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The Chemical Separation of Boron Isotopes

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THE CHEMICAL SEPARATION OF BORON ISOTOPES

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ABSTRACT

This is the final report of the research performed at ORNL on the chemical fractionation of boron isotopes between BF_3 gas and the liquid molecular addition compounds of BF_3. Thirty compounds were studied — ten of them in detail. Graphs and equations are given for variation of isotopic equilibrium constant, vapor pressure, and BF_3 solubility as a function of temperature. Rate of isotopic exchange and melting points were determined. Several of the compounds are likely candidates for use in a gas-liquid counter-current exchange system for large-scale separation of boron isotopes.

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SEPARATION OF BORON ISOTOPES

A. A. Palko

SUMMARY

This report deals with the studies performed at ORNL concerning the chemical fractionation of boron isotopes between BF_3 gas and the liquid molecular addition compounds of BF_3. Thirty compounds were examined for suitability — ten of them in detail. Included in the study were ethers, sulfides, amines and selenides. Graphs and equations are given for changes in isotopic equilibrium constant, vapor pressure, and BF_3 solubility with temperature. Rate of exchange and melting points were determined. This research resulted in the development of several new separation processes which are superior to methods previously employed to produce boron-10.

INTRODUCTION

This investigation of boron isotope separation schemes grew out of a desire by the U. S. Atomic Energy Commission early in the 1950's to have available, if the need should arise, chemical exchange processes capable of concentrating any or all of the isotopes of the lighter elements of the periodic table through calcium.

Boron isotopes were of particular interest because of their contrasting nuclear properties. ^{10}B with a natural abundance of 19.8% has a cross section of 3837 barns for thermal neutron capture while ^{11}B with a natural abundance of 80.2% has a cross section of only 0.005 barns.[1] The reaction

$$({}^{10}_{5}B + {}^{1}_{0}n \rightarrow ({}^{11}_{5}B) \rightarrow {}^{7}_{3}Li + {}^{4}_{2}He + 2.4\ MeV)$$

yields no secondary radiation effects and the α rays produced are easily stopped. Consequently, ^{10}B ranks high on the list of effective neutron capture materials. It is useful for reactor control rods, neutron shielding, and instrumentation both for neutron density and neutron dosage. For a given thickness, ^{10}B is 20 times more effective than lead and nearly 500 times as effective as concrete as a neutron shield. Consequently, from the nuclear engineers' viewpoint, separation of boron isotopes was not only desirable but imperative.

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Historical Background

In 1943 in the early stages of the Manhattan Project, a group was established at Columbia University to study the problem of boron isotope separation. Various approaches were undertaken but exchange distillation of the dimethyl ether-BF_3 complex was finally decided upon as being the most direct method to produce boron-10. Accordingly, laboratory development on the system was done at Columbia, while pilot plant testing was conducted by Standard Oil Company of Indiana (1944-46). A full-scale plant was operated by Hooker Electrochemical Company at Niagara Falls, New York, from 1953-1958. Although many difficulties were encountered, the plant was successfully operated and several hundred kilograms of 90-95% ^{10}B metal were produced. Details of these ventures may be found elsewhere.[2-5]

Exchange Distillation of $Me_2O{\cdot}BF_3$

Dimethyl ether reacts with BF_3 to form a "complex" which freezes at -12°C and "boils" at 127°C; 13.6 kcal of heat are released per mole of reactants.[6] At the boiling point, the complex is approximately 60% dissociated in the vapor phase. Passage of the vapor in a column countercurrent to the liquid complex effects a separation of the boron isotopes. ^{10}B concentrates in the descending liquid phase and ^{11}B concentrates in the upflowing gas phase. The effective single-stage isotopic separation factor is 1.016 even though the true isotopic equilibrium constant is 1.027 at the boiling point of the complex. This lowering is due to incomplete dissociation of the vapor phase which consists of BF_3, dimethyl ether and complex.

If the system is operated at atmospheric pressure, approximately 50% of the complex is decomposed in 24 hours. Products of decomposition are methyl fluoride and methyl borate. Methyl fluoride is an inert gas while methyl borate has a boiling point (80°C) that is much lower than that of the complex (127°C). Fortunately, both compounds accumulate at the waste end of the system and can be removed continuously. In order to decrease the rate of decomposition to a tolerable level, the distillation must be carried out at reduced pressure (∿200 torr).

However, lowering the pressure on the system immediately poses another serious problem. Any leak in the apparatus brings air and water into the process streams. Water causes another kind of decomposition. Boric acid, fluoroboric acid, hydrofluoric acid, and hydrofluoroboric acid are some of the products formed. Some are solids and tend to clog the distillation column; some are liquids, highly corrosive to materials of construction. All contain product ^{10}B which must be recovered. Hence, it becomes apparent immediately that water must be eliminated if the process is to function. (This is true, however, for any known gas-liquid system to concentrate boron isotopes.)

Because ^{10}B concentrates in the liquid phase, one other difficulty is encountered in the methyl ether-BF_3 distillation; namely, recovery of ^{10}B quantitatively. The dimethyl ether-BF_3 complex cannot be decomposed either quantitatively or easily, and losses of product are high at the recovery cycle. Hence, one can see that the methyl ether system is far from ideal as a process to enrich boron-10.

Purpose of Present Study

Early in the 1950's, it became apparent that if ton quantities of separated boron isotopes were required rather than kilogram quantities, a better, more efficient, less cumbersome method would be required for production than the methyl ether-BF_3 distillation. Accordingly, the present investigation of boron isotope chemistry was undertaken with special emphasis on gas-liquid counter-current, chemical exchange processes which could be thermally refluxed and operated at atmospheric pressure and ambient temperature.

Scope of Investigation

A brief survey of the literature brought to light the BF_3 addition compounds of anisole, phenol, and butyl sulfide. All are stable liquids at room temperature and all can be thermally dissociated with slight decomposition of the organic. Since the b.p. of the organic adduct is so high; the vapor phase contains essentially pure BF_3. Hence, each is a likely candidate for gas-liquid, counter-current ^{10}B enrichment. Laboratory experiments with the anisole complex were so encouraging that a bench-scale semi-pilot plant was built to test the system. This investigation indicated that the anisole system was indeed superior to the methyl ether·BF_3 distillation process. The single stage isotopic equilibrium constant was much larger and the exchange could be carried out at room temperature or below and at atmospheric pressure, thereby greatly simplifying plant operation. Furthermore, ^{10}B product recovery was much easier since the anisole·BF_3 complex could be quantitatively dissociated simply by heating. However, it is a foregone conclusion that water must be eliminated if decomposition is to be controlled. Details of the anisole process can be found elsewhere.[7-12]

Armed with early success, a systematic reinvestigation of BF_3 addition compounds was undertaken in 1956 in order to gain an insight into the exchange processes and to determine the best types of compounds for use in ^{10}B-^{11}B exchange. BF_3 forms such a large number of stable addition compounds that it affords an ideal system for study of isotope exchange chemistry. Initially, ten compounds were chosen for intensive study. Later, several more were added as research directed. These are shown in Table I. Periodically as research on each compound was completed, reports were published[13-23] in the open literature. A more detailed account of this work, however, is contained in this report. Except for nitrobenzene, ethyl mercaptan and butyl mercaptan, the compounds in the second part of this table will not be discussed here. A detailed report on these compounds can be found in ref. 22.

Table II is a compilation of the main physical and chemical properties used as a guide in this investigation. Every compound was studied only in such detail as the desirability for the compound warranted. Some compounds were examined in minute detail, others were merely screened. Details of the spectral studies may be found elsewhere.[17-19, 24-26]

The boron halide addition compounds chosen for intensive study not only encompass the whole range of stabilities exhibited by such compounds, but also cover a wide range of elemental coordination bond types; namely, B-O, B-S, B-Se, B-Te, and B-N. The only other elements known to coordinate directly with BF_3 are P, Cl, F, and H.[27] Stability of BF_3 complexes may be classed as follows:

Table I. Boron Halide Addition Compounds Investigated as Possible ^{10}B—^{11}B Isotopic Exchange Systems

Examined in Detail	Screened or Briefly Studied
1. Anisole·BF_3	1. Nitrobenzene·BF_3
2, n-Butyl sulfide·BF_3	2. Diphenyl ether·BF_3
3. Phenol·BF_3	3. Diphenyl ether·BCl_3
4. Ethyl sulfide·BF_3	4. Diphenyl sulfide·BF_3
5. Ethyl amine·BF_3	5. Diphenyl sulfide·BCl_3
6. Ethyl ether·BF_3	6. Thiophenol·BF_3
7. Tetrahydrofuran·BF_3	7. Thiophenol·BCl_3
8. Methyl selenide·BF_3	8. N-methyl diphenyl amine·BF_3
9. Methyl sulfide·BF_3	9. N,N'-dimethylphenyl amine·BF_3
10. Methyl ether·BF_3	10. Methyl isocyanide·BF_3
11. n-Butyl ether·BF_3	11. Acetyl chloride·BCl_3
	12. Methyl telluride·BF_3
	13. Ethyl mercaptan·BF_3
	14. Butyl mercaptan·BF_3
	15. Ethyl formate·BF_3

1. Compounds completely dissociated by heating. Vapor phase contains only BF_3 and traces of organic.
   Examples: anisole·BF_3, phenol·BF_3, n-butyl sulfide·BF_3
2. Compounds completely dissociated by heating. Vapor phase contains organics as well as BF_3.
   Examples: ethyl sulfide·BF_3, methyl sulfide·BF_3, methyl selenide·BF_3.

3. Compounds only partially dissociated by heating. Vapor contains BF_3, organic, complex.
   Examples: ethyl ether·BF_3, methyl ether·BF_3.
4. Compounds essentially undissociated by heating but may be distilled unchanged.
   Examples: tetrahydrofuran·BF_3, ethyl amine·BF_3.

The unstable boranes and the highly stable borates were not included in this study. Kiss studied the latter extensively.[28]

Table II. Properties of Boron Halide Addition Compounds Used as a Guide for Study

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1. Change in isotopic equilibrium constant with temperature.
2. Solubility of halide in organic adduct.
3. Vapor pressure of mixtures of halide and organic.
4. Rate of isotopic exchange between halide and complex.
5. Melting point of halide complexes.
6. Decomposition of complex (irreversible).
7. Calculation of heat of vaporization or dissociation.
8. Calculation of thermodynamic functions for exchange reaction.
9. Spectra of ^{10}B—^{11}B labeled addition compounds (infrared and Raman).
10. Calculation of isotopic equilibrium constants from spectral data.
11. Measurements of N.M.R. spectra of mixtures of BF_3 and selected pairs of ethers.
12. Calculation of reaction kinetics from N.M.R. data.

EXPERIMENTAL

Materials and Methods

The organic chemicals used in these experiments were analytical grade reagents. The dimethyl selenide, dimethyl telluride, and methyl isocyanide were prepared at Oak Ridge National Laboratory by the Analytical Chemical Division.[29-31] The dimethyl sulfide, furnished free by Crown Zellerback Corporation, Camas, Washington, was 99.8% pure. The dimethyl ether, BF_3 and BCl_3, were purchased from Matheson Chemical Company. All materials were purified and made anhydrous before use by standard techniques. Azeotropic distillation was used when applicable to remove water very effectively. The phenol-water azeotrope boils at 100°C and contains 91% H_2O while the anisole-water azeotrope boils at 95° and contains 59.5% H_2O. The two organics boil at 182° and 154°C, respectively. Aliphatic ethers were dried by refluxing over metallic sodium and the amines by refluxing over calcium hydride or calcium carbide. The sulfides were refluxed with metallic sodium and bright copper shot to remove both water and mercaptan.[32] The dried organic compounds were fractionated at atmospheric pressure under a blanket of dry nitrogen and then distilled directly into pre-dried reaction flasks. High-vacuum techniques were used throughout the experiments for transfer of BF_3, BCl_3 and the organic compounds. Stopcocks and ball joints were lubricated with Kel-f or Flurothene-G[33] stopcock grease. Break seal, glass sample tubes were used to transfer BF_3 samples from the reaction manifold to the mass spectrometer for assay.

Two different techniques were used to measure the amount of organic admitted to the reaction flask. For high boiling relatively non-volatile liquids, the organic was distilled into a pre-dried weighed reaction flask and the number of moles of organic were calculated from the weight. In the second method used for measurements of highly volatile liquids, a flask containing the liquid was attached to the vacuum system, the system evacuated, and a predetermined amount of organic was distilled into a volumetric graduated tube incorporated into the vacuum system. The tube was then equilibrated at a known constant temperature. The volume was measured and the organic was transferred to the reaction flask. From the temperature-volume-density relationship the amount of organic was determined. Both methods was quite satisfactory.

Apparatus

The apparatus used for these experiments is shown in Figure 1. It was made from Pyrex. The volume of the entire apparatus was calibrated and the volume of each section was known. The volume of the α measuring system was 320 cc and the volume of the vapor pressure system was 56 cc. Both reaction flasks were double walled with provisions for circulating constant temperature coolant through the jacket. Teflon-coated magnets were placed inside the flasks when made for stirring of the liquid phase. The break-seal tubes used for gas sampling were 10 mm O.D. and contained about 10 cc volume. Vacuum stopcocks were used throughout. Fluorothene ball joint and stopcock grease being polyfluorinated did not react with most of the BF_3 addition compounds and was quite satisfactory even at liquid nitrogen temperatures.

Determination of Isotopic Separation Factor

The single stage isotopic equilibrium constant, α, for the reaction

$$\begin{aligned} {}^{10}BF_3(\text{gas}) + {}^{11}BF_3\cdot\text{org. adduct(liq.)} &\rightleftarrows \\ {}^{11}BF_3(\text{gas}) + {}^{10}BF_3\cdot\text{org adduct(liq.)} & \qquad \text{(I)} \end{aligned}$$

may be written as a ratio of ratios thus:

$$\alpha = \frac{{}^{10}B/{}^{11}B(\text{liquid})}{{}^{10}B/{}^{11}B(\text{gas})} = \frac{{}^{10}B/{}^{11}B(\text{gas before equilibration})}{{}^{10}B/{}^{11}B(\text{gas after equilibration})} \qquad \text{(II)}$$

If the amount of BF_3 in the gas phase is kept small compared to the amount of BF_3 as complex in the liquid phase, then the second relationship above may be assumed, for mathematically it can be shown that essentially all the isotopic change takes place in the gas phase. For boron exchange processes, this gas-liquid ratio may be as small as 1:25. However, it is desirable to keep the ratio as high as 1:50 or 1:100.

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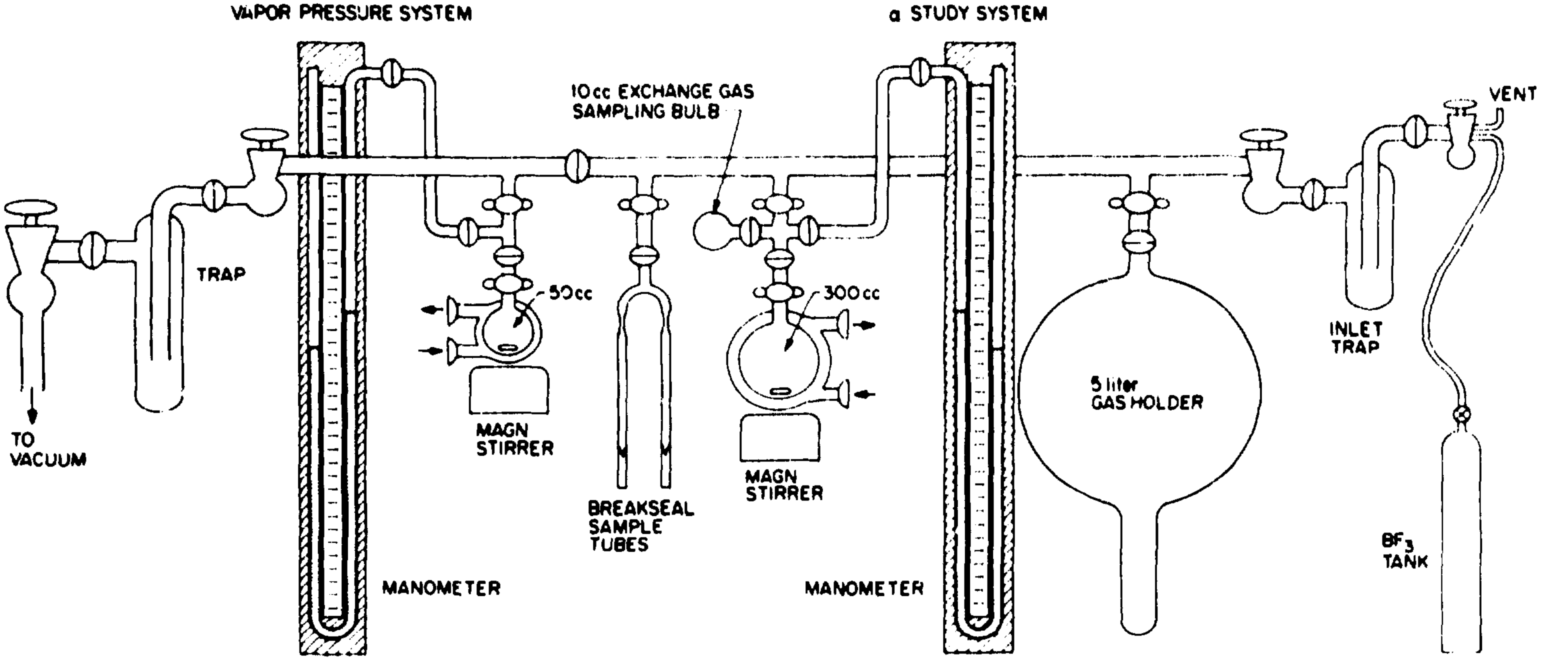

Fig. 1. Apparatus used to study BF_3 addition compounds.

Measurement of $^{10}B/^{11}B$ ratios of only the gas phase before and after equilibration greatly simplified determination of α, especially for systems containing compounds which cannot be easily dissociated into BF_3 and organic. One precaution must be observed however. The amount of gas removed from the gas phase during equilibration must be so small that isotopic equilibrium is not disturbed during sampling. Otherwise normal BF_3 is "boiled" from solution to contaminate the enriched gas phase. For example, in the experiment shown in Fig. 2, four gas samples were taken consecutively at 5-second intervals. The total volume of the gas samples was equal to the volume of the gas phase. Temperature of the experiment was 27°C. The α is lowered in direct proportion to the amount of sample taken from the gas phase. The data are taken from α determinations for the anisole-BF_3 system.

Single-stage isotopic equilibrium constants were determined for the exchange between BF_3 gas and eleven BF_3 addition compounds. Data were corrected where necessary for solubility of excess BF_3 in the liquid phase. Corrected data are shown in Tables III and IV. In some cases the data are different from those published earlier. This is due to the fact that much of the early data was reevaluated in the light of ten years' experience in isotopic chemistry. Then, too, some questionable experiments were rerun. All sets of data were fitted by least squares to the equation

$$\log \alpha = b/T - a \tag{III}$$

The ORNL 1604 computer was employed in these calculations. Table III is a summary of the computer calculations along with calculated values for ΔH, ΔF, and ΔS for the exchange reaction; data points were weighed as $1/\sigma^2$ in the least-squares treatment; in Table IV each point was treated equally. Results in the two cases are essentially identical. Raw data are given in Appendix A.

Procedure for Measuring α

Procedure for making an α determination was as follows. A predetermined amount of the purified anhydrous organic was admitted directly into a clean, dry 300 ml reaction flask. (About 30 ml, or enough organic, was

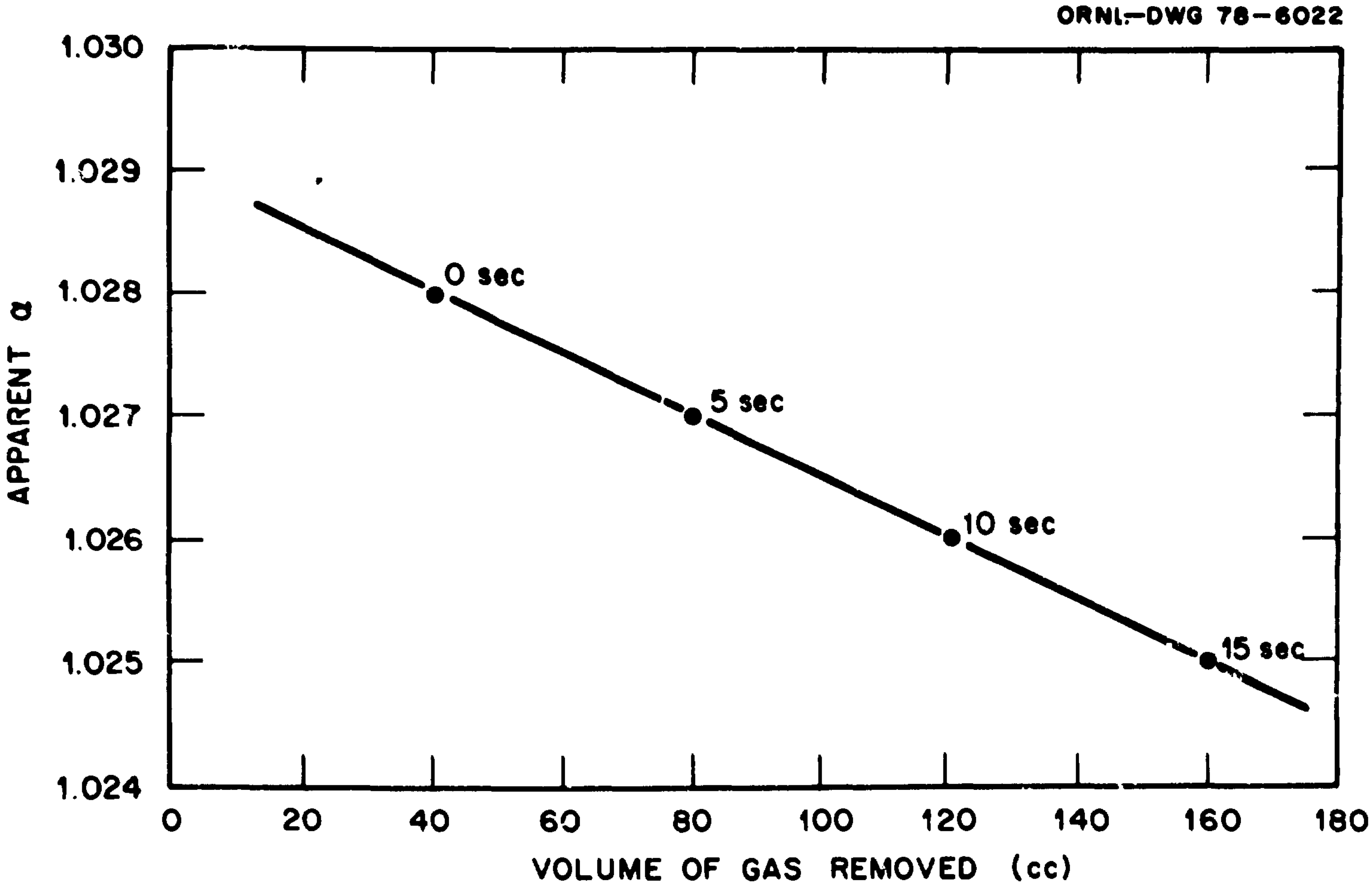

Fig. 2. Apparent change in α with volume of sample removed from gas phase.

Table III. Thermodynamic Functions for the Boron Isotopic Exchange Reaction

BF_3 Complex	b	(-)a	ΔH 2.303 Rb (cal.)	ΔF RTln α (cal.)	ΔS $\frac{\Delta H - \Delta F}{T}$	α_{30}	α_0
Methyl ether	8.7553 ± 1.49	0.01788 ± 0.005	-40.1	-15.3	-0.082	1.0260	1.0332
Methyl sulfide	10.7165 ± 1.05	0.01976 ± 0.004	-49.0	-21.6	-0.090	1.0366	1.0459
Methyl selenide	8.1345 ± 0.36	0.01307 ± 0.001	-37.2	-19.1	-0.059	1.0322	1.0393
Ethyl ether	7.1166 ± 1.27	0.01011 ± 0.005	-32.6	-18.5	-0.047	1.0313	1.0374
Ethyl sulfide	8.4920 ± 0.55	0.01195 ± 0.002	-38.9	-21.9	-0.056	1.0371	1.0427
Triethyl amine	6.4495 ± 0.49	0.01165 ± 0.002	-29.5	-13.4	-0.053	1.0224	1.0280
n-Butyl sulfide	9.6388 ± 1.16	0.01816 ± 0.005	-44.10	-18.9	-0.083	1.0319	1.0402
Phenol	10.1257 ± 0.32	0.02327 ± 0.001	-46.3	-14.0	-0.106	1.0236	1.0355
Anisole	10.4902 ± 1.83	0.02201 ± 0.006	-48.0	-17.5	-0.101	1.0295	1.0385
Tetrahydrofuran	6.0057 ± 1.78	0.00888 ± 0.006	-27.5	-15.2	-0.041	1.0255	1.0306

Data points weighed as $1/\sigma^2$. Log $\alpha = b/T - a$.

Table IV. Thermodynamic Functions for the Boron Isotopic Exchange Reaction

BF_3 Complex	b	(-)a	ΔH 2.303 Rb (cal.)	ΔF_{30} RTln α (cal.)	ΔS $\frac{\Delta H - \Delta F}{T}$	α_{30}	α_0
Methyl ether	7.78486 ± 1.487	0.01409 ± 0.005	-35.6	-16.1	-.064	1.0270	1.0337
Methyl sulfide	10.7142 ± 1.16	0.01974 ± 0.004	-49.0	21.7	.090	1.0366	1.0460
Methyl selenide	8.55388 ± 0.624	0.01452 ± 0.002	-39.2	-19.0	-.067	1.0321	1.0394
Ethyl ether	9.65068 ± 1.511	0.01956 ± 0.006	-44.2	-17.0	-.090	1.0287	1.0370
Ethyl sulfide	10.71682 ± 1.117	0.02006 ± 0.004	-49.1	-21.2	-.092	1.0358	1.0452
Triethyl amine	6.014386 ± 0.410	0.01022 ± 0.001	-27.5	-13.3	-.047	1.0224	1.0275
n-Butyl sulfide	7.7482 ± 1.38	0.01145 ± 0.005	-35.5	19.6	.052	1.0330	1.0395
Phenol	9.65331 ± 1.004	0.02147 ± 0.003	-44.2	-14.4	-.098	1.0242	1.0325
Anisole	10.5823 ± 1.26	0.02245 ± 0.004	-48.4	17.3	.103	1.0291	1.0382
Tetrahydrofuran	5.35707 ± 2.101	0.00660 ± 0.007	-24.5	-15.4	-.030	1.0258	1.0304
Butyl ether	1.6	-0.0059	(-7)	-	-	-	-
Phenetole	12.918	.0257	-59.1	-26.0	-0.01	1.039	1.051(38)

Data points treated as unity. Log $\alpha = b/T - a$.

used to "complex" about 8 liters of BF_3.) The flask with the organic was attached to the vacuum system (cf Fig. 1), the organic frozen and the entire apparatus evacuated. The flask was then isolated from the rest of the system and a predetermined pressure of BF_3 was admitted into the measuring system and was purified from noncondensable gases by a series of condensations and expansions with removal of inert material in between. Eight "tank" samples were taken and then the temperature and the volume of the BF_3 was determined. From pressure, temperature, and volume considerations, the amount of BF_3 in the system was determined. The BF_3 was then allowed to react slowly with the organic by opening the stopcock (partially) on the reaction flask. Enough BF_3 was added to the reaction flask to bring the pressure of the system to slightly more than atmospheric. Meanwhile coolant was circulated through the jacket of the reaction flask at the temperature for the experiment. When the desired temperature and pressure were reached, the reaction flask was isolated from the rest of the apparatus and the two phases equilibrated with the magnetic stirrer.

When the gas-liquid phases had been equilibrated for the desired length of time, a predetermined amount of gas was admitted into the 10 cc gas sampling bulb. This gas was subsequently transferred with liquid N_2 to the two break-seal tubes provided for the purpose. Equilibration continued and the system sampled again after the desired interval of time. Usually four sets of samples were taken at each temperature. The total amount of gas removed from the system per temperature sampling was approximately 20 ml, or about 1 part in 400 of the total.

After the desired number of samples had been obtained at a given temperature, the temperature was changed and the equilibration and sampling was repeated. Equilibrium constants were determined at 3 or 4 temperatures per run and usually about 3 runs were made per system studied. Runs were made from both ends of the temperature scale. If a run was started at a low temperature, it was not necessary to add more BF_3 as the temperature was raised. The amount of BF_3 evolved or dissociated from solution was more than enough to keep the pressure above atmospheric. When a run was started at high temperature, then more BF_3 had to be added to the system as the temperature was lowered. When an α run was completed,

$^{10}B/^{11}B$ ratio for the tank and exchange samples were determined by mass spectrometry and α's were calculated from these ratios.

Corrections

In most cases measured boron α's are not true equilibrium constants for the isotopic exchange reaction given in equation I. The effective measured α may be written:

$$\alpha_{(meas.)} = \alpha_1 M_1 + \alpha_2 M_2 \qquad \text{(IV)}$$

α_1 = K for reaction $^{10}BF_3(g) + {}^{11}BF_3\cdot Org.(liq.\ complex) \overset{\alpha_1}{\rightleftharpoons} {}^{10}BF_3\cdot Org.(liq.\ complex) + {}^{11}BF_3(gas)$

α_2 = k for reaction $^{10}BF_3(gas) + {}^{11}BF_3(diss.\ gas) \underset{\alpha_2}{\rightleftharpoons} {}^{10}BF_3(diss.\ gas) + {}^{11}BF_3(gas)$

M_1 = mole fraction of complexed BF_3 in solution.

M_2 = mole fraction of dissolved BF_3 in solution.

Normally, α_2 is very small, on the order of 1.002. In making corrections, α_2 was assumed to be 1.000 and it was also assumed that excess dissolved BF_3 was not bonded as a complex.

Obviously, if very little excess BF_3 is dissolved, the correction is small; if a large amount is dissolved, then the correction is large. A typical set of experimental data are shown in Table V. These data are from the Et_2O-BF_3 system where solubilities as high as 30% excess were encountered. With other compounds, such as phenol-BF_3, methyl sulfide·BF_3, triethyl amine-BF_3, and anisole-BF_3, no excess BF_3 was dissolved and measured α's are taken as true equilibrium constants.

Isotopic Analysis

During the initial part of this study we did not have control over a mass spectrometer and, hence, all isotopic analyses were performed by the Analytical Chemistry Division. Mass assays for boron were made on a modified G.E. consolidated 6", 60° sector mass spectrometer with a molecular leak. Measurements were made at m/e 48-49, which correspond to the $^{10}BF_2^+$ and $^{11}BF_2^+$ ions. These measurements were barely satisfactory, for

Table V. Observed and Corrected α Values for the System $BF_3(gas) \rightleftarrows Et_2O \cdot BF_3(liq.)$

Temp. °C	Obs. α	Corrected α	(P = 745 Torr) m. fr. cx'd BF_3 / m. fr. diss. BF_3	Total ($M\ BF_3/M\ Et_2O$)
22*	1.0308	1.0326	0.9438/0.0562	1.06
	1.0343	1.0363		
	1.0286	1.0303		
	1.0341	1.0361		
	1.0309	1.0327		
-3	1.0289	1.0343	0.8429/0.1571	1.19
	1.0315	1.0374		
	1.0327	1.0388		
	1.0356	1.0422		
	1.0361	1.0428		
-10	1.0296	1.0371	0.7972/0.2028	1.22
	1.0268	1.0336		
	1.0394	1.0494		
	1.0281	1.0352		
	1.0310	1.0389		
-22	1.0292	1.0388	0.7522/0.2478	1.33
	1.0282	1.0375		
	1.0292	1.0388		
	1.0304	1.0404		
	1.0315	1.0419		
	1.0325	1.0432		
-32	1.0387	1.0553	0.7004/0.2996	1.43
	1.0393	1.0561		
	1.0341	1.0487		
	1.0378	1.0540		
	1.0383	1.0547		
	1.0327	1.0467		

*Replicate samples

precision and reliability of mass assays depends to a large part on the past history of the mass spectrometer. If BF_3 samples are mixed indiscriminately with other samples, especially those containing traces of water or SO_2, then severe contamination of the m/e 48, 49 positions results. In the mass spectrometer water reacts with BF_3 to produce BFO and BFOH species. It also reacts to form HF which attacks any glass present to form SiF_4. Both sets of ions give m/e peaks in the 47, 48, 49 range. SO_2 gives a peak at m/e 48 only. Consequently, unless one has strict control of what goes into a mass spectrometer used for BF_3 analysis, serious doubt is cast upon the reliability of the mass measurements.

In 1958 a mass spectrometer built to specifications by Nuclide Analysis Associates, College Park, PA was acquired. It was a 6", 60° sector Nier-type ratio machine with dual viscous leaks and dual collectors. Isotopic analysis of boron, however, had to be performed by peak height measurement due to memory effects. It was decided, too, that assays be performed at m/e positions 10, 11 where contamination is essentially nonexistent.

To check the desirability of using m/e 10, 11, a series of samples were measured at both m/e 48-49 and at 10-11 positions. These data are shown in Tables VI and VII. As can be seen, the spread within a given set of samples is much greater than the spread between the 48/49 and 10/11 ratios. One observation was made, however, that m/e 10/11 peaks could not be used for absolute mass measurements due to discrimination of the machine at these positions. Since only ratios were desired, m/e 10/11 measurements were quite satisfactory.

Determination of Physical Constants

Solubility of BF_3

Before corrections for solubility in the isotopic equilibrium constant can be made, it is necessary to know quantitatively how much BF_3 is dissolved in the complex. Accordingly, a series of solubility measurements were made at 760 and 400 Torr over a wide temperature range for the $Me_2O\cdot BF_3$, $Et_2O\cdot BF_3$, $Et_2S\cdot BF_3$, $THF\cdot BF_3$, and $PhNO_2\cdot BF_3$ systems. Other

Table VI. Comparison of Boron Mass Analyses at m/e 10/11 and 48/49 for the Exchange $THF\cdot BF_3(\ell) \rightleftarrows BF_3(gas)$

Sample		m/e 10/11	m/e 48/49
7°C	1*	1.0270	1.0285
	2	1.0275	1.0286
	3	1.0280	1.0296
	4	1.0301	1.0286
	5	1.0275	1.0248
	6	1.0266	1.0268
Average		1.0278	1.0278
14°C	1	1.0259	1.0275
	2	1.0274	1.0291
	3	1.0269	1.0243
	4	1.0276	1.0241
	5	1.0281	1.0276
	6	1.0268	1.0235
Average		1.0271	1.0260
19°C	1	1.0219	1.0224
	2	1.0250	1.0253
	3	1.0265	1.0276
	4	1.0261	1.0258
	5	1.0218	1.0215
	6	1.0240	1.0196
	7	1.0234	1.0217
Average		1.0241	1.0238

*Replicate samples

Table VII. Comparison of Boron Mass Analyses at m/e 10/11 and 48/49 for the $Et_2O \cdot BF_3(\ell)$ - BF_3(gas) Exchange

Sample		m/e 10/11	m/e 48/49
22°C	1*	1.0241	1.0202
	2	1.0298	1.0317
	3	1.0321	1.0366
	4	1.0288	1.0284
	5	1.0334	1.0347
	6	1.0312	1.0305
Average		1.0299	1.0303
-3°C	1	1.0284	1.0293
	2	1.0307	1.0323
	3	1.0330	1.0323
	4	1.0343	1.0368
	5	1.0344	1.0378
Average		1.0322	1.0337
-32°C	1	1.0433	1.0340
	2	1.0418	1.0368
	3	1.0336	1.0345
	4	1.0382	1.0373
	5	1.0376	1.0389
	6	1.0305	1.0349
Average		1.0375	1.0361

*Replicate samples

compounds studied either dissolved no excess BF_3 or the amount dissolved was so small as to make solubility corrections to "α" impractical.

Procedure for making a solubility determination was quite simple. After a known amount of organic was transferred to a 50-ml reaction flask on the vacuum system, the sample was frozen and the entire apparatus was out-gassed, BF_3 was admitted at constant pressure to the flask held at constant temperature. After equilibrium was reached and no more BF_3 was absorbed, the amount of BF_3 which had reacted was determined. The temperature was then changed and the process was repeated. Measurements were made from +30 to -30°C in most cases.

Solubility data are shown in Tables VIII-XV. In some instances, as for the $Et_2O{\cdot}BF_3$ complex, solubility at lower temperatures is quite high--1.43 moles of BF_3 for a mole of Et_2O at -32°C. In fact, Wirth and Jackson have found that at -78°, 1 mole of Et_2O complexes 3 moles of BF_3.[34] Preliminary results with ethyl mercaptan-BF_3 indicate that even though no BF_3 is absorbed at room temperature, sizable amounts are absorbed at low temperatures, as shown in Table XIII.

Vapor Pressure of BF_3 Complexes

The vapor pressure of a BF_3 addition compound is a measure of its relative stability when compared to other similar compounds. Then, too, in cases where a compound dissociates according to the reaction below,

$$\text{ab(liq.)} \rightleftarrows \text{a(liq.)} + \text{b(gas)} \qquad \text{(V)}$$

where all the pressure may be attributed to the gas, vapor pressure data may be used to estimate the heat of dissociation for the compound. Accordingly, vapor pressure measurements were taken for several addition compounds over the temperature range - 60 to +40 and mole ratios of BF_3 to organic ranging from 0.1 to 1.06.

Procedure

Procedure for making a vapor pressure measurement was quite simple. After a known amount of dry, purified organic was admitted to a 50 cc reaction flask in the vac system, it was frozen and outgassed. A predetermined amount of BF_3 was admitted to the flask and allowed to

Table VIII. Solubility of BF_3 in THF (moles BF_3/mole THF)

Temp. °C	400 Torr	760 Torr
22	1.005	1.0316
14	1.0111	1.0476
8	1.0206	1.0622

Table IX. Solubility of BF_3 in Me_2O (moles BF_3/mole Me_2O)

Temp. °C	400 Torr	760 Torr
31	1.027	-
30	-	1.038
22	1.034	1.050
6.0	1.051	-
5.5	-	1.085
-8.1	-	1.133
-9.0	1.082	-
-16.5	1.103	-
-19.0	-	1.201

Table X. Solubility of BF_3 in Et_2O
(moles BF_3/mole ether)

Temp. °C	400 Torr	760 Torr
22	1.043	1.070
22	1.043	-
5.5	-	1.117
5.5	1.069	1.116
6.0	1.069	-
-8.5	1.106	1.182
-9.5	-	1.185
-10.0	1.111	-
-19	1.159	-
-19	1.161	1.271
-20	-	1.276

Table XI. Solubility of BF_3 in Et_2S
(moles BF_3/mole sulfide)

Temp. °C	400 Torr	760 Torr
31.5	0.857	-
31.0	-	0.950
23.0	0.938	-
22.5	0.936	0.996
11.0	-	1.038
10.5	0.997	1.032
6.0	1.019	-
4.0	-	1.060
-6.0	-	1.092
-7.0	1.046	-
-8.0	1.052	-
-16.0	-	1.138
-16.5	1.071	-
-17.0	1.085	-
-25.0	1.116	-

Table XII. Solubility of BF_3 in $PhNO_2$ (moles BF_3/mole $PhNO_2$)

Temp. °C	400 Torr	760 Torr
25	0.0253	0.0506
21	0.0327	0.0597
21	0.0310	-
14	0.0458	0.0838
11	0.0562	-
11	0.0520	0.0948
11	0.0532	-
7.0	-	0.1146
1.1	0.0792	-
1.1	0.871	-
-4	0.2278*	-
-4	0.2134*	0.7650*

*BF_3 added to solid solution, hence equilibrium may not have been reached. The $BF_3 \cdot PhNO_2$ mixture freezes at 0°C.

Table XIII. Solubility of BF_3 in EtSH at 760 Torr

Temp. °C	m BF_3/m EtSH
25	0
0	0.03
-50	2.6
-78	3.4

Table XIV. Solubility of BF_3 in Pentafluoro Anisole
@ 760 Torr

Temp. °C	m BF_3/m PFA
24	0.0092
-21	0.156
-28	0.289

Table XV. Solubility of BF_3 in Bu_2O
@ 760 Torr

Temp. °C	m BF_3/m Bu_2O
24	1.0006
8	1.010
-7	1.062
-20	1.081

react slowly with the organic. The flask and contents were then temperature equilibrated and a pressure measurement was made. The temperature was changed and the process repeated. Pressure measurements were made both ascending and descending the temperature scale.

Vapor pressure composition curves for the anisole, phenol, butyl sulfide, ethyl sulfide, methyl sulfide, and methyl selenide systems with BF_3 are shown in Tables XVI-XXII. Each set of data is a composite of several days of observation at any particular mole ratio. By taking readings over several days time, an estimate of the stability of the system could be made. The data were fitted to the log P = a + b/T equation by least squares. Figures 3-6 are a correlation of the vapor pressures of some of the 1:1 complexes of BF_3. Vapor pressures of the BF_3 compounds with Me_2O, Et_2O, and THF were found in the open literature.[6, 35-37] Raw data are shown in appendix A.

Melting Point

Melting points of the 1:1 addition compounds were determined both from cooling curves and by direct observation of the freezing-thawing cycle. A brown electronic recorder (0-1 mv full) scale aided in taking cooling curves. A calibrated, copper constantan thermocouple was used. Absolute temperature measurements were made with a K-2 potentiometer. Melting point data are shown in Table XXIII, along with available heats of dissociation for the BF_3 addition compounds studied.

Rate of Exchange

A rapid rate of $^{10}B-^{11}B$ exchange is a necessary criterion for any system used in a boron isotope separation process. Not only must the isotopic equilibrium constant differ from unity, but the rate of isotopic exchange must be so rapid that exchange be complete as soon as the two phases are contacted in a suitable apparatus, whether the phases be gas-gas, gas-liquid, or liquid-liquid. Qualitative observations made during equilibrium constant determinations indicated that the $^{10}B-^{11}B$ rate of exchange for highly dissociated compounds such as anisole-BF_3, Bu_2S-BF_3, or phenol-BF_3 was extremely rapid, while exchange rates for compounds such as Et_3N-BF_3 was considerably slower. It was, therefore, desirable to determine exactly how fast boron exchanged between the gas-liquid phases.

Table XVI. Vapor Pressure of Phenol-BF_3 Solutions from -10 to +40°C; $\log p = a - b/T$

(m BF_3/m phenol)	a	b	2.303 R b
0.165	10.686	2999	(-)13.7
0.205	10.753	2968	13.6
0.286	11.288	3037	13.9
0.309	11.075	2919	13.4
0.383	11.668	2989	13.7
0.489	11.294	2708	12.4
0.502	11.135	2626	12.0
0.587	10.419	2292	10.5
0.622	10.262	2204	10.1
0.683	9.703	1982	9.1
0.747	9.732	1912	8.8
0.792	9.858	1899	8.7
0.810	9.936	1899	8.7

Table XVII. Vapor Pressure of Anisole-BF_3 Solutions from -25 to +50°C; $\log p = a - b/T$

(m BF_3/m anisole)	a	b	2.303 R b
0.21	10.561	2681	(-)12.27
0.75	11.158	2623	12.00
0.80	10.659	2347	10.74
0.86	10.153	2172	9.94
0.92	10.116	2140	9.79
0.87	10.727	2339	10.70

Table XVIII. Vapor Pressure of Et_2S-BF_3 Solutions from -60 to + 30°C; $\log p = a - b/T$

(m BF /m sulfide)	a	b	2.303 R b
0	8.109	1890	(-)8.65
0.230	9.173	2164	9.90
0.530	10.400	2494	11.41
0.804	11.369	2703	12.37
0.881	12.006	2838	12.99
0.896	11.126	2576	11.79
0.941	12.069	2788	12.76
0.972	11.833	2677	12.25
1.000	10.030	2111	9.66
1.008	9.522	1959	8.96

Table XIX. Vapor Pressure of Me_2S-BF_3 Solutions from -20 to +26°C; $\log p = a - b/T$

(m BF_3/m Me_2S)	a	b	2.303 R b
Pure Me_2S	7.878	1546	(-) 7.1
0.303	7.837	1557	7.1
0.458	7.780	1556	7.1
0.537	7.819	1577	7.2
0.827	7.989	1665	7.6
0.850	8.377	1796	8.2
0.903	9.241	2056	9.4
0.961	9.982	2236	10.2
0.990	10.164	2209	10.1

Table XX. Vapor Pressure of Bu_2S-BF_3 Solutions from -30 to +30°C; $\log p = a - b/T$

($m\ BF_3/m\ Bu_2S$)	a	b	2.303 R b
0.229	11.497	2871	(-)13.14
0.471	11.418	2764	12.65
0.493	11.024	2636	12.06
0.712	11.818	2797	12.80
0.726	11.710	2753	12.60
0.955	10.677	2310	10.57
0.984	10.984	2383	10.90
0.998	10.388	2174	9.95
1.010	9.970	2039	9.33
1.060	8.653	1603	7.34
1.069	8.519	1563	7.15

Table XXI. Vapor Pressure of Me_2Se-BF_3 Solutions from -35 to +30°C; $\log p = a - b/T$

($m\ BF_3$/m selenide)	a	b	2.303 R b
0	7.861	1643	(-)7.72
0.086	9.552	2013	-9.21
0.356	10.376	2146	-9.82
0.415	10.215	2084	-9.54
0.933	10.444	1991	-9.11
0.995	9.945	1824	-8.35

Table XXII. Vapor Pressure Curves for Some 1:1 BF_3 Addition Compounds; Log p = a - b/T

Compound	a	b	Ref.
$Bu_2O\cdot BF_3$	5.56 ± 0.05	1006 ± 15	this work
$Et_2O\cdot BF_3$	10.082	2879	6
$Me_2O\cdot BF_3$	9.806	2775	6
$THF\cdot BF_3$	9.734	3126	32
$Me_2S\cdot BF_3$	10.164 ± 0.001	2209 ± 70	this work
$Et_2S\cdot BF_3$	10.030 ± 0.004	2111 ± 21	this work
$Bu_2S\cdot BF_3$	10.388 ± 0.064	2174 ± 19	this work
$Me_2Se\cdot BF_3$	9.945 ± 0.005	1824 ± 25	this work
$PhOMe\cdot 0.9\ BF_3$	10.116 ± 0.107	2140 ± 33	this work
$PhOH\cdot 0.8\ BF_3$	9.936 ± 0.008	1899 ± 16	this work
$PhOEt\cdot BF_3$	10.9	2575	38
$MeCO_2Et\cdot BF_3$	7.20	1870	39
$Et_2CO_2\cdot BF_3$	9.83	2726	39

Table XXIII. Melting Point and Heat of Dissociation BF_3 Addition Compounds

Complex	Melting Point (°C)	ΔH Dissoc. (kcal/m)	Ref.
Anisole-BF_3	∼ 2	-12.4	
Butyl sulfide-BF_3	<-60	-12.8	
Phenol-BF_3	-15	∼ -8	
2 Phenol-BF_3	-5	∼-14	
Methyl ether-BF_3	-12	-13.6	6,32
Ethyl ether-BF_3	-59	-11.9	6,32
Butyl ether-BF_3	∼-30		
Tetrahydrofuran-BF_3	+12	-16.8	6,32
Ethyl sulfide-BF_3	-62	∼ -9.6	
Methyl sulfide-BF_3	-19.6	∼-10.0	
Methyl selenide-BF_3	-43.3	∼ -8.4	
Ethyl amine-BF_3	19.6	-35.7	33
nn dimethyl analine-BF_3	92		
n methyl diphenyl amine-BF_3	86-100		
Diphenyl ether-BCl_3	∼ 4	∼ -5.3	
Diphenyl sulfide-BCl_3	{+42 +50	∼ -8.7	
Nitrobenzene-BF_3	∼ 0		
Phenetole-BF_3		-11.7	38
Ethyl acetate-BF_3	-27.5	-8.5	39
Ethyl propionate-BF_3	42.8	-12.6	39

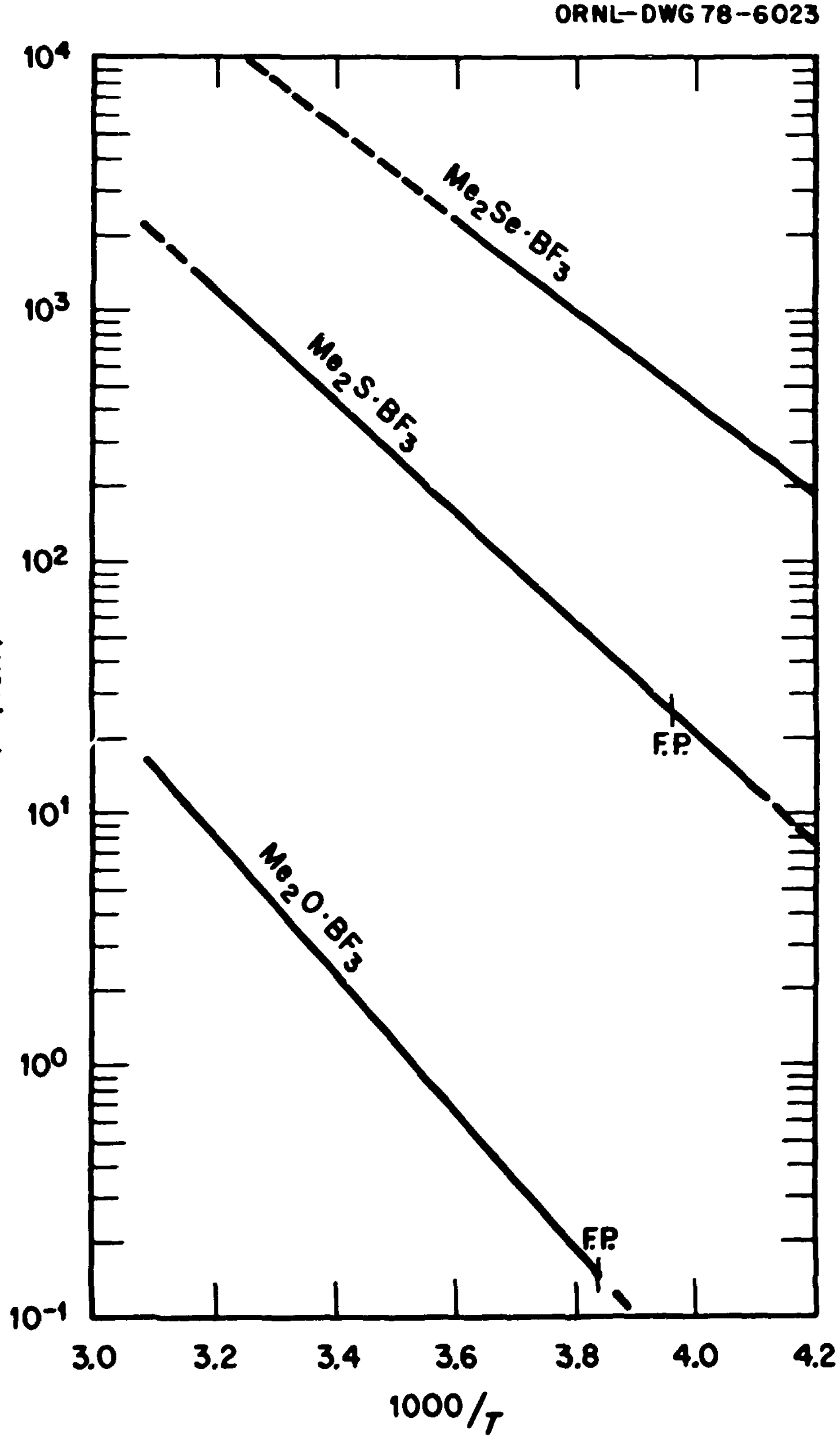

Fig. 3. Comparison of vapor pressures of $Me_2O \cdot BF_3$, $Me_2S \cdot BF_3$ and $Me_2Se \cdot BF_3$

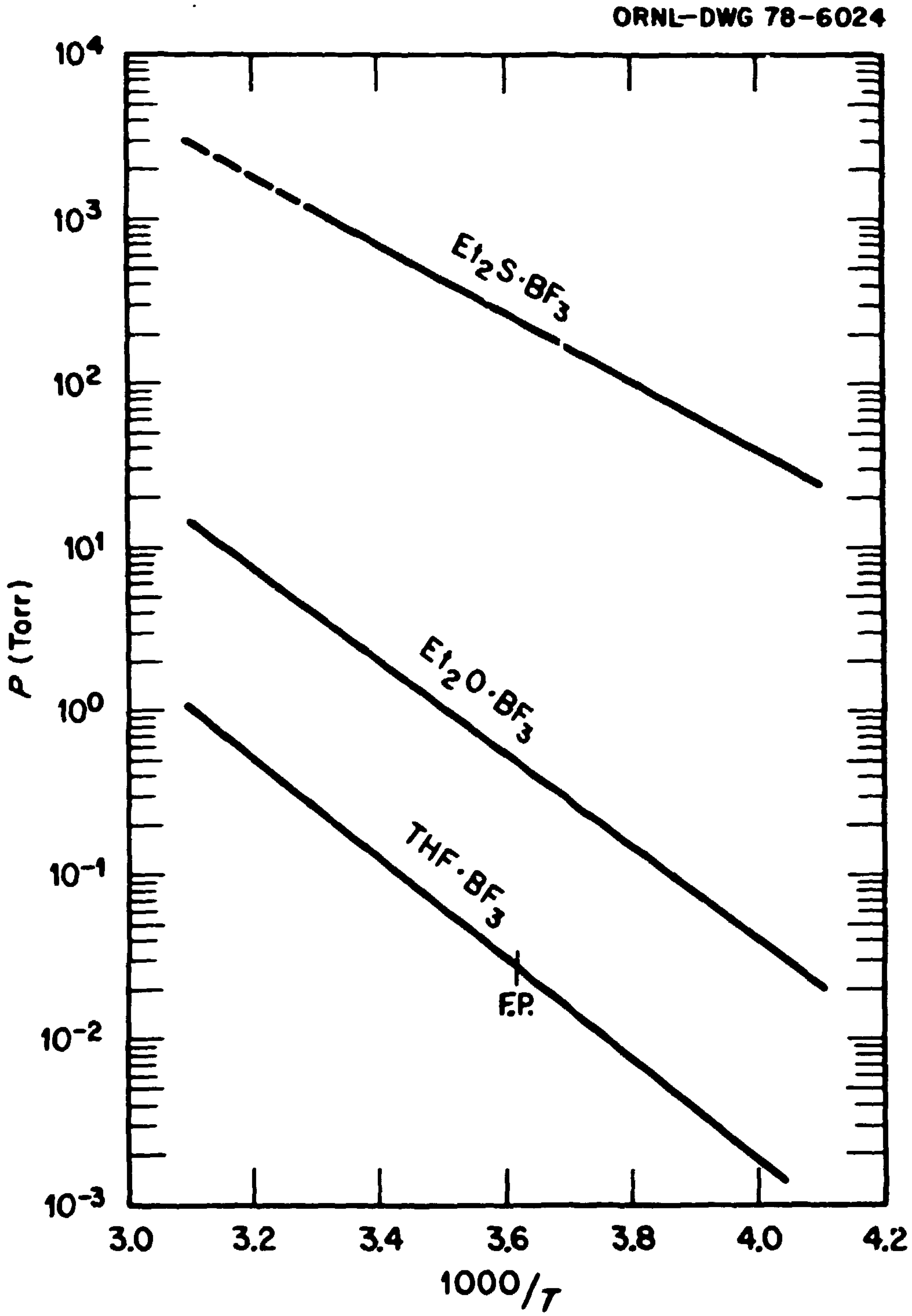

Fig. 4. Comparison of the vapor pressures of $ET_2O \cdot BF_3$, $Et_2S \cdot BF_3$, and $THF \cdot BF_3$.

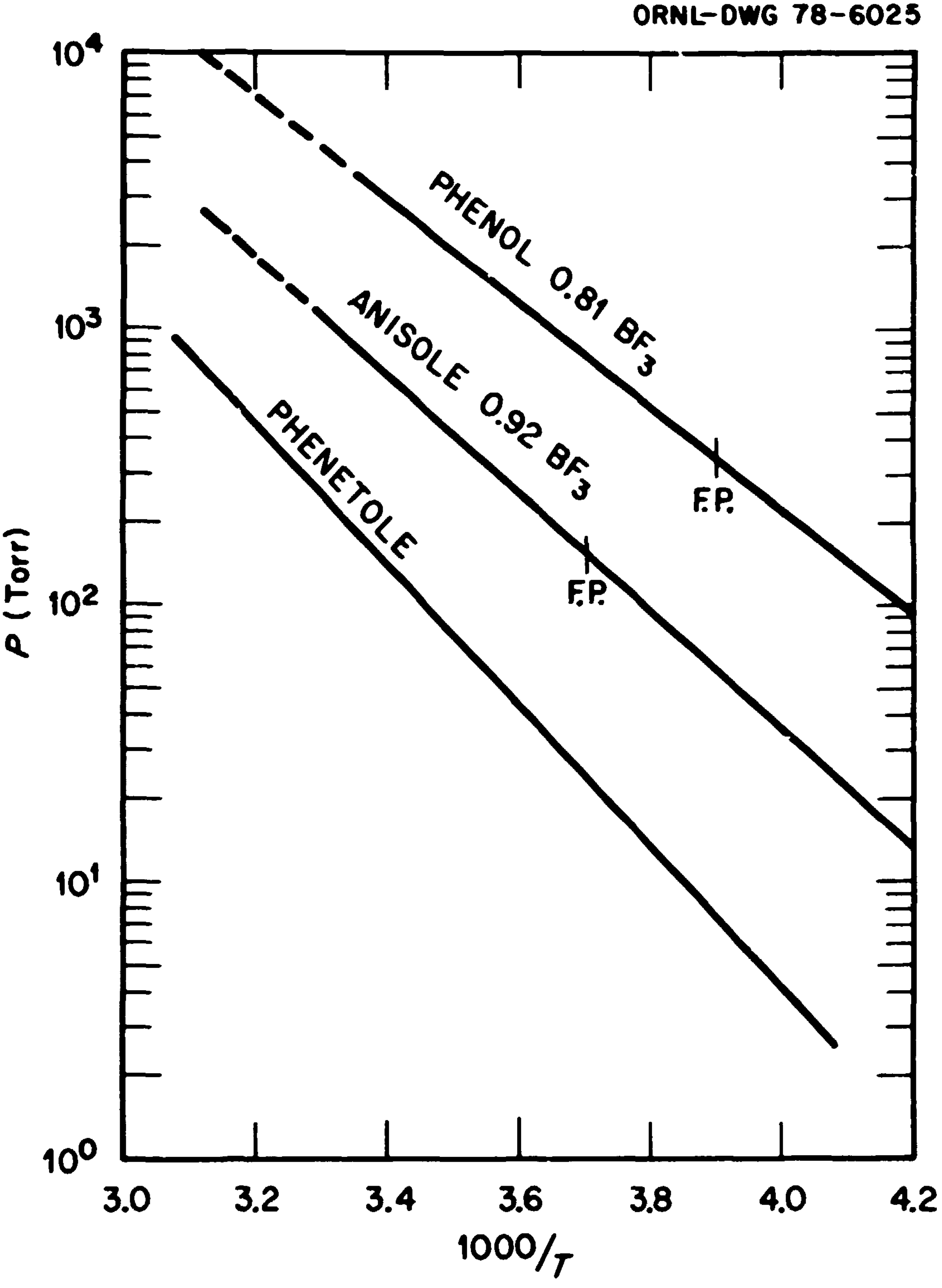

Fig. 5. Comparison of vapor pressure of anisole·BF$_3$ phenol·BF$_3$, and phenetole·BF$_3$ (38). Pressure of the 1:1 complexes for anisole and phenol is so high that it was not practical to measure in glass apparatus.

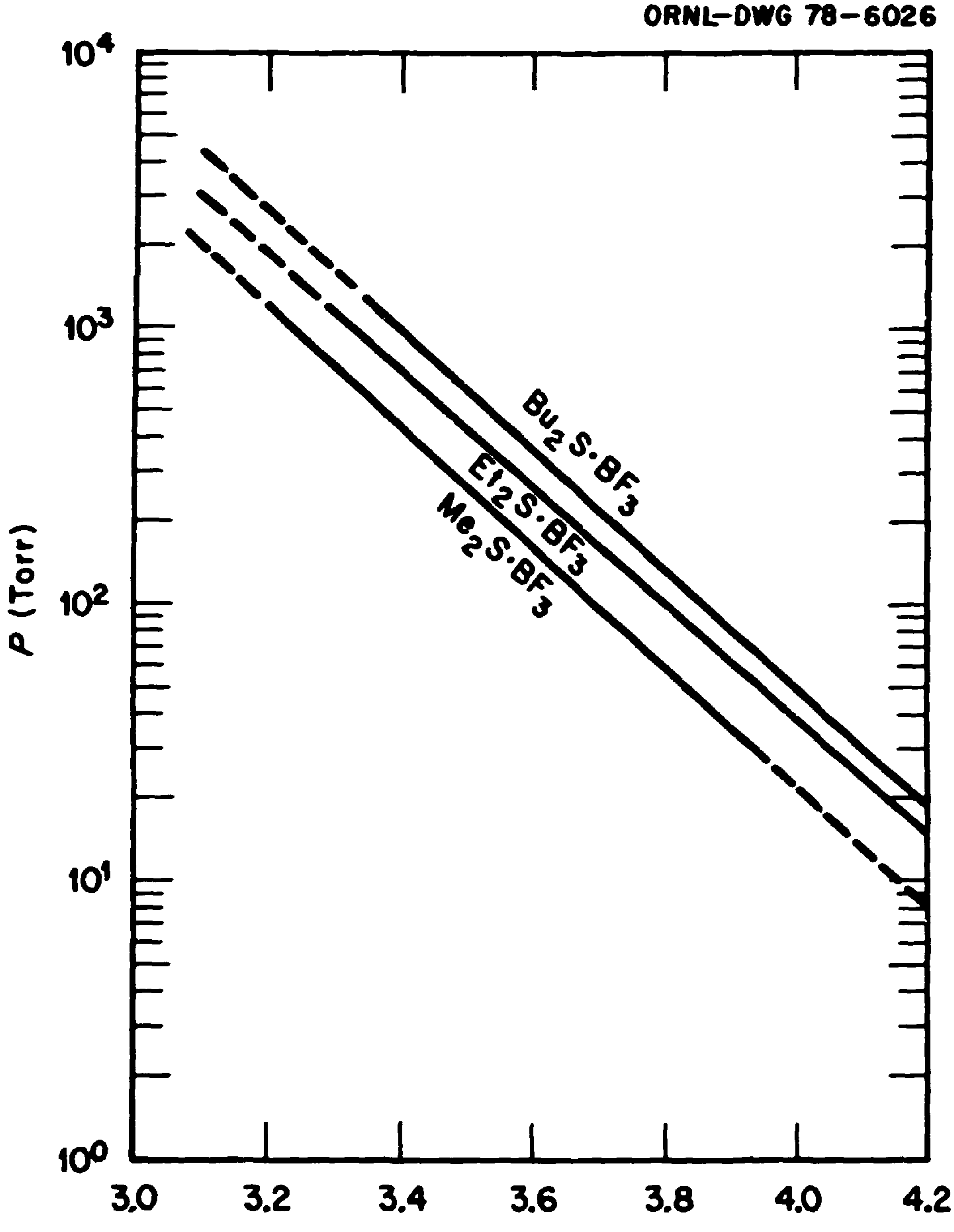

Fig. 6. Comparison of the vapor pressures of $Me_2S \cdot BF_3$, $ET_2S \cdot BF_3$, and $Bu_2S \cdot 13F_3$.

Since anisole-BF_3 and triethyl amine-BF_3 were at opposite ends of the stability scale, so to speak, these two compounds were chosen for rate studies.

Rate of exchange was determined by contacting normal BF_3 complex with enriched $^{10}BF_3$ gas. This was done in the apparatus shown in Fig. 7. To determine rate of exchange, a weighed amount of normal BF_3 complex was transferred to the thin-walled break tube and the tube attached to the flask as shown. The flask was then attached to a vacuum system, a set of sample tubes put in place, the entire apparatus evacuated, and the sample tubes isolated from the flask. A predetermined amount of spiked $^{10}BF_3$ (about 40% ^{10}B) was then admitted to the flask, the stopcock closed, and the flask removed from the vacuum manifold. To contact the two phases, the ball joint was turned in such a manner that the thin-walled tube was broken, allowing the normal complex to react with the enriched gas. The flask was vigorously shaken by hand for a desired interval of time and then the stopcock to the sample tubes opened momentarily to sample the gas phase. From a knowledge of the amount of complex and gas present and the isotopic analysis of each, an equilibrium isotopic composition could be calculated. Analysis of the gas phase after contact showed how much exchange actually took place. Thus time needed for complete exchange could be calculated. Approximately 4 seconds were required for manipulation of stopcocks, etc. Hence exchange time shorter than 4 seconds could not be measured by this technique. For the anisole system, half time for complete exchange was much less than 4 seconds. In fact, exchange was contact limited, i.e., mixing of the phases governed the exchange time. For the ethyl amine system, a half time of about 50 minutes was estimated. Data for the two systems are shown in Table XXIV.

DISCUSSION

A detailed discussion of the data presented in this report can be found in ACS publication #89, Advances in Chemistry Series; Isotope Effects in Chemical Processes, 1969, Chapter 3, by A. A. Palko and J. S. Drury. Hence, the discussion will not be repeated here.

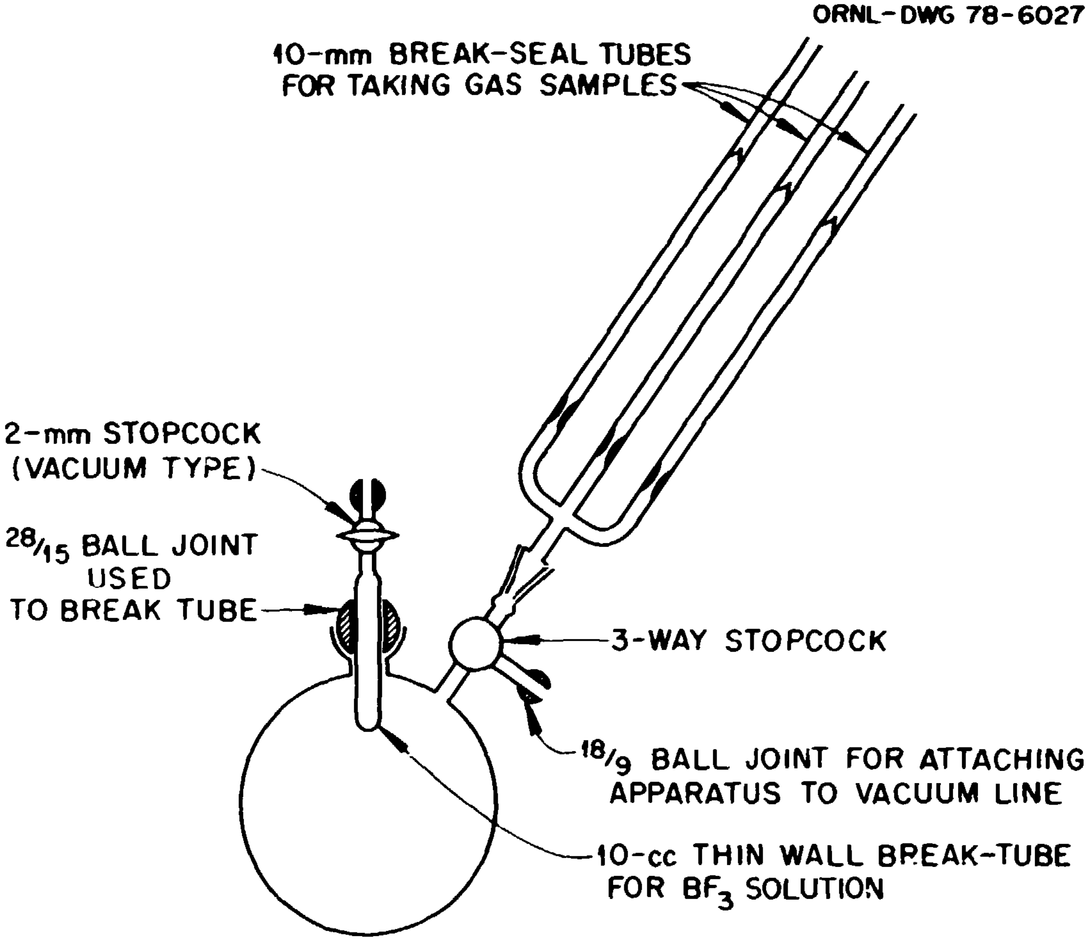

Fig. 7. Apparatus used to study exchange rate

Table XXIV. Rate of Exchange for the Reaction
$^{10}BF_3(gas) + {}^{11}BF_2\cdot Complex(liq) \rightleftarrows {}^{10}BF_3\cdot Complex(liq) + {}^{11}BF_3(gas)$

Weight of Complex (g)	Vol. BF_3 cc STP	Time of Expt.	Meas. % ^{10}B Before	After	Calc. % ^{10}B at Equil.	Calc. % Exchange
Anisole						
9.04(a)	170.6	2 min.	1.034(b)		-	-
10.523	224.5	15 sec.	40.71	23.05	23.2	100
10.207	164.0	7 sec.	40.82	23.96	23.45	90
Triethyl amine						
10.48(c)	128.6	15 sec.	47.19	44.41	21.70	10.9
11.296	160.3	30 sec.	47.19	44.12	22.03	12.2
12.737	147.8	5 min.	25.26	23.55	20.10	33.1
12.083	126.3	30 min.	25.26	23.14	20.05	40.7
(same expt.)		60 min	25.26	22.46	20.05	53.6

a. Complex was 35.2% BF_3 = 0.87 m. BF_3/m. anisole.

b. $^{10}B/^{11}B$(before $^{10}B/^{11}B$(after) = 1.034 total separation.

c. Complex 1:1 $Et_3N:BF$ = 169.01 g./m.

It is appropriate, however, that we present a visual comparison of the major results of this study. Figure 8 is a composite of all the α data. Figure 9 shows variations of α with heat of association of the donor molecule. Figure 10 shows differences in the slope of the α curves when the data points are treated differently in making the least-squares calculations. Ethyl ether and ethyl sulfide showed the greatest discrepancy between the two methods of treatment. The unity treatment more nearly approximated the graphical solution. Tables III and IV are a compilation of the two treatments. Figures 11-14 show the effect of donor atom and of the substitution of various groups on that atom. Figures 15 and 16 show the minimum number of theoretical stages and the reflux ratio required to achieve a given enrichment for a given effective single stage separation factor.

Figure 17 shows the only conclusive data we obtained for a BCl_3 organic complex that showed any degree of stability. Boron trichloride is much more reactive than BF_3 and hence most BCl_3 complexes dissociate with irreversible decomposition or do not form at all. The BCl_3 reacting with the organic rather than adding to it.

Vapor pressure as a function of temperature and composition for various BF_3 complexes is shown in Figures 18-23.

The author would like to thank Larry Landau for the many isotopic analyses he performed during this study. He would also like to thank J. S. Drury, who was our group leader, for his suggestions and criticism and Dr. Taylor, our director, for his leadership.

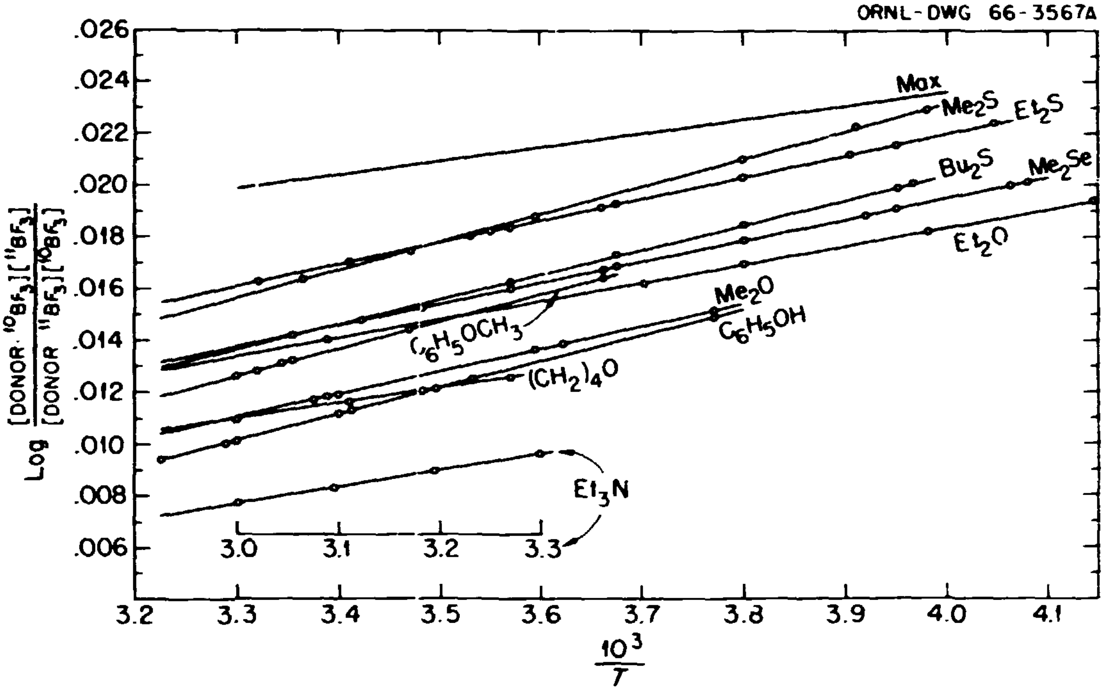

Fig. 8. Composite of all "α" data

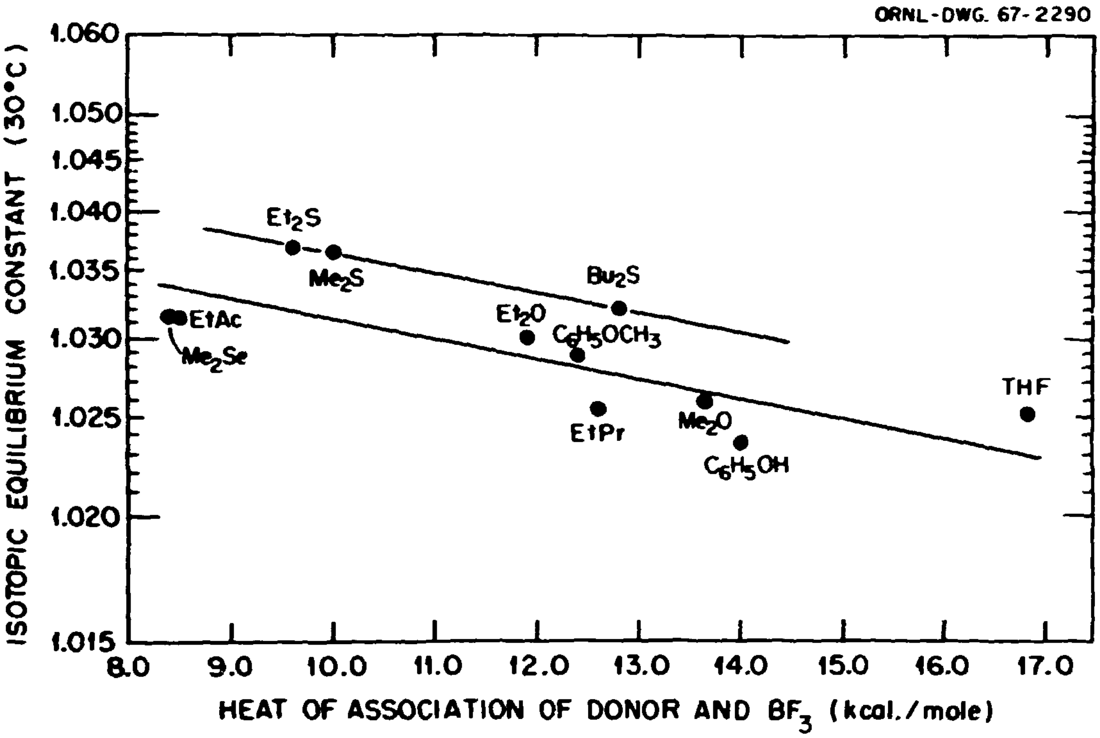

Fig. 9. Variation of isotopic separation factor with heat of association of BF_3 complex.

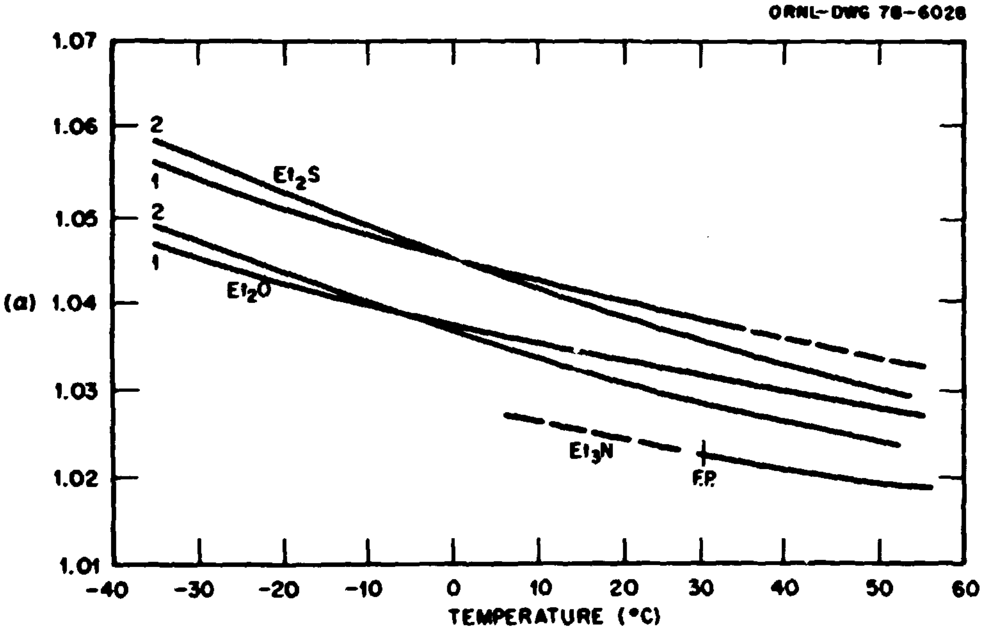

Fig. 10. Comparison of α curves for the Et_2O, Et_2S, Et_3N-BF_3 systems. (1) Data points weighed as $1/\sigma^2$, (2) data points weighed as unity.

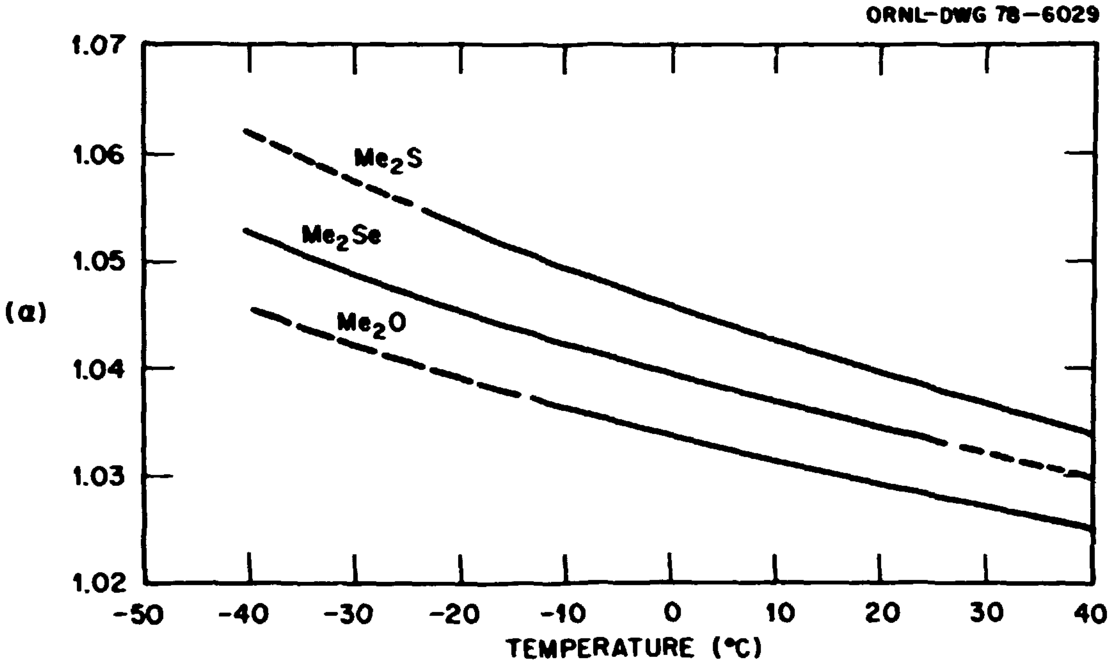

Fig. 11. Comparison of the α curves for the Me_2O, Me_2S, and Me_2Se-BF_3 systems.

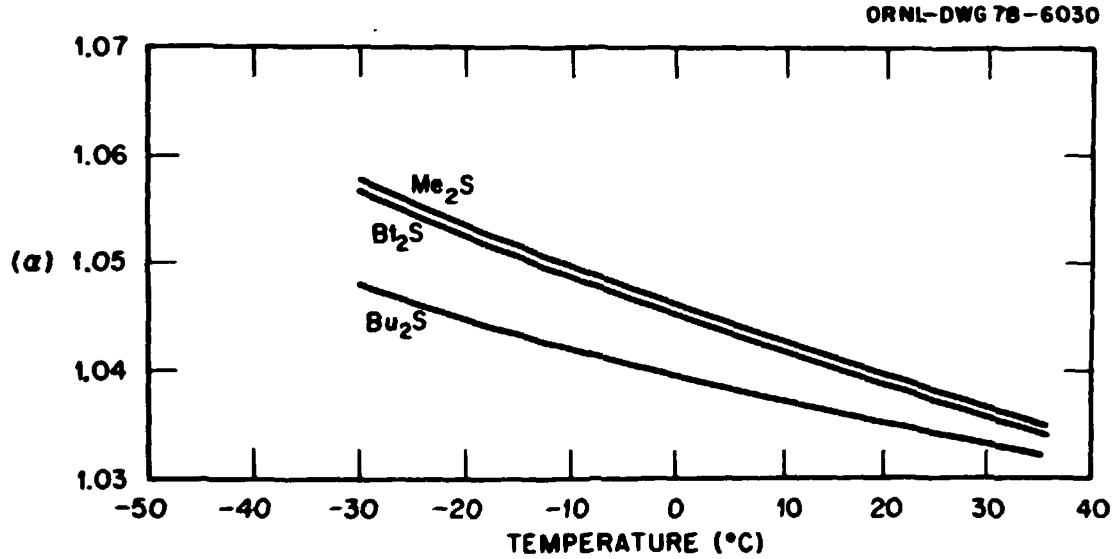

Fig. 12. Comparison of α curves for Me_2S, Et_2S, and Bu_2S-BF_3 systems

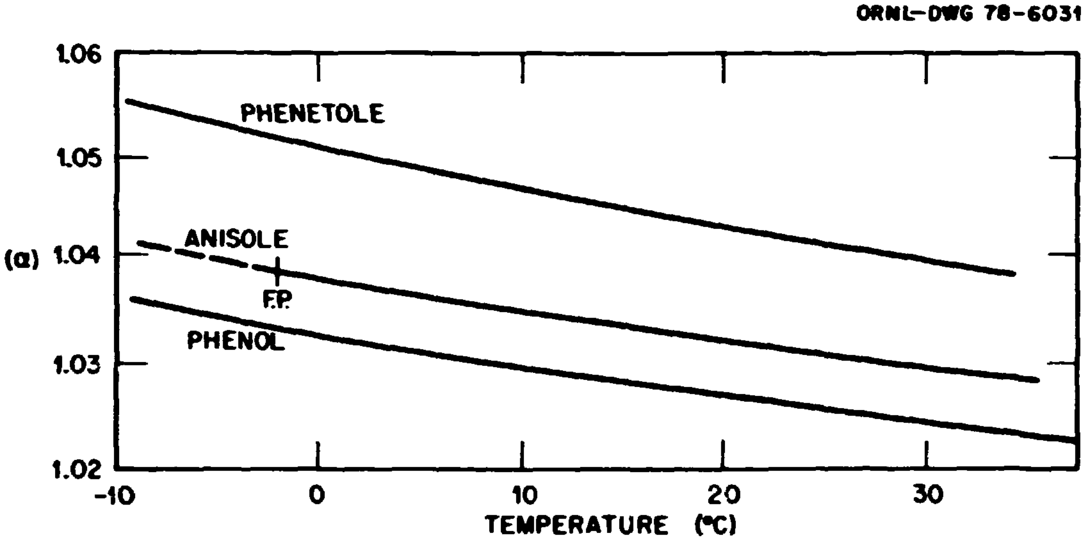

Fig. 13. Comparison of α curves for PhOMe, PhOH, and PhOEt·BF₃ systems.

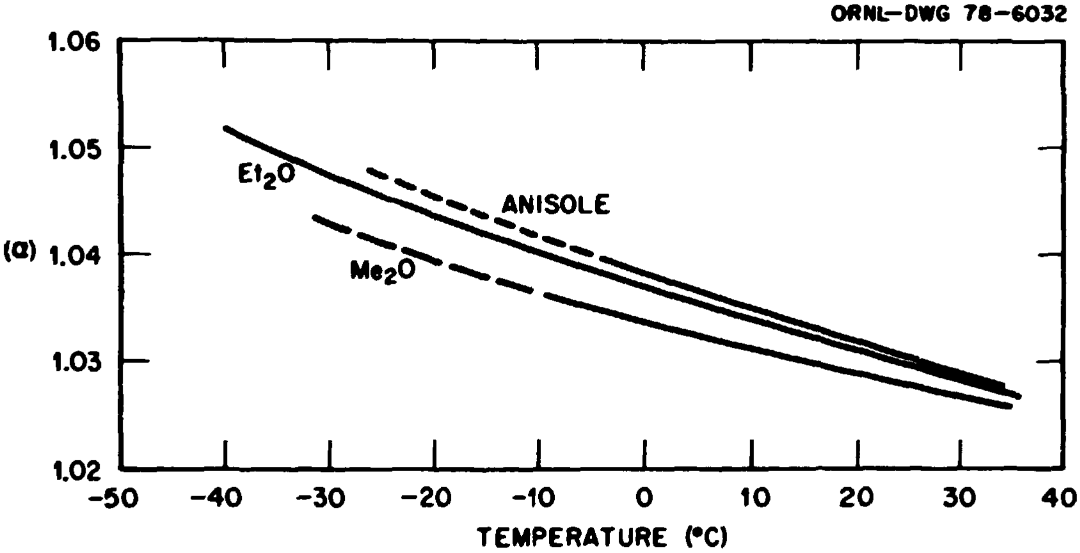

Fig. 14. Comparison of α curves for the Me_2O, Et_2O, anisole-BF_3 systems.

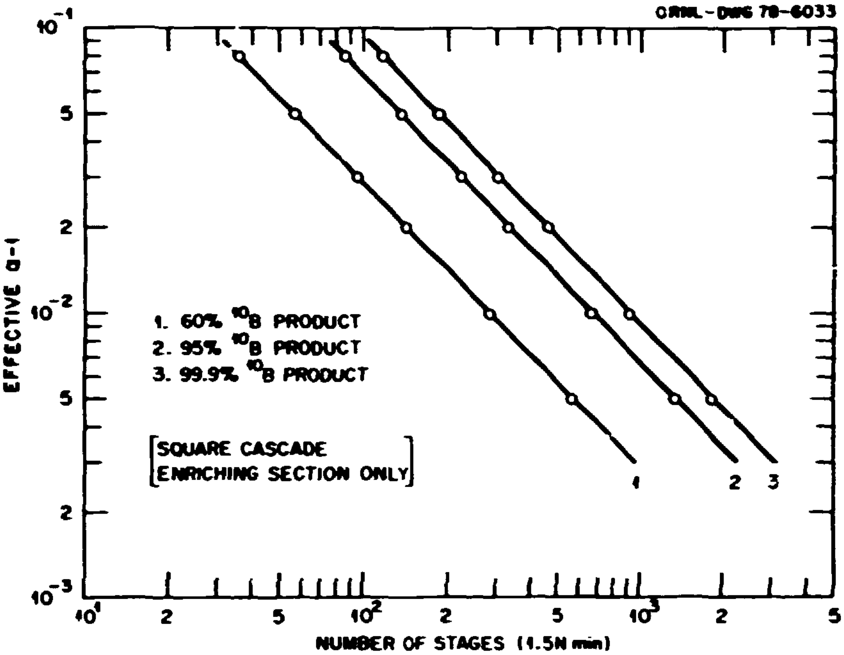

Fig. 15. Number of stages required as a function of effective α and degree of enrichment for a ^{10}B plant.

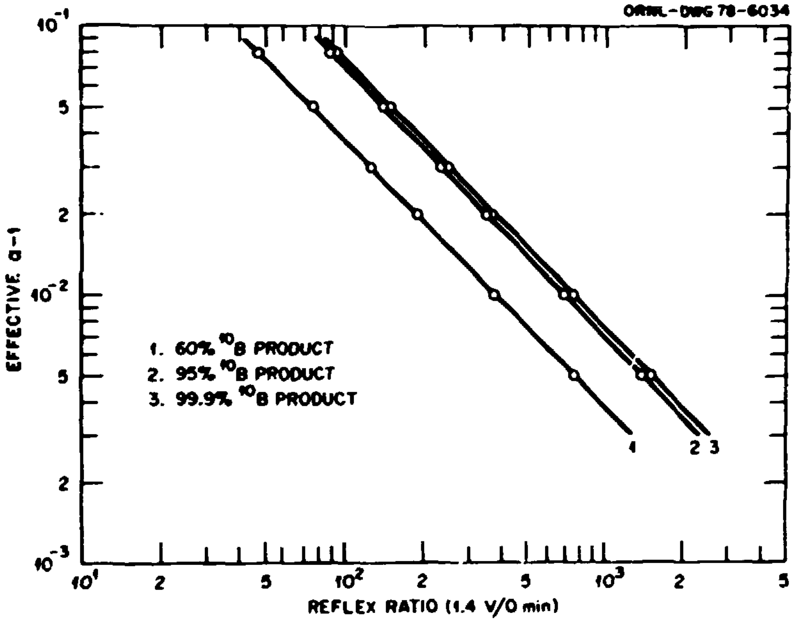

Fig. 16. Reflux ratio as a function of effective and degree of enrichment for a ^{10}B plant.

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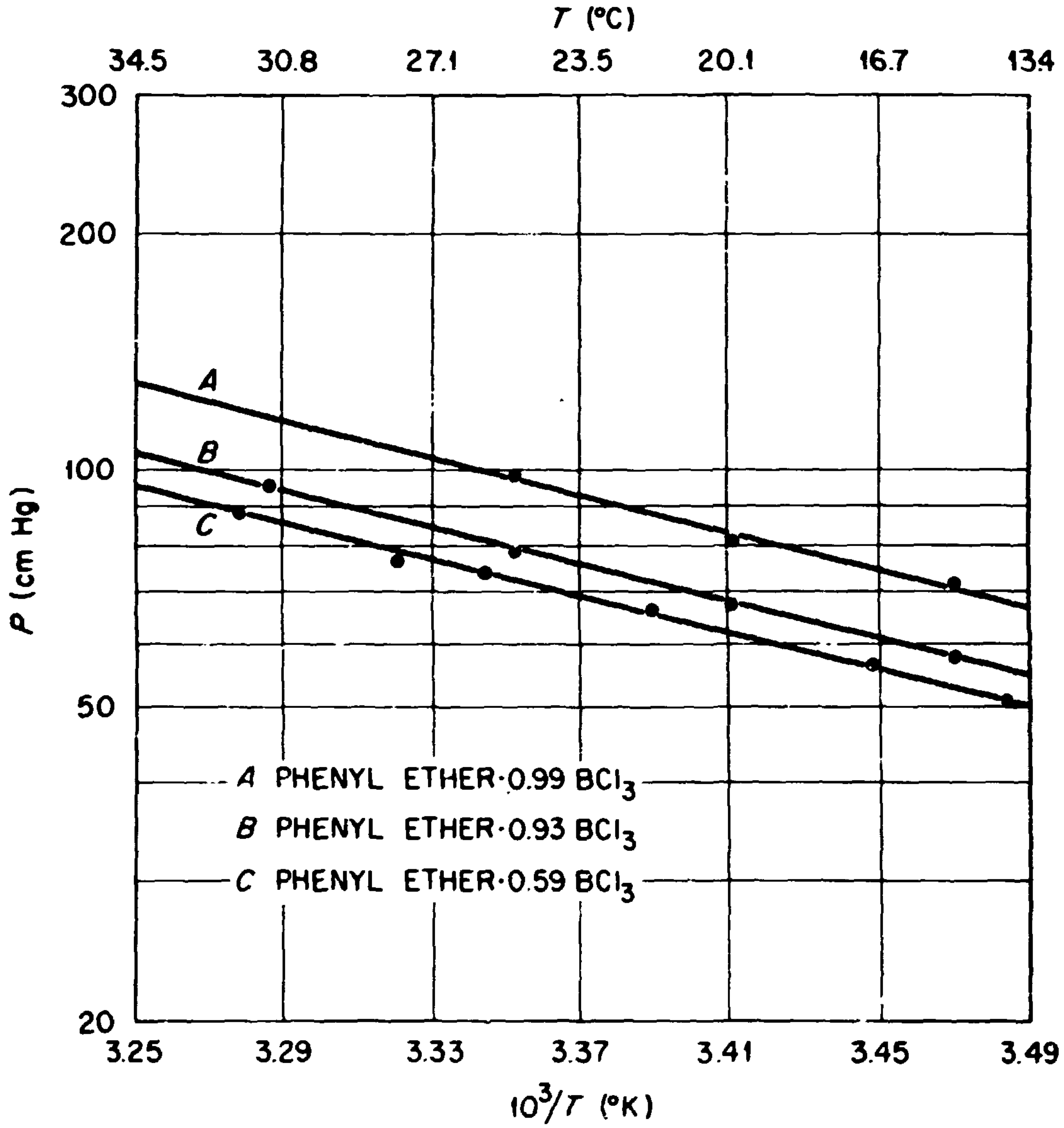

Fig. 17. Vapor pressure - composition for diphenyl ether-BCl_3.

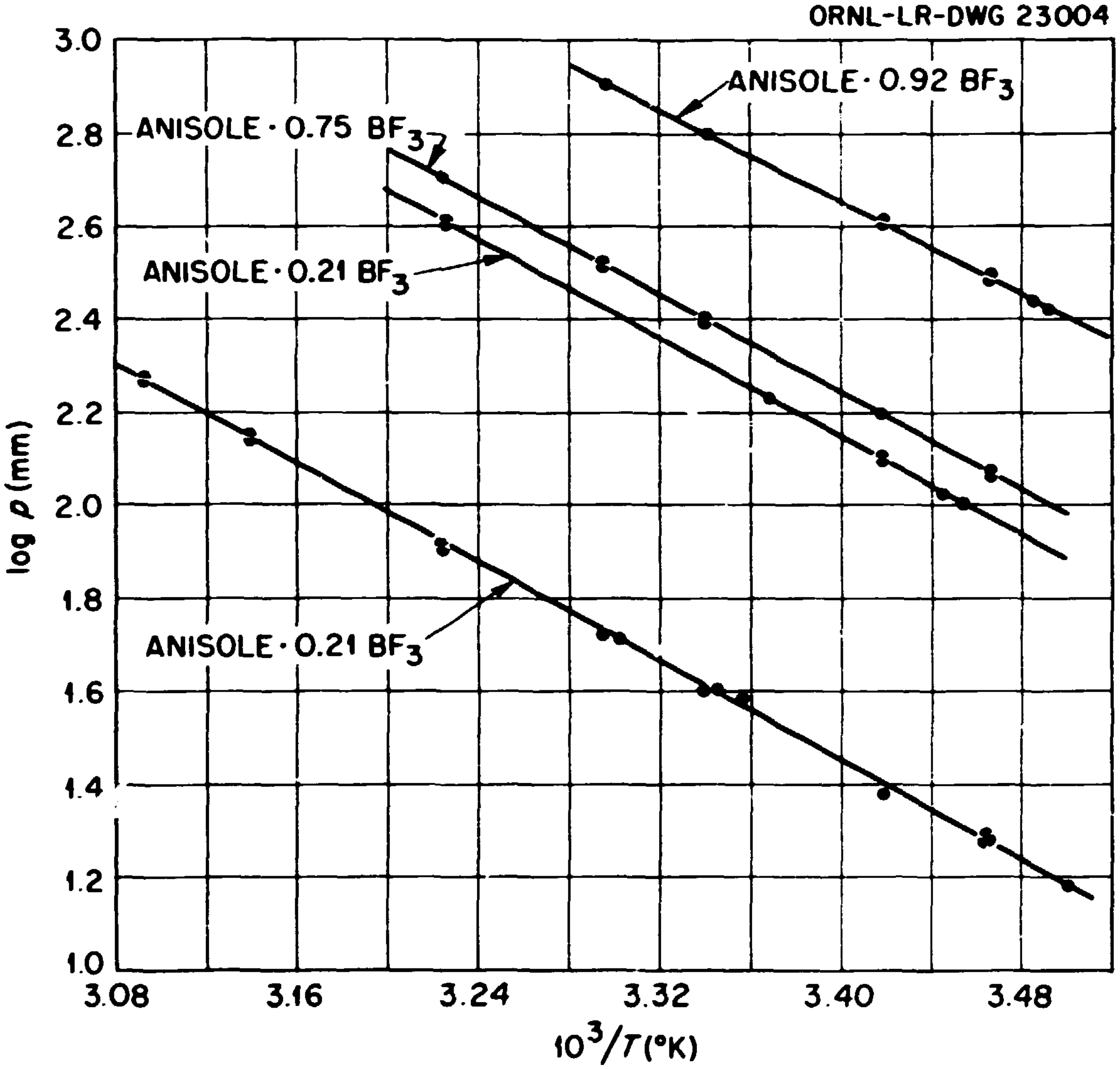

Fig. 18. Vapor pressure of anisole-BF$_3$ solutions.

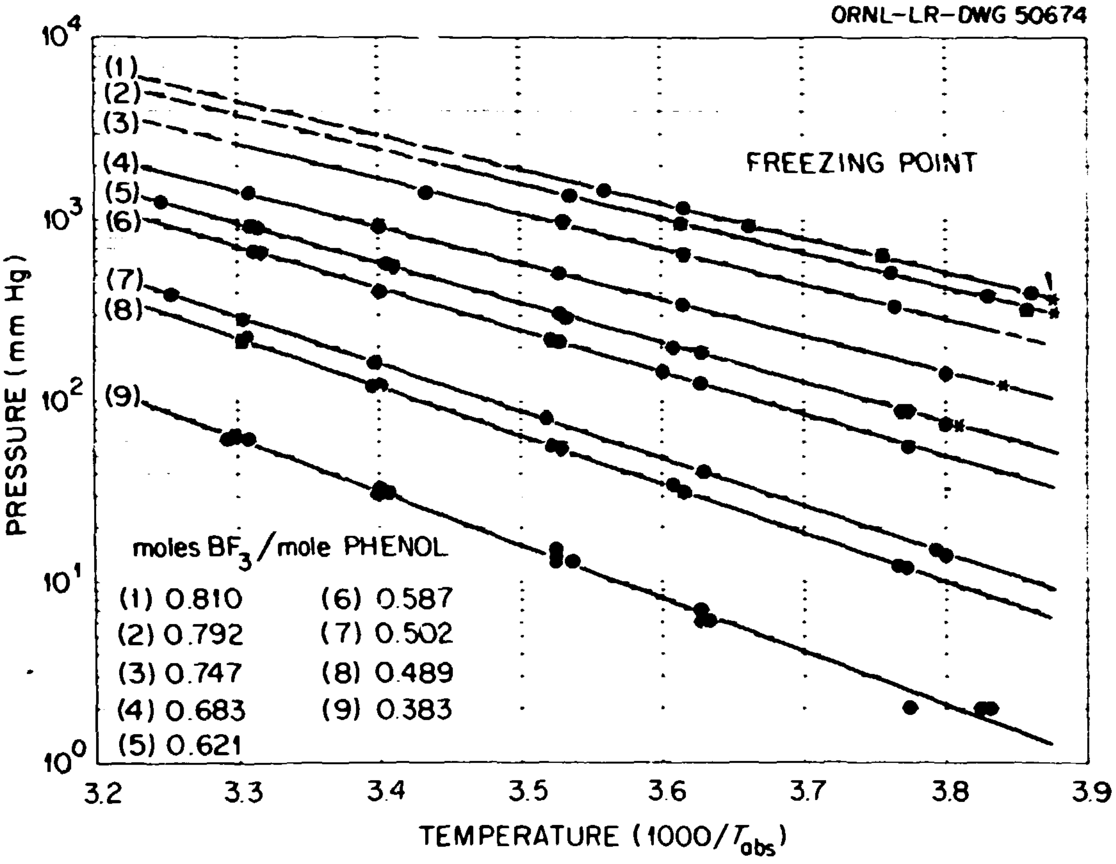

Fig. 19. Vapor pressure of phenol-BF_3 solutions

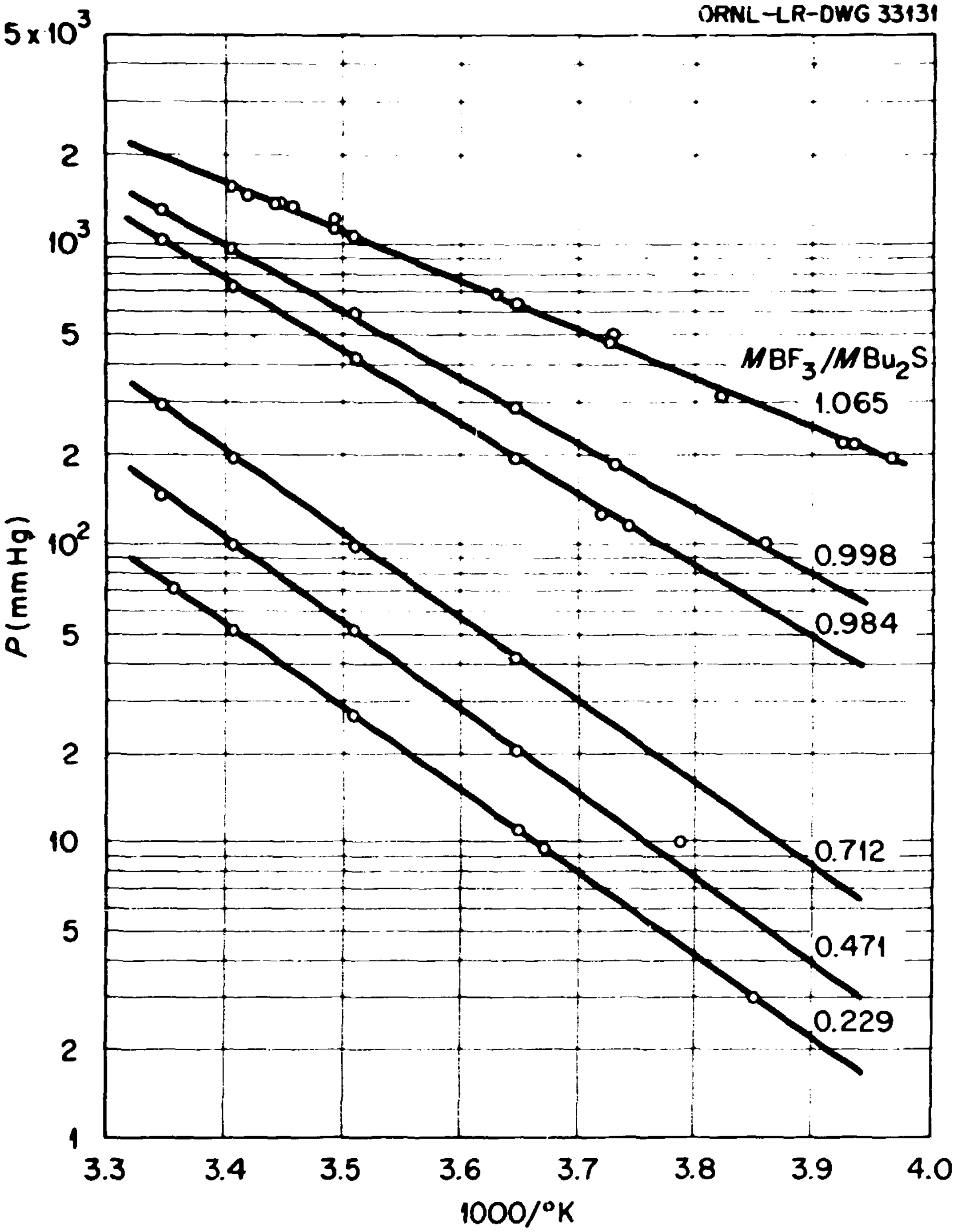

Fig. 20. Vapor pressure of n-butyl sulfide-BF₃ solutions

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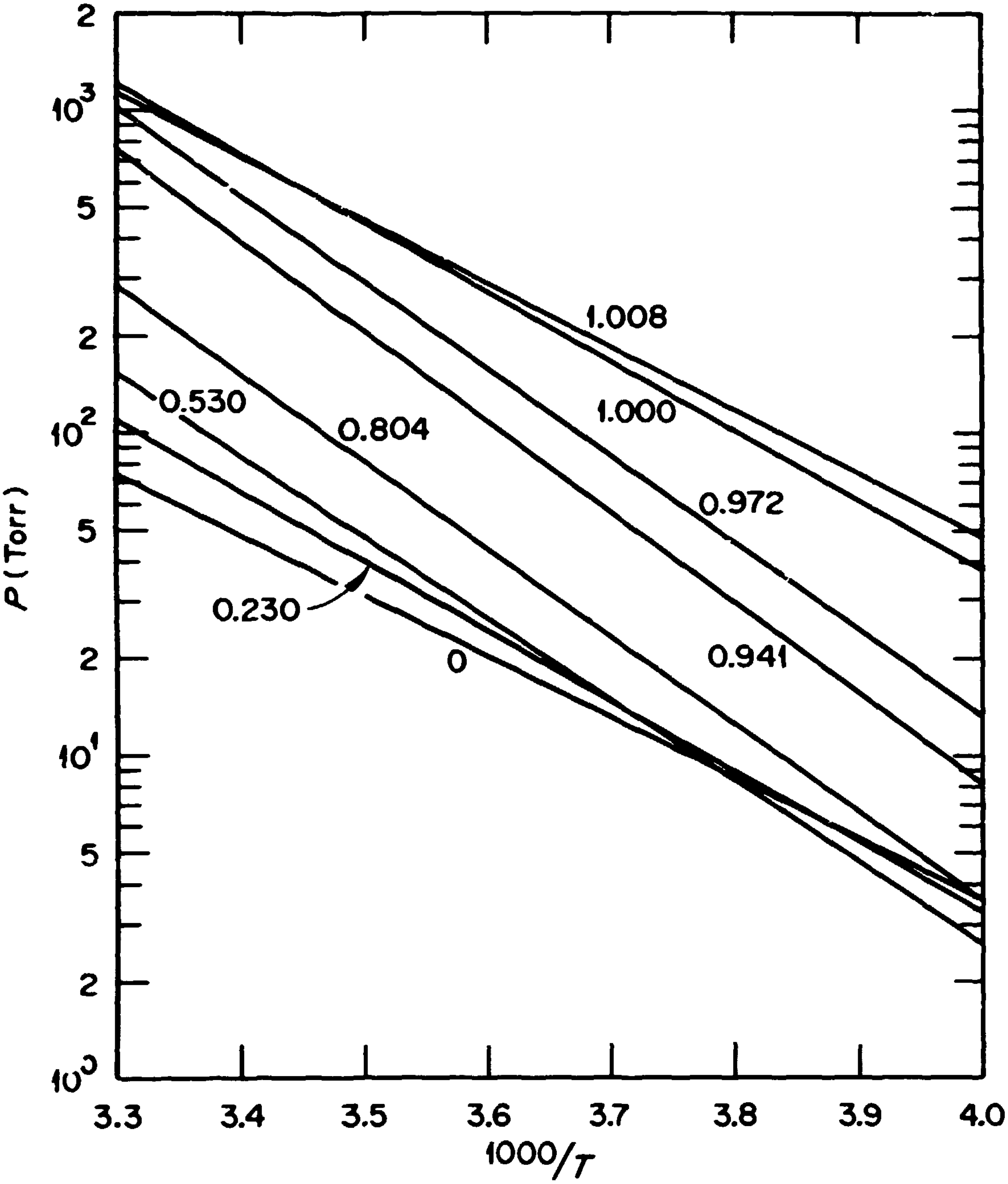

Fig. 21. Vapor pressure for Et_2S-BF_3 solutions (moles BF_3/mole sulfide.

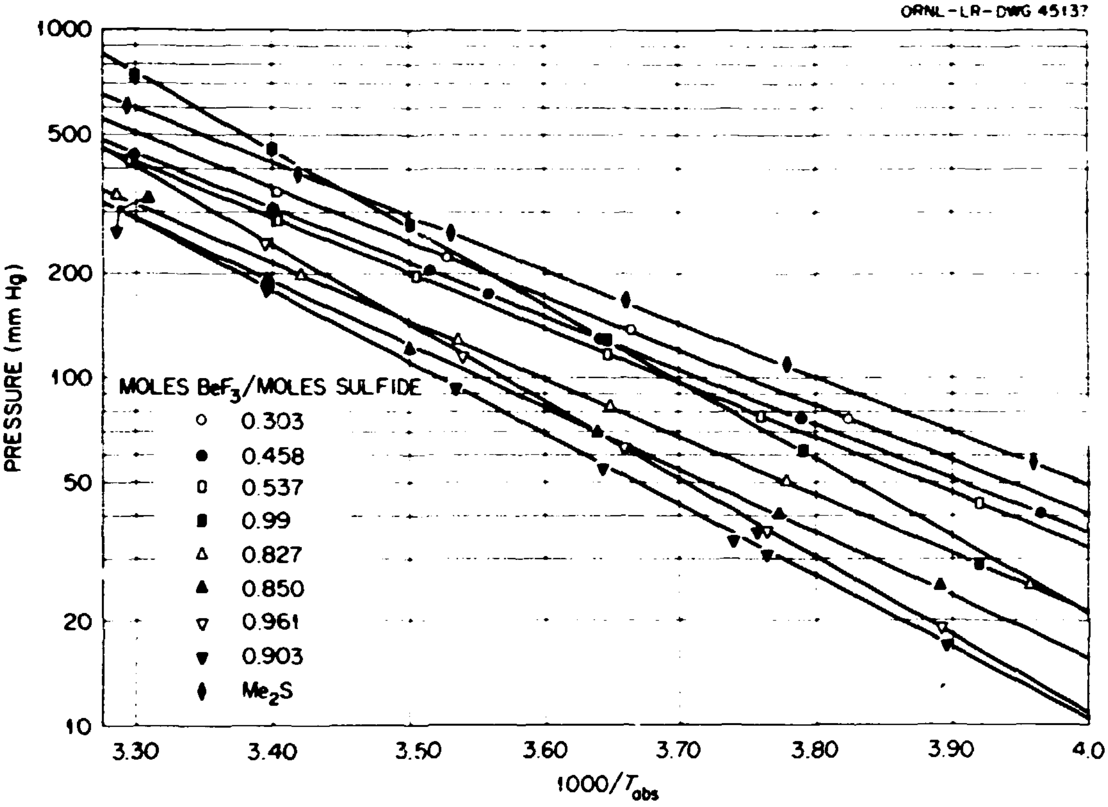

Fig. 22. Vapor pressure of Me_2S-BF_3 solutions.

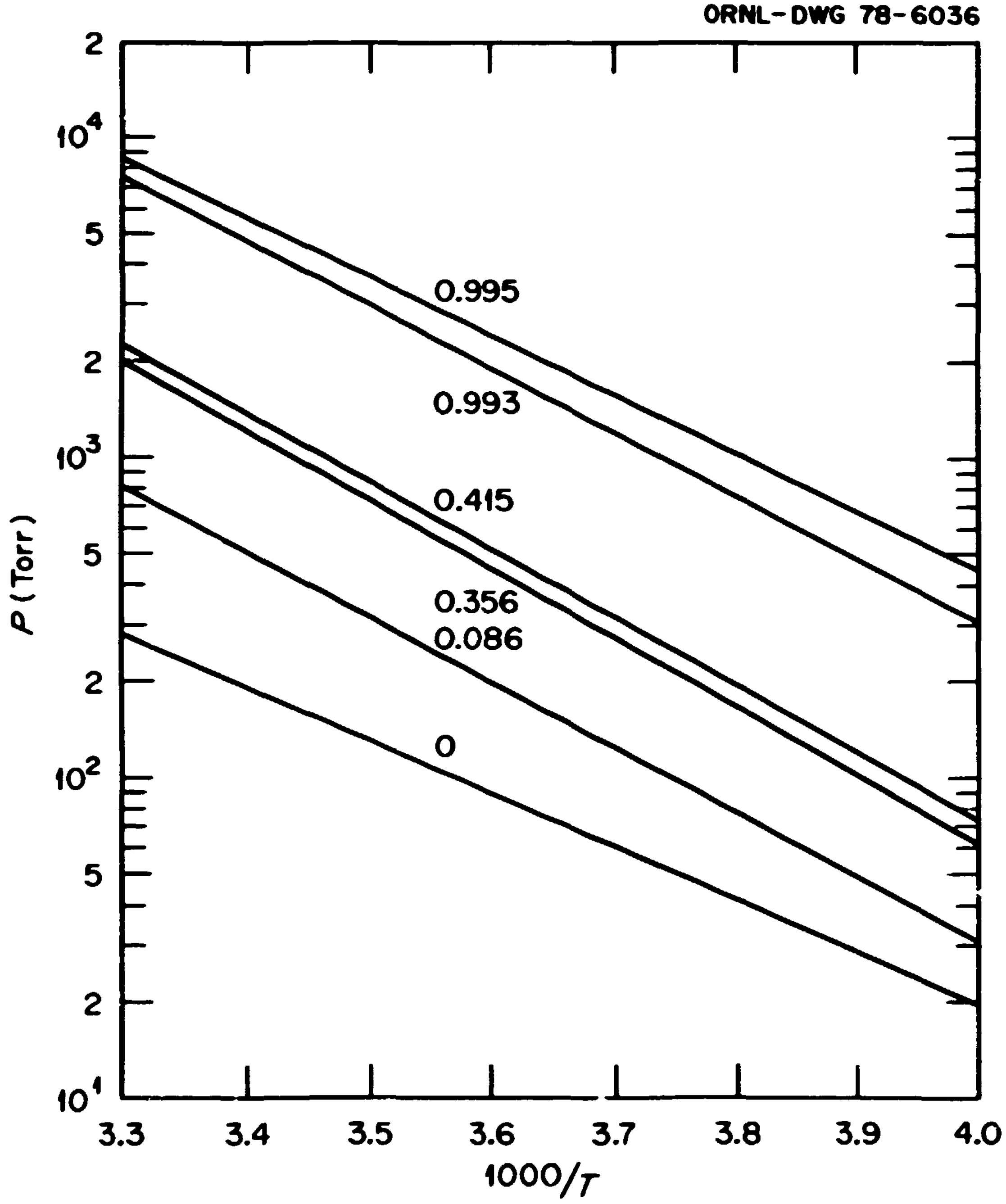

Fig. 23. Vapor pressure of Me_2Se-BF_3 solutions (moles BF_3/mole Me_2Se.

APPENDIX A

Tables of raw α and vapor pressure data for the various compounds covered during this research.

Table XXV. Summary of α Studies $ET_2O\cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α
22	1.0326
	1.0363
	1.0303
	1.0361
	1.0327
-3	1.0343
	1.0374
	1.0388
	1.0422
	1.0428
-10	1.0371
	1.0336
	1.0494
	1.0352
	1.0389
-22	1.0388
	1.0375
	1.0388
	1.0404
	1.0419
	1.0432
-32	1.0553
	1.0561
	1.0487
	1.0540
	1.0547
	1.0467

Table XXVI. Summary of α Studies $Bu_2S\cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α
25	1.0321
	1.0335
	1.0372
	1.0361
7	1.0332
	1.0393
	1.0391
	1.0383
-1	1.0354
	1.0381
	1.0388
	1.0404
-10	1.0374
	1.0481
	1.0488
-20	1.0471
	1.0486
	1.0490
	1.0475
-21	1.0406
	1.0427
	1.0454
	1.0408

Table XXVII. Summary of α Studies
$Et_2S\cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α	Temp. °C	α	Temp. °C	α
28	1.0305	7.0	1.0474	-17	1.0483
	1.0329		1.0449		1.0502
	1.0351				1.0498
	1.0337	0	1.0400		1.0490
			1.0404		1.0504
20	1.0318		1.0539		1.0530
	1.0485		1.0493		
	1.0344		1.0459	-20	1.0454
	1.0367		1.0378		1.0469
	1.0376				1.0694
	1.0364	-1	1.0462		1.0628
	1.0372		1.0456		
	1.0370		1.0476	-26	1.0519
	1.0361		1.0486		1.0525
			1.0475		1.0513
10	1.0448		1.0478		1.0515
	1.0545		1.0491		1.0535
	1.0415		1.0491		1.0533
	1.0388				1.0527
	1.0463	-10	1.0449		1.0531
	1.0476		1.0476		
			1.0467	-34	1.0514
8.5	1.0386		1.0481		1.0524
	1.0378		1.0476		1.0524
	1.0402		1.0618		1.0575
	1.0434		1.0522		
	1.0424		1.0471		
	1.0435				

Table XXVIII. Summary of α Studies
$Me_2O \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α	Temp. °C	α
23	1.0293	3	1.0305
	1.0207		1.0338
	1.0338		1.0285
	1.0348		1.0321
	1.0329		1.0297
	1.0253		
		-8	1.0330
22	1.0264		1.0343
	1.0340		1.0426
	1.0313		1.0345
			1.0339
21	1.0263		1.0328
	1.0259		1.0346
	1.0315		1.0403
	1.0245		1.0397
	1.0250		1.0387
			1.0325
5	1.0373		1.0346
	1.0384		1.0382
	1.0328		1.0333
	1.0328		1.0367
	1.0286		

Table XXIX. Summary of α Studies
$Me_2Se \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α	Temp. °C	α	Temp. °C	α
19	1.0313	7	1.0377	-10	1.0434
	1.0334		1.0369		1.0460
	1.0341		1.0417		1.0508
	1.0354		1.0378		
	1.0300		1.0389	-18	1.0411
	1.0340				1.0436
	1.0326	0	1.0383		1.0417
	1.0313		1.0441		1.0452
			1.0400		
14	1.0377		1.0437	-20	1.0483
	1.0374				1.0457
	1.0365	-1	1.0355		1.0460
	1.0358		1.0424		
	1.0335		1.0387	-27	1.0475
	1.0387		1.0412		1.0496
	1.0356		1.0353		1.0495
	1.0348				
		-10	1.0383	-28	1.0477
10	1.0366		1.0376		1.0453
	1.0391		1.0404		1.0458
			1.0398		
7	1.0371		1.0440	-33	1.0478
	1.0378		1.0486		1.0485
	1.0370		1.0448		1.0493

Table XXX. Summary of α Studies
$PhNO_2 \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α
7	1.0315
	1.0321
	1.0347
	1.0353
	1.0328
	1.0310
	1.0284
	1.0312
	1.0308
	1.0312
	1.0299
	1.0300

Table XXXI. Summary of α Studies
$Et_3N \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α
50	1.0182
	1.0193
	1.0195
	1.0195
	1.0197
	1.0197
	1.0197
40	1.0200
	1.0210
	1.0210
30	1.0219
	1.0222
	1.0226
	1.0227
	1.0227
	1.0226

Table XXXII. Summary of α Studies
$Me_2S \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α
24	1.0366
	1.0402
	1.0387
	1.0355
15	1.0407
	1.0439
	1.0420
	1.0449
5	1.0448
	1.0434
	1.0424
-10	1.0489
	1.0519
	1.0470
	1.0486
	1.0466
	1.0501
-18	1.0547
	1.0503
	1.0471
	1.0541
	1.0462
	1.0474
-22	1.0544
	1.0613
	1.0579
	1.0596

Table XXXIII. Summary of α Studies
$PhOH \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α	Temp. °C	α	Temp. °C	α
37	1.0230	30	1.0224	11	1.0289
	1.0260				1.0287
	1.0285	25	1.0221		1.0262
	1.0268				
	1.0196	21	1.0270	10	1.0259
	1.0238		1.0278		1.0354
			1.0249		1.0380
31	1.0293		1.0253		1.0330
	1.0238		1.0249		1.0226
	1.0289		1.0240		1.0248
	1.0259		1.0256		
	1.0276			0	1.0317
	1.0208	20	1.0252		1.0297
	1.0238		1.0239		1.0308
	1.0208		1.0218		1.0370
	1.0228		1.0235		1.0261
	1.0204				1.0388
	1.0234	19	1.0267		1.0376
					1.0370
30	1.0226	13	1.0291		
	1.0245		1.0266	-8	1.0353
	1.0234		1.0283		1.0345
	1.0248		1.0296		1.0351
	1.0236		1.0304		1.0355
	1.0246				
	1.0241	11	1.0282		
	1.0250		1.0297		
	1.0238				

Table XXXIV. Summary of α Studies
$PhOMe \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α	Temp. °C	α	Temp. °C	α
30	1.0319	25	1.0345	20	1.0266
	1.0289		1.0351		1.0275
	1.0284		1.0331		1.0278
	1.0282				1.0283
	1.0271	22	1.0367		1.0284
	1.0274		1.0352		
	1.0274		1.0316	15	1.0351
	1.0277		1.0344		1.0340
					1.0344
28	1.0304	20	1.0248		1.0332
	1.0316		1.0301		1.0325
	1.0323		1.0305		1.0334
	1.0327		1.0303		
	1.0326		1.0290	0	1.0393
	1.0329		1.0311		1.0408
	1.0315		1.0315		1.0403
	1.0401		1.0263		1.0413
			1.0283		1.0427
26	1.0271		1.0302		1.0408
	1.0282		1.0292		1.0421
	1.0282		1.0353		1.0403
	1.0281		1.0286		1.0366
			1.0299		1.0371
25	1.0350		1.0294		1.0372
	1.0350		1.0280		1.0366
	1.0345		1.0289		1.0356
	1.0332		1.0297		1.0366
	1.0335		1.0288		

Table XXXV. Summary of α Studies
$THF \cdot BF_3(\ell) \rightleftarrows BF_3(g)$

Temp. °C	α	Temp. °C	α
30	1.0259	20	1.0298
	1.0245		1.0327
	1.0232		1.0315
	1.0220		
	1.0214	14	1.0273
	1.0191		1.0288
	1.0291		1.0290
	1.0317		1.0306
	1.0313		1.0282
	1.0319		1.0290
			1.0295
20	1.0226		1.0281
	1.0259		1.0255
	1.0274		1.0253
	1.0270		1.0290
	1.0232		1.0247
	1.0262		
	1.0285	7	1.0286
	1.0267		1.0291
	1.0226		1.0297
	1.0249		1.0319
	1.0243		1.0302
	1.0223		1.0303
	1.0202		1.0314
	1.0225		1.0303
	1.0320		1.0292
	1.0322		1.0282
	1.0308		1.0263
	1.0312		1.0284
	1.0330		

Table XXXVI. Vapor Pressure for the Anisole-BF_3 System
Temp., °C, Pressure, Torr

0.21*		0.75*		0.80*		0.87*	
Temp.	P	Temp.	P	Temp.	P	Temp.	P
12.4	15.1	15.4	115.1	1.1	125	0.3	140
15.4	19.0		115.1	1.2	117		140
15.6	18.9		116.0	1.3	117		132
15.6	19.4	19.4	156.1	15.5	323	11.0	298
19.4	23.7	26.3	249	16.6	357	18.5	503
24.8	38.3		248	17.0	363	21.3	603
25.8	39.8		249	19.4	435	21.5	614
26.3	39.5		249	19.5	436	25.8	799
29.2	52	30.4	327	19.6	440	26.2	823
30.5	53		328	19.6	453	26.5	839
37.1	82	37.1	502	19.7	448	30.4	1059
37.1	82		503	27.1	709	30.6	1064
45.4	138			27.3	715	30.8	1080
45.5	139			30.8	827	35.4	1384
45.5	140			31.5	905	35.5	1383
50.2	186			32.8	975		
	186			33.8	1035		
				34.7	1083		
				35.0	1114		
				35.5	1139		
				35.7	1133		
				36.3	1175		

*Moles BF_3/Mole Anisole

Table XXXVII. Vapor Pressure for the Anisole-BF_3 System
(Continued)

0.86*		0.86 con'td.		0.92*		0.92 con'td.	
Temp.	P	Temp	P	Temp.	P	Temp.	P
0.3	145	25.1	741	0.2	167	27.0	1002
	146		741		167		1002
0.5	149	28.2	902	0.3	172	27.7	1040
0.7	149	28.9	936		172	28.9	1109
0.4	143	29.0	936		172	30.8	1218
	145		937	6.0	256	30.9	1230
	145		936	6.1	261	30.8	1226
3.0	169	30.8	1023		259	34.2	1451
8.0	256	30.6	1008	14.2	438	34.3	1451
10.0	288	30.7	1013		443	34.4	1448
11.0	308		1013	20.1	674	34.4	1443
12.0	335	35.0	1286		676	35.7	1478
12.5	362		1284	20.2	681	35.8	1483
14.2	399	35.1	1286	21.7	741	35.8	1481
16.7	451	35.0	1285	21.3	679	35.9	1544
	451	36.4	1363		681	35.9	1536
19.7	546		1363	21.4	683	35.9	1537
19.6	546		1363	22.3	765		
19.7	543	37.4	1434	25.2	859		
19.3	543	37.8	1462	25.9	874		
	543		1464				
20.0	559	37.9	1475				
20.2	564		1471				
	567	39.0	1543				
25.1	741		1543				
			1543				

*Moles BF_3/Mole Anisole

Table XXXVIII. Vapor Pressure for the Butyl Sulfide-BF_3 System
Temp., °C; Pressure, Torr

0.7696* 0.3795 0.493		0.7696* 0.5590 0.726		0.7696* 0.7350 0.955			
Temp.	P	Temp.	P	Temp.	P	Temp.	P
-50	0	-40	0	-40	3	0	156
-40	2	-30	2	-39	6	5	208
-38	4	-20	6	-37	8		208
-35	4		6	-31	10	5.5	217
	4		6		10	8	241
-21	5	-10	15	-26	11	10	356
-20	5		15	-25	12		358
	5	0	44	-20	24		355
-16	7		39		24	14	444
	7		43		26	15	462
-8	12		43		26		469
	12		41		28		453
0	23	10	96		30		444
	23		98		24	17	504
	23		96		24		504
	23	16	155		21	17.5	556
10	50		155		21	18	595
	52	18	181		30		597
	51		181		29		597
15	75	24	280		27		597
	75	25	297		27	18.3	607
19	101		297	-10	59	19	650
	102		297		59	21	626
23	132				52	22	700
	132				52	23	720
					53	24	766
				-0.5	125		760
					123	25	819
				0.0	164		819
					164	26	893
					167	27	940

*moles sulfide
moles BF_3
moles BF_3/mole sulfide

Table XXXIX. Vapor Pressure for the Butyl Sulfide-BF_3 System (continued)

0.8577		0.8577		0.8577		0.8577	
0.1962		0.4040		0.6107		0.8430	
0.229		0.471		0.712		0.984	
Temp.	P	Temp.	P	Temp.	P	Temp.	P
-13.5	3	-8.5	10	1.0	42	-5.5	116
	3	1.0	20		42	-4.3	126
-1.5	10		20		45		128
	9		22	11.8	100	1.2	196
0.5	10		21		102		196
1.5	11	11.8	52		100	11.8	422
	11		52		100	20.2	730
11.7	27		54	20.2	190		731
11.8	27	20.2	99		190		730
20.2	52		98	20.5	195		711
	52		100		195		711
20.5	51	25.7	146	25.8	291	25.8	1023
24.8	70		148		291		1028
30.4	111		147				1028
							1030
							1028

Table XI. Vapor Pressure for the Butyl Sulfide-BF_3 System (continued)

0.8577 0.8568 0.998		0.8577 0.9124 1.060				0.7573 0.7650 1.01	
Temp.	P	Temp.	P	Temp.	P	Temp.	P
-30	13	-41.5	62	1.0	638	-3	271
-12	106		62	1.0	640		270
-5	183	-35	86		641	11.8	645
1.0	284		86	2.4	691		644
11.8	571	-26.5	141		696	19.5	1015
	573		140	11.2	1048		1005
20.1	947		140		1049		1005
	947	-21.2	196	11.8	1053		
20.2	944		196		1053		
	944		196		1053		
25.8	1293	-19	216		1051		
	1292		216		1052		
		-18.5	217	13.2	1133	Temp.	P
			217	15	1224		
			216	16.9	1331		
		-11.5	315		1332	-4.8	500
			315		1334		500
			315	17	1337		501
		-4.8	484	17.2	1342	11.7	1067
			484		1341		1068
			490		1341		1067
			490	19.3	1485	20.2	1547
			483		1486		1542
			483		1486		

Table XLI. Vapor Pressure for the Ethyl Sulfide-BF_3 System
Temp., °C; Pressure, Torr

0.151* 0		0.1509* 0.1328 0.881		0.1376* 0.1106 0.804		0.1376* 0.1232 0.895	
Temp.	P	Temp.	P	Temp.	P	Temp.	P
-17	3	-36	0	-47	1	-46	0
-16.8	4	-28	2.5	-33.5	3.5	-32.5	2
	4.5	-26	3.5	-33.5	3.5	-32.8	2
-16.5	5	-23.5	4.5	-18	6.5	-37.2	4
-16.5	4	-20.5	6	-17.9	6.5		4
-6.5	9.5	-20	6		6.5	-17.5	9
-6.2	9.5		6	-16.9	7.0	-12.2	15
3.0	17	-19	7	-16.8	6.5	-12.1	15
	17		8	-16.7	6.5	-5.5	32
3.2	18	-11.1	15	-12.0	9.5		32
	18	-10	16		9.5	2.5	57
11.2	28.5		16		10		57
	28.5	2.2	50		11	9.8	105
	28.5	3.2	52		11		108
11.7	26.5		52	2.6	36.5		108
23.1	47.5	9.8	93	2.8	34		108
23.1	47.5		93		35	10	109
23.2	48	21.3	233		36.5		109
23.5	48	21.5	248	9.2	60.5	21.0	254
		22.2	251		61.5		254
			255	9.8	62.5	21.2	258
			255		62.5		258
					62	21.5	257
					62	21.5	259
				21.0	158	30.2	484
					158		486
					159		486
				21.2	154		489
					156		
				30.6	300		
				30.6	300		
				30.8	303		
				30.8	303		

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*Moles sulfide
Moles BF_3
Moles BF_3/mole sulfide

Table XLII. Vapor Pressure for the Ethyl Sulfide-BF_3 System (continued)

0.1611*		0.1611*		0.1611*		0.1859*	
0.0365		0.0850		0.1623		0.1807	
0.227		0.530		1.007		0.972	
Temp.	**P**	**Temp.**	**P**	**Temp.**	**P**	**Temp.**	**P**
-51	0	-52	0	-51.8	5	-32.8	4
-39	1	-36.5	1	-32.7	22		4
-39	1.5		1		22	-33	5
27	3.0	-30.5	1.5	-32.8	24		5
	3.0		1.5		24	-18.2	20
-16	4.0	-20	3.0	-18	67		20
	3.0		3.0		67	-18.9	23
-16.8	6.5	-16	5.0	-4.8	169	-18.2	23
	6.0		5.0		169	-18.9	23
	6.0	-4.8	14	11.8	448	-4.5	76
-5.0	11.5	-4.9	14		448		77
-4.5	11.5	2.0	21.5	21.3	739	-4.8	79
11	33		21.5		739		80
	33	13.0	48			-4.7	82
13.4	37	13.1	48			11.2	277
	37	13.5	48			11.5	279
21	61	13.5	47				280
	61	21.8	87				279
30.0	108		87			21	514
30.0	108		89				516
30.8	108	22.0	89				519
		30.5	158				518
			158				516
			159			30.5	993
			159				998
							993
							1000
							1000

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*Moles sulfide
Moles BF_3
Moles BF_3/mole sulfide

Table XLIII. Vapor Pressure for the Ethyl Sulfide-BF_3 System (continued)

0.1376*		0.1509*		0.1512*		0.1859*	
0.1377		0.509		0.1512		0.1750	
1.0007		1.0003		1.000		0.9414	
Temp.	**P**	**Temp.**	**P**	**Temp.**	**P**	**Temp.**	**P**
-44.8	7	-42.7	3	-54	3	-53	0
-44.5	6		3	-51	3.5	-32.9	3
-38.5	11	-41.2	4	-49	4.5		3
-36	13	-40	5		4.5	-33.5	4.5
-34	28	-33	13	-43	7.5		4.5
-31	23		13		7.5	-18.1	12
	23	-29.2	21		8.0		12
-17	72		21		8.0	-18.5	13
	72	-20.1	46	-36	14		13
	71		46		14	-18.2	15
	71	-19.2	50	-29.5	26		15
-16.8	72		50		26	-5	46
-5.0	162	-10.8	93		25		46
-4.8	164		93		25		48
2.8	261		92	-18	60		48
	261		91		60	-4.2	49
3.1	264	-0.8	186	-11.5	91	-4.8	48
10.2	401	2.8	239		91	12.2	190
10.0	403		237	-11.7	93		190
	406		249		93	12.5	193
21	720	3.2	253	0	199		194
	720		249		199	12.3	192
30.1	1130	9.3	359		197		192
	1128		360		199	13	207
	1130	10.6	400		197	21	375
	1126	10.7	400		203		377
	1128	20.8	709	10.0	362		373
	1128		707	10.2	373	21.2	376
		21.0	704		375		376
			704		372		378
					371		378
				20.5	668	30.2	678
					668		682
				21	679		680
					678	30.5	686
				22.5	720		688
				27.2	924		690
					920		688
				27.5	926		688

*Moles sulfide
Moles BF_3
Moles BF_3/mole sulfide

Table XLIV. Vapor Pressure of Me_2S

Temp	P	Temp.	P	Temp.	P
-36.5	21	-8.3	111	10.1	263
	21		111		266
	21		111		266
				18.8	382
	21		114		382
-35.5	23	-0.5	162		382
	23		162	19.0	386
	23		163		387
-21.5	53		163		388
	53		163		389
	53	0.0	168		389
-20.5	57		169	19.2	390
	57		171		390
	57		172		390
	57		174		390
	56		178	19.4	394
	56	9.5	251		394
	56		255	30.5	598
-8.5	106		255		601
	106		256		601
	106	9.7	260		601
	107		260	31	609
	108		260		610
-8.3	110		260		613
	110		261		613
	110		263		

Table XLV. Vapor Pressure for Me_2S-BF_3 System
Temp., °C; Pressure, Torr

0.3170^a		0.3170^a		0.2789^a		0.1770^a	
0.0962		0.2095		0.1497		0.1504	
0.304		0.661		0.537		0.850	
Temp.	P	Temp.	P	Temp.	P	Temp.	P
-37	18	-33.4	18	-41.5*	10	-42.8	12
	18		18		10	-32.9	16
-30	27		18		10		15.5
	27	-29.7	23	-30.5*	21		16
-29.5	28		23		21		15.5
	28		23		22	-30.1	18
	28	-23.4	29		20		18
	28		29		21	-17.7	25
-11.5	75		29	-18	42		24
	75	-17.2	40		42		24
-11.3	76		41	-17	45		25
	76		41		45	-8.8	40
	76	-16.8	42	-73	77		40
-11.0	78		42		77		41
0.0	135		42		77		40
	135		42		77		41
	135		42	1.0	116	1.5	69
0.1	138	-11.5	56		116		69
	140		56		118		69
	141		56		117		69
	141		56		116		69
0.2	142		56		117	12.6	108
10.1	217		56		118		108
	217		58		116	12.8	121
	218	0.2	96	12.0	196		121
	218		96		197		120
10.3	224		97		193	21.8	189
	224		97	12.5	199		189
	225		97	20.3	278		188
	225		97		278		188
10.8	229		97	20.9	284		188
20.5	337	10.7	151		285		188
	337		153	30.3+	413	30.7+	307
	339		155		425		308
20.7	346		155		426		306
	346		155	35.0+	489		306
	348		155		493		
			156	35.3+	504		
		21.1	239		504		
		21.2	240				
		21.3	241				
		21.6	243				
			244				
			244				

[a] Moles sulfide
Moles BF_3
Moles BF_3/mole sulfide

*Below freezing point of system.

+Above R.T., hence some condensate in manometer. Not used in calculating vapor pressure curves.

Table XLVI. Vapor Pressure for Me_2S-BF_3 System
(continued)

0.3396[a]		0.3396[a]		-			
0.1555		0.2808		-		1:1	
0.458		0.827		1.00			
Temp.	P	Temp.	P	Temp.	P	Temp.	P
-29.6	25	-42[*]	9	-22.5	23	20.5	450
	25		9		23		449
	25		10		23		417
	25	-33.5[*]	13		22	20.7	422
	25		13		23		422
-20.9	40		13	-21	30		440
	41		13		29	21.3	428
	40				29		455
	41			-20.5	29	21.4	455
-9.4	74	-29.7[*]	15		29	21.5	425
	74		15	-13	58		450
	74		15	-12.5	58	30.0	726
-9.5	80		15		54		724
	80	-22.2	19		53	30.3	687
1.4	128		19		53		686
	128	-20.4	25	-12	58		740
	128		25		59		738
	128		25	0	120		701
7.5	173		25		120		701
	173	-9.5	50		123	34.8	863
	173		50	0.5	128		863
	173		50		130	36	885
11.2	203		50		132		885
	203		50	11.7	252	35.2	910
	203		50	12.0	254		910
	203	1.0	82		255	36.2	922
	205		82	12.2	287		922
20.8	307		82	12.3	280		
	307		82	12.6	275		
	307	9.6	127		258		
	307		127	13.0	263		
30.8[+]	437		127	13.3	285		
	437		127	12.5	287		
	437		127	13.0	259		
35.6[+]	534	19.2	196				
	529		196				
	530		196				
	532		196				
		31.1[+]	332				
			332				
			332				
		37.3[+]	446				
			446				
			446				
			446				

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[a] Moles sulfide
Moles BF_3
Moles BF_3/mole sulfide

[*] Below freezing point of system.

[+] Above R.T., hence some condensate in manometer. Not used in calculating vapor pressure curves.

Table XLVII. Vapor Pressure for Me_2S-BF_3 System
(continued)

0.6062^a 0.6014 0.992		0.2704^a 0.2600 0.962		0.2012^a 0.1822 0.906		0.3541 0.3194 0.903		0.3541^a 0.3538 0.999		0.2473^a 0.2307 0.933	
Temp.	P	Temp.	P	Temp.	P	Temp.	P	Temp.	P	Temp.	P
-16.5	38	-16.4	19	-16.5	17	-57*	3	-17.1	23	-17.5	17
-16.8	38		19		17	-43*	4		23		17
-15.1	49		19		17	-32.5*	12		23		17
-14.6	50		20	-7.5	31		14		23		15
-9	66		19		31	-25*	12	-7.9	62	-9.5	30
	66	-7.5	36		31		12		62		30
	66		36	-7.0	36		12		62		30
-8.9	69		36		36		12		62	1.9	59
	69		35		36		12		63		58
0.6	132	0.1	63	1.0	54	-6.3	34	2.4	127		59
	134		63		54		34		130		60
0.8	135		63		54		34		130	10.1	98
	137		64		55	1.5	56		128		99
12.4	292	9.5	116		55		56		134		100
13.4	297		116	9.8	91		56	10	216		100
12.7	296		116		91	8.5	92		220	21	198
13.4	299		116		91	9.0	94		220		202
21.0	478	20.2	246		90		94		216		200
21.4	478		246	20.9	173	10	95		223		204
21.1	486		246		174		96	21.5	433	30	362
21.6	486				173		96		433		362
				30.5	304	21.2	182		433		366
					304		186		433	30.5	370
					304		186		439		372
							182	30.5	735		372
						30.5	315		732		
							320		737		
									735		

^{a}Moles sulfide
Moles BF_3
Moles BF_3/mole sulfide

*Below freezing point of system
$^+$Above R.T., hence some condensate in manometer
Not used in calculating vapor pressure curves.

Table XLVIII. Vapor Pressure for Dimethyl Selenide-BF_3 System
Temp., °C; Pressure, Torr

0.120*		0.1323*		0.2366*	
0		0.047		0.2352	
0		0.355		0.994	
Temp.	P	Temp.	P	Temp.	P
-27.3	13.5	-26.6	46	-31.6	245
-27.4	13.5		46	-31.4	248
-27.5	14.0		46	-31.2	248
-27.3	14.0		46	-31.1	248
-26.9	13.5	-27	48	-31.0	245
-10.5	40.5	-26.7	44		246
-10.3	40.5	-26.8	46	-23.8	449
-10.2	40.0	-26.8	46		449
-10.4	40.0	-10.5	164	-23.3	453
-10.4	40.5	-10.3	163		453
-10.6	40.0	-10.2	162	-23.2	463
-10.6	40.5	-10.6	164	-23	462
0.8	71.5	-10.1	161	-22.9	460
0.6	71.5	-10.5	164	-15.3	770
0.9	73.0	0.7	352		771
0.8	72.5	1.0	356	-14.8	774
3.1	81.5	1.3	358		775
3.3	82.0	0.3	341	-9.9	1067
3.0	81.0	0.7	349		1067
3.1	81.0	0.4	344	-9.6	1071
10.2	118	0.6	348		1071
10.4	120	0.7	343	-8.5	1136
10.2	119	11.2	672		1136
10.2	117	10.6	656	-7.9	1144
10.6	120	10.7	658		1142
10.2	117	20.9	1178	-3.5	1524
21.3	194	21.4	1195		1515
21.2	194	20.9	1182		1525
21.0	192	21.4	1195		1520
21.0	192	20.9	1181		1521
24.9	227				1524
25.5	228				1522
24.9	227			03.0	1532
25.5	228				1531
30.4	286				1529
30.6	288				1533
30.4	284				1535
30.6	387				1526
b.p. 57.3°C				(f.p. = -43.2°C)	
at 760 mm Hg.					

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*Moles selenide
Moles BF_3
Moles BF_3/moles selenide

Table XLIX. Vapor Pressure for Dimethyl Selenide-BF_3 System
(continued)

0.1323*		0.2673*		0.2673*	
0.1234		0.0228		0.1108	
0.933		0.085		0.415	
Temp.	P	Temp.	P	Temp.	P
-32.8	138	-28.5	22	-10.3	196
	138	-28	22	-10.2	192
	142	-27.8	24	-9.9	197
-32.6	144	-27.6	24	-9.8	194
	144	-27.5	20	1.8	433
-31.9	148	-9.6	84		435
-31.8	148	-9.6	81		435
-31.8	150	-9.2	84	2.5	444
-26.9	232	-9.6	82		444
	228	1.6	167	10.3	726
	232	2.4	174		720
	228	2.6	176	10.6	743
	231	2.1	178	10.7	742
-26.8	233	2.4	178		742
-10.2	756	10.4	287	10.9	744
-9.6	768	10.9	293	11.1	761
-9.5	768	21.1	499		762
-10.5	752	21.2	505	20.9	1347
-9.8	770	20.9	499		1348
-10.3	754	21.2	505	21.4	1359
-9.8	756				1368
-9.8	758				1368
-9.7	770			21.9	1378
1.2	1449				
0.6	1430				
0.4	1426				
1.2	1447				

(solution slushy at -38°C)

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*Moles selenide
Moles BF_3
Moles BF_3/mole selenide

Table L. Vapor Pressure for the Phenol-BF$_3$ System
Temp., °C; Pressure, Torr

0.1897*
0.0727
0.383

Temp.	P
-8.2	2
	2
	2
-2.5	6
	6
2.6	7
	7
	7
	7
	7
	7
9.8	13
	13
	13
10.5	14
	14
	14
	14
10.6	15
	15
	15
21.2	31
	31
	31
	31
21.6	32
	32
	32
	32
	32
	32
30.6	61
	61
	61
29.2	62
	62
	62
	62
30.2	63

0.1896*
0.0924
0.489

Temp.	P
-8	12
	12
-7.5	12
	12
	12
3.5	32
	32
	32
4.0	35
	35
10.3	56
	56
	56
10.8	57
	57
21.2	120
	120
	120
	120
	120
29.3	223
29.6	224
	224
	224
	224

0.231*
0.0385
0.165

Temp.	P
20.6	3
	3
28.5	5.5
	5.5
35.3	9
41	14

0.1897*
0.1113
0.587

Temp.	P
-14.8	35
	35
	35
-12.2	41
	41
-8.1	57
	57
	56
	57
	57
2.7	127
	127
	127
4.8	142
	142
10.5	212
	212
	212
10.8	215
	215
	215
20.9	399
	399
	399
	399
	399
	400
28.5	648
	650
	652
28.8	660
	660
	662
	662

0.6585*
0.2677
0.4065

Temp.	P
0.8	9
1.2	9
1.4	9
12.7	23
13	24
12.8	24
12.4	25
13	25
12.6	25
21.4	44
20.9	44
21.1	44
21.3	46
21.2	47
20.6	47
30.8	87
31.0	86
30.6	86
30.5	87
30.8	87
30.7	87
35.4	114
35.4	115
35.6	115

0.2331*
0.0668
0.287

Temp.	P
10.9	4
	4
	4
21.4	9
	9
	9
30.0	19
	19
	19

---

*Moles phenol
Moles BF$_3$
Moles BF$_3$/mole phenol

Table LI. Vapor Pressure for the Phenol-BF_3 System (continued)

0.2260*		Cont.		0.2562*		1.2483*	
0.1688				0.2059		0.6265	
0.747		0.747		0.804		0.502	
Temp.	P	Temp.	P	Temp.	P	Temp.	P
-16.6	168	17.9	1429	(f.p. -15°C)		-9.5	14
-16.9	170	18.1	1432	-14	402		15
-17.1	179	18.1	1436		402		15
-16.8	179	17.9	1436		402		15
-17.2	179	17.9	1435		402	2.5	41
-7.7	342	17.9	1429	-6.8	654		41
-7.4	342	18.0	1427		654		41
-7.6	342	18.1	1431	-6.6	654		41
-7.5	356	18.2	1433	-6.8	654	108	82
-7.2	356	18.4	1436	0	940		82
-7.5	357	18.1	1444		940		82
-7.1	351	18.4	1443		940		82
-7.3	357	18.1	1429		940	20.6	162
3.5	675	18.3	1431	3.4	1201		162
3.0	679	18.3	1433		1201		162
3.3	678	17.9	1431		1201		162
3.3	678	17.9	1427	3.2	1190	29.6	280
3.7	678			3.6	1195		281
3.4	683			3.9	1193		281
3.5	683			3.3	1195		281
4.0	683			3.8	1199	34.2	383
3.4	675			7.6	1470		383
3.8	676			7.8	1473		383
3.2	678			7.6	1476		383
3.3	678			7.7	1476		
10.5	985			7.7	1476		
				7.7	1476		
10.2	985						
10.4	985						
10.3	983						
10.1	983						
9.9	983						
10.1	984						
9.9	972						
10.2	975						
10.2	975						

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*Moles phenol
Moles BF_3
Moles BF_3/mole phenol

Table LII. Vapor Pressure for the Phenol-BF_3 System (continued)

0.2290*
0.0470
0.205

Temp.	P
11.0	2
	2
	2
20.8	4
	4
	4
21	4.5
	4.5
29.8	9.5
	9.5
	9.5
40.7	19
	19
	19

0.2290*
0.1425
0.622

Temp.	P
-7.9	90
	90
	90
4.0	201
	201
	201
10.0	309
	309
	310
	571
20.6	571
	571
	572
30.0	907
	907
	907

0.2260*
0.1544
0.683

Temp.	P
-8.0	110
	110
	111
-5.8 f.p.	
3.1	343
3.3	343
3.5	343
3.5	343
3.7	349
4.0	351
4.0	351
10.1	519
10.4	519
10.5	519
10.6	522
20.8	908
	909
21.0	906
	906
	909
	908
21.1	907
	913
28.9	1395
	1400
29.0	1407
	1409
	1409
29.3	1408
29.5	1394
	1400
29.8	1409

0.2260*
0.1789
0.792

Temp.	P
(f.p. -15°C)	
-13.5	337
-13.7	334
-14.1	333
-13.7	332
-13.5	329
-14.0	329
-13.8	337
-13.8	337
-14.1	333
-7.4	533
-6.9	533
-7.1	536
-7.3	537
-7.4	536
-7.4	536
-7.4	537
3.8	984
3.4	984
4.0	986
3.7	982
3.7	986
3.3	985
3.6	983
4.0	983
3.8	987
3.4	987
10.4	1385
10.1	1382
9.8	1385
10.1	1381
10.2	1381

0.2290
0.0707
0.309**

Temp.	P
10.3	6
	6
10.4	6
	6
	6
21.2	14
	14
	14
20.8	14
	14
28.0	25
	25
	25
28.2	25
	25
40.6	58
	58
	58
	58

0.620
m.BF_3/m.

Temp.	P
2.5	199
	199
	198
9.6	308
	308
10.0	312
	312
20.2	571
	573
	573
29.6	909
	909
	909
35	1197
	1210
	1211

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*Moles phenol
Moles BF_3
Moles BF_3/mole phenol

**Solid below 0°C

Table LIII. Vapor Pressure for the System Bu_2O-BF_3
1:1 Complex; Temp., °C; Pressure, Torr
(composite of several runs) log p = (5.56±.05) - (1006±15)

Temp.	P	Temp.	P
-55	3	-7.0	72
-48	2	-6.5	72
-45	6	-0	100
-36	8	+3	107
-33*	16	7	119
-32	29	8	119
-26	41	13.5	134
-21	41	14	142
-20	41.4	18.5	166
-16.5	56	19	168
-9	74	23.5	175
-7.5	80	24	186
		30.5	212

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*mp. of complex

REFERENCES

1. BNL-325, Sec. Edit., Neutron Cross Sections, Vol. I (1964).
2. Separation of the Boron Isotopes, NNES III-5, McGraw-Hill, N. Y. (1952).
3. A. L. Conn and J. E. Wolf, Ind. Eng. Chem. 50, 1231 (Sept. 1958).
4. G. T. Miller, R. J. Kralik, B. A. Belmore, and J. S. Drury, 2nd Geneva Conference, Pergamon Press, London, p. 585-94.
5. C. H. Chilton, Chem. Engineering (Prog. & Tech.) 148-50, 176-8 (May 1957).
6. D. E. McLaughlin and N. Tamres, J. Amer. Chem. Soc. 82, 5618 (1960).
7. R. M. Healy, A. A. Palko, and E. F. Joseph, ORNL-2069 (April 1956).
8. A. A. Palko, Ind. Eng. Chem. 51, 121 (1959).
9. R. G. Jordan, KC718 (May 1964).
10. J. R. Merriman, J. H. Pashley, and N. W. Snow, K1653 (April 1966).
11. R. M. Healy and A. A. Palko, J. Chem. Phys. 28, No. 2, 211-13 (1958), Part 1.
12. A. A. Palko, R. M. Healy, and L. Landau, J. Chem. Phys. 28, 214-17 (1958), Part 2.
13. A. A. Palko, J. Chem. Phys. 30, 1187-89 (1959), Part III.
14. A. A. Palko and J. S. Drury, J. Chem. Phys. 33, 779-81 (1960), Part IV.
15. A. A. Palko, J. S. Drury, and W. E. Bull, J. Chem. Phys. 35, 103-5 (1961, Part V).
16. A. A. Palko and J. S. Drury, J. Chem. Phys. 40, 278-81 (1964), Part VI.
17. G. M. Begun, W. H. Fletcher, and A. A. Palko, Spec. Chim. Acta 18, 655-65 (1962).
18. A. A. Palko, G. M. Begun, and L. Landau, J. Chem. Phys. 37, 552-55 (1962).
19. G. M. Begun and A. A. Palko, J. Chem. Phys. 38, 2112-2117 (1963).
20. A. A. Palko and J. S. Drury, J. Chem. Phys. 47, 8, 2561-66 (Oct. 1967).
21. A. A. Palko and J. S. Drury, Advances in Chemistry Series, 40-56, ACS Publication #89 (1969).

22. A. A. Palko, J. Inorg. and Nucl. Chem. 27, 287-92 (1965), Part VII.
23. A. A. Palko, J. Chem. Phys. 46, 2297-2300 (1967), Part VIII.
24. A. C. Rutenberg, A. A. Palko, and J. S. Drury, J. Amer. Chem. Soc. 85, 2702 (1963) I.
25. A. C. Rutenberg, A. A. Palko, and J. S. Drury, J. Phys. Chem. 68, 976 (1964) II.
26. A. C. Rutenberg and A. A. Palko, J. Phys. Chem. 69 (1965) III (in press).
27. N. N. Greenwood and R. L. Martin, Quarterly Rev. 8, 1-39 (1954).
28. I. Kiss, I. Opanszky, and L. Matush, Atomnaya Energiza 10, 1, 73-75 (1961).
29. H. L. Holsopple, ORNL-60-10-26 (1960).
30. H. L. Holsopple, ORNL-61-2-7 (1961).
31. H. L. Holsopple, ORNL-TM-777 (1964).
32. D. W. Osborne, R. N. Doescher, and D. M. Yosh, J. Amer. Chem. Soc. 64, 169-72 (1942).
33. Manufactured by Union Carbide Corporation at K-25, Oak Ridge, Tennessee.
34. H. E. Wirth, M. H. Jackson, and H. W. Griffiths, J. Phys. Chem. 62, 871 (1958).
35. H. C. Brown and R. M. Adams, J. Amer. Chem. Soc. 64, 2557 (1942).
36. D. E. McLaughlin, M. Tamres, and S. Searles, J. Amer. Chem. Soc. 82, 5621 (1960).
37. A. C. Boyd, Ph.D. Thesis, Purdue University (1957) (DDS pb. 22, 248).
38. S. G. Katal'nikov and R. M. Paramonov, Zhur. Fiz. Khim 40, 401-6 (1966).
39. S. G. Katal'nikov and Kung Chih Ch'in, Zhur. Fiz. Khim 39, 6 (1965).