An analysis of chemical exchange systems for the separation of boron isotopes
by Ronald Scott Herbst

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering
Montana State University
© Copyright by Ronald Scott Herbst (1992)

Abstract:

Chemical exchange between gaseous BF3 and the liquid BF3 •dimethyl ether complex is currently used commercially for the fractionation of boron isotopes. Several compounds never before studied as donors in the isotope exchange reaction were examined to determine if they were viable replacements for the currently used dimethyl ether system. The evaluation of these materials as potential donors was based on experimental studies and modelling and analysis of large scale fractionation cascades.

For the first time, ketones were studied as donors in the boron isotope exchange reaction. The ketones examined were: acetone, methyl isobutyl ketone (HIBK), and diisobutyl ketone (DIBK). The ideal single stage separation factor, α, for these ketones was between α = 1.038 and α = 1.043 at 30°C. The observed separation factor for a fourth donor system, nitromethane, was α = 1.067 at 30°, well above that predicted by theory or observed for any known BF3/donor system. For each of the systems studied, the separation factors were greater than the value of α = 1.027 reported for the dimethyl ether/BF3 system at 30°C. In view of the experimentally observed separation factors, these donor systems are potential replacements for dimethyl ether in large scale boron isotope fractionation schemes.

Modelling and analysis of large scale fractionation cascades based on the values of a experimentally observed for the different donors indicated plant size could be greatly reduced using these donors rather than dimethyl ether. Ideal, constant recycle, and squared off cascade configurations utilizing counter current flow were examined. The two section squared off cascade reduced the ideal number of stages by 8% to 11% and required 13% more total interstage flow than the ideal cascade. Stripping in the various cascades was estimated to account for as much as 30% of total cascade size. The ideal cascade was shown to be the most energy efficient of the recycle cascade configurations studied. These results indicate the directions cascade design must take if maximally efficient large scale facilities are to be built and operated.

AN ANALYSIS OF CHEMICAL EXCHANGE SYSTEMS FOR THE SEPARATION OF BORON ISOTOPES

by

Ronald Scott Herbst

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Doctor of Philosophy

in

Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

November 1992

D378
H4174

APPROVAL

of a thesis submitted by

Ronald Scott Herbst

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

11-30-92 — FP McCandless

Date — Chairperson, Graduate Committee

Approved for the Major Department

11-30-92 — John F Mandell

Date — Head, Major Department

Approved for the College of Graduate Studies

12/14/92 — RL Brown

Date — Graduate Dean

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a doctoral degree at Montana State University, I agree that the Library shall make it available to borrowers under rules of the Library. I further agree that copying of this thesis is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for extensive copying or reproduction of this thesis should be referred to University Microfilms International, 300 North Zeeb Road, Ann Arbor, Michigan 48106, to whom I have granted "the exclusive right to reproduce and distribute copies of the dissertation in and from microfilm and the right to reproduce and distribute by abstract in any format."

Signature ______________________

Date Nov 30, 1992

TABLE OF CONTENTS

Page

LIST OF TABLES vi

LIST OF FIGURES vii

ABSTRACT ix

INTRODUCTION 1

Historical Background 2
Literature Review 4
Isotope Exchange Processes 5
Selection of X 6
Donor Selection 7
Effect of Temperature and Pressure on K_{eq} 13
Kinetics of Isotope Exchange Reactions 14
Theory of Isotope Exchange Reactions 15

PURPOSE AND SCOPE OF PRESENT STUDY 22

EXPERIMENTAL DETERMINATION OF SEPARATION FACTORS 25

Experimental Reagents, Equipment and Procedures 26
Experimental Reagents 26
Experimental Equipment and Procedures 27
Mass Spectroscopic Isotopic Abundance Analysis 31
Results and Discussion 34
The Phenetole/BF_3 System 34
The Acetone/BF_3 System 39
The Acetophenone/BF_3 System 42
The MIBK/BF_3 System 43
The DIBK/BF_3 System 47
The Nitromethane/BF_3 System 50
The DMSO/BF_3 System 54
Comparison of Experimentally Studied Systems 55

TABLE OF CONTENTS--Continued

Page

MODELLING AND ANALYSIS 61

- Terminology 62
  - Ideal Stages 62
  - Separation Factors 64
- Countercurrent Recycle Cascade 65
  - Material Balances 68
  - Recycle Ratio 69
    - Providing Recycle in the Cascade 72
  - Number of Separation Stages 73
  - Total Interstage Flow 74
  - Practical Recycle Ratio 75
- Cascade Models 80
  - Ideal Cascade 82
    - Heads Separation Factor 82
    - The Ideal Cascade Model 89
    - Results and Discussion of the Ideal Cascade Calculations 91
  - Constant Recycle Cascade 96
    - The Constant Recycle Model 96
    - Results and Discussion of the CRC Calculations . 98
  - Squared Off Cascade 103
    - The Squared Off Model 104
    - Results and Discussion of the SOC Calculations 108
- Comparison of Cascade Models 117
- Effect of the Stripping Section 124
  - Addition of Square Sections to the Stripper 124
  - Elimination of the Stripping Section 132
    - The Ideal Cascade Without Stripping 134
    - The CRC Without Stripping 136
    - The SOC Without Stripping 138
  - Energy Requirements 142
    - Energy Requirements for Providing Recycle in the Cascade 143
    - Energy Requirements for Stagewise Separation of Components 147

CONCEPTUAL BORON ISOTOPE ENRICHMENT PLANT 158

CONCLUSIONS 168

RECOMMENDATIONS FOR FURTHER STUDY 170

REFERENCES CITED 171

LIST OF TABLES

Table Page

1 Review of previously studied donor molecules in the isotopic exchange reaction (4) 8

2 Ratios of the vibrational partition function for BF_3 and BF_3^* at 303K and 250K [32] 19

3 Calculated and observed values of the isotopic equilibrium constant for reaction (4) at 303K [32] 19

4 Minimum ideal stage requirements with different donors for a boron isotope fractionation cascade operating at total reflux 58

5 Ideal cascade results for the various BF_3/donor systems . . 92

6 Constant recycle cascade results for the various BF_3/donor systems 99

7 Summary of the results from the squared off cascade calculations for the various BF_3/donor systems 109

8 Comparison of the various BF_3/donor systems in different models 118

9 Comparison of the results from the SOC models with the stripping section squared off for the various BF_3/donor systems. 127

10 Ideal cascade results for the various BF_3/donor systems without a stripping section 135

11 Constant recycle cascade results for the various BF_3/donor systems without a stripping section 137

12 Squared off cascade results for the various BF_3/donor systems without a stripping section 139

13 Comparison of different types of energy input and total interstage flow for the various cascade configurations with the nitromethane/BF_3 donor system 151

LIST OF FIGURES

Figure		Page
1	Schematic of the test cell used to obtain experimental data .	30
2	Experimental results for the Phenetole/BF_3 system	36
3	Experimental results for the Acetone/BF_3 system	40
4	Experimental results for the MIBK/BF_3 system	44
5	Experimental results for the DIBK/BF_3 system	48
6	Experimental results for the Nitromethane/BF_3 system	51
7	Comparison of experimental systems studied in isotope exchange.	56
8	Single separating stage and associated nomenclature.	63
9	Flow schematic of the countercurrent recycle cascade.	67
10	Inverse multiplication factor vs. total interstage flow and number of ideal stages for the dimethyl ether/BF_3 system .	77
11	Inverse multiplication factor vs. total interstage flow and number of ideal stages for the nitromethane/BF_3 system . .	78
12	Mole ratios in a section of an ideal cascade	83
13	Effect of the exponential factor, q, on the recycle ratio versus stage number curve for the ideal cascade	86
14	Effect of the exponential factor, q, on total interstage flow rate in the ideal cascade	88
15	Recycle ratio versus stage number for the ideal cascade with the different donors	94
16	Recycle ratio versus stage number for the constant recycle cascade with the different donor systems	102

LIST OF FIGURES--Continued

Figure Page

17 Recycle ratio vs. stage number for the SOC with the nitromethane/BF_3 donor system 112

18 Recycle ratio vs. stage number for the SOC with the DIBK/BF_3 donor system 113

19 Recycle ratio vs. stage number for the SOC with the MIBK/BF_3 donor system 114

20 Recycle ratio vs. stage number for the SOC with the acetone/BF_3 donor system 115

21 Recycle ratio vs. stage number for the SOC with the dimethyl ether/BF_3 donor system 116

22 Comparison of recycle ratio versus stage number for the nitromethane/BF_3 donor system with the ideal, CRC and 3 & 4 section SOC models 121

23 Comparison of recycle ratio versus stage number for the dimethyl ether/BF_3 system with the ideal, CRC and 2 & 5 section SOC models 122

24 Effect of adding square sections to the stripping portion of the nitromethane/BF_3 SOC 130

25 Effect of adding square sections to the stripping portion of the dimethyl ether/BF_3 SOC 131

26 Typical stage from a countercurrent recycle cascade 148

27 Ideal energy, separative energy and total interstage flow as a function of inverse recycle factor (1/A) for the CRC with the nitromethane/BF_3 donor system 154

28 Recycle and separative energy as a function of recycle ratio for the CRC with the nitromethane/BF_3 donor system . . . 156

29 Process flow schematic for the two section SOC with the nitromethane/BF_3 donor system 159

30 Process flow schematic for the two section SOC with the dimethyl ether/BF_3 donor system 163

ABSTRACT

Chemical exchange between gaseous BF_3 and the liquid BF_3·dimethyl ether complex is currently used commercially for the fractionation of boron isotopes. Several compounds never before studied as donors in the isotope exchange reaction were examined to determine if they were viable replacements for the currently used dimethyl ether system. The evaluation of these materials as potential donors was based on experimental studies and modelling and analysis of large scale fractionation cascades.

For the first time, ketones were studied as donors in the boron isotope exchange reaction. The ketones examined were: acetone, methyl isobutyl ketone (MIBK), and diisobutyl ketone (DIBK). The ideal single stage separation factor, α, for these ketones was between $\alpha = 1.038$ and $\alpha = 1.043$ at 30°C. The observed separation factor for a fourth donor system, nitromethane, was $\alpha = 1.067$ at 30°, well above that predicted by theory or observed for any known BF_3/donor system. For each of the systems studied, the separation factors were greater than the value of $\alpha = 1.027$ reported for the dimethyl ether/BF_3 system at 30°C. In view of the experimentally observed separation factors, these donor systems are potential replacements for dimethyl ether in large scale boron isotope fractionation schemes.

Modelling and analysis of large scale fractionation cascades based on the values of α experimentally observed for the different donors indicated plant size could be greatly reduced using these donors rather than dimethyl ether. Ideal, constant recycle, and squared off cascade configurations utilizing counter current flow were examined. The two section squared off cascade reduced the ideal number of stages by 8% to 11% and required 13% more total interstage flow than the ideal cascade. Stripping in the various cascades was estimated to account for as much as 30% of total cascade size. The ideal cascade was shown to be the most energy efficient of the recycle cascade configurations studied. These results indicate the directions cascade design must take if maximally efficient large scale facilities are to be built and operated.

INTRODUCTION

Naturally occurring boron is comprised of two isotopic forms. The mass 10 isotope, ^{10}B, has a relative abundance of 19.8 atom % while the remainder or 80.2% consists of the mass 11 isotope, ^{11}B.

The impetus for the isotopic fractionation of boron arises primarily from a contrasting difference in thermal neutron capture cross sections. Boron-10 has a thermal neutron capture cross section of 3837 barnes, while that of ^{11}B is only 0.005 barnes. As a composite of the two isotopes, naturally occurring boron has a thermal neutron capture cross section of approximately 750 barnes. Subsequently, ^{10}B is roughly 5 times more effective than naturally occurring boron, 20 times more effective than lead, and nearly 500 times more effective than concrete as a neutron shielding material. It is precisely this propensity for thermal neutron capture which makes ^{10}B enriched materials a useful commodity.

The nuclear related industries are the predominant consumers of ^{10}B. Enriched boron-10 compounds are used for standby liquid control systems in boiling water reactors. Breeder reactors use ^{10}B enriched carbide for control rods. Boron-10 enriched boric acid is used as a chemical shim for reactivity control in pressurized water reactors. Boron-10 enriched alloys are used for criticality control in nuclear fuel casks, as construction material in storage racks, and as neutron shielding around reactors. It is also used in instrumentation for both neutron density and dosage. Medical research with ^{10}B enriched compounds has indicated a promising method for the non-surgical removal of malignant brain tumors.

The goals of this study included examination of several isotope exchange systems which have not been previously reported in the literature. The second objective was to examine modelling and analysis of a production scale counter current cascade process for boron isotope separation by gas-liquid isotope exchange.

Historical Background

The quest for a suitable method for the large scale separation of boron isotopes began in 1943. At that time, the U.S. War Department, as a result of the war effort, requested 50 kg of crystalline boron containing not less than 90% ^{10}B. Accordingly, research was initiated at Columbia University, under a classified program of the Manhattan Project, to develop a suitable scheme for the separation of boron isotopes. Six different separation schemes were investigated during the initial stages of the project. These were: (1) thermal diffusion of BF_3; (2) distillation of BF_3; (3) distillation of methyl borate, $(CH_3O)_3B$; (4) steam distillation of boric acid, H_3BO_3; (5) isotope exchange between dimethyl ether-BF_3 complex, $(CH_3)_2O \cdot BF_3$, and BF_3; and (6) isotope exchange between ethyl borate-BF_3 complex, $(C_2H_5O)_3B \cdot 2BF_3$ and BF_3 gas.

The "distillation" of dimethyl ether-BF_3 complex was selected as the most efficient method of separation, primarily due to a lower rate of irreversible chemical decomposition. As a result of this work, Standard Oil Company (Indiana) designed and operated the first large scale boron isotope fractionating facility. The initial order from the War Department was filled in May 1945. That plant was subsequently dismantled in 1948. A second, larger facility was constructed and operated by Hooker

Electrochemical Corp. from 1953 to 1958 at Model City, New York. That plant successfully produced several hundred kilograms of 90-95% ^{10}B metal utilizing the "distillation" of dimethyl ether-BF_3 complex. A complete account of the above ventures is available in the open literature (1-3).

It is interesting to note that the rapidity with which a suitable method for the large scale separation of boron isotopes was established is indicative that many potential methods were not investigated.

In 1977, Eagle-Pitcher Industries reconstructed and began operation of the Model City plant at Quapaw, Oklahoma. This facility relies on the same gas-liquid partitioning process as its predecessors, e.g. isotope exchange between dimethyl ether-BF_3 complex and BF_3 gas to fractionate the isotopes of boron. To increase capacity, two new separation cascades were designed and added to the plant. These cascades are identical, each consisting of two packed columns in series. The first column is 50.8 cm ID with a packed height of 42 meters, while the second is 30.5 cm ID with 27.4 meters of packing. The operating pressure throughout the system is 27 kPa (200 torr) with boilup at 96°C. Fourteen days are required from startup for the process to reach steady state operation. The capacity of this plant is reported to be in excess of two metric tons/year of boron metal enriched to 95% ^{10}B with production costs of \$5 to \$15 per gram of ^{10}B, depending on the degree of enrichment [4,36].

Problems associated with the process used at the Quapaw plant include irreversible decomposition of the dimethyl ether-BF_3 complex to form undesired reaction products. Furthermore, quantitative recovery of BF_3 from the complex is difficult. The equilibrium constant for the $(CH_3)_2O\cdot BF_3$ exchange system is $K_{eq} = 1.027$. Ideally, the single stage separation factor, α, would be identical to K_{eq}. However, the gas phase contains approximately 40% undissociated complex, which effectively lowers the single stage separation factor to $\alpha = 1.014$ [4].

Due to the nomenclature used in the early literature, the isotope exchange process is often referred to as "distillation". It must be emphasized that the separation is based on chemical reaction equilibrium rather than phase equilibrium. Consequently, this is not a distillation process. In fact, it is distillation (the vaporization of complex without dissociation) which is responsible for lowering the single stage separation factor and thus decreasing the process efficiency.

Literature Review

Many studies have been initiated in quest of an "improved" boron isotope separation scheme. A survey of the literature indicates several active areas of study regarding boron isotope separation. These areas are conveniently divided into three categories:

(1) Photochemical induced separations or laser based separations where tunable lasers are used to separate isotopes by making use of the small differences in the absorption spectra of ^{10}B and ^{11}B or one of their compounds.

(2) Chromatographic separations where isotopic fractionation is facilitated by small differences in the retention times of boron isotopes in the liquid phase on chromatographic resins.

(3) Isotopic equilibrium or isotope exchange reactions where separation is affected by the isotope exchange equilibrium between boron in a liquid and a gaseous phase.

Numerous publications, process and process equipment patents exist in each of these three areas. Despite the fact that other technologies apparently exist for the large scale separation of boron isotopes, commercial success has been realized only with the isotope exchange process used by the Eagle-Picher Company as previously described.

This study is characterized by boron isotope separation schemes involving isotope exchange reactions. Accordingly, only the literature pertinent to this area will be reviewed.

Isotope Exchange Processes

Isotope exchange processes are characterized by reactions of the type:

$$^{10}BX_{3(g)} + {}^{11}BX_3\cdot Donor_{(l)} \rightleftharpoons {}^{11}BX_{3(g)} + {}^{10}BX_3\cdot Donor_{(l)} \qquad (1)$$

where X is generally H, CH_3 or a halogen. The "complex", $BX_3\cdot$Donor, is a molecular addition compound, and the donor is a Lewis base or electron pair donor. The equilibrium constant for reaction (1) is given by:

$$K_{eq} = \frac{[{}^{11}BX_{3(g)}]\ [{}^{10}BX_3\cdot Donor_{(l)}]}{[{}^{10}BX_{3(g)}]\ [{}^{11}BX_3\cdot Donor_{(l)}]} = \frac{[{}^{10}B/{}^{11}B]_{(l)}}{[{}^{10}B/{}^{11}B]_{(g)}} \qquad (2)$$

where square brackets represent the equilibrium concentrations of the respective species.

Most known exchange systems pertinent to boron isotopes have values of the equilibrium constant in the range of $1 \leq K_{eq} < 1.06$. That the equilibrium lies slightly to the right in reaction (1) forms the basis for the separation. The small value of K_{eq} suggests the need of a multistage exchange process in order to obtain a significant degree of separation.

Utilization of the isotopic exchange reaction requires the passage of gaseous BX_3 and liquid complex in a stagewise process. Thus, ^{10}B concentrates in the liquid phase while ^{11}B concentrates in the gaseous phase. Pertinent considerations focus primarily on the selection of X and the donor molecule in reaction (1). These considerations include:

(a) The largest possible value of the equilibrium constant, K_{eq}, in order to minimize the necessary number of stages for a given enrichment.

(b) The equilibrium must be rapidly established, e.g. isotopic exchange need be kinetically rapid, in order to maintain a high throughput in a continuous system.

(c) BX_3 must be readily liberated from the complex for product recovery, recirculation and reuse of the separative agent or donor. In this regard, it is desirable that the formation reaction:

$$BF_3 + \text{Donor} \rightleftharpoons BF_3 \cdot \text{Donor} \qquad (3)$$

be quantitatively reversible simply by addition or removal of heat.

(d) The BX_3·donor complex must be sufficiently stable so as not to decompose into unwanted reaction products. Such irreversible decomposition would result in ^{10}B enriched product losses with the attendant loss of BX_3 and donor.

Selection of X

Virtually all systems studied to date have used the first member of the halogen family, fluorine, for X in the isotopic exchange reaction. This consideration largely stems from criteria (a) and (d) above and is associated with the excellent electron acceptor capabilities of BF_3 [6,7]. Use of BF_3 as the Lewis acid in the isotope exchange reaction has been justified on theoretical grounds as well (*vide infra*). Consequently, the isotope exchange reaction may be rewritten for subsequent discussions as:

$$^{10}BF_{3(g)} + {}^{11}BF_3 \cdot Donor_{(\ell)} \rightleftharpoons {}^{11}BF_{(3)} + {}^{10}BF_3 \cdot Donor_{(\ell)} \qquad (4)$$

In addition to BF_3, several brief studies utilizing BCl_3 as the Lewis acid in the isotopic exchange reaction have been conducted [6,7,13,15]. In all reported instances, the equilibrium constant for the BF_3 systems was larger than for similar BCl_3 systems. Consequently, the use of BCl_3 as the acid in isotopic exchange was largely abandoned.

Donor Selection

The species $BF_3 \cdot Donor$ in equation (4) is a molecular adduct formed between BF_3 and an electron pair donor. This type of compound formation is a classical example of Lewis acid-base chemistry. Here, the Lewis acid, BF_3, accepts a lone electron pair from the basic donor atom which is typically bound in a molecular species.

Boron trifluoride has been touted as the most powerful acceptor molecule (Lewis acid) known, while the number of atomic species capable of donating electrons to BF_3 is relatively small [5]. The nine elements H, N, O, F, P, S, Cl, Se, and Te, in certain of their compounds, have been found capable of donating electrons to BF_3 [6].

Of the aforementioned criteria, (a) and (d) limit the donor atom to predominantly N, O, or S, although systems containing other donors have been examined [6,7]. Table 1 lists the donor molecules which have been studied, the associated equilibrium constants which were reported and the literature references for the pertinent study.

Table 1. Review of previously studied donor molecules in the isotopic exchange reaction (4).

Donor		K_{eq}†		
		30°C	0°C	Reference
Oxygen Donors				
1. Methyl Ether	$(CH_3)_2O$	1.027	1.034	6,7,12
2. Ethyl Ether	$(C_2H_5)_2O$	1.031	1.037	6,7,17
3. n-Butyl Ether	$(C_4H_9)_2O$	-	-	6,7,12
4. Tetrahydrofuran	$(CH_2)_4O$	1.026	1.031	6,7,13
5. Phenol	C_6H_5OH	1.024	1.040	6,7,14,15
6. Anisole	$C_6H_5OCH_3$	1.030	1.039	6,7,15,16
7. Phenetole	$C_6H_5OC_2H_5$	1.039 1.042 (25°C)	1.051	6,7,8
8. n-Butyl phenyl ether	$C_6H_5OC_4H_9$	1.026 (25°C)	-	7,10
9. Ethyl formate	$HCOOC_2H_5$	1.029 (20°C)	-	7,11,12
10. Ethyl acetate	$CH_3COOC_2H_5$	1.033 (28°C)	-	7,9
11. Ethyl propionate	$C_2H_5COOC_2H_5$	1.019 (43°C)	-	7,9
12. Sulfur dioxide	SO_2	-	-	20,21
13. Dimethyl sulfoxide‡	$(CH_3)_2SO$	1.040	1.036	19
14. Diphenyl ether	$(C_6H_5)_2O$	-	-	6
15. Nitrobenzene	$C_6H_5NO_2$	1.03 (7°)	-	6,13
Sulfur Donors				
16. Methyl sulfide	$(CH_3)_2S$	1.037	1.046	6,7,12,23
17. Ethyl Sulfide	$(C_2H_5)_2S$	1.037	1.043	6,7,17
18. n-Butyl sulfide	$(C_4H_9)_2S$	1.032	1.040	6,7,15,18
19. Diphenyl sulfide	$(C_6H_5)_2S$	-	-	6,13
20. Thiophenol	C_6H_5SH	-	-	6,13
21. Ethyl mercaptan	C_2H_5SH	-	-	6
22. Butyl mercaptan	C_4H_9SH	-	-	6
Nitrogen Donors				
23. Triethyl amine	$(C_2H_5)_3N$	1.022	1.028	6,7,17
24. N-Methyl diphenyl amine	$(C_6H_5)_2NCH_3$	-	-	6,13
25. N,N-Dimethyl aniline	$C_6H_5N(CH_3)_2$	-	-	6,13
Miscellaneous				
26. Methyl selenide	$(CH_3)_2Se$	1.032	1.039	6,7,12
27. Methyl telluride	$(CH_3)_2Te$	-	-	6,12
28. Methyl isocyanide	CH_3NCO	-	-	6,13

†Equilibrium temperatures other than 30°C or 0°C are denoted by brackets.

‡Isotopic equilibrium between the gas and solid phases:

$$^{10}BF_{3(g)} + {}^{11}BF_3\cdot DMSO_{(s)} \rightleftharpoons {}^{11}BF_{3(g)} + {}^{10}BF_3\cdot DMSO_{(s)}$$

The standard by which an "improved" isotope separation process is compared is the current production scale method involving BF_3 and the BF_3-dimethyl ether complex. From Table 1, the equilibrium constant at 30°C for this system is $K_{eq} = 1.027$. The actual separation factor observed for the process is $\alpha = 1.014$ with the reduction due primarily to incomplete dissociation of the complex in the vapor phase and solubility of BF_3 in the liquid complex [1,6].

A second drawback associated with the dimethyl ether system results from irreversible decomposition of the complex. At atmospheric pressure, roughly 50% of the dimethyl ether-BF_3 complex is decomposed to methyl fluoride and methyl borate in 24 hours [6]. In order to decrease the decomposition rate to tolerable levels, the process is operated at subatmospheric pressure of approximately 200 torr. Thus, in accord with criterion (d) above, an improved system would be amenable to operation at conditions of ambient temperature and pressure.

With regard to irreversible decomposition, it is a forgone conclusion that water must be carefully excluded from the system [1,6]. Boron trifluoride readily reacts with water, even in the presence of atmospheric moisture, to form a number of acidic hydrolysis products such as hydrofluoric, hydrofluoroboric, fluoroboric and boric acid. Several of these are highly corrosive to process construction materials, some may cause or catalyze decomposition of the complex, and others are solids which tend to plug the process equipment [6].

The literature data presented in Table 1 indicates that the equilibrium constant for reaction (4) varies with temperature, donor atom, and donor substituents. Palko and Drury have indicated [7,32] that a variation of donor atom and donor substituents affects the relative bond strength between the donor atom and boron in the molecular addition compound. The bond strength is therefore a measure of the relative stabilities of the various BF_3 adducts. In general, the more stable or stronger the boron to donor bond for a particular adduct, the less prone the adduct is towards isotope exchange, resulting in a lower value of the equilibrium constant than for a similar, less stable complex.

Palko et. al. [7] indicated that the variation in stability with different donor atoms increased in the order N > O > S and that stronger molecular addition compounds (in terms of bond strength or stability) resulted in smaller values of the equilibrium constant. Consequently, triethyl amine was more stable than diethyl ether which in turn was more stable than diethyl sulfide. As a result of this difference in stability, the value of the equilibrium constant increased in the order $(C_2H_5)_2S$ > $(C_2H_5)_2O$ > $(C_2H_5)_3N$ at 30°C. In accord with theoretical considerations (*vide infra*), the increase in K_{eq} with different donors in the order S > O > N can be attributed to the fact that substitution of the heavier donor atom simultaneously increases the reduced mass of the molecular addition compound and decreases the donor to boron force constant resulting in a weaker or less stable adduct with a concomitant increase in the equilibrium constant [32].

The stability of BF_3 adducts containing the same donor atom indicates variations with substituents attached to the basic center in the donor molecule. This variation has been explained in terms of inductive and steric effects associated with various donor substituents [7,37]. An electrophilic (electron withdrawing) group attached to the basic center decreased basicity, and resulted in a weakened adduct. Consequently, $(CH_3)_2O \cdot BF_3$ is more stable than $C_6H_5OCH_3 \cdot BF_3$ and $(C_6H_5)_2O \cdot BF_3$ does not form at -40°C. Accordingly, the largest equilibrium constant is associated with the weakest adduct, $C_6H_5OCH_3 \cdot BF_3$ in this case (refer to Table 1).

Conversely, a nucleophilic or electron donating group attached to the basic center is expected to increase the basicity and stabilize the resulting adduct [7]. Table 1 indicates that the stabilities of the alkyl substituted etherates increase in the order $(CH_3)_2O \cdot BF_3 > (C_2H_5)_2O \cdot BF_3$, apparently due to increased steric interferences, despite the increased inductive effect of the larger alkyl group. Apparently, the β-carbon in the ethyl group of the latter compound interferes with the normal positioning of the fluorine atoms in the complex [7]. For the analogous thioether series, Table 1 indicates that the stability of the alkyl substituted thioethers increases in the order $(C_4H_9)_2S \cdot BF_3 > (C_2H_5)_2S \cdot BF_3 > (CH_3)_2S \cdot BF_3$ at 0°C. The fact that the expected inductive/stability order is observed in the alkyl substituted thioethers is attributed to the larger size of the central sulfur atom, which overcomes the steric hinderance encountered in the analogous ether systems.

The above concepts regarding donor atom and inductive and steric effects of substituent groups on the equilibrium constant provide useful guidelines for evaluating potential behavior of unstudied compounds in isotope exchange. Furthermore, these guidelines are of practical interest in the selection of potentially useful donors for experimental testing.

The list of donor species presented in Table 1 were studied pursuant to development of an improved separation process with respect to the dimethyl ether-BF_3 system. The improved system would be subject to all criteria previously outlined. Examination of Table 1 is indicative that a number of exchange systems possess a larger equilibrium constant (criterion a) than the dimethyl ether system. Most of these systems were dismissed based on failure to meet one or another of the remaining criteria presented. In a number of cases, a donor was eliminated prior to obtaining experimental equilibrium data.

Studies with anisole as the donor species in the isotope exchange reaction indicated that this system was indeed superior to the dimethyl ether system [6,16]. The promising experimental results for the anisole-BF_3 exchange reaction prompted both bench scale and pilot plant studies with this system [24,25]. The final conclusion from these studies was that the anisole process was a definite improvement over the dimethyl ether system and was amenable to plant scale application.

It was postulated that phenetole would be a better donor for isotope fractionation than anisole, but the appropriate bench scale and pilot plant studies have not yet been performed [7].

Despite the positive results suggesting the use of anisole as the separative agent for large scale fractionation of the boron isotopes, its use has not been incorporated into the process. A satisfactory answer regarding why anisole has not been incorporated into the separation scheme is unavailable in the literature. It is therefore postulated that the reason involves economic considerations.

Effect of Temperature and Pressure on K_{eq}

Examination of the available equilibrium constant data in Table 1 indicates that K_{eq} increases as temperature decreases. The only exception to this observation is for the dimethyl sulfoxide (DMSO) system. Thus, in all but this one instance, the isotopic exchange reaction is exothermic. In the case of the DMSO system, examination of the original literature [26] indicates that this data was obtained by parametric pumping studies based on isotopic equilibrium between $DMSO \cdot BF_3$ complex in the solid state and gaseous BF_3. This is the only known instance of equilibrium constant determination between the gaseous and solid states, and is therefore indicative that the isotope exchange reaction in such systems may indeed be endothermic.

Studies regarding the effect of pressure on the equilibrium constant for isotope exchange are extremely limited. Only one literature reference to such a study was obtained [27], and the nature of this source left much to be desired. In that study, the equilibrium constant (system unknown) was measured over a pressure range of 1 to 4.5 atmospheres. The equilibrium constant was observed to decrease from $K_{eq} = 1.027$ at 1 atm to $K_{eq} = 1.017$ at 4.5 atm. This decrease was presumed to be due to increased solubility of gaseous BF_3 in the liquid complex. This observation was explained in terms of competing isotope exchange reactions between BF_3 bound in the complex with gaseous BF_3 and BF_3 dissolved in the liquid phase:

$$^{10}BF_{3(diss.\ gas)} + {}^{11}BF_3 \cdot Donor_{(l)} \rightleftharpoons {}^{11}BF_{3(diss.gas)} + {}^{10}BF_3 \cdot Donor_{(l)} \tag{5}$$

$$^{10}BF_{3(g)} + {}^{11}BF_3 \cdot Donor_{(l)} \rightleftharpoons {}^{11}BF_{3(g)} + {}^{10}BF_3 \cdot Donor \tag{6}$$

The equilibrium constant for the liquid phase exchange (reaction 5) was reported as 1.003 at 25°C [27].

Palko et al. [6,22] has observed that BF_3 is quite soluble in several of the liquid complexes studied and that the solubility generally increases with decreasing temperature. The increased solubility results in a lowering of the observed equilibrium constant. In agreement with the above pressure study, Palko indicated the equilibrium constant for the liquid phase exchange reaction (reaction 5) was small, on the order of 1.002 [6].

Based on the above discussions, the effect of pressure on the equilibrium constant may vary considerably depending on the solubility of BF_3 gas in the liquid phase.

Kinetics of Isotope Exchange Reactions

In order to achieve a high throughput of process materials in isotope exchange, the rate of exchange in such systems must be rapid. From the standpoint of process application, it is desirable that the rate of isotopic exchange be so rapid that exchange be completed as soon as the two phases are contacted in the suitable process equipment, i.e., the exchange reaction must be mass transfer limited as opposed to kinetically limited.

Literature references to kinetic studies of the isotope exchange reaction are virtually non-existent. Palko [6] examined the exchange rate for the anisole-BF_3 and triethyl amine-BF_3 systems. The technique used in that study was not amenable to measurement of exchange times less than 4 seconds. For the anisole-BF_3 system, isotopic exchange occurred much faster than 4 sec and exchange was determined to be contact limited. In the case of the triethyl amine-BF_3 system a half time for exchange of about 50 minutes was reported.

Qualitative observations indicate that the rate of ^{10}B-^{11}B exchange for highly dissociated complexes is extremely rapid, while exchange rates for the more stable complexes were considerably slower [6]. Thus, the kinetics of the isotopic exchange reaction is intimately connected to the relative strength of the BF_3-donor bond. This observation is supported by kinetic studies pertaining to BF_3 exchange between mixtures of oxygen containing donors in the liquid phase [28,29,30].

Theory of Isotope Exchange Reactions

Isotope exchange reactions are not unique to boron and are documented for the isotopes of many of the lighter elements [31]. The observed thermodynamic phenomena are a manifestation of small differences in the energy states of isotopically different molecules. Thus, the equilibrium constant is adequately correlated with the energy states of the molecules as secured from spectral data. Statistical thermodynamics provides the medium through which spectral data is related to the thermodynamic equilibrium constant. The generalized theory of equilibrium constants for isotope exchange reactions has been eloquently presented by Urey [31].

Palko and Drury [32] have proposed a model of isotope exchange which adequately accounts for the observed variation in the equilibrium constant and explains the behavior of the different boron halides in isotope exchange reactions. This model is supported by theoretical calculations based on spectral data. A development of this isotope exchange model follows.

Consider first the electronic and structural details of BF_3 and its constituent atoms. The free boron atom has three valence shell electrons in the nominal configuration $2s^2p^1$. The free fluorine atom has seven valence shell electrons with the nominal $2s^2p^5$ configuration. When a molecule of BF_3 is formed, the boron valence shell electrons are promoted to sp^2 hybridized orbitals and three boron to fluorine bonds are formed by sharing the unpaired fluorine electrons. The resulting BF_3 molecule is planar with the nominal 120° central bond angle and an empty boron p orbital protruding from the plane of the molecule at 90°. Each fluorine atom in BF_3 has three non-bonding electron pairs, and due to the small size of fluorine, the electron pairs are crowded much closer together than in any other element. Consequently, the repulsive forces between these lone pairs are much greater in fluorine than in any other element. Due to the large repulsive forces, a fluorine lone pair of electrons occupies the empty boron p orbital in the BF_3 molecule. One fluorine atom is therefore essentially double bonded to boron while the remaining two fluorines have conventional sigma bonds. There are three such configurations possible and resonance occurs between them [34]. The associated resonance energy has been estimated to be 48 kcal/mol [35]. This resonance energy is much greater than the energy involved in formation of the BF_3-donor bond upon adduct formation and is directly responsible for the enrichment of the lighter isotope in the liquid phase.

The boron p orbital used for π-bonding to one of the fluorines in BF_3 must be available for formation of the coordinate covalent bond between BF_3

and a Lewis base. Thus, the π-bond energy associated with BF_3 must be released and the energy associated with adduct formation must be absorbed when the $BF_3\cdot$donor molecular addition compound is formed. It is convenient to regard these energy changes as occurring in separate, discrete steps. The isotope exchange reaction discussed previously:

$$^{11}BF_3\cdot Donor_{(\ell)} + {}^{10}BF_{3(g)} \rightleftharpoons {}^{10}BF_3\cdot Donor_{(\ell)} + {}^{11}BF_{3(g)} \tag{4}$$

may therefore be rewritten as a composite of the two reactions:

$$^{10}BF_{3(g)} + {}^{11}BF_3{}^*{}_{(g)} \rightleftharpoons {}^{11}BF_{3(g)} + {}^{10}BF_3{}^*{}_{(g)} \tag{7}$$

$$^{11}BF_3{}^*{}_{(g)} + {}^{10}BF_3\cdot Donor_{(\ell)} \rightleftharpoons {}^{10}BF_3{}^*{}_{(g)} + {}^{11}BF_3\cdot Donor_{(\ell)} \tag{8}$$

where $BF_3{}^*$ is a hypothetical intermediate in which no π-bonding occurs, e.g. a molecule in which all fluorines are attached to boron with a conventional sigma bond. The respective equilibrium constants for reactions (7) and (8) are given by:

$$K_{eq}\ (7) = \frac{Q(^{11}BF_3)}{Q(^{10}BF_3)} \Bigg/ \frac{Q(^{11}BF_3{}^*)}{Q(^{10}BF_3{}^*)} \tag{9}$$

$$K_{eq}\ (8) = \frac{Q(^{11}BF_3\cdot Donor)}{Q(^{10}BF_3\cdot Donor)} \Bigg/ \frac{Q(^{11}BF_3{}^*)}{Q(^{10}BF_3{}^*)} \tag{10}$$

where Q represents the vibrational partition function of the indexed isotopic species. The ratio of these equilibrium constants is the equilibrium constant for the overall isotope exchange reaction, reaction (4):

$$K_{eq}\ (4) = \frac{K_{eq}\ (7)}{K_{eq}\ (8)} = \frac{Q(^{11}BF_3)}{Q(^{10}BF_3)} \Bigg/ \frac{Q(^{11}BF_3\cdot Donor)}{Q(^{10}BF_3\cdot Donor)} \tag{11}$$

At a specific temperature, K_{eq} (7) is fixed and the value of K_{eq} (8) will depend on the magnitude of the vibrational partition function ratio for the isotopic species in the molecular addition compound. The value of the numerator in equation (10) will depend on the specific donor and will be largest for strongly bound molecular addition compounds. Note that as K_{eq} (8) approaches unity as a limit, the observed equilibrium constant K_{eq} (4) approaches K_{eq} (7). Thus, K_{eq} (7) represents the maximum value the observed equilibrium constant, K_{eq} (4), may assume.

If the appropriate spectroscopic data is available, values for the ratios of the partition functions in equations (9), (10), and (11) can be calculated using the relationships of statistical thermodynamics. In the case of the hypothetical BF_3^* intermediates, partition function ratios were empirically evaluated from BF_3 and BF_4^- spectroscopic data. Thus, equations (9) through (11) provide the theoretical basis for estimating the maximum obtainable equilibrium constant, K_{eq} (7), and the expected equilibrium constant for any BF_3-donor system, K_{eq} (4), at a specified temperature.

Palko and Drury [32] have calculated values for the ratios of the vibrational partition functions in equation (9) at temperatures of 303K and 250K from the appropriate spectroscopic data and determined the theoretical maximum value the equilibrium constant may assume at these temperatures. These results are summarized in Table 2.

The linear extrapolation of $K_{eq}(7)$ as a function of temperature through the two points listed in Table 2 is of some interest, given by:

$$\ln \alpha = \frac{12.233}{T(K)} + 0.00556 \tag{12}$$

Equation (12) represents the theoretical maximum value the equilibrium constant may assume for a specific temperature.

Table 2. Ratios of the vibrational partition function for BF_3 and BF_3^* at 303K and 250K [32].

	Temperature	
Vibrational Partition Function	303K	250K
$Q(^{11}BF_3)/Q(^{10}BF_3)$	1.2046	1.2680
$Q(^{11}BF_3^*)/Q(^{10}BF_3^*)$	1.1506	1.2006
$K_{eq}(7) = \dfrac{Q(^{11}BF_3)}{Q(^{10}BF_3)} \Big/ \dfrac{Q(^{11}BF_3^*)}{Q(^{10}BF_3^*)}$	1.047	1.056

Table 3. Calculated and observed values of the isotopic equilibrium constant for reaction (4) at 303K [32].

Donor	$\dfrac{Q(^{11}BF_3 \cdot Donor)}{Q(^{10}BF_3 \cdot Donor)}$	$\dfrac{Q(^{11}BF_3)}{Q(^{10}BF_3)} \Big/ \dfrac{Q(^{11}BF_3 \cdot Donor)}{Q(^{10}BF_3 \cdot Donor)}$	Exptl. Obs. $K_{eq}(4)$
$(CH_3)_2O$	1.1706	1.2046/1.1706 = 1.029	1.027
$(CH_2)_4O$	1.1789	1.2046/1.1789 = 1.022	1.026

If the spectroscopic data for the isotopic forms of the $BF_3 \cdot$Donor complexes are available, the equilibrium constant for reaction (4), $K_{eq}(4)$, may also be calculated. Begun and Palko [33] have obtained and interpreted the necessary spectra for the BF_3 complexes of diethyl ether and tetrahydrofuran and calculated theoretical values of the equilibrium constants for these systems (Table 3). The calculated and experimental values are in excellent agreement.

The effect of temperature on the partition function ratios is apparent from Tables 2 and 3. As temperature increases, the ratio of the partition functions decreases. The corresponding effect is a reduction of the equilibrium constant, K_{eq} (4), as temperature increases. This trend is expected since the vibrational partition function depends inversely on temperature. Therefore, as temperature increases, the value of the partition function decreases and their ratio approaches unity.

It is appropriate at this point to consider the substitution of one of the other boron halides for BF_3 in the isotopic exchange reaction. As previously expressed, the BF_3 exchange reaction proceeds as observed due to electrostatic relaxation when a fluorine electron pair occupies the empty boron p orbital. The magnitude of the electrostatic repulsions between non-bonding electron pairs progressively decreases moving down the periodic table from fluorine to iodine due to increasing atomic radius. Thus, the ratio of area to pairs for non-bonding electrons increases by factors of 2, 3, and 4, respectively. Consequently, the π-bond energy and the B-X stretching force constant decreases as progressively heavier halogens are substituted for fluorine in BX_3. In terms of the two step mechanism previously described for isotope exchange, the equilibrium constant for reaction (7), K_{eq} (7), tends to unity as the B-X stretching force constant decreases. At the same time, the molecular adduct is becoming more stable due to increased strength of the Lewis acid with the heavier halogens. Thus, the equilibrium constant for reaction (8), K_{eq} (8), is becoming larger. When K_{eq} (8) is equal to K_{eq} (7), isotopic fractionation will cease to occur in reaction (4) and the overall equilibrium constant, K_{eq} (4), will be unity. It is therefore reasonable to expect that the equilibrium constant will decrease as BCl_3, BBr_3, or BI_3 are substituted for BF_3 in the isotope exchange reaction for a particular donor species. Furthermore, the heavy isotope of boron, ^{11}B, is expected to concentrate in the liquid phase at some point in this substitution process.

There is little data in the literature to support the above predictions, primarily because the heavier boron trihalides are such strong Lewis acids that they tend to decompose most donors. Two systems with BCl_3 as the Lewis acid have been reported [15]. The exchange reactions and equilibrium constants are:

$$(C_6H_5)_2O\cdot{}^{11}BCl_{3(\ell)} + {}^{10}BCl_{3(g)} \rightleftharpoons (C_6H_5)_2O\cdot{}^{10}BCl_{3(\ell)} + {}^{11}BCl_{3(g)} \qquad (12)$$

$$K_{eq} = 1.002 \ (28°C)$$

$$CH_3COCl\cdot{}^{11}BCl_{3(\ell)} + {}^{10}BCl_{3(g)} \rightleftharpoons CH_3COCl\cdot{}^{10}BCl_{3(\ell)} + {}^{11}BCl_{3(g)} \qquad (13)$$

$$K_{eq} = 0.996 \ (25°C)$$

It is apparent that the equilibrium constants for reactions (12) and (13) are much smaller than for similar BF_3 reactions. Furthermore, for the acetyl chloride system, the reversal in the direction of isotopic enrichment is observed.

It can be concluded that isotopic fractionation in the exchange reaction is a quantum mechanical effect. This effect is amplified with BF_3 as the Lewis acid due to the unique electronic characteristics of boron and fluorine. The above described model adequately accounts for the observed behavior of the isotopic exchange reaction. It is possible to theoretically estimate the expected equilibrium constant for $BF_3\cdot$Donor systems solely from spectroscopic data. The theory of isotope exchange provides valuable insight regarding the expected trends in the evaluation of equilibrium constants for previously unstudied BF_3-donor systems.

PURPOSE AND SCOPE OF PRESENT STUDY

The purpose for the current study was twofold. First, several previously unstudied donors, predominately ketones, were examined to determine if such donors would be viable replacements for the dimethyl ether/BF_3 system. The separation factor, α, was experimentally measured for the new donors to accomplish this goal. Secondly, modelling and analysis of large scale boron isotope separation facilities were performed to examine potential methods of increasing the efficiency of such systems.

As previously mentioned, the ideal single stage separation factor, α, associated with prevalent process equipment is expected to be identical to K_{eq} for the isotope exchange reaction. Deviations between these two values may occur due to solubility of the ^{11}B enriched gas phase in the ^{10}B enriched liquid phase, essentially "diluting" the isotopic constitution of the liquid complex. Furthermore, incomplete dissociation of the complex in the vapor phase can cause a dilution of the ^{11}B enriched gas phase with ^{10}B enriched complex. Both phenomena result in a lowering of α from the "true" value of K_{eq}, i.e. the value of the equilibrium constant in the absence of these effects. From the standpoint of the design and operation of a large scale facility, the single stage separation factor, α, is the more desirable quantity to have readily available since the phenomenon responsible for lowering α from the equilibrium constant would be expected to operate in the prevalent process equipment. Consequently, the scope of the experimental study focussed on the evaluation of α and not on the measurement of the "true" equilibrium constant, K_{eq}.

Besides the measurement of separation factors associated with the isotope exchange reaction, the relative stability of the BF_3·donor complexes studied were qualitatively examined. In the experimental procedure used, the various complexes were in contact with BF_3 gas for several days or weeks. Thus, the mass spectroscopic analysis procedure was used to examine any irreversible decomposition of the molecular addition compounds over extended periods of time. As previously discussed in conjunction with the currently used dimethyl ether large scale fractionation system, irreversible decomposition of BF_3 complex results in a number of processing problems. A goal in this portion of the study was to gain at least a qualitative idea of the relative stability of the BF_3·donor complexes examined experimentally.

Various large scale boron isotope fractionating facilities based on chemical exchange between BF_3 and the BF_3·dimethyl ether complex have been in operation in the U.S. for nearly 50 years. Despite this fact, detailed modelling and analysis studies of these systems are nonexistent in the open literature. The need for such studies is mandatory if efficient commercial plants are to be built and operated. It is possible that the required studies have been conducted, but this information is proprietary and therefore has not appeared in the open literature. Modelling and analysis of plant scale separation cascades based on chemical exchange was therefore conducted as the second aspect of this research program. Results from this portion of the study are expected to facilitate the design of future experiments on both the bench and pilot plant scale. Furthermore, these studies provide insight regarding the size and design of separation columns in plant scale systems based on chemical exchange.

The scope of the modelling and analysis portion of this study included generating computer models for several different counter current recycle cascade configurations typically encountered in large scale isotope separations. These models were based on the separation factors evaluated for the donor systems studied experimentally. Of necessity, these models were based on the concept of ideal stages where the streams exiting each stage were in chemical equilibrium. Only ideal stages could be considered since no experimental data pertaining to stage efficiency was obtained in this research.

These computer models were used to determine the ideal stage and total interstage flow requirements associated with each of the different cascade configurations. The number of ideal stages provides a measure of the height of the fractionating column while the total interstage flow is a measure of the amount of material processed by the cascade. A knowledge of the ideal stage and total interstage flow requirements indicates the relative size of the separation system associated with a given donor system. For comparison, models based on the literature value of the separation factor for the dimethyl ether/BF_3 system were also included in this study.

Within the confines of the experimental data available, an analysis of plant size based on the computer models was possible. The effects that the different donor systems had on the size of the separation plant were evaluated. The analysis was also extended to examine the pros and cons of incorporating a stripping section in the separation system. Ultimately, such an analysis is beneficial in establishing an efficient cascade design for large scale boron isotope separation based on chemical exchange.

EXPERIMENTAL DETERMINATION OF SEPARATION FACTORS

The number of molecular species capable of forming complexes with BF_3, and thus potentially useful as donors in the isotope exchange reaction, is virtually limitless. As indicated previously (refer to Table 1), only a select few of the vast number of potentially useful donor compounds have been examined in the isotope exchange reaction. The systematic examination of each possible donor compound would be a horrendous undertaking. Rather, a more prudent approach is the systematic examination of a number of species from characteristic classes of compounds to determine the potential usefulness of these materials in the exchange reaction. This is apparently the approach taken by previous researchers in this area, and a number of classes of compounds have been examined, e.g. ethers, amines, sulfides, etc.

Examination of the relevant literature is indicative that carbonyl compounds have never been studied as donor species in boron isotope exchange reactions. Furthermore, studies utilizing ketones as the donor have never been reported. Molecular addition compounds between BF_3 and the carbonyl groups of acetone, acetaldehyde, trimethyl acetaldehyde, methyl nonyl ketone, and camphor are known [5]. A portion of this study was therefore directed at examining various carbonyl compounds, specifically ketones, as the donor species in the isotope exchange reaction. Emphasis was placed on determination of the separation factors for these $BF_3 \cdot$donor systems.

Numerous compounds were prescreened as donors to determine if the BF_3 complexes with these materials actually existed. Once the existence of the complex was established, the molar ratio of BF_3 absorbed per mole of donor material and the freezing point of the resultant liquid complex were also determined. These prescreening experiments provided a measure of the solubility of gaseous BF_3 in the liquid complex and were used to determine the appropriate temperatures at which gas/liquid equilibrium data could be obtained.

Prescreening experiments with acetone, acetophenone, methyl isobutyl ketone (MIBK), diisobutyl ketone (DIBK), nitromethane, and dimethyl sulfoxide (DMSO) were performed. Based on these initial experiments, the systems selected for study in equilibrium experiments were: acetone/BF_3, MIBK/BF_3, DIBK/BF_3, and nitromethane/BF_3. The acetophenone/BF_3 and DMSO/BF_3 systems were found to be unsuitable for boron isotope fractionation by chemical exchange methods.

Experimental Reagents, Equipment and Procedures

Experimental Reagents

The following compounds were obtained for use in the experimental examination of separation factors. Unless otherwise noted, materials were used as received with no attempt at further purification.

Boron trifluoride, BF_3, was obtained from the Matheson Gas Company, Inc. and was of chemical purity (c.p.) grade with a minimum reported purity of 99.5% BF_3. This gas was used as the boron feed in all experiments. Mass spectral analysis indicated the boron isotopes were present in approximately the natural abundance (19.7% ^{10}B, 80.3% ^{11}B).

High purity helium was obtained from the Linde Company with a minimum reported purity of 99.995% He. The high purity helium (HP He) was used as a purge gas to eliminate entrained air, and thus atmospheric moisture, from experimental equipment prior to use of BF_3.

Phenetole or ethyl phenyl ether, $C_6H_5OC_2H_5$, was obtained from the Aldrich Chemical Company. The reported purity was 99% phenetole.

Reagent grade acetone, $(CH_3)_2CO$, was obtained from the J. T. Baker Company with a minimum reported purity of 99.6% acetone.

Dimethyl sulfoxide, $(CH_3)_2SO$, was obtained from the Crown Zellerbach Company Incorporated.

Acetophenone or methyl phenyl ketone, $C_6H_5COCH_3$, was obtained from the Aldrich Chemical Company with a reported purity of 99.5%.

Methyl isobutyl ketone (4-methyl-2-pentanone, $(CH_3)_2CHCH_2COCH_3$, or MIBK) was obtained from the Aldrich Chemical Company.

Diisobutylketone (2,6-dimethyl-4-heptanone, $(CH_3)_2CHCH_2COCH_2CH(CH_3)_2$, or DIBK) was obtained from the Union Carbide Corporation.

Nitromethane, CH_3NO_2, was obtained from the Aldrich Chemical Company with a reported purity of 96%. This material was redistilled by the organic group in the Chemistry Department of Montana State University to remove residual water. This purified or redistilled material was used in all subsequent equilibrium experiments.

Experimental Equipment and Procedures

The separation factor for the exchange reaction being discussed:

$$^{10}BF_{3(g)} + {}^{11}BF_3 \cdot Donor_{(\ell)} \rightleftharpoons {}^{11}BF_{(3)} + {}^{10}BF_3 \cdot Donor_{(\ell)} \qquad (4)$$

is given by:

$$\alpha = \frac{[^{10}B/^{11}B]_{(\ell)}}{[^{10}B/^{11}B]_{(g)}} \approx \frac{[^{10}B/^{11}B]_{(\text{gas before equilibration})}}{[^{10}B/^{11}B]_{(\text{gas after equilibration})}} \qquad (15)$$

The approximation in the second relationship can be assumed only in the case where the amount of BF_3 in the gas phase is small compared to the amount of BF_3 tied up as complex in the liquid phase. This assumption is valid since it has been shown that essentially all the isotope exchange occurs in the vapor or gaseous phase [6]. It is desirable to keep the ratio of gas to liquid as high as 1:50 or 1:100 to insure that the approximation in equation (15) is valid.

Due to the difficulties associated with the quantitative recovery of BF_3 from the liquid complex, analysis of the $^{10}B/^{11}B$ ratios of only the gas phases greatly simplifies the determination of the separation factor, α. However, caution must be used in sampling the equilibrated gas phase. The sample removed after equilibration must be small and must be rapidly removed so as not to disturb the equilibrium compositions. Otherwise, BF_3 is "boiled off" of the liquid complex, contaminating the ^{11}B enriched gas phase.

Using elaborate vacuum equipment and appropriate experimental techniques, all previous investigators have determined values of α based on the approximation given in equation (15). Primarily due to equipment limitations, numerous attempts to reproduce literature values of α for the phenetole/BF_3 system in this laboratory by the above method of sampling only the gaseous phases failed. Although isotopic fractionation occurred in the "proper" direction, e.g. ^{10}B concentrated in the liquid phase while ^{11}B concentrated in the gaseous phase, the experimentally determined values of α were consistently low. This problem was attributed to the inability to adequately control the amount of BF_3 added to the cell, thus the BF_3 gas to liquid ratio was too high, and the approximation in equation (15) was invalid.

The experimental equilibrium cell designed to obtain separation factors associated with the isotope exchange reaction is shown in Figure 1. The cell consisted of a cylindrical vessel machined from 316 stainless steel. The internal volume of the cell was approximately 265 ml. The cell lid was secured by machine screws and incorporated a viton o-ring to facilitate a leak free seal. The cell lid contained gas inlet and outlet ports, a thermowell and a pressure transducer port. A liquid circulating pump withdrew the liquid phase from a port near the bottom of the cell body and returned the liquid near the top of the cell through a sparger placed in the vapor space just under the cell lid. The circulation and sparging action of the liquid phase provided agitation of the cell contents. A valved, small diameter tube placed in the circulating pump return line between the pump and the cell body provided a simple means of removing a small amount of the liquid complex for the isotopic abundance analysis (*vide infra*).

The first step in the experimental procedure was to place a known volume (≈45 ml to 65 ml) of the donor liquid into the equilibrium cell. The cell lid was then sealed in place. The cell was purged with high purity helium and evacuated under vacuum to remove any entrained air (and thus atmospheric moisture) from the cell. Once the cell was evacuated, only the pure donor material remained sealed in the equilibrium cell. Donor losses were expected during the evacuation process, but the amount of material lost was unknown.

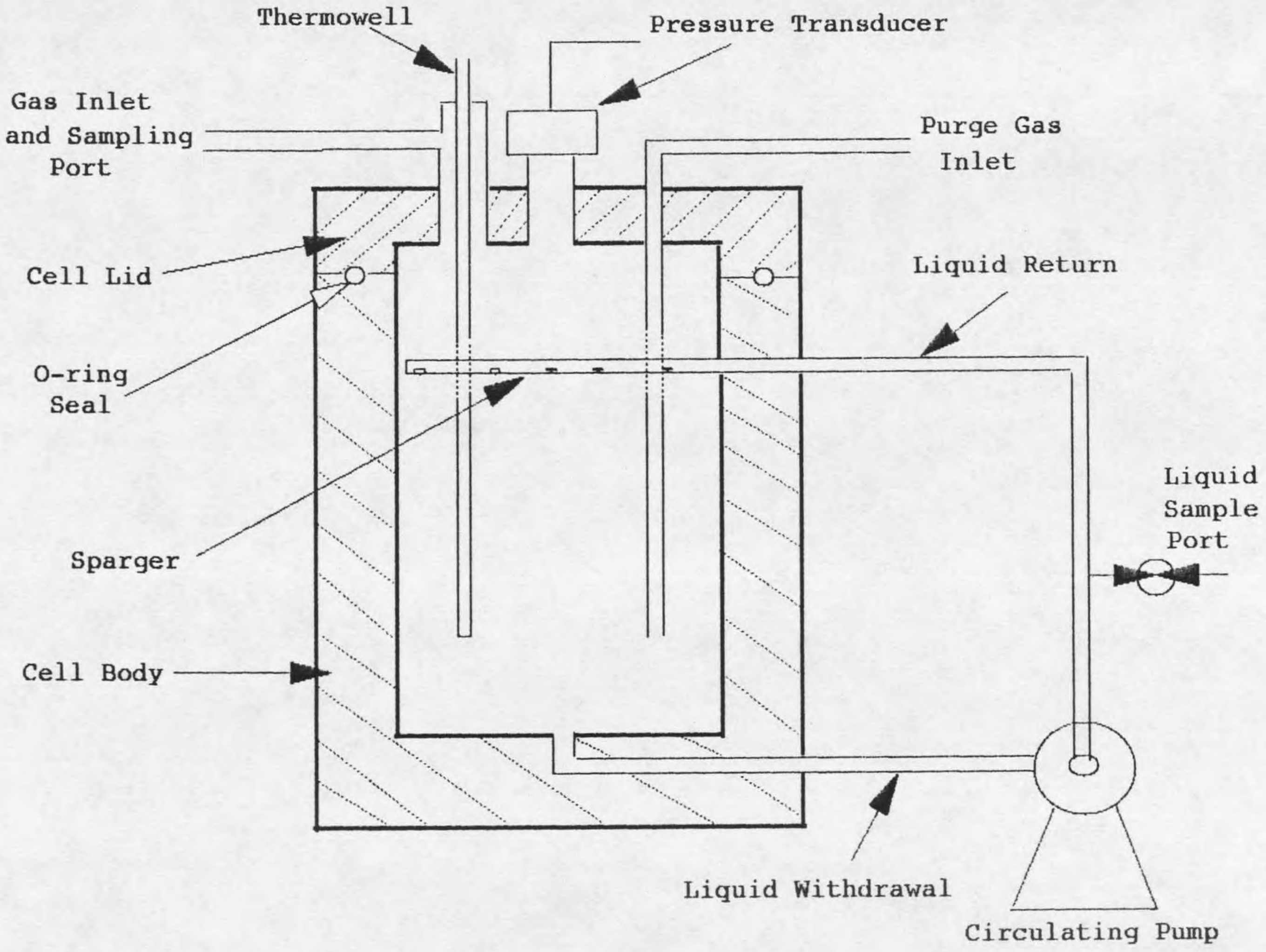
Thermowell
Pressure Transducer
Gas Inlet and Sampling Port
Purge Gas Inlet
Cell Lid
Liquid Return
O-ring Seal
Liquid Sample Port
Sparger
Cell Body
Liquid Withdrawal
Circulating Pump

Figure 1. Schematic of the test cell used to obtain experimental data.

The cell was then placed in a constant temperature bath preset to the desired equilibrium temperature. Once the cell and its contents reached the temperature of the bath, BF_3 was slowly added to the system. The internal pressure was monitored with the pressure transducer as BF_3 was added to the cell. Thus, the liquid complex was formed *in situ* and once the pressure stabilized at between 8 to 14 psig, the complex formation process was assumed complete and the BF_3 feed to the cell was shut off.

The cell and its contents were then allowed to stand at the desired equilibrium temperature for an appropriate length of time. Usually 12 to 24 hours were allowed to establish the isotopic equilibrium between the two phases. Samples of both the gas and liquid phases were withdrawn from the cell and the boron isotopic ratios determined by mass spectroscopy. The separation factor for the given BF_3/donor at the specific equilibrium temperature was then evaluated from this information. The sampling/analysis process was repeated several times at a given equilibrium temperature. The temperature was then changed and the associated separation factor determined in an analogous manner at the new equilibration temperature. Thus, a single experiment provided the separation factor for a particular BF_3/donor system as well as the temperature dependance of α.

Mass Spectroscopic Isotopic Abundance Analysis

Since no attempt was made in the above outlined experimental procedure to control the BF_3 ratio between the gas and liquid phases, the approximation in equation (15) could not necessarily be assumed. Thus, an analysis of the boron isotope abundance ratio for both the gas and liquid phases was required. The associated separation factor was evaluated from the relationship:

$$\alpha = \frac{[^{10}B/^{11}B]_{(l)}}{[^{10}B/^{11}B]_{(g)}} \tag{16}$$

which is merely the equality in equation (15). In the above outlined procedure, the value of α was determined directly by equation (16) from mass spectroscopic analysis of the two phases. Consequently, the molar quantities of BF_3 and pure donor in the equilibrium cell were not required for the evaluation of α. It was only necessary that an excess amount of gaseous BF_3 be present in the cell for exchange with the BF_3 bound in the liquid complex.

The analysis of the isotopic ratio in the liquid phase, $[^{10}B/^{11}B]_{(l)}$, presents a number of problems due to the difficulties associated with sampling the liquid phase and quantitative recovery of BF_3 from the liquid complex. Therefore, previous researchers have not attempted isotopic analysis of the liquid molecular addition compound.

These problems were overcome by developing a novel analytical technique for determining the boron isotopic ratio in the equilibrated liquid phase. The liquid phase was sampled by withdrawing a small amount (≈ 0.6 ml) from the cell through a needle port. This sample was added to a small amount of the pure liquid donor compound (≈ 0.3 ml) in a sample vial. The excess liquid donor in the sample vial insured that any dissolved BF_3 remained bound as complex in the sample. This measure prevented isotopic fractionation from occurring in the sample vial prior to completion of the isotopic analysis.

The isotopic analysis of the liquid phase was accomplished by injecting an appropriate amount of the liquid sample, taken and prepared as described above, directly into the septum inlet port of the mass spectrometer. The mass spectrometer gas reservoir was maintained at a constant temperature of 200°C and pressure of 10^{-2} torr. These conditions provided a convenient *in situ* method for thermally and quantitatively decomposing the liquid complex into the BF_3 gas and donor compound. The analysis appeared to provide accurate and reproducible results for the isotopic abundance of boron in the liquid complex and was advantageous in that the isotopic abundance of the liquid phase could be determined directly. The evaluation of the liquid phase isotopic composition in the above manner constituted the first known attempt at such an analysis. Consequently, this work was expected to provide the actual value of α for the first time since the approximation in equation (15) was unnecessary.

The mass spectrum of the $BF_3 \cdot$donor liquid complex obtained in the above manner was the superimposed spectra of the donor compound and BF_3. The liquid analysis procedure required that the donor compounds had no characteristic mass spectral peaks at m/z 48^+ and 49^+, since these signals are attributed to the $^{10}BF_2^+$ and $^{11}BF_2^+$ ions, respectively, and are used for the isotopic abundance analysis of boron. If the donor species has contributions to the mass spectrum of the liquid complex at these masses, alternate methods must be employed for the boron isotopic abundance analysis. Such alternate methods might include correcting the signals for contributions from the donor, using high resolution mass spectroscopy to separate the donor and BF_3 peaks of nearly the same mass, or calibrating the mass spectrometer to use different masses in the isotopic abundance determination. Fortunately, the donor materials that were used in this study exhibited no interferences at the BF_2^+ positions in the mass spectra.

Sampling of the equilibrated BF_3 gas phase was accomplished by removing 1 to 2 cc of the gas from the cell into a clean, dry gas sampling reservoir. The mass spectral procedure for the determination of isotopic abundance in gaseous BF_3 was developed during the early stages of this research program. In this procedure, BF_3 gas was bled into the ionization chamber of the mass spectrometer from a gas sample reservoir through a leak valve. The leak valve used was a series 203 variable leak manufactured by the Granville-Phillips Company. The variable leak is simply a very low conductance valve used for sensitive control of gas flows across the extreme pressure drop from the gas sample tube ($\approx$ 1 atm) to the mass spectrometer ionization chamber ($\approx 10^{-7}$ torr).

Results and Discussion

The Phenetole/BF_3 System

Since the experimental and analytical techniques used to study chemical exchange in this research were new and untested, it was necessary to establish the validity of these procedures. This task was readily accomplished by examination of a BF_3/donor system studied by previous researchers with results available in the literature. Once the validity of the experimental and analysis procedures were proven, new systems could be confidently examined with these techniques.

The BF_3/phenetole system was chosen to further develop and test the experimental and analytical techniques. Phenetole was chosen as the donor material since the $BF_3\cdot$phenetole complex is reported to have a respectable separation factor of $\alpha = 1.051$ at 0°C [6]. Furthermore, this liquid complex is reportedly quite stable with regards to irreversible decomposition [7].

Several experiments were conducted to establish the validity of the new experimental technique and analytical procedure with the phenetole/BF_3 isotope exchange system. The separation factor was determined as a function of temperature by the above described analytical and experimental techniques for this system. The results of these experiments are presented in Figure 2. The best fit straight line through the experimental data is also indicated. The equation of this line, obtained by linear regression analysis, is given by:

$$\ln \alpha = \frac{23.94}{T\ (K)} - 0.03489 \qquad (17)$$

The best fit line through the literature data taken from Table 1 for the phenetole/BF_3 system is also shown in Figure 2. The equation of this line is given by:

$$\ln \alpha = \frac{30.42}{T\ (K)} - 0.06158 \qquad (18)$$

As indicated in Figure 2 and by comparison of the above linear equations, the experimental and literature data show reasonable agreement. The slope of the two lines are approximately equal, indicating consistency between the two data sets. The experimental data is consistently somewhat higher than the corresponding literature data. This may be attributed to the fact that the experimental data was obtained directly by analysis of both gas and liquid isotopic abundance ratios without the need for the approximation previously discussed in conjunction with equation (15).