
55	0.05031	145	0.05573
60	0.05057	150	0.05609
65	0.05083	155	0.05646
70	0.05110	160	0.05684
75	0.05137	165	0.05722
80	0.05165	170	0.05762
85	0.05193	175	0.05802
90	0.05221	180	0.05844
95	0.05250		
100	0.05280		
105	0.05310		

Table XXIX

PREDICTED SATURATED VAPOR VOLUME FOR
BROMINE PENTAFLUORIDE

The saturated vapor volumes for bromine pentafluoride were found by substituting pressures and temperatures from the vapor pressure equation into the low-pressure form of the Berthelot equation of state:

$$P V = R T [1 + (9/128) (T_c/T) (P/P_c) (1 - 6T_c^2/T^2)]$$

where P = pressure, atm

T = temperature, °K

R = 62.361 (mm)(liters)/(°K),

T_c = predicted critical temperature, 486°K,

P_c = predicted critical pressure, 47 atm.

Temperature, °C	Sat'd Vapor Volume (liters/gm mol)	Temperature, °C	Sat'd Vapor Volume (liters/gm mol)
20	54.759	95	5.397
25	45.010	100	4.787
30	37.288	105	4.258
35	31.112	110	3.799
40	26.136	115	3.398
45	22.094	120	3.047
50	18.789	125	2.739
55	16.067	130	2.467
60	13.808	135	2.227
65	11.927	140	2.014
70	10.348	145	1.825
75	9.016	150	1.657
80	7.887	155	1.507
85	6.926		
90	6.104		

Table XXX

PREDICTED SATURATED VAPOR VOLUME FOR
BROMINE TRIFLUORIDE

The saturated vapor volumes for bromine trifluoride were found by substituting pressures and temperatures from the vapor pressure equation into the low-pressure form of the Berthelot equation of state:

$$P V = R T [1 + (9/128) (T_c/T) (P/P_c) (1 - 6T_c^2/T^2)]$$

where P = pressure, atm.

T = temperature, °K,

R = 62.361 (mm)(liters)/(°K),

T_c = predicted critical temperature, 612°K,

P_c = predicted critical pressure, 69 atm.

Temperature, °C	Sat'd Vapor Volume (liters/gm mol)	Temperature, °C	Sat'd Vapor Volume (liters/gm mol)
20	3387.2	110	52.779
25	2470.9	115	44.808
30	1826.4	120	38.225
35	1367.0	125	32.760
40	1035.21	130	28.200
45	792.57	135	24.377
50	613.15	140	21.155
55	478.97	145	18.429
60	377.64	150	16.112
65	300.34	155	14.134
70	240.83	160	12.441
75	193.93	165	10.984
80	158.46	170	9.727
85	129.91	175	8.638
90	107.21	180	7.692
95	89.029		
100	74.377		
105	62.487		

Table XXXI

ENTHALPY OF VAPORIZATION OF BROMINE PENTAFLUORIDE

The enthalpy of vaporization of bromine pentafluoride was calculated at 5° C intervals by means of the Clausius-Clapeyron equation,

$$(H_v - H_l) = J(dp_l/dt) T(V - v) \quad ,$$

where $(H_v - H_l)$ = the enthalpy of the saturated vapor minus the enthalpy of the saturated liquid in (calories)/(gram mole),

$(V - v)$ = the saturated vapor volume minus the saturated liquid volume in (liters)/(gram mole),

(dp_l/dt) = the temperature derivative of the vapor pressure curve in (atm)/(°C),

T = the temperature in °K, and

J = the energy equivalent, 24.218 (calories)/(liter-atmosphere).

<u>Temperature, °C</u>	<u>$(H_v - H_l)$</u>	<u>Temperature, °C</u>	<u>$(H_v - H_l)$</u>
20	7194	95	6074
25	7119	100	5993
30	7045	105	5909
35	6972	110	5824
40	6900	115	5736
45	6828	120	5647
50	6756	125	5555
55	6684	130	5462
60	6610	135	5365
65	6537	140	5267
70	6463	145	5166
75	6388	150	5062
80	6311		
85	6234		
90	6156		

Table XXXII

ENTHALPY OF VAPORIZATION OF BROMINE TRIFLUORIDE

The enthalpy of vaporization of bromine trifluoride was calculated at 5°C intervals by means of the Clausius-Clapeyron equation,

$$(H_v - H_l) = J(dp_2/dt) T(V - v) \quad ,$$

where $(H_v - H_l)$ = the enthalpy of the saturated vapor minus the enthalpy of the saturated liquid in (calories)/(gram mole),

$(V - v)$ = the saturated vapor volume minus the saturated liquid volume in (liters)/(gram mole),

(dp_2/dt) = the temperature derivative of the vapor pressure curve in (atmospheres)/(°C),

T = the temperature in (°K), and

J = the energy equivalent, 24.218 (calories)/(liter-atmosphere)

<u>Temperature, °C</u>	<u>$(H_v - H_l)$</u>	<u>Temperature, °C</u>	<u>$(H_v - H_l)$</u>
20	11586	110	10200
25	11489	115	10131
30	11396	120	10062
35	11306	125	9992
40	11220	130	9920
45	11137	135	9849
50	11057	140	9774
55	10978	145	9699
60	10901	150	9623
65	10827	155	9545
70	10754	160	9465
75	10683	165	9383
80	10613	170	9299
85	10543	175	9213
90	10474	180	9124
95	10405		
100	10337		
105	10269		

Table XXXIII

ENTROPY OF VAPORIZATION OF BROMINE PENTAFLUORIDE

The entropy of vaporization of bromine pentafluoride was calculated at 5°C intervals from the enthalpy of vaporization,

$$(S_v - S_l) = (H_v - H_l)/T \quad ,$$

where $(H_v - H_l)$ = enthalpy of the saturated vapor and liquid, respectively, of bromine pentafluoride in (calories)/(gram mole),

$(S_v - S_l)$ = entropy of the saturated vapor and liquid, respectively, of bromine pentafluoride in (calories)/(gram mole)(°K), and

T = temperature, °K.

Temperature, °C	$(S_v - S_l)$ (cal)/(gm mol)(°K)	Temperature, °C	$(S_v - S_l)$ (cal)/(gm mol)(°K)
20	24.54	95	16.50
25	23.88	100	16.06
30	23.04	105	15.63
35	22.63	110	15.20
40	22.03	115	14.78
45	21.46	120	14.36
50	20.91	125	13.95
55	20.37	130	13.55
60	19.84	135	13.15
65	19.33	140	12.75
70	18.83	145	12.35
75	18.35	150	11.96
80	17.87	155	11.57
85	17.41		
90	16.95		

Table XXXIV

ENTROPY OF VAPORIZATION OF BROMINE TRIFLUORIDE

The entropy of vaporization of bromine trifluoride was calculated at 5°C intervals from the enthalpy of vaporization,

$$(S_v - S_l) = (H_v - H_l)/T \quad ,$$

where $(S_v - S_l)$ = the entropy of the saturated vapor minus the entropy of the saturated liquid in (calories)/(gram mole)(°K),

$(H_v - H_l)$ = the enthalpy of the saturated vapor minus the enthalpy of the saturated liquid in (calories)/(gram mole), and

T = temperature, °K.

<u>Temperature, °C</u>	<u>$(S_v - S_l)$</u>	<u>Temperature, °C</u>	<u>$(S_v - S_l)$</u>
20	39.52	110	26.62
25	38.53	115	26.10
30	37.59	120	25.59
35	36.69	125	25.09
40	35.83	130	24.61
45	35.00	135	24.13
50	34.21	140	23.66
55	33.45	145	23.19
60	32.72	150	22.74
65	32.02	155	22.29
70	31.34	160	21.85
75	30.68	165	21.41
80	30.05	170	20.98
85	29.44	175	20.56
90	28.84	180	20.14
95	28.26		
100	27.70		
105	27.16		

Table XXXV

LIQUID-VAPOR EQUILIBRIA, 25° C ISOTHERM; SYSTEM: BrF₅ - BrF₃

Compositions calculated from correlation assuming ideal gases.

Mole Fraction BrF ₅ in Liquid	Mole Fraction BrF ₅ in Vapor	Pressure, mm
0.000	0.000	7.522
0.001	0.072	8.094
0.002	0.134	8.666
0.003	0.188	9.237
0.005	0.279	10.381
0.007	0.352	11.522
0.010	0.437	13.232
0.015	0.539	16.075
0.020	0.610	18.911
0.025	0.663	21.74
0.030	0.703	24.56
0.040	0.761	30.18
0.050	0.800	35.76
0.070	0.851	46.84
0.100	0.893	63.21
0.150	0.929	89.82
0.200	0.948	115.56
0.250	0.959	140.38
0.300	0.967	164.25
0.350	0.973	187.1
0.400	0.978	209.0
0.450	0.981	229.8
0.500	0.984	249.5
0.550	0.986	268.1
0.600	0.988	285.7
0.650	0.990	302.1
0.700	0.991	317.5
0.750	0.993	332.0
0.800	0.994	345.9
0.850	0.995	359.4
0.900	0.996	373.1
0.950	0.998	387.8
1.000	1.000	405.1

Table XXXVI

LIQUID-VAPOR EQUILIBRIA, 50°C ISOTHERM; SYSTEM: BrF₅ - BrF₃

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF₅ in Liquid</u>	<u>Mole Fraction BrF₅ in Vapor</u>	<u>Pressure, mm</u>
0.000	0.000	32.81
0.001	0.046	34.35
0.002	0.088	35.89
0.003	0.126	37.42
0.005	0.194	40.49
0.007	0.252	43.56
0.010	0.325	48.14
0.015	0.420	55.77
0.020	0.492	63.37
0.025	0.549	70.94
0.030	0.594	78.58
0.040	0.663	93.50
0.050	0.712	108.40
0.070	0.778	137.86
0.100	0.837	181.23
0.150	0.888	251.2
0.200	0.917	318.3
0.250	0.935	382.4
0.300	0.947	443.5
0.350	0.956	501.3
0.400	0.963	556.1
0.450	0.968	607.6
0.500	0.973	656.0
0.550	0.976	701.2
0.600	0.980	743.4
0.650	0.982	782.6
0.700	0.985	819.3
0.750	0.987	853.8
0.800	0.989	887.0
0.850	0.991	919.4
0.900	0.993	952.8
0.950	0.996	989.1
1.000	1.000	1031.5

Table XXXVII

LIQUID-VAPOR EQUILIBRIA, 75° C ISOTHERM; SYSTEM: BrF₅ - BrF₃

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF₅ in Liquid</u>	<u>Mole Fraction BrF₅ in Vapor</u>	<u>Pressure, mm</u>
0.000	0.000	111.45
0.001	0.032	114.98
0.002	0.062	118.52
0.003	0.090	122.05
0.005	0.141	129.08
0.007	0.187	136.10
0.010	0.247	146.63
0.015	0.331	164.11
0.020	0.398	181.51
0.025	0.453	198.83
0.030	0.500	216.1
0.040	0.572	250.3
0.050	0.627	284.3
0.070	0.705	351.2
0.100	0.776	449.4
0.150	0.843	606.5
0.200	0.881	755.6
0.250	0.905	896.7
0.300	0.922	1029.6
0.350	0.935	1154.3
0.400	0.944	1270.9
0.450	0.952	1379.7
0.500	0.958	1480.5
0.550	0.964	1573.9
0.600	0.968	1660.2
0.650	0.972	1740.2
0.700	0.976	1814.5
0.750	0.979	1884.4
0.800	0.982	1951.5
0.850	0.986	2018
0.900	0.989	2087
0.950	0.994	2162
1.000	1.000	2249

Table XXXVIII

LIQUID-VAPOR EQUILIBRIA, 100°C ISOTHERM; SYSTEM: BrF_5 - BrF_3

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF_5 in Liquid</u>	<u>Mole Fraction BrF_5 in Vapor</u>	<u>Pressure, mm</u>
0.000	0.000	309.7
0.001	0.024	316.9
0.002	0.046	324.1
0.003	0.068	331.3
0.005	0.109	345.6
0.007	0.146	360.0
0.010	0.196	381.4
0.015	0.268	417.0
0.020	0.329	452.4
0.025	0.381	487.6
0.030	0.425	522.6
0.040	0.498	592.1
0.050	0.554	660.8
0.070	0.638	795.9
0.100	0.718	992.9
0.150	0.797	1305.9
0.200	0.843	1599.8
0.250	0.873	1895.0
0.300	0.895	2131
0.350	0.911	2369
0.400	0.923	2589
0.450	0.933	2792
0.500	0.941	2978
0.550	0.948	3149
0.600	0.954	3305
0.650	0.960	3449
0.700	0.964	3581
0.750	0.969	3706
0.800	0.974	3826
0.850	0.978	3946
0.900	0.984	4071
0.950	0.991	4206
1.000	1.000	4363

Table XXXIX

LIQUID-VAPOR EQUILIBRIA, 125°C ISOTHERM; SYSTEM: BrF₅ - BrF₃

Compositions calculated from correlation assuming ideal gases.

Mole Fraction BrF ₅ in Liquid	Mole Fraction BrF ₅ in Vapor	Pressure, mm
0.000	0.000	742.7
0.001	0.019	756.1
0.002	0.037	769.5
0.003	0.054	782.9
0.005	0.087	809.7
0.007	0.118	836.3
0.010	0.161	876.2
0.015	0.224	942.4
0.020	0.278	1008.1
0.025	0.325	1073.4
0.030	0.367	1138.3
0.040	0.437	1266.8
0.050	0.493	1393.5
0.070	0.579	1642.3
0.100	0.665	2003
0.150	0.753	2571
0.200	0.805	3099
0.250	0.841	3588
0.300	0.866	4038
0.350	0.885	4451
0.400	0.900	4828
0.450	0.912	5171
0.500	0.922	5483
0.550	0.931	5766
0.600	0.938	6022
0.650	0.945	6256
0.700	0.951	6471
0.750	0.957	6673
0.800	0.963	6868
0.850	0.969	7062
0.900	0.977	7265
0.950	0.987	7484
1.000	1.000	7730

Table XL

LIQUID-VAPOR EQUILIBRIA, 150°C ISOTHERM; SYSTEM: BrF₅ - BrF₃

Composition calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF₅ in Liquid</u>	<u>Mole Fraction BrF₅ in Vapor</u>	<u>Pressure, mm</u>
0.000	0.000	1580.0
0.001	0.016	1603.4
0.002	0.031	1626.5
0.003	0.045	1649.9
0.005	0.073	1696.2
0.007	0.100	1742.3
0.010	0.136	1811.3
0.015	0.192	1925.9
0.020	0.241	2040
0.025	0.284	2152
0.030	0.323	2264
0.040	0.389	2485
0.050	0.444	2703
0.070	0.530	3129
0.100	0.619	3743
0.150	0.712	4703
0.200	0.770	5584
0.250	0.809	6389
0.300	0.838	7123
0.350	0.860	7788
0.400	0.877	8387
0.450	0.891	8926
0.500	0.902	9410
0.550	0.912	9844
0.600	0.921	10233
0.650	0.929	10584
0.700	0.936	10907
0.750	0.943	11208
0.800	0.951	11498
0.850	0.959	11787
0.900	0.969	12087
0.950	0.982	12407
1.000	1.000	12753

Table XLI

LIQUID-VAPOR EQUILIBRIA, 1/8 Atm ISOBAR; SYSTEM: BrF₅ - BrF₃

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF₅ in Liquid</u>	<u>Mole Fraction BrF₅ in Vapor</u>	<u>Temperature, °C</u>
0.000	0.000	71.47
0.001	0.034	70.75
0.002	0.066	70.04
0.003	0.096	69.34
0.005	0.153	67.98
0.007	0.205	66.68
0.010	0.275	64.80
0.015	0.374	61.88
0.020	0.455	59.20
0.025	0.521	56.73
0.030	0.576	54.43
0.040	0.661	50.38
0.050	0.723	46.83
0.070	0.806	40.96
0.100	0.874	34.23
0.150	0.927	26.27

Table XLII

LIQUID-VAPOR EQUILIBRIA, 1/4 Atm ISOBAR; SYSTEM: BrF₅ - BrF₃

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF₅ in Liquid</u>	<u>Mole Fraction BrF₅ in Vapor</u>	<u>Temperature, °C</u>
0 000	0.000	87.53
0.001	0.027	86.88
0.002	0.054	86.24
0.003	0.079	85.60
0.005	0.127	84.37
0.007	0.172	83.17
0.010	0.232	81.43
0.015	0.320	78.71
0.020	0.394	76.17
0.025	0.457	73.82
0.030	0.511	71.62
0.040	0.598	67.65
0.050	0.663	64.13
0.070	0.754	58.19
0.100	0.834	51.22
0.150	0.902	42.83
0.200	0.935	36.78
0.250	0.955	32.14
0.300	0.966	28.42
0.350	0.971	25.35

Table XLIII

LIQUID-VAPOR EQUILIBRIA, 1/2 Atm ISOBAR; SYSTEM: BrF₅ - BrF₃

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF₅ in Liquid</u>	<u>Mole Fraction BrF₅ in Vapor</u>	<u>Temperature, °C</u>
0.000	0.000	105.51
0.001	0.023	104.92
0.002	0.044	104.33
0.003	0.066	103.75
0.005	0.106	102.62
0.007	0.144	101.51
0.010	0.196	99.90
0.015	0.274	97.35
0.020	0.341	94.96
0.025	0.400	92.71
0.030	0.451	90.60
0.040	0.536	86.72
0.050	0.602	83.24
0.070	0.698	77.27
0.100	0.788	70.12
0.150	0.869	61.30
0.200	0.910	54.83
0.250	0.935	49.83
0.300	0.952	45.84
0.350	0.963	42.55
0.400	0.971	39.78
0.450	0.977	37.41
0.500	0.981	35.36
0.550	0.984	33.58
0.600	0.987	32.02
0.650	0.989	30.64
0.700	0.991	29.41
0.750	0.993	28.31
0.800	0.994	27.30
0.850	0.996	26.37
0.900	0.997	25.45

Table XLIV

LIQUID-VAPOR EQUILIBRIA, 1 Atm ISOBAR; SYSTEM: BrF_5 - BrF_3

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF_5 in Liquid</u>	<u>Mole Fraction BrF_5 in Vapor</u>	<u>Temperature, °C</u>
0.000	0.000	125.71
0.001	0.019	125.16
0.002	0.037	124.61
0.003	0.055	124.07
0.005	0.089	123.02
0.007	0.121	121.99
0.010	0.166	120.48
0.015	0.235	118.09
0.020	0.295	115.82
0.025	0.349	113.68
0.030	0.396	111.65
0.040	0.477	107.88
0.050	0.543	104.46
0.070	0.641	98.50
0.100	0.738	91.21
0.150	0.830	82.02
0.200	0.880	75.18
0.250	0.912	69.85
0.300	0.932	65.55
0.350	0.947	62.00
0.400	0.957	59.00
0.450	0.965	56.45
0.500	0.971	54.24
0.550	0.976	52.22
0.600	0.979	50.64
0.650	0.983	49.16
0.700	0.986	47.85
0.750	0.988	46.67
0.800	0.991	45.59
0.850	0.993	44.57
0.900	0.995	43.56
0.950	0.998	42.50
1.000	1.000	41.32

Table XLV

LIQUID-VAPOR EQUILIBRIA, 2 Atm ISOBAR; SYSTEM: BrF_5 - BrF_3

Compositions calculated from correlation assuming ideal gases.

Mole Fraction BrF_5 in Liquid	Mole Fraction BrF_5 in Vapor	Temperature, °C
0.000	0.000	148.63
0.001	0.016	148.11
0.002	0.031	147.60
0.003	0.046	147.08
0.005	0.075	146.08
0.007	0.103	145.10
0.010	0.142	143.67
0.015	0.202	141.38
0.020	0.256	139.21
0.025	0.304	137.14
0.030	0.346	134.92
0.040	0.424	131.48
0.050	0.487	128.12
0.070	0.585	122.18
0.100	0.686	114.81
0.150	0.787	105.34
0.200	0.846	98.18
0.150	0.883	92.53
0.300	0.908	87.95
0.350	0.926	84.16
0.400	0.940	80.96
0.450	0.950	78.23
0.500	0.958	75.88
0.550	0.964	73.84
0.600	0.970	72.06
0.650	0.974	70.48
0.700	0.978	69.08
0.750	0.982	67.81
0.800	0.985	66.63
0.850	0.988	65.51
0.900	0.992	64.40
0.950	0.996	63.23
1.000	1.000	61.91

Table XLVI

LIQUID-VAPOR EQUILIBRIA, 4 Atm ISOBAR, SYSTEM: BrF_5 - BrF_3

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF_5 in Liquid</u>	<u>Mole Fraction BrF_5 in Vapor</u>	<u>Temperature, °C</u>
0.070	0.530	148.82
0.100	0.634	141.36
0.150	0.741	131.65
0.200	0.806	124.23
0.250	0.849	118.31
0.300	0.879	113.50
0.350	0.901	109.50
0.400	0.918	106.13
0.450	0.931	103.26
0.500	0.941	100.79
0.550	0.949	98.65
0.600	0.956	96.76
0.650	0.962	95.11
0.700	0.968	93.63
0.750	0.972	92.29
0.800	0.977	91.03
0.850	0.981	89.83
0.900	0.986	88.61
0.950	0.992	87.33
1.000	1.000	85.89

Table XLVII

LIQUID-VAPOR EQUILIBRIA, 8 Atm ISOBAR; SYSTEM: BrF_5 - BrF_3

Compositions calculated from correlation assuming ideal gases.

<u>Mole Fraction BrF_5 in Liquid</u>	<u>Mole Fraction BrF_5 in Vapor</u>	<u>Temperature, °C</u>
0.250	0.812	147.73
0.300	0.846	142.72
0.350	0.871	138.56
0.400	0.890	135.06
0.450	0.906	132.09
0.500	0.919	129.55
0.550	0.929	127.34
0.600	0.938	125.42
0.650	0.946	123.72
0.700	0.952	122.20
0.750	0.959	120.81
0.800	0.967	119.50
0.850	0.972	118.23
0.900	0.979	116.94
0.950	0.988	115.57
1.000	1.000	114.06

VI. EXPERIMENTAL ERRORS AND COMPARISON WITH OTHER WORK

The prior work in this field consists of vapor pressure data on bromine pentafluoride and bromine trifluoride. These data are compared with the values found in the present investigation. No previous work has been reported on the liquid-vapor equilibria of the binary system.

An estimate is made of the experimental errors involved in this investigation. A brief estimate is also made of the uncertainty caused by these experimental errors in the calculated quantities which are listed in the various tables.

A. Comparison with Previous Work

Vapor Pressure of Bromine Pentafluoride. The vapor pressure of bromine pentafluoride was measured for the range 25 to 146°C and fitted with the equation

$$\log_{10}p_1 = 6.4545 + 0.001101t - 895/(t + 206) \quad ,$$

where p_1 is the pressure in mm and t is the temperature in °C.

The data previously available were those of Ruff and Menzel.⁽²⁾ Their measurements were made for the range -60 to 25°C and they fitted the data with the equation

$$\log_{10}p_1 = 8.0716 - 1627.7/(t + 273) \quad ,$$

where the symbols have the same meaning as above. Although the ranges for the two sets of data do not overlap, the equation used to represent the data of the present investigation was extrapolated to lower temperatures and the extrapolated values are compared with the observed values of Ruff and Menzel.

This is considered to be excellent agreement between the two sets of data. The modified Antoine equation is seen to be of an excellent type for purposes of extrapolation.

Although the vapor pressure data of bromine pentafluoride are found to be more accurate at lower pressure, it is estimated that the accuracy is approximately 0.1 per cent in pressure, or 0.02 to 0.05°C.

Table XLVIII
Comparison of Vapor Pressure Equation of Bromine
Pentafluoride with Data of Ruff and Menzel

Temp. °C	Pressures		100 $\frac{(\text{Obs } p_1 - \text{Calc } p_1)}{(\text{Calc } p_1)}$
	Observed by Ruff and Menzel, mm	Extrapolated Pressures, mm	
-10.8	73.0	72.0	1.4
- 6.0	95.1	93.9	1.3
0.0	130.3	128.8	1.2
5.6	171.7	170.2	0.88
9.1	203.1	201.2	0.94
13.1	244.2	242.1	0.87
15.4	269.6	268.5	0.41
17.3	293.2	292.1	0.38
19.4	320.6	320.0	0.19
21.8	356.5	354.5	0.56
24.0	390.3	388.7	0.41

Vapor Pressure of Bromine Trifluoride. The vapor pressure of bromine trifluoride was measured for the range 65 to 180°C and fitted with the equation,

$$\log_{10} p_2 = 7.65757 - 1627.5/(t + 215) \quad ,$$

where p_2 is the pressure in mm and t is the temperature in °C.

Ruff and Braida⁽²²⁾ measured the vapor pressure of bromine trifluoride for the range -5 to 80°C and fitted their data with the equation

$$\log_{10} p_2 = .841954 - 2220.2/(t + 273) \quad ,$$

where the symbols have the same meaning as above. The equation used to represent the data of the present investigation was extrapolated somewhat, and the values calculated from the equation are compared with the observed values of Ruff and Braida.

This is very poor agreement and may be due to impurities in the samples of bromine trifluoride used by Ruff and Braida. Bromine trifluoride has a considerable solubility for metal salts and this would cause the static method used by Ruff and Braida to give incorrect results. Contamination by volatile impurities such as bromine and bromine pentafluoride would also make the results uncertain.

Table XLIX
Comparison of Vapor Pressure Equation of Bromine
Trifluoride with Data of Ruff and Braidà

Temp. °C	Pressures Observed by Ruff and Braidà, mm	Calculated Pressures, mm	100 $\frac{(\text{Obs } p_2 - \text{Calc } p_2)}{(\text{Calc } p_2)}$
25	10.3	7.5	37
30	13.7	10.3	33
35	17.5	14.0	25
40	23.8	18.8	27
45	30.5	25.0	22
50	41.0	32.8	25
60	63.0	54.9	15
70	94.5	88.5	7
80	136.0	138.2	-2

Another set of data available previous to the present investigator was that of Oliver and Grisard.⁽³⁾ They measured the vapor pressure of bromine trifluoride for the range 37 to 155°C and fitted their data with the equation

$$\log_{10} p_2 = 7.74853 - 1685.8/(t + 220.57) \quad ,$$

where the symbols have the same meaning as above. The equation used to represent the data of the present investigation was extrapolated to somewhat lower temperatures and the values calculated from the equation are compared with the observed values of Oliver and Grisard.

This is excellent agreement between the two sets of data. The only significant differences were temperatures below 50°C, where it was necessary to calculate the pressure by extrapolation. Although there are experimental difficulties encountered in the measurement of the very low vapor pressures, the equation of Oliver and Grisard is probably somewhat more accurate for temperatures below 50°C.

In the present investigation, vapor pressures at temperatures as high as 225°C were measured. Although steady temperatures were recorded, it was evident from the operation of the equipment that the bromine trifluoride was present in a partially decomposed state, and data points above 200°C were not used in fitting the vapor pressure equation. It is estimated that the vapor pressure data are accurate to approximately 0.2 per cent in pressure, or 0.04 to 0.07°C.

Table L
Comparison of Vapor Pressure Equation of Bromine
Trifluoride with Data of Oliver and Grisard

Temp. °C	Pressures Observed by Oliver and Grisard, mm	Calculated Pressures, mm	$100 \frac{(\text{Obs } p_2 - \text{Calc } p_2)}{(\text{Calc } p_2)}$
38.716	17.67	17.50	0.97
49.097	31.46	31.26	0.64
57.000	47.25	46.22	0.06
66.226	74.07	74.20	-0.18
76.355	117.80	117.92	-0.10
84.935	170.05	170.37	-0.19
91.837	225.05	225.66	-0.27
101.748	330.15	330.69	-0.16
111.848	475.93	476.64	-0.15
121.961	671.68	672.40	-0.11
126.841	787.57	788.10	-0.07
131.857	923.3	923.5	-0.02
137.301	1092.1	1091.3	0.07
148.295	1507.0	1505.7	0.09
154.822	1808.0	1806.3	0.09

B. Experimental Errors

Vapor Pressure Data. It is estimated that the experimental error involved in the vapor pressure measurements for bromine pentafluoride is 0.1 per cent in pressure. The error in temperature will vary from 0.03 to 0.05°C for the range 25 to 150°C. For bromine trifluoride, it is estimated that the error involved in the vapor pressure measurements is 0.2 per cent in pressure. This corresponds to an error in temperature of 0.04 to 0.07°C for the range 50 to 150°C. These estimated errors are taken large enough to include slight systematic errors that may be present in the data as well as the deviations from the vapor pressure equations.

Liquid-Vapor Equilibria. No previous liquid-vapor equilibria measurements are available on the binary system bromine pentafluoride-bromine trifluoride. Thus only the estimated experimental errors in this investigation can be discussed.

The equipment used for pressure and temperature measurement were capable of much finer accuracy than could be actually realized. There are two main reasons for this. The analytical technique was of less precision than the pressure and temperature measurements. The second source of inaccuracy was the ability of the still to give samples that actually represent a separation of one theoretical plate between the liquid and vapor compositions, and a temperature that is the true boiling temperature of the liquid sample.

The auxiliary equipment was capable of giving an accuracy of 0.01°C , 0.02 per cent in pressure, and 0.3 to 0.5 per cent in composition. It is estimated that the accuracy actually obtained corresponds to approximately 0.3 to 0.5°C , 1 per cent in pressure, and 1 per cent in composition.

The above estimates were obtained by noting that the average deviation of the observed compositions from the vapor liquid correlation was approximately 1 per cent. The accuracy in temperature and pressure corresponding to 1 per cent are the values mentioned above. It was possible to check the still on the systems ethanol-water and n-heptane-toluene within the limit of error claimed above.

C. Errors in Calculated Quantities

For the purpose of calculating some of the quantities listed in the section on calculated results, it was necessary to have information on the saturated vapor volumes. Except for several vapor densities for bromine pentafluoride at low pressure, no experimental data are available. These several measurements serve only to show that bromine pentafluoride does not appreciably dimerize under these conditions. In Appendix B, critical constants as listed below are estimated. These are used with the low-pressure form of the Berthelot equation of state to estimate the non ideal vapor volumes. These values are listed here with an estimate of their accuracy since they will determine, in part, the error of some of the calculated quantities.

For bromine pentafluoride,

$$T_c = 486 \pm 20^{\circ}\text{K} \quad , \text{ and}$$

$$P_c = 47 \pm 10 \text{ atm} \quad .$$

For bromine trifluoride,

$$T_c = 612 \pm 40^{\circ}\text{K} \quad , \text{ and}$$

$$P_c = 69 \pm 20 \text{ atm} \quad .$$

The saturated vapor volumes for bromine pentafluoride and bromine trifluoride were calculated by substituting the predicted critical constants into the low pressure form of the Berthelot equation of state. The error in the vapor volumes can be calculated from the estimated errors in the critical constants. For bromine pentafluoride, the error in the volume is found to vary from 0.2 per cent at 25°C to 3 per cent at 150°C. For bromine trifluoride, the error in the volume is found to vary from 0.01 per cent at 25°C to 0.4 per cent at 150°C. These results may be stated in another manner. For both bromine pentafluoride and bromine trifluoride, the error in the volumes calculated in the above manner will be only 0.1 as large as the error involved in calculating the volumes from the ideal gas law; that is, the difference in saturated vapor volume due to the estimated error in the critical constants is only 0.1 as large as the difference between the predicted nonideal volume and the ideal gas volume.

Saturated liquid densities at higher temperatures were estimated by extrapolating the liquid densities reported by Stein, Vogel and Ludewig.⁽¹⁶⁾ Besides the extrapolations used in the section on method of calculation, densities were also extrapolated assuming that the expansion factor is a linear function of temperature. Although the expansion factor is rather poorly represented by a linear function, it is felt that the difference in densities predicted by the two methods would be a reliable measure of the accuracy of the reported extrapolation. For bromine pentafluoride, the error is found to be 0.02 per cent at 25°C, where Stein, Vogel and Ludewig reported the density to approximately 3 per cent at 150°C. For bromine trifluoride, the error is found to be 0.02 per cent at 50°C, where Stein, Vogel and Ludewig reported the density to 0.6 per cent at 150°C.

The error in the slope of the vapor pressure curve can be calculated from the error in the vapor pressure equation itself. Assuming the error in pressure is 0.1 per cent for bromine pentafluoride, the error in the slope of the vapor pressure curve will also be approximately 0.1 per cent. It was previously estimated that the error in pressure for the vapor pressure of bromine trifluoride was 0.2 per cent. In this case the error in the temperature derivative of the vapor pressure equation will be approximately 0.2 per cent.

The entropy and enthalpy of vaporization for bromine pentafluoride and bromine trifluoride were calculated from the Clausius-Clapeyron equation. For the most part, the error in the entropy and enthalpy of vaporization is due to the error in the saturated vapor volumes which were substituted into the Clausius-Clapeyron equation. For bromine pentafluoride, the error in the entropy and enthalpy of vaporization was found to vary from 0.5 per cent at 50°C to 3 per cent at 150°C. For bromine trifluoride, the error in the entropy and enthalpy of vaporization was found to vary from 0.2 per cent at 50°C to 0.5 per cent at 150°C.

VII. THEORY

A very brief survey is made of the available information concerning the chemical behavior of bromine pentafluoride and bromine trifluoride. A short account is given of bromine monofluoride for the sake of completeness, although it has not been isolated in the pure state and no data were taken in this investigation on its physical properties. The entropy of vaporization of bromine pentafluoride and bromine trifluoride are compared by the Hildebrand rule with normal liquids. Bromine pentafluoride is found to exhibit a small excess entropy of vaporization over that expected of a normal liquid, and bromine trifluoride is found to show considerable excess entropy of vaporization. The liquid vapor equilibrium data on the system bromine pentafluoride-bromine trifluoride is compared with the liquid vapor equilibrium behavior predicted for the system by the regular solution theory. The experimental data show far less deviation from ideality than predicted theoretically and it is suggested that the cause may be a specific interaction between the unlike molecules of the solution.

A. Chemical Behavior of the Interhalogens.

Bromine and fluorine react to form three interhalogen compounds, bromine monofluoride, bromine trifluoride, and bromine pentafluoride. Their properties are typical of the interhalogens in general and their thermal stability increases with increasing fluorine content. The thermal stability is important since it limits the conditions under which their properties may be studied. Bromine monofluoride has been reported to decompose completely to bromine and higher fluorides at 50°C. Bromine trifluoride will begin to decompose at about 170 to 180°C. Bromine pentafluoride is the most stable and shows no signs of decomposition at 400°C.

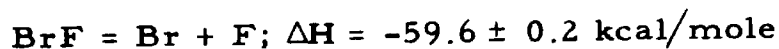
Bromine Monofluoride. Bromine monofluoride has never been isolated in the pure state and therefore no experimental data are reported in this investigation on its properties. However, for the sake of completeness, a few remarks concerning its physical properties will be given. Ruff and Braida⁽²²⁾ were first to claim the preparation of bromine monofluoride. Fluorine and bromine were diluted with nitrogen and allowed to react at 10°C. The product was collected by fractional condensation in traps held at successively lower temperatures. Ruff and Braida concluded that almost 50% of the fraction condensed in the trap held at -120°C was bromine monofluoride.

Ruff and Braida described bromine monofluoride as a reddish-brown gas or red liquid which crystallizes to a solid having the color of potassium dichromate. They found that when the mixture was cooled, it separated into a solid, bromine-rich phase and a phase containing bromine monofluoride with the pentafluoride as impurity. The latter phase could be liquified by heating to -35°C and the authors concluded that the melting point of bromine

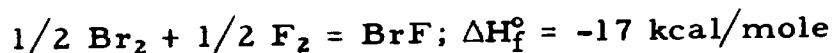
monofluoride is in the neighborhood of -33°C . From the temperature variation of the vapor pressure of this sample, and extrapolation to 760 mm, a temperature of about 20°C was estimated for the boiling point.

The lack of success of later investigators in isolating bromine monofluoride casts doubt on the interpretation of Ruff and Braida of their experimental work. It seems quite possible that the experimental work of Ruff and Braida could be interpreted by assuming that what they considered to be bromine monofluoride was actually a eutectic mixture of bromine and bromine pentafluoride. Ruff and Braida concluded that the monofluoride decomposed completely at 50°C . It would seem, however, that it is still an open question whether its stability is less or greater at higher temperature.

The band spectrum of bromine monofluoride in the visible region has been analyzed by Brodersen and Schumacher^(23,24) and leads to an energy of dissociation into normal atoms of



If the dissociation energies of bromine and fluorine be taken as -45.5 and -39.8 kcal/mole, respectively, then the heat of formation of bromine monofluoride from its elements in the gaseous phase is



The uncertainty arises from the use of the dissociation energy of fluorine, but the calculation shows that the formation of bromine monofluoride is associated with considerable exothermicity and the instability of the compound would have to be explained by the greater stability of the higher fluorides rather than to the weakness of the Br-F bond.

From the band spectrum, Brodersen and Schumacher⁽²³⁾ calculated the internuclear distance to be $1.74 \text{ \AA}$. A more accurate value is obtained from the microwave spectrum by Smith, Tidwell and Williams:⁽²⁵⁾ $r_e = 1.759 \text{ \AA}$. The thermodynamic functions await evaluation from the spectroscopic data. The dipole moment of bromine monofluoride, as determined by microwave spectroscopy, is 1.29D . In this work no attempt was made to isolate the monofluoride, the bromine and fluorine were simply added in equimolar proportions.

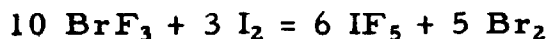
Bromine Trifluoride. The preparation of bromine trifluoride by combination of the elements was first carried out by Lebeau⁽¹⁾ and later by Ruff and Menzel.⁽²⁾ Present practice calls for the use of a water-cooled tubular copper reactor which is inclined at a slight angle from the horizontal. Bromine is brought into the upper end of the reactor, and fluorine is introduced near the lower end from which the bromine trifluoride is withdrawn.

When pure, bromine trifluoride is a pale yellow liquid which solidifies to prisms of the same color. The vapor pressure and density of bromine trifluoride are reported in other sections of this report. Early values of the boiling point were several degrees too high and this was probably due to the fact that the boiling point was obtained by extrapolation from lower temperatures. Grisard and Oliver⁽³⁾ reported that at 165°C the bromine trifluoride appeared to decompose into more volatile products and was carried over into the cold trap. In the present investigation, the samples were not lost from the ebulliometer, but evidence of decomposition was noted. It was found that in the range of 160 to 180°C too much heat added to the boiler of the ebulliometer caused the condensation temperature to drop. Below 180°C it was possible to find a range of heat input that gave a constant condensation temperature. Above 180°C, this was no longer possible, even though the temperature measured was fairly constant with time.

A reason for this behavior of the metal ebulliometer might be tentatively suggested. The decomposition occurring in the boiler depends on the rate of heat input, and recombination occurs in the upper part of the ebulliometer. The equilibrium between the decomposition and the recombination is determined by the heat input. The fact that the temperature is fairly constant with time, in spite of the fact that it is not a true condensation temperature, would suggest that the decomposition reaction or reactions are reversible and rapid. It would be further suggested that the decomposition products are more volatile than bromine trifluoride. This is not of great significance, however, since all of the possible decomposition products, bromine monofluoride, bromine, and bromine pentafluoride are more volatile than bromine trifluoride. A reddish color observed in bromine trifluoride at higher temperature might suggest bromine or bromine monofluoride.

Electron diffraction studies have been made by Rogers, Wahrhaftig, and Schomaker,⁽²⁶⁾ and interpreted on the basis of a pyramidal model with the bond distance Br-F = 1.78 Å as contrasted with 1.76 Å for bromine monofluoride. The angle F-Br-F is interpreted to be 86 degrees.

The heat of formation of bromine trifluoride is not yet known although ways of determining it have been suggested by Emeleus and Woolf.⁽²⁷⁾ The reaction of chlorine trifluoride with alkali halides used by Schmitz and Schumacher⁽²⁸⁾ to determine the heat of formation of chlorine trifluoride would not be applicable with bromine trifluoride because of the formation of complexes.⁽²⁹⁾ The criteria for ready reaction of an oxide with bromine trifluoride is that a volatile fluoride be produced, or that the fluoride formed be soluble in the reagent. The heat evolved in the simplest of these reactions, the hydrolysis of iodine pentafluoride, has been measured by Woolf.⁽³⁰⁾ The heat of formation of bromine trifluoride, which cannot be determined by simple hydrolysis since the products of this reaction (bromine, oxygen, hydrobromic and bromic acids) are formed in variable amounts, may be determined from the heat of the reaction,



now that the heat of formation of the pentafluoride is known.

Bromine Pentafluoride. Ruff and Menzel⁽²⁾ were first to prepare bromine pentafluoride. The preparation was carried out by direct combination of bromine and fluorine to form bromine pentafluoride in copper apparatus at 200°C. This is essentially the same as present practice. The compound is very stable to heat, showing no sign of decomposition at 400°C.

A single measurement of the gas density of bromine pentafluoride was made by Ruff and Menzel⁽²⁾ from which they concluded that at 29°C and 330 mm there was no association of the gas molecules. This has since been confirmed at approximately the same conditions.⁽⁴⁾ The vapor pressure of bromine pentafluoride was determined by Ruff and Menzel for temperatures below 20°C. Their data were accurate in the range of measurement but gave a boiling point approximately 2°C too low when extrapolated to 1 atmosphere pressure.

When pure, the liquid bromine pentafluoride is colorless and freezes to a whitish solid. No information is available on the internuclear distances, bond angles or heat of formation for bromine pentafluoride.

B. Comparison with "Normal" Liquids.

According to the crude Trouton rule, the entropy of vaporization at the normal boiling point is the same for a great many liquids. An obvious generalization of Trouton's rule is that the entropy of vaporization is a function of pressure only. A better rule is that first suggested by Hildebrand,⁽³¹⁾ which states that the entropy of vaporization per mole is the same for all normal liquids if measured, not at their boiling points, but at temperatures at which their vapors have equal molar volumes. The comparison is usually made at relatively low temperatures where lack of knowledge concerning the vapor volume will not cause a large uncertainty in the calculation of the entropy of vaporization. Hildebrand⁽³²⁾ suggests the value 20.1 calories gram mole⁻¹ degree Kelvin⁻¹ as a normal value for the entropy of vaporization, when the volume of the vapor is 49.5 liters gram mole⁻¹. The excess in entropy of vaporization above 20.1 may be taken as indicating a degree of order.

For bromine pentafluoride, the saturated vapor volume is 49.5 liters gram mole⁻¹ at 22.6°C and the entropy of vaporization is found to be 24.1 calories gram mole⁻¹ degree Kelvin⁻¹. For bromine trifluoride, the saturated vapor volume is 49.5 liters gram mole⁻¹ at 112.0°C and the entropy of vaporization is found to be 26.4 calories gram mole⁻¹ degrees Kelvin⁻¹. Hildebrand⁽³³⁾ states that bromine pentafluoride is not quite a normal liquid, showing evidence of a little excess entropy of vaporization that might be

attributed to lack of a center of symmetry, only a plane of symmetry, and somewhat ionic bonds. Bromine trifluoride shows a considerable excess entropy of vaporization and is definitely not a normal liquid.

C. Comparison with Regular Solution Theory

The liquid-vapor equilibria data for the system bromine pentafluoride-bromine trifluoride is correlated by fitting the data with van Laar equations in the form given by Carlson and Colburn:⁽²⁰⁾

$$\log_{10} \gamma_1 = A / (1 + Ax_1/Bx_2)^2, \text{ and}$$

$$\log_{10} \gamma_2 = B / (1 + Bx_2/Ax_1)^2,$$

where $\gamma_1 = Py_1/p_1x_1$, and $\gamma_2 = Py_2/p_2x_2$. The constants A and B represent the logarithm of the activity coefficients in infinitely dilute solution for bromine pentafluoride and bromine trifluoride, respectively. These constants were fitted as functions of temperature by the equations,

$$A = 0.112 + 0.00168t, \text{ and}$$

$$B = 0.450 + 0.00100t,$$

where t is the temperature in °C.

It will now be seen how well these experimental results for the liquid-vapor equilibria of the system bromine pentafluoride-bromine trifluoride can be predicted by assuming that they form a regular solution. Scatchard⁽³⁴⁾ derived an equation in which all the constants represent physical properties for systems in which the change of entropy on mixing is the same as that for an ideal mixture, designated a "regular solution" by Hildebrand:

$$RT \ln \gamma_1 = v_1 b z_2^2,$$

$$RT \ln \gamma_2 = v_2 b z_1^2,$$

where

$$b = [(\Delta E_1/v_1)^{1/2} + (\Delta E_2/v_2)^{1/2}]^2$$

E_1, E_2 = the energy of vaporization of the liquid to zero pressure for bromine pentafluoride and bromine trifluoride, respectively,

v_1, v_2 = the liquid volume of pure bromine pentafluoride and bromine trifluoride, respectively,

z_1, z_2 = the volume fractions of bromine pentafluoride and bromine trifluoride, respectively.

Since partial molal volumes are not usually available, it is assumed that no volume change occurs in mixing, and the volume fraction is defined by

$$z_1 = x_1 v_1 / (x_1 v_1 + x_2 v_2), \text{ and } z_2 = x_2 v_2 / (x_1 v_1 + x_2 v_2).$$

The terms $(\Delta E_1/v_1)$ and $(\Delta E_2/v_2)$ have the dimensions of calories/cc and are sometimes called the "cohesive energy density." Values are listed below at 25°C intervals.

Table LI			
Cohesive Energy Densities			
Temperature °C	$\Delta E_1/v_1$	$\Delta E_2/v_2$	b
25	91.98	223.07	28.57
50	83.11	208.07	28.19
75	74.50	194.55	28.27
100	65.92	181.89	28.82
125	57.22	169.55	29.78
150	48.33	157.10	31.16

The equations derived by Scatchard may be rewritten in a form more easily compared with the van Laar equations. These may be written as

$$\log_{10} \gamma_1 = (0.4343 b v_1 / RT) z_2^2, \text{ and}$$

$$\log_{10} \gamma_2 = (0.4343 b v_2 / RT) z_1^2,$$

where the quantity $(0.4343 b v_1 / RT)$ is the logarithm of the activity coefficient for bromine pentafluoride at infinite dilution, and likewise the quantity $(0.4343 b v_2 / RT)$ is the logarithm of the activity coefficient for bromine trifluoride at infinite dilution. Though the non-symmetry expressed by the equations above is not comparable with the non-symmetry expressed by the van Laar equations, the logarithm of the activity coefficients at infinite dilution may be used for comparison of the experimentally and theoretically predicted liquid-vapor equilibria behavior of the system (see Table LII).

The agreement is very poor. Various reasons may be suggested to account for the poor agreement, but not a great deal is yet known concerning these compounds and the suggestions must not be taken too seriously. The treatment presented for the application of the regular solution theory has of necessity been rather superficial. The form of the equations derived by Scatchard is such that if the two components of the system approach each other in physical properties, then the activity coefficients predicted approach unity. Thus, as a limiting case, the treatment reduces to the Raoult's law approximation.

Table LII

ACTIVITY COEFFICIENTS AT INFINITE DILUTION

Temperature °C	<u>Calc. from Exp. Data</u>		<u>Theoretical Prediction</u>	
	<u>BrF₅</u>	<u>BrF₃</u>	<u>BrF₅</u>	<u>BrF₃</u>
25	*0.070	*0.425	1.489	1.023
50	0.196	0.500	1.408	0.954
75	0.238	0.510	1.368	0.912
100	0.212	0.550	1.364	0.891
125	0.314	0.600	1.394	0.889
150	0.372	0.600	1.462	0.903

* Extrapolated values.

No attempt has been made in applying the regular solution theory to the system bromine pentafluoride-bromine trifluoride to account for specific interactions such as solvation and association. The high entropy of vaporization of bromine trifluoride suggests association in the liquid phase and this effect would influence the behavior of solutions which contain bromine trifluoride. The fact that the deviations from ideal behavior are less than theoretically predicted would suggest that some sort of interaction is present between unlike molecules in the solution. It is of interest to point out that two immiscible liquid phases are theoretically predicted over the entire temperature range involved and the failure of these to appear would have to be attributed to a specific interaction between unlike molecules of the solution.

VIII. CONCLUSIONS

The vapor pressures of the two pure components of the system bromine pentafluoride-bromine trifluoride were measured and are compared with the previously available vapor pressure information on these compounds. The liquid-vapor equilibria data for the system were measured at temperatures of 50, 75, 100, 125 and 150°C, and at a pressure of 1 atm. The 5 isotherms were each fitted with a set of van Laar equations and the constants of the van Laar were fitted as functions of temperature. The van Laar equations were used in the form suggested by Carlson and Colburn⁽²⁰⁾ so that the constants represent the logarithm of the activity coefficients in infinitely dilute solution. This correlation of the liquid-vapor equilibria data was used to calculate the smoothed isothermal and isobaric diagrams. It is considered that the correlation can be extrapolated to 25°C, making it possible to compare it with the entire 1 atm experimental isobaric diagram. The correlation was not extrapolated above 150°C, since bromine trifluoride shows thermal instability at high temperatures and the procedure would be questionable. Some of the isobaric diagrams calculated would exceed the temperature range of the correlation. Therefore only the part of the isobaric diagrams falling in the range of 25 to 150°C are tabulated in the tables. No apology should be necessary since this is the part of the isobaric diagrams that should prove useful.

The correlation of liquid-vapor equilibria data was carried out with the assumption that the vapor phase behaves ideally. In the worst case, that is, at high temperature and bromine pentafluoride-rich solutions, the vapor volumes are only about 80% of the ideal gas volume. However, the fact that the correlation is used in turn to calculate the isothermal and isobaric diagrams should cause most of the error to cancel. For the purpose of calculating entropies and enthalpies of vaporization, it is felt that considerable increase in accuracy is obtained by estimating the nonideal vapor volumes. The vapor volumes are estimated by the use of the low-pressure form of the Berthelot equation of state in conjunction with predicted critical constants.

The entropies of vaporization for bromine pentafluoride and bromine trifluoride were compared with the value suggested by Hildebrand for normal liquids. Bromine pentafluoride was found to exhibit a slightly greater entropy of vaporization than is expected for a normal liquid and bromine trifluoride showed a considerable excess entropy of vaporization. Bromine trifluoride is definitely not a normal liquid.

The experimentally determined data on the liquid-vapor equilibria of the system bromine pentafluoride-bromine trifluoride were compared with the liquid-vapor equilibria behavior predicted by the regular solution theory. The theoretically predicted behavior was found to offer a very poor approximation and the reasons are not completely clear. In the treatment

of the regular solution theory that was used, no attempt was made to account for specific interactions. The excess entropy of vaporization that was found for bromine trifluoride suggests that there is considerable association in the condensed phase. This effect would be expected to carry over into solutions in which bromine trifluoride is a component. The regular solution theory predicts that the system will have two immiscible liquid phases. The much smaller deviations from ideality that were actually observed and the failure of the system to exhibit immiscible liquid phases might be explained by a specific interaction of unlike molecules in the solution.

An attempt was made to estimate the errors in the experimental data and in the calculated quantities. In comparing the data from the present investigation with prior work, the vapor pressures reported are in general more accurate than those previously available. No previous data are available on the liquid-vapor equilibria of the system, but it is possible to check published values for the systems ethanol-water and n-heptane-toluene within the accuracy claimed for the bromine pentafluoride-bromine trifluoride system.

APPENDIX A

SAFETY PRECAUTIONS

The interhalogen compounds of bromine and fluorine are extremely reactive fluorinating agents and react with many materials in explosive fashion. Either the interhalogen liquid or vapor will cause serious burns if allowed to contact any part of the body. The safety precautions that must be followed are intended to minimize injury to personnel. The health hazards and first aid treatment will be discussed first, and secondly the handling techniques which should prevent accidental injury.

Health hazards. The maximum allowable concentration of interhalogen in the air that is breathed by personnel is generally accepted to be one part per million for an eight-hour period. This hazard is not difficult to control since the odor is so pungent that it is physically uncomfortable to remain in a room with a dangerous concentration of interhalogen in the air. As far as is known, the effects are not cumulative and the sense of smell does not seem to be deadened by smelling traces of interhalogens over a long period.

The interhalogens, as liquid or vapor, cause severe thermal and chemical burns upon contact with any part of the body. The thermal burn is due to the heat of reaction of the interhalogen with the flesh and causes the intense pain that accompanies the burn. The more serious aspect of the burn is the chemical burn which is caused by hydrofluoric acid and should be treated as such. The acid burn may not be noticeable for several hours and by this time treatment will not be nearly as effective as immediate treatment. For this reason inexperienced personnel must be thoroughly instructed in proper handling of interhalogen compounds and hydrofluoric acid. The proper first aid treatment should be given to even the most minor appearing burns.

First aid. When any part of the body has contacted an interhalogen, the area must be subjected immediately to a drenching shower of water. The clothing over the area should be removed immediately, even while drenching with water, and medical assistance should be obtained immediately. It is essential that the exposed area be washed with copious quantities of water for a sufficient period of time to remove all hydrofluoric acid from the skin. Following this, a saturated solution of magnesium sulfate (Epsom salt) or iced 70% alcohol should be applied for 15 minutes. If the burn is in such an area that it is impracticable to immerse the part, then the iced alcohol or magnesium sulfate should be applied with compresses, which should be changed at least every two minutes. This treatment should be continued for 30 minutes. The victim should be referred to a physician, even when immediate injury seems slight, and the physician should be given a detailed account of the accident.

Medical treatment. If there is a possibility of an acid burn, the physician will inject a calcium gluconate solution (1 gram calcium gluconate in 10 cc water) by infiltrating the skin and subcutaneous tissue in the same manner as in the injection of a local anesthetic subcutaneously. All skin which has been exposed to the acid, including at least 1/4 to 1/2 inches around the area, should be infiltrated. This treatment will usually prevent the development of severe burns by tying up the fluoride ion with the calcium to form the inert calcium fluoride.

Protective Equipment. Employees should never expose the skin when working with interhalogens, and should wear full coverage of clothing at all times. Working without safety glasses, face shield and leather gloves should never be permitted. If the concentration surpasses the maximum allowable limit in the working area, the area should be temporarily abandoned. If it is essential that the worker enter the area, a gas mask of the assult type or oxygen-supplied type should be worn. Assult type gas masks should be used only when it is certain that the concentration of vapor is less than 2% by volume and the oxygen content is not less than 16%, and then only for exposures not exceeding one-half hour. In an emergency, the oxygen supplied type should be worn.

The personal protective equipment consists of

- a. Safety glasses
- b. Plastic face shield
- c. Leather gauntlet gloves
- d. Leather jacket
- e. Leather trousers
- f. Safety shoes
- g. Gas mask-assult type or oxygen supplied type depending upon the service.

None of the equipment will completely resist the action of the interhalogens, but will slow down the reaction and enable one to get his hands out of the gloves before the gloves burn through to the skin. The same is true of the other articles of protective clothing.

Handling. The following precautions and handling techniques must be observed for safety reasons regardless of the particular manipulation or measurement being made. Techniques peculiar to interhalogens which are necessary to obtain accurate data will not be discussed in this section.

Besides the danger of burns to personnel already discussed, there is the possibility of fire and explosion. Bromine trifluoride and pentafluoride are in themselves nonflammable; however, the heat evolved during any

fluorination reaction is sufficient to bring some metals to their ignition point and all organic materials will ignite. Upon contact with any organic material such as wood or inorganic material like concrete, the interhalogen will react with explosive violence and splatter in all directions. Each drop-let so scattered again reacts with the material with which it comes into contact and further splattering occurs. If the reaction is confined in any way an explosion will result.

Bromine pentafluoride and trifluoride are classified by the Interstate Commerce Commission as corrosive liquids. They are packed and shipped in a manner similar to anhydrous hydrofluoric acid. One, fifteen and one hundred pound steel containers are used for shipment. All containers received from the manufacturer carry the ICC white acid label. The small one-pound cylinders are boxed when received. The larger fifteen and one hundred pound cylinders are shipped unboxed with a valve cap over the plug. Re-distilled and other interhalogen stored in the laboratory are kept in welded nickel or monel vessels. The cylinders should be stored away from any other materials and preferably in an aluminum or mild steel box completely closed on the bottom. It is very important never to fill any container more than 80% full, since the interhalogen liquid expands appreciably on heating and a ruptured cylinder might result.

Interhalogen waste should be discarded only after it has been hydrolyzed with an aqueous solution and neutralized. Weak solutions of hydrofluoric acid (a product of hydrolysis) are exceedingly corrosive to ceramic materials and to ferrous metals. Bromine pentafluoride and trifluoride if allowed to stand in an open beaker in a well-ventilated hood will slowly hydrolyze and the fumes evacuate through the ducts. This is not a recommended procedure since the hydrofluoric acid will corrode the ducts as well as the beaker. Most metals owe their resistance to interhalogens and hydrofluoric acid to a thin film of metallic fluoride on the surface and this film is not stable in the presence of moisture in the air.

Personnel should not be permitted to work alone since help may be needed immediately in case of accident and not be available.

APPENDIX B

PREDICTION OF CRITICAL CONSTANTS

It is necessary for the calculation of entropies and enthalpies of vaporization to have some method available for estimation of the nonideal volume of the interhalogen vapors. A convenient representation of the pressure-volume-temperature relationship at low pressures is the low pressure form of the Berthelot equation of state. The Berthelot equation of state requires the knowledge of the critical temperature and pressure for its employment. Since these values have not been measured for the bromine fluorides it was necessary to predict values for the critical constants.

The prediction of critical constants from information which is far removed from the critical region is in any event subject to large errors. Meissner and Redding⁽³⁵⁾ have recently reviewed the procedures for predicting critical constants and have proposed a procedure which seems most reasonable to them. After a study of these methods, it becomes apparent that the best procedure in any particular case depends on the kind and extent of the information already available on the compound. Meissner and Redding have restricted their treatment to the use of data that are generally available.

A point worth mentioning is that the methods suggested in the literature are of an almost entirely empirical nature. Thus the usual approach is to collect information on a wide variety and large number of compounds. The critical constants are then plotted against a number of different physical and structural properties. In short, the relationships found are usually of most accuracy and value when used with homologous series or at least somewhat similar compounds. As especially bad example is the fact that water does not fit any of these correlations well. This is mentioned not to disparage the work that has been done in this field but rather to point out that very likely interhalogens will not fit correlations which have been derived from data on other compounds. Furthermore, bromine trifluoride in particular may emulate water in its failure to behave in a normal fashion.

In spite of the difficulties mentioned above, it is still felt that it should be possible to predict critical constants that will enable the prediction of PVT behavior much better than the ideal gas law allows. The low pressure form of the Berthelot equation of state requires the knowledge of only the critical temperature and pressure. Thus no attempt will be made to predict critical volume. One of the most accurate and complete pieces of information available, in the present case, is the vapor pressure data. It was felt therefore that the critical temperature and pressure should be made to obey the vapor pressure equations. This leaves only one critical constant to be determined, and for this constant the critical temperature was chosen.

Meissner and Redding⁽³⁵⁾ suggest for compounds containing halogens or sulfur, the equation

$$T_C = 1.41 T_B + 66 - 11 F,$$

where, T_C = predicted critical temperature °K,

T_B = normal boiling temperature °K, and

F = number of fluorine atoms in the molecule.

Substitution into this equation gives,

$T_C = 454^\circ\text{K}$ for bromine pentafluoride, and

$T_C = 595^\circ\text{K}$ for bromine trifluoride.

The Guldberg three-halves rule states that the critical temperature can be approximated by taking for the critical temperature three-halves of the normal boiling point when measured in absolute temperature. From this rule, we have

$T_C = 472^\circ\text{K}$ for bromine pentafluoride, and

$T_C = 598^\circ\text{K}$ for bromine trifluoride.

Stein, Vogel and Ludewig⁽¹⁶⁾ have reported the densities of bromine pentafluoride at 0 and 25°C and bromine trifluoride at 25 and 50°C. These were used in the section on calculations to extrapolate the liquid density to higher temperatures. The equations used for this purpose required knowledge of the critical temperature. The critical temperatures which allow the equations to fit Stein, Vogel and Ludewig's data are

$T_C = 499^\circ\text{K}$ for bromine pentafluoride, and

$T_C = 643^\circ\text{K}$ for bromine trifluoride.

If the expansion factor, as defined by Watson,⁽³⁶⁾ can be represented by the linear function

$$w = 0.1745 - 0.0838(T/T_C)$$

in the range of low temperature and pressure. Then the densities reported by Stein would predict the values

$T_C = 483^\circ\text{K}$ for bromine pentafluoride, and

$T_C = 638^\circ\text{K}$ for bromine trifluoride.

From consideration of the previous predictions, the best values for the critical constants were obtained and are listed below.

For bromine pentafluoride,

$$T_c = 486 \pm 20^\circ\text{K}, \text{ and}$$

$$P_c = 47 \pm 10 \text{ atmospheres.}$$

For bromine trifluoride,

$$T_c = 612 \pm 40^\circ\text{K}, \text{ and}$$

$$P_c = 69 \pm 20 \text{ atmospheres.}$$

The critical pressures were calculated by substituting the critical temperatures into the respective vapor pressure equations.

APPENDIX C

SAMPLE EQUILIBRIUM STILL DATA SHEET

Run No. 6

Resistance Thermometer 1031564

June 8, 1952

Time (min)	Resistance Thermometer Readings	
	Equilibrium Still	Metal Steam Ebulliometer
13.6	N 35.5634	
14.8	R 35.5628	
21.7		R 40.6360
22.2		N 40.6368
31.0	N 35.5688	
31.8	R 35.5682	
42.6		R 40.6362
43.4		N 40.6369
49.2	N 35.5699	
49.9	R 35.5695	
57.8		R 40.6365
58.5		N 40.6370
73.1	N 35.5701	
74.2	R 35.5698	
81.0		R 40.6364
81.8		N 40.6368

Equilibrium Still, Aver. Res. = 35.5678
 Temperature = 99.74°C

Metal Steam Ebulliometer, Aver. Res. = 40.6366
 Temperature = 151.417°C
 Pressure = 3708.1 mm

APPENDIX C (contd.)

SAMPLE ANALYTICAL DATA SHEET

Sample No. V-6

June 8, 1952

Measurement of prism angle

1) 280°18'	1) 160°12'	120°6'	59°54'	59°54' = ϕ
2) 100°15'	2) 340°9'	120°6'	59°54'	
1) 280°13'	1) 160°10'	120°3'	59°57'	59°56.5' = ϕ
2) 100°12'	2) 340°8'	120°4'	59°56'	
1) 280°15'	1) 160°10'	120°5'	59°55'	59°55.5' = ϕ
2) 100°13'	2) 340°9'	120°4'	59°56'	

Measurement of angle of deviation of light beam

1) 84°3'	1) 57°28'	26°35'	26°34' = δ
2) 264°4'	2) 237°31'	26°33'	
1) 237°4'	1) 263°38'	26°34'	26°34.5' = δ
2) 57°2'	2) 83°37'	26°35'	

$$\phi = 59^\circ 55.3' \quad \phi/2 = 29^\circ 57.6' \quad \delta = 26^\circ 34.2' \quad \frac{\delta + \phi}{2} = 43^\circ 14.8'$$

$$\log_{10} \sin \frac{\delta + \phi}{2} = 9.83578$$

$$\log_{10} \sin \phi/2 = 9.69846$$

$$\log_{10} \eta = \log_{10} \sin \frac{\delta + \phi}{2} - \log_{10} \sin \phi/2 = 0.13732$$

$$\eta = 1.3719$$

Mole per cent $\text{BrF}_5 = 75.2$ Mole per cent $\text{BrF}_3 = 24.8$

REFERENCES

1. Lebeau, P., Compt. rend., 141 1018 (1905).
2. Ruff, O. and Menzel, W., Z. anorg. allgem. Chem., 202 49 (1931).
3. Grisard, J. W. and Oliver, G. D., "The Vapor Pressure and Heat of Vaporization of Bromine Trifluoride," (K-766), Carbide and Carbon Chemicals Company, K-25 Plant, June 8, 1951.
4. Steunenbergh, R. K., Argonne National Laboratory, Private communication.
5. Barber, E. J. and Cady, G. H., J. Am. Chem. Soc., 73 4247-50 (1951).
6. Dorsey, N. E., "Properties of Ordinary Water Substance," Reinhold Publishing Corporation (1940).
7. Leach and Lythgoe, J. Am. Chem. Soc., 27 964 (1905).
8. Chu, J. C., "Distillation Equilibrium Data," Reinhold Publishing Corporation (1950).
9. Carey, J. S. and Lewis, W. K., Ind. Eng. Chem., 24 882 (1932).
10. Noyes, W. A. and Warfle, R. R., J. Am. Chem. Soc., 23 463 (1901).
11. Jones, C. A., Schoenberg, E. M. and Colburn, A. P., Ind. Eng. Chem., 35 666 (1943).
12. Hipkin, H. and Myers, H. S., Ind. Eng. Chem., 46 2524 (1954).
13. Steinhauser, H. H. and White, R. H., Ind. Eng. Chem., 41 2912 (1949).
14. Bromiley, E. C. and Quiggle, D., Ind. Eng. Chem., 25 1136 (1933).
15. Stein, L., Private Communication.
16. Stein, L. Vogel, R. C. and Ludewig, W. H., J. Am. Chem. Soc., 76 4287-89 (1954).
17. Weissburger, A., "Physical Methods of Organic Chemistry," 2rd. Ed., Vol. I, Part I, Interscience Publishers (1949).
18. Thomson, G. W., unpublished work based on Watson's Table I of Ind. Eng. Chem., 35 398 (1943).
19. Reilly, J., and Rae, W. N., "Physico-Chemical Methods," 3rd. Edition, Vol. I, Van Nostrand (1939).

20. Carlson, H. C. and Colburn, A. P., Ind. Eng. Chem., 34 581 (1942).
21. Laar, J. J. van, "Sechs Vorträge über das thermodynamische Potential," Braunschweig (1906)
22. Ruff, O. and Braida, A., Z. anorg. Chem., 206 59 (1932).
23. Brodersen, P. H. and Schumacher, H. J., Z. Naturforsch., 2a 358 (1947).
24. Brodersen, P. H. and Schumacher, H. J., Anales a soc. quim. argentina, 38 52 (1950).
25. Smith, D. F., Tidwell, M. and Williams, D.V.P., Phys. Rev., 77 420 (1950).
26. Rogers, M. T., Wahrhaftig, A. L. and Schomaker, V., Abstr. Atlantic City Meeting, Amer. Chem. Soc., April 21P (1947).
27. Emeleus, H. G. and Woolf, A. A., J. Chem. Soc., 164 (1950).
28. Schmitz, A. and Schumacher, H. J., Z. Naturforsch., 2a 362 (1947).
29. Shraper, A. G. and Emeleus, H. G., J. Chem. Soc., 2135 (1948).
30. Woolf, A. A., J. Chem. Soc., 231-2 (1951).
31. Hildebrand, J. H., J. Am. Chem. Soc., 37, 970 (1915); 40, 45 (1918).
32. Hildebrand, J. H. and Scott, R. L., "The Solubility of Nonelectrolytes," Reinhold Publishing Corporation (1950).
33. Hildebrand, J. H., Private Communication.
34. Scatchard, G., Chem. Rev., 8 321-33 (1931).
35. Meissner, H. P. and Redding, E. M., Ind. Eng. Chem., 34 521 (1942).
36. Watson, K. M., Ind. Eng. Chem., 35 398 (1943).