



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
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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 (HIBK), 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 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.

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APPROVAL

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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.

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TABLE OF CONTENTS

	<u>Page</u>
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

	<u>Page</u>
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

<u>Table</u>		<u>Page</u>
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

<u>Figure</u>		<u>Page</u>
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

<u>Figure</u>		<u>Page</u>
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, $(\text{CH}_3\text{O})_3\text{B}$; (4) steam distillation of boric acid, H_3BO_3 ; (5) isotope exchange between dimethyl ether- BF_3 complex, $(\text{CH}_3)_2\text{O} \cdot \text{BF}_3$, and BF_3 ; and (6) isotope exchange between ethyl borate- BF_3 complex, $(\text{C}_2\text{H}_5\text{O})_3\text{B} \cdot 2\text{BF}_3$ 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 $(\text{CH}_3)_2\text{O}\cdot\text{BF}_3$ exchange system is $K_{\text{eq}} = 1.027$. 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.

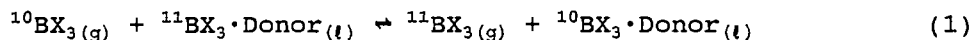
(3) Isotopic equilibrium or isotope exchange reactions where separation is affected by the isotope exchange equilibrium between boron in a liquid and a gaseous phase.

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:



where X is generally H, CH₃ or a halogen. The "complex", BX₃·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:

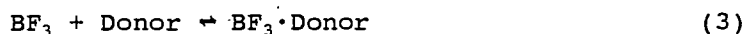
$$K_{\text{eq}} = \frac{[^{11}\text{BX}_3(\text{g})] [^{10}\text{BX}_3 \cdot \text{Donor}(\text{l})]}{[^{10}\text{BX}_3(\text{g})] [^{11}\text{BX}_3 \cdot \text{Donor}(\text{l})]} = \frac{[^{10}\text{B}/^{11}\text{B}] (\text{l})}{[^{10}\text{B}/^{11}\text{B}] (\text{g})} \quad (2)$$

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 $1 \leq K_{\text{eq}} < 1.06$. 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:



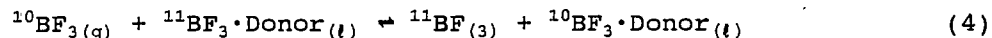
be quantitatively reversible simply by addition or removal of heat.

- (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:



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 $\text{BF}_3\cdot\text{Donor}$ 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		$K_{eq}^{\dagger}$		Reference
		30°C	0°C	
<i>Oxygen Donors</i>				
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	1.051	6,7,8
		1.042 (25°C)		
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
<i>Sulfur Donors</i>				
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
<i>Nitrogen Donors</i>				
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
<i>Miscellaneous</i>				
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:



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 $K_{\text{eq}} = 1.027$. 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 $\text{N} > \text{O} > \text{S}$ 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 $(\text{C}_2\text{H}_5)_2\text{S} > (\text{C}_2\text{H}_5)_2\text{O} > (\text{C}_2\text{H}_5)_3\text{N}$ at 30°C . In accord with theoretical considerations (*vide infra*), the increase in K_{eq} with different donors in the order $\text{S} > \text{O} > \text{N}$ 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, $(\text{CH}_3)_2\text{O} \cdot \text{BF}_3$ is more stable than $\text{C}_6\text{H}_5\text{OCH}_3 \cdot \text{BF}_3$ and $(\text{C}_6\text{H}_5)_2\text{O} \cdot \text{BF}_3$ does not form at -40°C . Accordingly, the largest equilibrium constant is associated with the weakest adduct, $\text{C}_6\text{H}_5\text{OCH}_3 \cdot \text{BF}_3$ 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 $(\text{CH}_3)_2\text{O} \cdot \text{BF}_3 > (\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$, 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 $(\text{C}_4\text{H}_9)_2\text{S} \cdot \text{BF}_3 > (\text{C}_2\text{H}_5)_2\text{S} \cdot \text{BF}_3 > (\text{CH}_3)_2\text{S} \cdot \text{BF}_3$ 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.

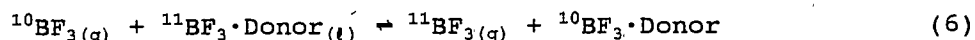
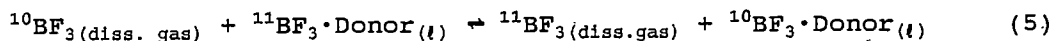
It was postulated that phenetole would be a better donor for isotope fractionation than anisole, but the appropriate bench scale and pilot plant studies have not yet been performed [7].

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:



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-BF₃ system a half time for exchange of about 50 minutes was reported.

Qualitative observations indicate that the rate of ¹⁰B-¹¹B 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 BF₃-donor bond. This observation is supported by kinetic studies pertaining to BF₃ 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].

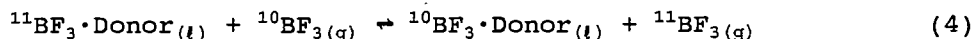
Palko and Drury [32] have proposed a model of isotope exchange which adequately accounts for the observed variation in the equilibrium constant and explains the behavior of the different boron halides in isotope exchange reactions. This model is supported by theoretical calculations

based on spectral data. A development of this isotope exchange model follows.

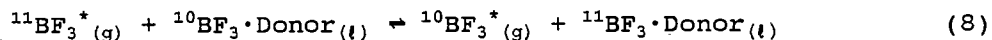
Consider first the electronic and structural details of BF_3 and its constituent atoms. The free boron atom has three valence shell electrons in the nominal configuration $2s^2p^1$. The free fluorine atom has seven valence shell electrons with the nominal $2s^2p^5$ configuration. When a molecule of BF_3 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 -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:



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



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:

$$K_{\text{eq}} (7) = \frac{Q(^{11}\text{BF}_3)}{Q(^{10}\text{BF}_3)} \bigg/ \frac{Q(^{11}\text{BF}_3^*)}{Q(^{10}\text{BF}_3^*)} \quad (9)$$

$$K_{\text{eq}} (8) = \frac{Q(^{11}\text{BF}_3 \cdot \text{Donor})}{Q(^{10}\text{BF}_3 \cdot \text{Donor})} \bigg/ \frac{Q(^{11}\text{BF}_3^*)}{Q(^{10}\text{BF}_3^*)} \quad (10)$$

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):

$$K_{\text{eq}} (4) = \frac{K_{\text{eq}} (7)}{K_{\text{eq}} (8)} = \frac{Q(^{11}\text{BF}_3)}{Q(^{10}\text{BF}_3)} \bigg/ \frac{Q(^{11}\text{BF}_3 \cdot \text{Donor})}{Q(^{10}\text{BF}_3 \cdot \text{Donor})} \quad (11)$$

At a specific temperature, $K_{\text{eq}} (7)$ is fixed and the value of $K_{\text{eq}} (8)$ 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:

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

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].

Vibrational Partition Function	Temperature	
	303K	250K
$Q(^{11}\text{BF}_3)/Q(^{10}\text{BF}_3)$	1.2046	1.2680
$Q(^{11}\text{BF}_3^*)/Q(^{10}\text{BF}_3^*)$	1.1506	1.2006
$K_{\text{eq}}(7) = \frac{Q(^{11}\text{BF}_3)}{Q(^{10}\text{BF}_3)} \bigg/ \frac{Q(^{11}\text{BF}_3^*)}{Q(^{10}\text{BF}_3^*)}$	1.047	1.056

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

Donor	$\frac{Q(^{11}\text{BF}_3 \cdot \text{Donor})}{Q(^{10}\text{BF}_3 \cdot \text{Donor})}$	$\frac{Q(^{11}\text{BF}_3)}{Q(^{10}\text{BF}_3)} \bigg/ \frac{Q(^{11}\text{BF}_3 \cdot \text{Donor})}{Q(^{10}\text{BF}_3 \cdot \text{Donor})}$	Exptl. Obs. $K_{\text{eq}}(4)$
$(\text{CH}_3)_2\text{O}$	1.1706	$1.2046/1.1706 = 1.029$	1.027
$(\text{CH}_2)_4\text{O}$	1.1789	$1.2046/1.1789 = 1.022$	1.026

If the spectroscopic data for the isotopic forms of the $\text{BF}_3 \cdot \text{Donor}$ complexes are available, the equilibrium constant for reaction (4), $K_{\text{eq}}(4)$, 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.

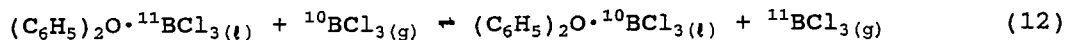
The effect of temperature on the partition function ratios is apparent from Tables 2 and 3. As temperature increases, the ratio of the

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:



$$K_{\text{eq}} = 1.002 \quad (28^\circ\text{C})$$



$$K_{\text{eq}} = 0.996 \quad (25^\circ\text{C})$$

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 -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/BF₃ 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 ¹¹B enriched gas phase in the ¹⁰B 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 ¹¹B enriched gas phase with ¹⁰B 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 -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, $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$, was obtained from the Aldrich Chemical Company. The reported purity was 99% phenetole.

Reagent grade acetone, $(\text{CH}_3)_2\text{CO}$, was obtained from the J. T. Baker Company with a minimum reported purity of 99.6% acetone.

Dimethyl sulfoxide, $(\text{CH}_3)_2\text{SO}$, was obtained from the Crown Zellerbach Company Incorporated.

Acetophenone or methyl phenyl ketone, $\text{C}_6\text{H}_5\text{COCH}_3$, was obtained from the Aldrich Chemical Company with a reported purity of 99.5%.

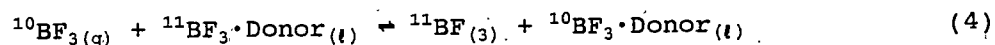
Methyl isobutyl ketone (4-methyl-2-pentanone, $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$, or MIBK) was obtained from the Aldrich Chemical Company.

Diisobutylketone (2,6-dimethyl-4-heptanone, $(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_2\text{CH}(\text{CH}_3)_2$, 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:



is given by:

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

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 $^{10}\text{B}/^{11}\text{B}$ 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.

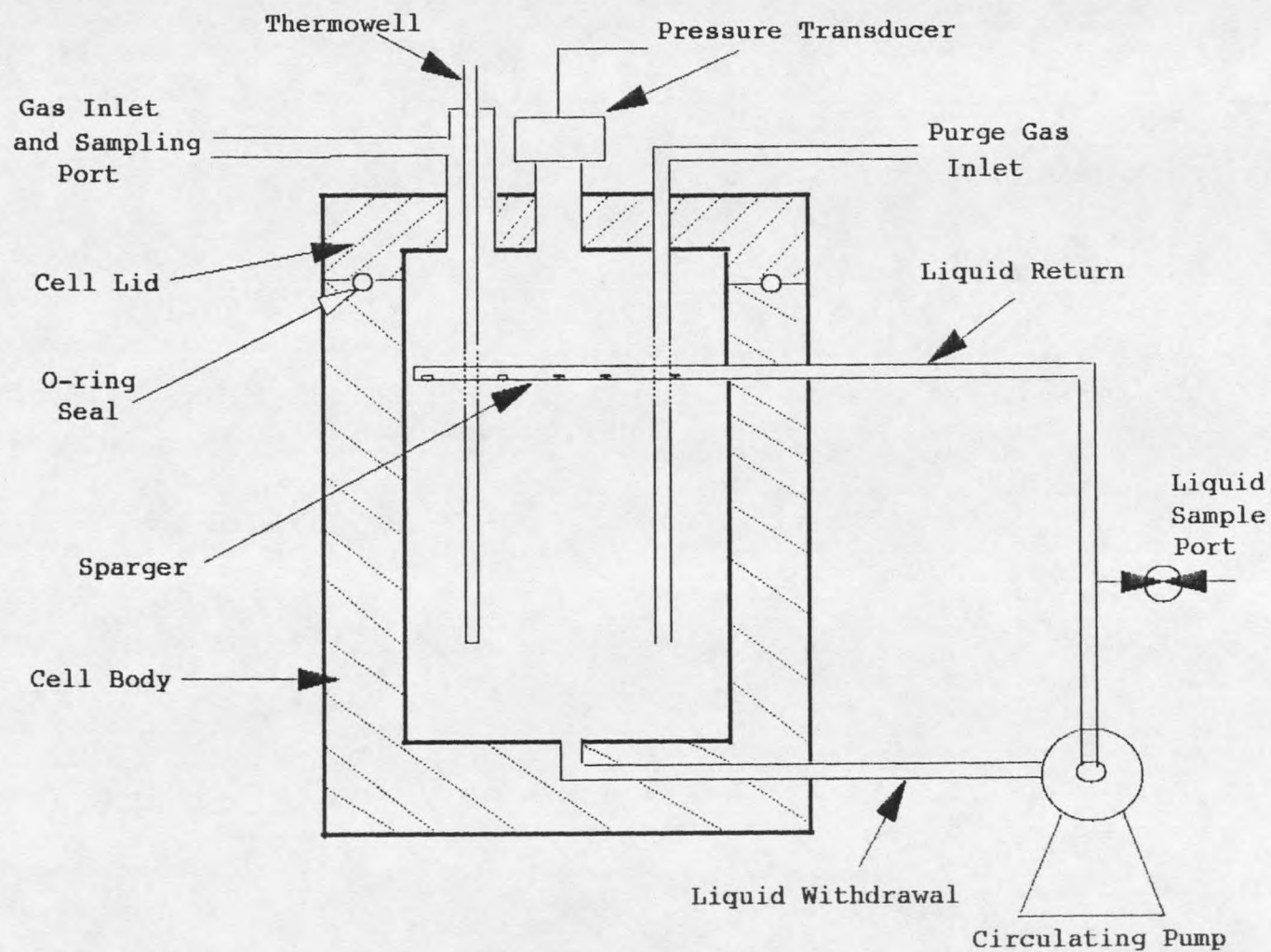


Figure 1. Schematic of the test cell used to obtain experimental data.

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:

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

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, $[^{10}\text{B}/^{11}\text{B}]_{(l)}$, 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 ·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 $^{10}\text{BF}_2^+$ and $^{11}\text{BF}_2^+$ 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 (≈ 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 -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:

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

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:

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

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).

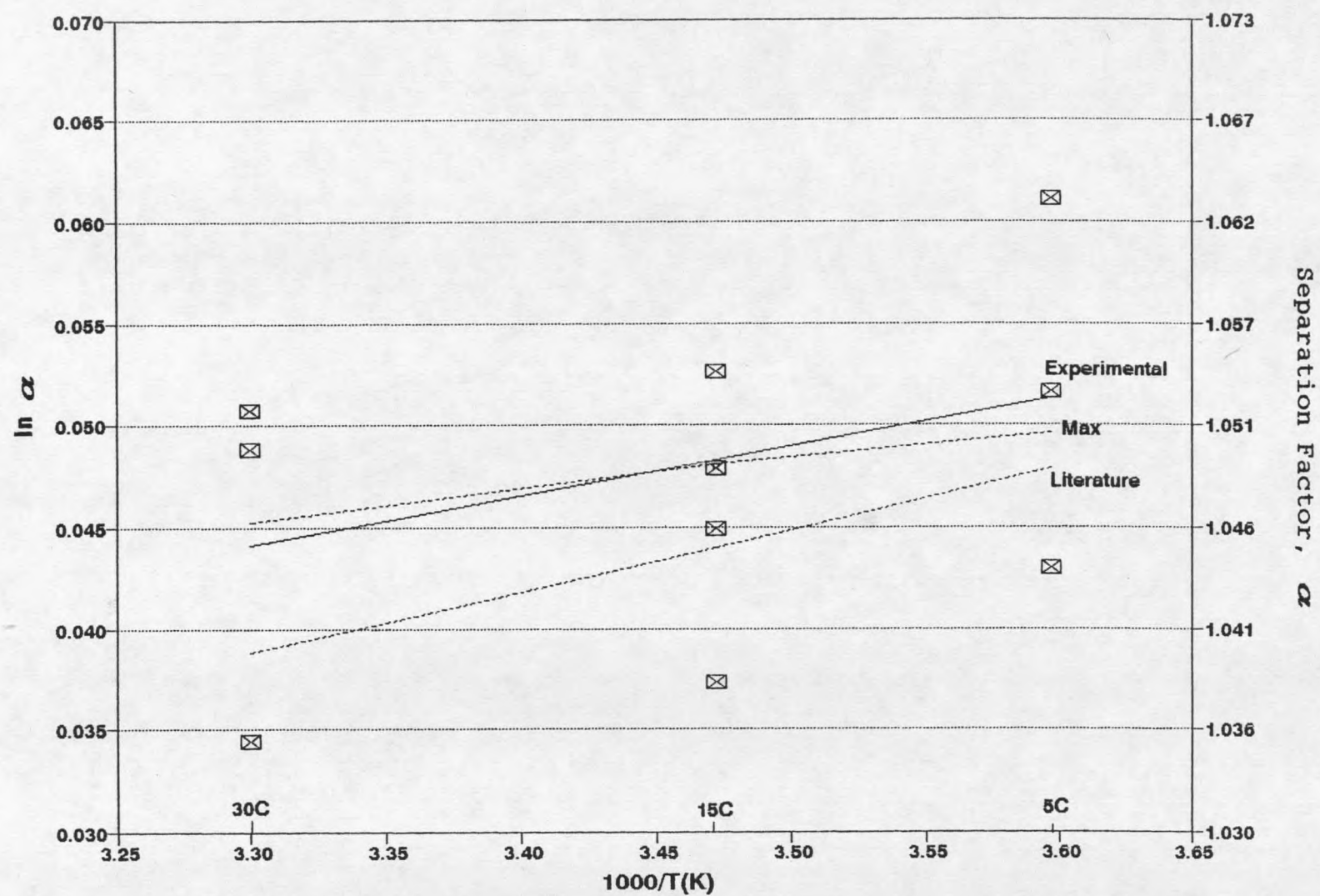


Figure 2. Experimental results for the Phenetole/BF₃ system.

Consequently, the experimental data may provide a more realistic measure of the actual behavior of the BF_3 /phenetole system.

The deviation or spread between the individual data points at each of the experimental temperatures is rather large. This discrepancy is attributed to problems associated with the sampling of the equilibrated gas phase. If too small a gas sample was removed, not enough BF_3 was present for a representative mass spectral analysis and the calculated separation factor was consistently higher than the corresponding literature value. If too much BF_3 gas was removed, BF_3 was "boiled" off of the liquid complex and this ^{10}B enriched material diluted the ^{11}B enriched gas phase. This invariably led to values of the experimental separation factors lower than the corresponding literature values. This problem was addressed by adjusting the size of the gas sample reservoirs and developing a technique to remove a consistent amount of the equilibrated gas from the equilibrium cell. The amount of equilibrated gas removed (≈ 1 cc) assured that there was an ample amount of gas for the isotopic analysis without removing enough to affect the isotopic constitution of the gas phase.

The line labelled "Max" in Figure 2 is a linear extrapolation of the two data points representing the theoretical maximum value that the separation factor may assume as given by equation (12) previously presented in the theoretical section. It is slightly disconcerting that the experimental best fit line crosses the theoretical maximum line. Recall that the theoretical maximum is based on only two points, and is prone to some uncertainty. The discrepancy between experimental data and the theoretical maximum may also be attributed to the uncertainties

associated with the size of the equilibrated gas sample removed for analysis in the experimental procedure as previously discussed.

In these experiments, gaseous BF_3 and the BF_3 ·phenetole complex were contacted in the equilibrium cell for up to 144 hours (6 days) at several different conditions of temperature and pressure. This length of time and variety of conditions allowed ample opportunity for irreversible decomposition of the liquid complex to occur. Since the gas and liquid samples are analyzed on the mass spectrometer, decomposition products would be expected to show up in the mass spectra of these samples. It was anticipated that the signal strength of peaks associated with any decomposition products would increase for samples taken at consecutively later times. Comparison of the initial mass spectra of the gas and liquid phases with those taken at all later times were indicative that no detectable decomposition of the complex had occurred. This observation is in line with literature reports attesting to the excellent stability of the BF_3 ·phenetole complex [6,7].

The agreement between the experimental separation factors and those reported in the literature for the BF_3 /phenetole system was sufficient to lend credibility to the newly developed experimental technique and analytical procedure. By exercising proper care in sampling the equilibrated gas phase, these techniques appear suitable for the examination of previously unstudied BF_3 /donor systems.

The Acetone/BF₃ System

Acetone was selected as the first donor for study in isotope exchange since the existence of the acetone·BF₃ complex is mentioned in the literature [5] and preliminary work in this laboratory indicated acetone readily absorbs gaseous BF₃ to form a liquid molecular addition compound. Prescreening studies indicated that 1 mole of acetone absorbed 1 mole of BF₃ gas. The resulting acetone·BF₃ molecular addition compound was a dark brown liquid with a freezing point of 16 to 18°C. The fact that 1 mole of acetone absorbed 1 mole of BF₃ is indicative that the resulting complex is a 1:1 molecular addition compound and gaseous BF₃ is not excessively soluble in the liquid complex. Furthermore, equilibrium experiments between gaseous BF₃ and the liquid acetone·BF₃ complex could be performed only at temperatures greater than the freezing point of the complex or approximately 20°C. Thus, the temperatures selected for the determination of experimental separation factors were 25°C, 35°C, and 45°C.

The experimentally determined separation factors are presented graphically in Figure 3. The best fit line through the experimental data, obtained from linear regression analysis, is also shown in Figure 3. The equation of this line is:

$$\ln \alpha = \frac{59.58}{T \text{ (K)}} - 0.1597 \quad (19)$$

Note that the experimental best fit line is consistently below the theoretical maximum. Furthermore, the slope of the experimental line is positive, indicating that α increases with decreasing temperature. Both of these observations are consistent with theoretical considerations and lend credibility to experimental data.

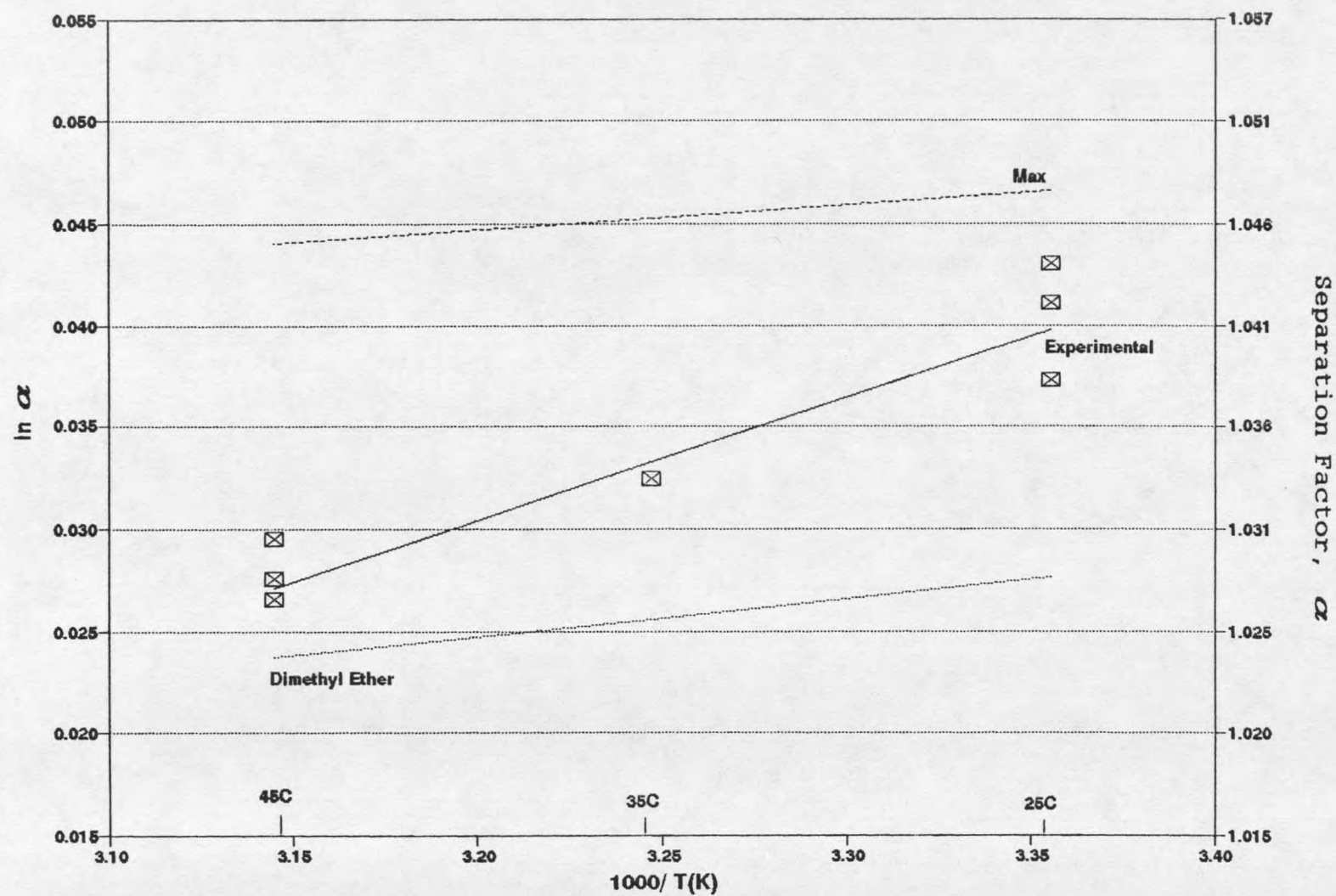


Figure 3. Experimental results for the Acetone/ BF_3 system.

In the experiment being discussed, the acetone·BF₃ complex and gaseous BF₃ were in contact in the equilibrium cell for 220 hours (≈ 9 days). Over this extended period of time, the appearance of decomposition products was noted in the mass spectral analysis of the liquid and gas phases. Furthermore, a lowering in the freezing point of the liquid complex present at the end of the experiment from that of the initial complex was noted. A color change of the final liquid complex was visually detected as well. These observations are indicative that the acetone·BF₃ complex undergoes slow, irreversible decomposition. No attempt was made at characterizing the decomposition mechanism or products.

Mass spectral analysis of the equilibrated gas phase consistently indicated the presence of acetone in the BF₃ gas samples. The presence of acetone in the equilibrated gas phase is indicative that the gaseous phase may contain undissociated acetone·BF₃ complex. It is therefore possible that the experimental separation factors may be lower than the "true" equilibrium constant for the acetone/BF₃ system in accordance with previous discussions [1]. No attempt was made to test this hypothesis or quantify these effects.

The best fit line through the equilibrium constant data for the dimethyl ether/BF₃ system is also indicated in Figure 3. In terms of separation factors, the acetone/BF₃ system consistently out performs the dimethyl ether system. Consequently, the experimental results for the acetone/BF₃ system are indicative that acetone, or perhaps other ketones, could provide superior donor properties as compared to the currently used dimethyl ether system for the large scale fractionation of boron isotopes.

The Acetophenone/BF₃ System

Based on the positive results obtained in experiments with the acetone/BF₃ system, the systematic examination of other ketones was warranted. Initially, acetophenone, (C₆H₅)COCH₃, and propiophenone, (C₆H₅)COC₂H₅, were to be examined as donors in the isotope exchange reaction. These materials were selected based on the excellent properties of the homologous ethers (anisole and phenetole) in the isotope exchange reaction. It was believed that these compounds would exhibit superior qualities compared to acetone as donor materials, much as the phenyl ethers showed enhanced properties as compared to dimethyl ether. Prior to testing these ketones in equilibrium experiments, acetophenone was prescreened to determine if the BF₃ complex even existed and if so, evaluate some of the physical properties of the resulting complex.

At 25°C, acetophenone readily absorbed BF₃ gas, forming a dark brown liquid. At the completion of the formation reaction, the complex was a very viscous, dark black material. Since the complex had the consistency of tar even at the elevated temperature of 100°C, the use of acetophenone as a possible donor in isotope exchange was eliminated. Due to the chemical similarity of propiophenone, this material was not prescreened. Based on these studies, testing of phenyl ketones in the isotope exchange process was abandoned.

The MIBK/BF₃ System

Because the positive nature of the experimental results with the acetone/BF₃ system indicated that ketones could be viable alternative donors in boron isotope exchange, 4-methyl-2-pentanone (methyl isobutyl ketone or MIBK) was prescreened as a potential donor material. The purpose for studying other ketone systems was to examine the effect substituting other functional groups for one or both of the methyl groups in acetone would have on the separation factor. The difference between acetone and MIBK is the substitution of an isobutyl group for a methyl group in acetone to form MIBK. The carbonyl oxygen provides the lone electron pair used to form the BF₃ addition compound in both ketone systems. Thus, any differences in the experimentally measured separation factors associated with the two systems could be attributed to differences in the functional groups attached to the carbonyl carbon.

The prescreening studies were indicative that one mole of MIBK absorbed 1.1 moles of BF₃. A 1:1 molar complex is therefore indicated with slight solubility of BF₃ gas in the liquid phase. The resultant MIBK/BF₃ complex was a dark reddish brown liquid exhibiting a freezing point of 16 to 18°C. Based on the freezing point of the complex, equilibrium temperatures of 25°C, 35°C and 45°C were selected for the experimental determination of separation factors.

The results of two separate equilibrium experiments with the MIBK/BF₃ system are presented in Figure 4. Note that there is significant variation in the individual data points for a specific temperature in the first MIBK/BF₃ experiment. This variation at a specified temperature results in uncertainties regarding the actual value of α and the position

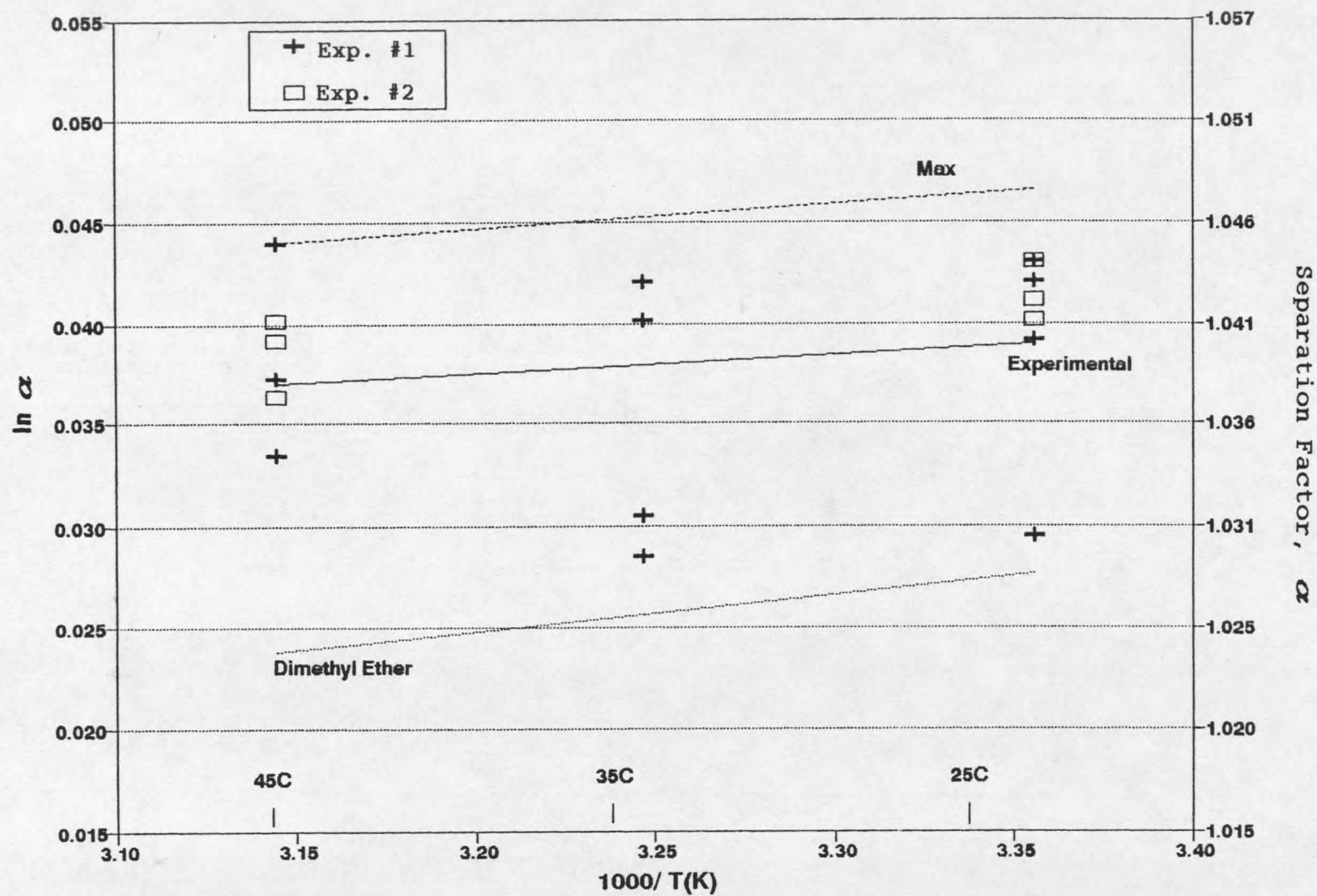


Figure 4. Experimental results for the MIBK/BF₃ system.

of the best fit straight line. The reasons for these variations are unclear, but inconsistencies in the sampling procedures for the equilibrated gas and liquid phases are suspect. Due to these uncertainties, the experiment was repeated with these results also indicated in Figure 4.

In the second MIBK/BF₃ equilibrium experiment, data was taken only at temperatures of 25°C and 45°C. It is apparent from Figure 4 that the agreement between α 's for a given temperature was much better in the second experiment. Furthermore, the agreement between the results from the independent experiments is very good. These observations reinforce the reliability of the individual data points and the best fit straight line through the data, also included in Figure 4.

The equation of the best fit line obtained by linear regression analysis is given by:

$$\ln \alpha = \frac{9.504}{T \text{ (K)}} + 0.0071 \quad (20)$$

This line lies below the theoretical maximum at all points. Furthermore, the slope of the best fit line is positive, indicating that α increases with decreasing temperature. Both observations are consistent with theoretical considerations and lend credibility to the experimental data.

The liquid complex was in contact with gaseous BF₃ for 192 hours ($\approx$ 8 days) in experiment #1 and for 96 hours ($\approx$ 4 days) in experiment #2. Decomposition products were not noted in the mass spectra of the equilibrated gas or liquid phase samples in either experiment. Further testing of the liquid phase was facilitated with gas chromatography/mass spectral (GC/MS) analysis. The GC was used to separate components in the

liquid phase, and the separated effluent from the GC was sent directly into the mass spectrometer such that the mass spectrum of the separated components could be obtained. The GC/MS analysis was performed on pure MIBK used to form the complex, the MIBK/BF₃ complex formed initially at the beginning of experiment #1, and the final complex from the conclusion of experiment #1. The gas chromatographs of each of the above liquids were identical, corresponding to pure MIBK (BF₃ is so volatile that it exits the GC column with or before the solvent). Thus, irreversible decomposition products were not detected in the liquid phase. It is therefore apparent that the MIBK/BF₃ system is quite stable with regards to irreversible decomposition.

MIBK was not observed in the mass spectral analysis of any of the equilibrated gas phase samples. This is indicative that undissociated complex does not exist in the vapor phase for the MIBK/BF₃ system. This observation, coupled with the limited solubility of BF₃ in the liquid phase are good indications that the experimentally determined α 's should closely approximate the actual values of the equilibrium constant for this system.

The best fit line based on literature data for the dimethyl ether/BF₃ system is indicated in Figure 4. The MIBK/BF₃ system provides larger values of the separation factor than the dimethyl ether system over the temperature range studied. Consequently, MIBK appears to be a better donor than dimethyl ether in the boron isotope exchange reaction. Furthermore, comparison of Figures 3 and 4 or equations (19) and (20) indicates that the results of the MIBK/BF₃ system are slightly higher than for the acetone system. The substitution of an isobutyl group for a methyl group in acetone appears to affect the donor to boron bond

stability in the complex and enhances the separation factor. Thus, MIBK appears to be a viable alternative to dimethyl ether and is comparable to acetone as a donor in chemical exchange.

The DIBK/BF₃ System

The acetone and MIBK experiments indicated that the BF₃/ketone molecular addition compound was destabilized by replacing a methyl group with an isobutyl group attached at the carbonyl carbon. The manifestation of this destabilizing effect was slightly larger separation factors at a specific temperature for the MIBK/BF₃ system as compared to the acetone/BF₃ system. To further examine this effect, 2,6-dimethyl-4-heptanone (diisobutyl ketone or DIBK) was selected as a donor compound for study in the exchange reaction. For DIBK, both methyl groups of acetone are replaced by isobutyl groups. It was anticipated that further destabilization of the BF₃ complex with DIBK would enhance the separation factor over that obtained with either the acetone/BF₃ or MIBK/BF₃ systems.

Prescreening studies were indicative that 1 mole of DIBK absorbed approximately 1.1 moles of BF₃ gas. Slight solubility of gaseous BF₃ in the liquid complex was therefore indicated. The resulting liquid complex was dark reddish brown in color and exhibited a freezing point of 16°C to 18°C. Based on the freezing point of the DIBK/BF₃ complex, the selected equilibration temperatures were identical to those used with the other ketone systems.

The experimental results from the equilibrium studies with the DIBK/BF₃ system are shown in Figure 5. The best fit linear equation for this system is given by:

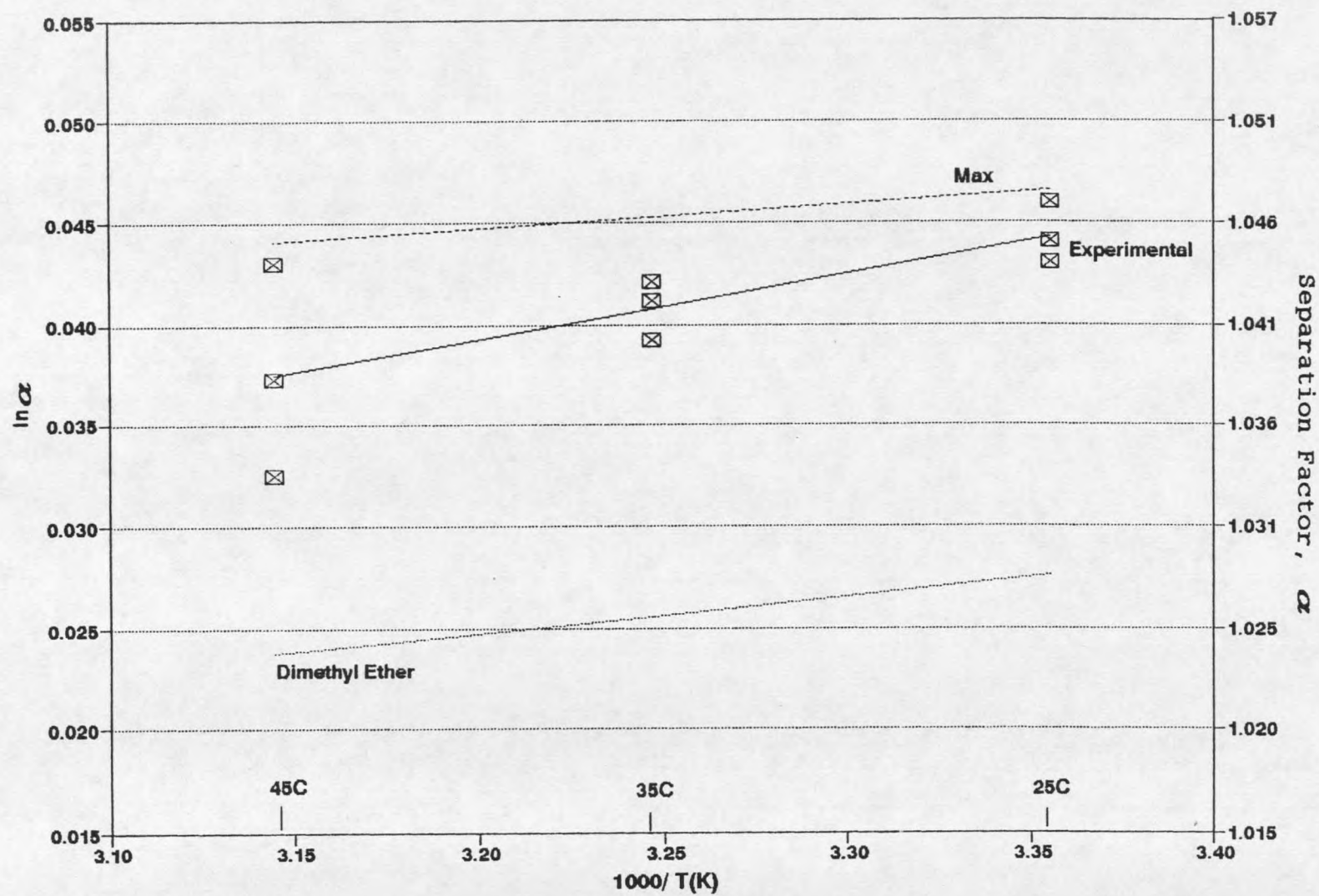


Figure 5. Experimental results for the DIBK/BF₃ system.

$$\ln \alpha = \frac{31.785}{T \text{ (K)}} - 0.0624 \quad (21)$$

This best fit line is also shown in Figure 5. As expected, this line lies below that of the theoretical maximum and has a positive slope. These observations are consistent with theoretical considerations and lend credibility to the experimental data.

During the course of the DIBK/BF₃ experiment, mass spectral analysis of the equilibrated gas indicated negligible amounts of DIBK were present in the vapor phase. This is indicative that the DIBK/BF₃ complex is not present in the vapor phase. Coupled with the limited solubility of BF₃ in the in the liquid complex, the experimentally measured separation factors are expected to represent the actual value of the equilibrium constant for the DIBK/BF₃ system.

The liquid DIBK/BF₃ complex was in contact with the gas phase for 216 hours ($\approx$ 9 days) during the equilibrium experiment. Decomposition products, expected to show up as increasing, time dependant signals in the mass spectra, were not detected in the equilibrated gas or liquid samples. The GC/MS analysis discussed previously was also used to examine the liquid phase for irreversible decomposition products. Samples of pure DIBK used to form the complex initially, the DIBK/BF₃ complex taken at the beginning of the experiment, and of the liquid phase after 216 hours in the equilibrium cell were submitted to the GC/MS analysis. The chromatographs and mass spectra for each sample were similar, and indicated only the DIBK donor was present in the liquid samples. Consequently, the DIBK/BF₃ complex is apparently very stable with regard to irreversible decomposition.

The best fit line representing literature data for the dimethyl ether/BF₃ system is indicated in Figure 5. As with the other ketone systems studied, the DIBK/BF₃ system exhibits separation factors larger than for the dimethyl ether system. By comparison of the available data, DIBK appears to be a significant improvement over dimethyl ether as the donor in boron isotope exchange.

The Nitromethane/BF₃ System

An interest in nitromethane (CH₃NO₂) as a potential donor species in boron isotope exchange developed from discussions with the organic chemistry group at Montana State University. A graduate student in that group had been working with solutions of nitromethane saturated with BF₃ gas in organic synthesis reactions. The reported properties of the nitromethane/BF₃ complex included excellent stability in regards to irreversible decomposition and a freezing point less than 0°C. One mole of nitromethane was reported to absorb 1.4 to 1.6 moles of BF₃ gas at 0°C [38]. These properties were confirmed in this laboratory, and the light brown liquid complex exhibited a freezing point of -46°C to -48°C.

The experimental results for the nitromethane/BF₃ system are presented graphically in Figure 6. The linear equation representing the best fit line through the experimental data is also shown. The equation of this line is:

$$\ln \alpha = \frac{33.257}{T \text{ (K)}} - 0.0452 \quad (22)$$

The slope of this line is positive in accord with theoretical considerations. The most striking aspect of these results is that they

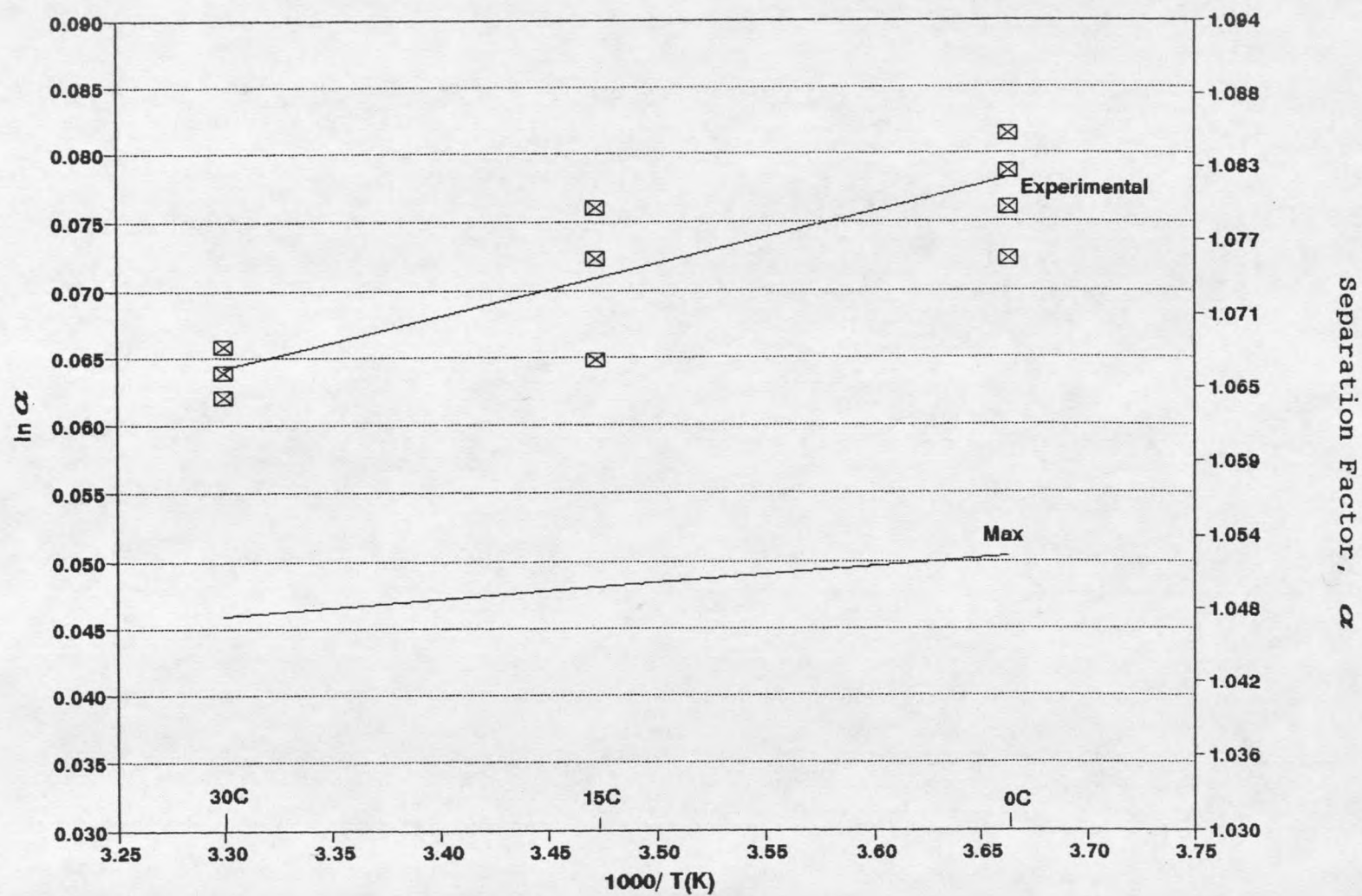


Figure 6. Experimental results for the Nitromethane/BF₃ system.

are substantially greater than those predicted by the theoretical maximum. The nitromethane/BF₃ system is the only known instance in BF₃ gas/liquid adduct isotope exchange where α 's in excess of the theoretical maximum have been observed. These extraordinary results may be justified based on the unique properties of the nitromethane molecule.

The donors which have been examined in this study, and nearly all of those examined by previous researchers, have been *single site* donors. That is, there is only one basic center containing the required lone pair of electrons necessary for bonding in formation of the BF₃-donor molecular addition compound. The nitromethane molecule contains two oxygen atoms, and consequently has two such donor sites available. It is conceivable that excess BF₃ dissolved in the liquid phase beyond that mandated by a 1:1 molar complex could be associated or weakly bound to the second oxygen of the nitromethane/BF₃ complex. The isotope effect between the complex and the excess BF₃ could potentially result in larger values of the separation factor than for the corresponding single site donors.

The only system similar to nitromethane which has been previously examined and is briefly described in the literature [13] is that of nitrobenzene, (C₆H₅)NO₂. In that work, a separation factor for the nitrobenzene/BF₃ system of 1.03 at 7°C was reported. This well below the theoretically predicted maximum of $\alpha = 1.05$ at 7°C. That study also reported BF₃ gas was virtually insoluble in the liquid nitrobenzene/BF₃ complex. Comparison of these two systems provides some evidence regarding the existence of a double site mechanism in isotope exchange for the nitromethane/BF₃ system. Furthermore, the dramatic effect of substituent groups attached to the basic donor center is indicated.

Any justification for such a mechanism must of course come from careful experimental observation. Determining the exact nature of the BF_3 -nitromethane bonding arrangement in the liquid complex would be the first step in evaluating the underlying principles involved. Such an undertaking is outside the scope of this project, but is strongly recommended in future work.

During the nitromethane/ BF_3 experiment, the liquid complex was in contact with the gas phase for 435 hours (≈ 18 days). During this extended period of time, decomposition products were never observed in the mass spectra of the equilibrated gas or liquid samples. It was concluded that this system was extremely stable with regards to irreversible decomposition of the complex. Furthermore, nitromethane was never observed in the gas phase samples, which indicated a relatively low vapor pressure for this complex.

The experimental evidence outlined above for the nitromethane/ BF_3 system strongly suggests much potential exists for the use of nitromethane as a viable alternative donor in the boron isotope fractionation scheme. Based on the extraordinary magnitude of the separation factor, it is conceivable that a "super donor" has been discovered in this system. Further work is certainly required and strongly suggested with the nitromethane/ BF_3 system to validate this supposition.

The DMSO/BF₃ System

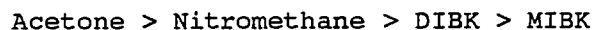
The previously cited literature data for the dimethyl sulfoxide (DMSO) system (refer to Table 1) was obtained for gas/solid isotope exchange. This is the only known instance where such a system has been examined experimentally and those results indicate that the separation factor increases with increasing temperature. This trend contradicts the theoretical predictions and experimental observations for gas/liquid exchange reactions. Based on the DMSO gas/solid data and the demonstrated behavior of similar gas/liquid systems, it was postulated that the separation factor, α , goes through a maximum at temperatures near the phase transition of the complex from the liquid to solid states. It is necessary to validate this hypothesis by experimental determination of the temperature dependence of α for the gas/liquid DMSO/BF₃ system.

The DMSO·BF₃ complex freezes to form a white crystalline solid at 53°C. The experimental apparatus developed in this study proved inadequate to obtain equilibrium data at these elevated temperatures. The complex froze in the circulating pump and pump lines external to the equilibrium cell. This complication made sampling of the liquid phase impossible since the complex solidified in the liquid sampling port as well. Consequently, experimentation with the DMSO/BF₃ system was discontinued. If experimentation is resumed at a future time, the experimental apparatus must be modified to accommodate the use of higher experimental temperatures.

Comparison of Experimentally Studied Systems

The scope of the experimental portion of this study focussed on the experimental determination of the separation factor as a function of temperature for the various systems examined. The temperature dependence and magnitude of the separation factor for the BF_3 /donor systems studied in this research are presented in Figure 7. Literature data for the dimethyl ether system is also indicated in Figure 7 for comparison.

As previously discussed, the separation factor, α , increases with decreasing temperature, as indicated by the positive slope of the lines shown in Figure 7. The positive slope indicates that the exchange process is exothermic. This trend is expected and predicted from theory and the results of previous researchers for similar exchange systems. Based on the slope of the experimental lines shown in Figure 7, the temperature dependence of separation factor varies from donor to donor and increases in the order:



Depending on the BF_3 /donor system, the variation of α with temperature may be an important consideration in the design and operation of a large scale cascade. For a strongly temperature dependent donor, such as acetone or nitromethane, a substantial increase in cascade performance may be realized by isothermal operation of the exchange column.

The magnitude of the separation factor at a specific temperature varies from donor to donor. In accord with previous discussions, the variation is a result of differences in substituent groups attached to the basic center in the donor molecule. The increasing inductive effect of

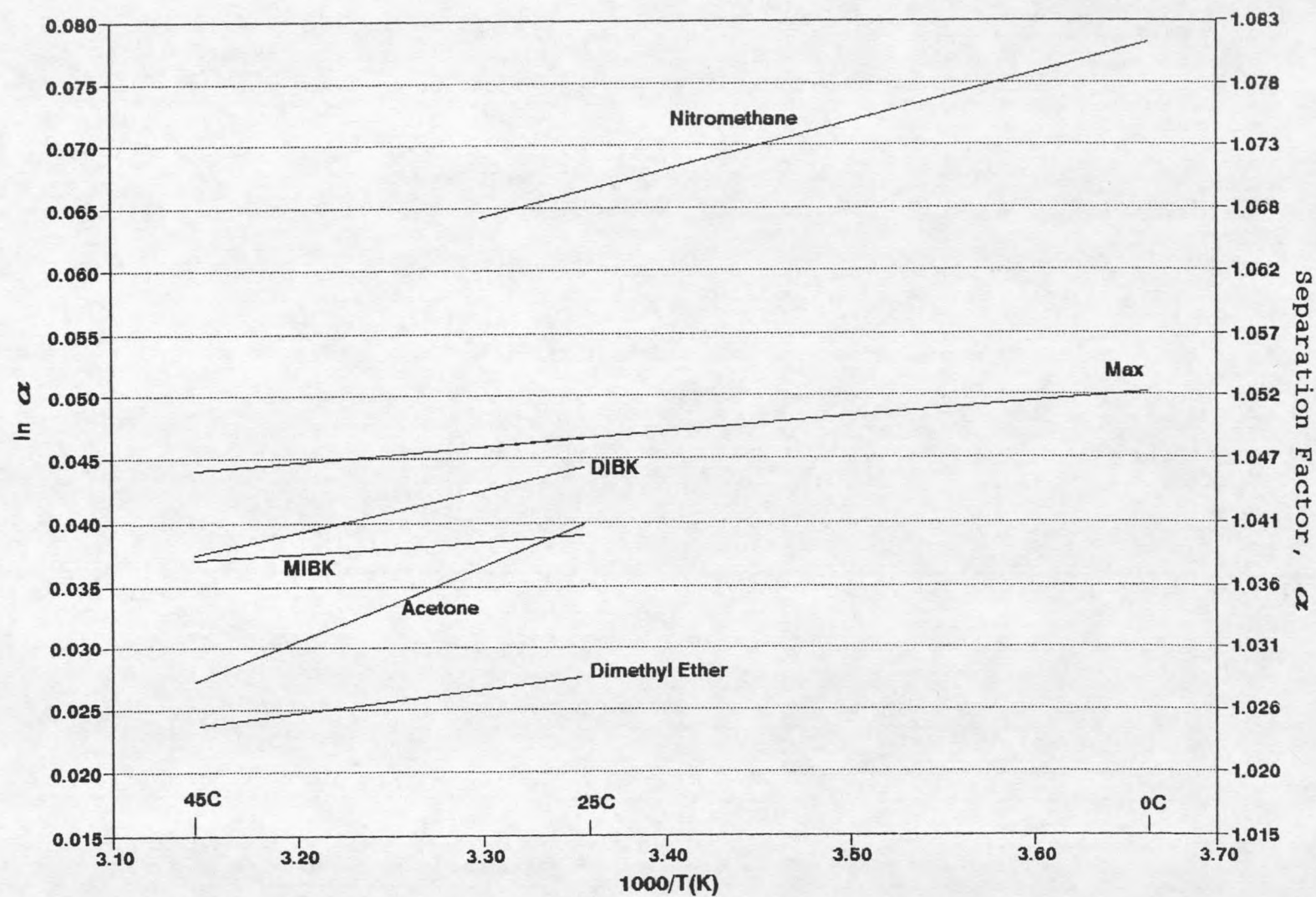


Figure 7. Comparison of experimental systems studied in isotope exchange.

larger alkyl groups should strengthen the BF_3 -donor bond and result in lower values of the separation factor. The opposite trend was observed with the ketones studied in this work, with separation factor increasing in the order $\text{DIBK} > \text{MIBK} > \text{Acetone}$. This is attributed to steric interferences, presumably between the β or γ -carbon in the isobutyl group and the normal positioning of fluorine in BF_3 .

It is apparent in Figure 7 that the separation factors associated with the nitromethane system are dramatically larger than those for the ketones. The cause of this anomaly is uncertain, and further experimental work is necessary to enhance understanding of this phenomenon.

The benefits of increasing the separation factor in large scale isotope fractionation is easily brought into perspective with a simple comparison based on the familiar Fenske-Underwood equation:

$$n = \frac{\ln[y_P(1-x_W)/(1-y_P)x_W]}{\ln \alpha} \quad (23)$$

Equation (23) provides the minimum number of ideal stages, n , required for a specified separation in a exchange column operated at total reflux. For a cascade producing 95% ^{10}B product ($y_P = 0.95$) and a 5% ^{10}B waste stream ($x_W = 0.05$), equation (23) can be simplified:

$$n = \frac{5.889}{\ln \alpha} \quad (24)$$

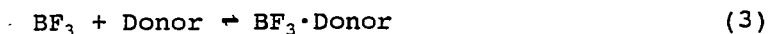
Minimum stage requirements are presented in Table 4 for the dimethyl ether, acetone, MIBK, DIBK and nitromethane systems based on reported values of the separation factor and evaluated from equation (24). It is apparent from the above comparison that a slight increase in separation

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

<u>Donor</u>	<u>α</u>	<u>Min N° of Ideal Stages</u>
Dimethyl ether	1.014	424
Acetone	1.041	147
MIBK	1.041	147
DIBK	1.045	134
Nitromethane	1.081	77

factor results in a concomitant decrease in the minimum ideal stage requirements. Consequently, a dramatic reduction in the size of the required process equipment is indicated if a ketone or nitromethane is used as the donor rather than dimethyl ether. An in-depth analysis of isotope fractionating cascades is the purpose of the second portion of this study and will be deferred to the subsequent section on modelling and analysis.

Other considerations besides the magnitude of the separation factor and hence the size of the process equipment required to effect a given separation are important in the selection of the an appropriate donor. Recall that the BF_3 bound in the liquid molecular addition complex must be readily liberated to effect product recovery and for the recirculation and reuse of the liquid donor. Consequently, the formation reaction:



should be quantitatively reversible simply by the addition or removal of heat. Reversible decomposition of the liquid complex into BF_3 and donor is tantamount to establishing the method recycle will be provided in large scale isotope fractionation.

Experiments to determine the reversibility of the formation reaction were undertaken in this study. The equilibrium cell previously described was fitted with a stainless steel condenser. A heating tape wrapped around the body of the cell provided a convenient method of heating the cell and its contents. The complex under consideration was formed *in situ* in the equilibrium cell. Then contents were then heated via the heating tape and gas was allowed to escape from the cell through the condenser under constant helium purge. In this manner, the cell was designed to operate in the fashion of a distillation flask. The idea was to thermally liberate gaseous BF_3 from the complex.

Liquid samples were taken at two hour intervals during the decomposition experiments for analysis of boron content. An analysis was attempted on the mass spectrometer previously used in conjunction with the isotopic abundance determinations. Boron content was to be determined by comparing the signal strength of the BF_3 peak to that of the base peak from the donor in the mass spectrum of the complex. In this manner, relative amounts of BF_3 present in the liquid compared to the donor were to be determined if the amount of donor in the cell was assumed constant.

Unfortunately, the experimental apparatus and the analysis procedure proved inadequate for the purpose of studying reversible decomposition. Refluxing the liquid complex in the cell could not be adequately controlled, primarily since visual inspection was not possible in the stainless steel vessel. In general, the complex was irreversibly decomposed or even scorched to the cell walls due to excessive temperatures, or in some instances the donor was boiled away with the BF_3 gas rendering the analysis useless. Consequently, the data obtained from

these experiments was very inconclusive but did indicate that the decomposition may be reversible if performed under the proper conditions.

Experimental methods and analytical techniques amenable to the study of irreversible decomposition of the liquid complexes are reported in the literature [1,5,24]. The appropriately modified equipment was outside the means of this project. The analytical techniques for determination of boron content in the liquid sample are extremely labor intensive and require specialized analytical equipment. Such experiments are best suited to a well equipped analytical laboratory. Consequently, a detailed study of reversible decomposition was abandoned but is strongly recommended as future work.

MODELLING AND ANALYSIS

The purpose of the modelling and analysis portion of this study was to compare the number of ideal chemical equilibrium stages and total interstage flow requirements for different recycle cascade configurations with the various BF_3 /donor systems examined experimentally. Total interstage flow and ideal stage requirements provide an estimate of the size of the separation plant necessary to fractionate the isotopes of boron. The previously discussed dimethyl ether system currently in commercial use provides a convenient basis for comparison of the plant size associated with the experimentally examined exchange systems. Such a study is beneficial in estimating the effect different donors has on the size, and hence design, of the necessary process equipment. Indeed, this type of analysis is tantamount to selecting the donor system to be used in large scale separation schemes, and generally must be conducted prior to a full scale design and economic evaluation.

The experimental portion of this work focussed primarily on the determination of the separation factor, α , associated with the different BF_3 /donor systems. With the values of α available, only ideal stages can be considered in this portion of the study since actual (non-ideal) stage requirements would rely on stage efficiency data obtained from pilot plant experiments. Furthermore, the physical properties (e.g. viscosity and density) as well as the reversibility and thermodynamics of the formation reaction for the different liquid BF_3 /donor complexes must be established prior to conducting a full scale design and economic evaluation. The

appropriate experiments and pilot plant studies necessary to determine these important operating parameters were outside the scope of this work. Despite these limitations, the results from this portion of the study are useful in planning future bench scale experiments or pilot plant studies and to evaluate the actual requirements of plant scale boron isotope separation systems.

The salient features of recycle cascades are set forth and discussed in the following sections. Detailed analysis and derivations of cascade theory can be found in the open literature [4,39,40]. These established relationships were used to propagate computer models for the stagewise behavior of several types of recycle cascades applicable to isotope fractionation. These models and the results are subsequently discussed.

Terminology

Ideal Stages

The fundamental element of an isotope separation plant which effects a portion of the overall separation of the process materials is a *separating unit* or *stage*. The simplest type of stage is one that receives a single feed stream and produces one heads stream enriched in the desired component and a single tails stream depleted in the desired component. Such a separating stage is depicted in Figure 8. The heads stream exits the stage with a flow rate denoted L , indicating a liquid stream in accord with chemical exchange, and is enriched in the desired isotope. The tails stream flow rate, denoted G to indicate a gas stream, is depleted in the desired isotope. The feed stream, F , is generally a mixture of two or more streams containing both gas and liquid fractions. In this study,

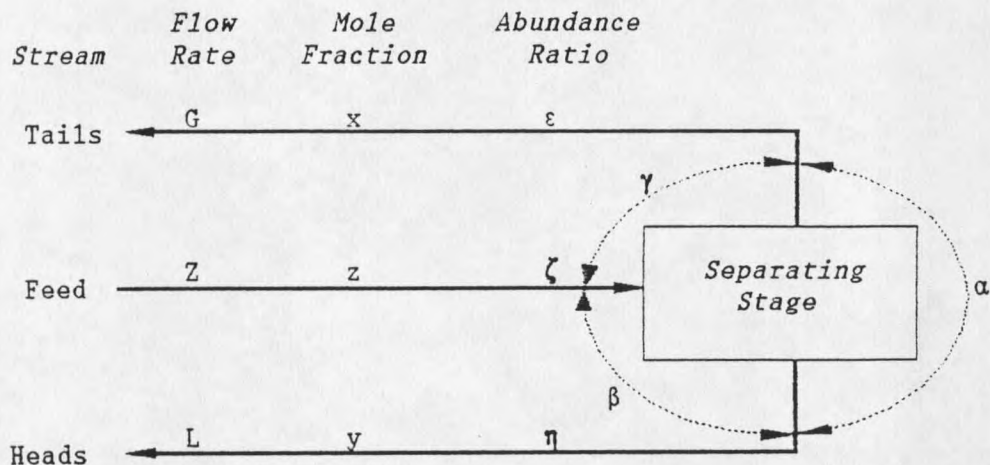


Figure 8. Single separating stage and associated nomenclature.

hourly molar flow rates were used exclusively, consequently L , G , and F have units of moles/hour.

For binary systems, as is the case of boron isotopes, it is commonplace to express mole fractions in terms of the desired isotope. The desired isotope was defined as ^{10}B for the purposes of this study. Accordingly, the mole fraction of ^{10}B was denoted as y in the heads stream, x in the tails stream and z in the feed stream as indicated in Figure 8. The mole fraction of ^{11}B is then expressed as $(1-y)$, $(1-x)$, or $(1-z)$ in the heads, tails and feed streams, respectively.

Certain relationships in separation cascades are simpler when expressed as mole ratios, defined as the ratio of the mole fraction of one component in a stream to the mole fraction of the second component in the same stream. The greek letters η , ϵ , or ζ are used to denote these ratios in the heads, tails, or feed streams, respectively. The mole ratios

corresponding to a given stream are indicated in Figure 8 and defined as follows:

$$\eta \equiv \frac{y}{(1 - y)} \quad (25)$$

$$\epsilon \equiv \frac{x}{(1 - x)} \quad (26)$$

$$\zeta \equiv \frac{z}{(1 - z)} \quad (27)$$

Emphasis in this portion of the study was placed on the concept of an *equilibrium* or *ideal stage*. In an ideal stage, the two streams exiting the stage are in equilibrium.

Separation Factors

The degree of separation achieved within a single ideal stage is measured by the *separation factor*, α . The separation factor is defined as the ratio of the heads stream mole fractions divided by the corresponding ratio in the tails stream. For the binary component mixture (^{10}B & ^{11}B) being discussed:

$$\alpha \equiv \frac{\eta}{\epsilon} = \frac{y/(1-y)}{x/(1-x)} = \frac{y(1-x)}{x(1-y)} \quad (28)$$

The separation factor defined in the above manner is useful since in many isotope separation processes it is independent of composition. In the models developed for this study, it was assumed that the separation factor α was a constant and known property of each ideal stage with a magnitude determined from experiment.

Other useful measures of the degree of separation obtained in a single stage are the *heads separation factor*, β :

$$\beta \equiv \frac{\eta}{\xi} = \frac{y/(1-y)}{z/(1-z)} = \frac{y(1-z)}{z(1-y)} \quad (29)$$

and the *tails separation factor*, γ :

$$\gamma \equiv \frac{\xi}{\epsilon} = \frac{z/(1-z)}{x/(1-x)} = \frac{z(1-x)}{x(1-z)} \quad (30)$$

The composition differences measured by the above defined separation factors are indicated by the dashed lines in Figure 8.

If one or more of the separation factors are known and assumed to be constant for a stage, the above definitions can be rearranged to provide *equilibrium expressions* relating the various mole fractions for an ideal stage:

$$y = \frac{\alpha x}{\alpha x + 1 - x} = \frac{\beta z}{\beta z + 1 - z} \quad (31)$$

$$x = \frac{y}{\alpha(1-y) + y} = \frac{z}{\gamma(1-z) + z} \quad (32)$$

$$z = \frac{y}{\beta(1-y) + y} = \frac{\alpha x}{\alpha x + \beta(1-x)} \quad (33)$$

Countercurrent Recycle Cascade

When the degree of separation effected by a single stage is smaller than the required amount of separation between the waste and product streams, it becomes necessary to connect a number of stages together in series to perform the required separation. A group of stages connected in series is referred to as a *cascade*. The countercurrent recycle cascades

examined in this study are represented schematically in Figure 9. The process scheme in Figure 9 represents the simplest type of recycle cascade in which the tails stream from stage $i-1$ (G_{i-1} in Figure 9) is recycled to form a portion of the feed to stage i . Experience indicates that counter current contacting is required for the efficient separation of many mixtures; continuous distillation with reflux is a typical example of a common counter current cascade. Consequently, the recycle flow scheme is often encountered in separation processes.

The countercurrent cascade shown in Figure 9 separates a *feed stream* with a ^{10}B mole fraction of z_F flowing at rate F into a *product stream* containing a mole fraction ^{10}B of y_P flowing at rate P and a *tails or waste stream* with a mole fraction ^{10}B of x_W flowing at rate W . These six flow rates and compositions are termed the *external variables* for the recycle cascade.

The feed to each stage is a combination of the tails stream from the next lower stage and the heads stream from the next higher stage. The flow rates and compositions are defined in exactly the same manner as for the single stage shown in Figure 8, except a subscript is used to indicate the stage number with which the flows and mole fractions are associated. These flow rates and compositions are referred to as the *internal variables* of the cascade.

The portion of the cascade from the product stage up to and including the feed stage is referred to as the *enriching section*. The purpose of the enriching section is to make isotopically enriched material of the desired product composition. The enriching section is therefore essential in making product of the required purity. The portion of the

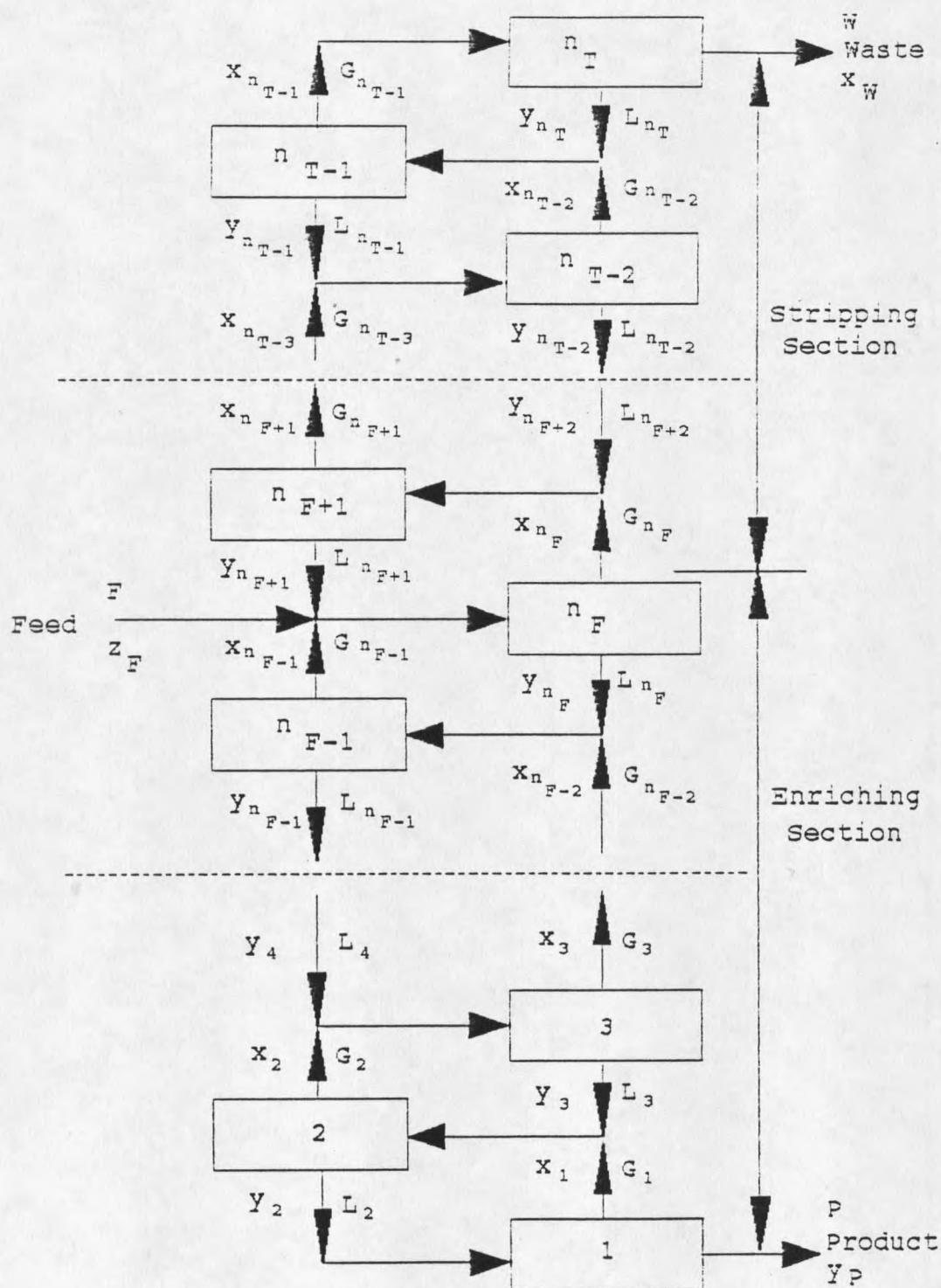


Figure 9. Flow schematic of the countercurrent recycle cascade.

cascade above the feed point is termed the *stripping section*. The purpose of the stripping section is to recover or strip the desired isotope from the feed stream. Therefore, the stripping section serves only to reduce the amount of fresh feed required to make a specified amount of product, and in certain instances it can be economically advantageous to eliminate this section altogether.

Material Balances

Two material balances may be written for the external process variables, e.g. the feed, waste and product streams, shown in Figure 9:

$$F = P + W \quad (34)$$

and
$$z_F F = y_P P + x_W W \quad (35)$$

Since there are two equations and six unknowns, it is possible to specify four of the external variables, the remaining two are fixed by the above material balance relations. If the product rate and composition, P and y_P respectively, the feed composition, z_F , and waste composition, x_W , are specified, the feed rate, F , and the waste rate, W , are given by:

$$F = \frac{P(y_P - x_W)}{z_F - x_W} \quad (36)$$

$$W = \frac{P(y_P - z_F)}{z_F - x_W} \quad (37)$$

It is also possible to write two material balances on the internal process variable for any stage in the cascade. Consider a portion of the enriching section from the product end up to and including stage i . The material balances for stage i :

$$L_{i+1} = G_i + P \quad (38)$$

$$Y_{i+1}L_{i+1} = x_iG_i + y_P P \quad (39)$$

may be combined resulting in the *enriching section material balance equation* valid for the heads composition exiting any stage up to and including the feed stage, n_F :

$$Y_{i+1} = \frac{x_i(G_i/P) + y_P}{(G_i/P) + 1} \quad (i = 1, 2, 3, \dots, n_{F-1}) \quad (40)$$

Equation (40) is often referred to as the *operating line equation* for the enriching section of a cascade.

Similarly, in the stripping section for any stage above the feed stage, n_F , the material balances are:

$$L_{i+1} + F = G_i + P \quad (41)$$

$$Y_{i+1}L_{i+1} + z_F F = x_iG_i + y_P P \quad (42)$$

The equations can be combined to give the *stripping section material balance equation* valid for the heads composition exiting stages in the stripping section:

$$Y_{i+1} = \frac{x_i(G_i/P) + y_P - z_F(F/P)}{(G_i/P) + 1 - (F/P)} \quad (i = n_F, n_{F+1}, n_{F+2}, \dots, n_{T-1}) \quad (43)$$

Equation (43) is often referred to as the *stripping section operating line equation*.

Recycle Ratio

The quantity G_i/P in equations (40) and (43) has special significance and was defined for the modelling purposes of this study as the *recycle ratio*, R_i :

$$R_i \equiv G_i/P \quad (44)$$

The number of ideal stages required to separate feed into product and waste of the specified compositions is a minimum at $R_1 \rightarrow \infty$. This condition is referred to as total reflux. The condition of total reflux is of theoretical interest since the absolute minimum number of ideal stages, n , required for a specified separation is mathematically easy to obtain from the familiar Fenske-Underwood equation, which was presented earlier:

$$n = \frac{\ln[y_P(1-x_W)/(1-y_P)x_W]}{\ln \alpha} \quad (23)$$

However, at total reflux, none of the product or waste is withdrawn from the cascade. Total reflux is therefore impractical in actual cascades.

At total reflux, the composition difference between corresponding streams on adjacent stages is a maximum and the required number of ideal stages is minimized. As the recycle ratio is decreased, this composition difference decreases and the required number of ideal stages increases. At some point the recycle ratio reaches a minimum value where the cascade just ceases to separate. This condition is known as minimum reflux, $(R_1)_{\min}$, and occurs at the point within the cascade where the composition difference between corresponding streams on adjacent stages is zero. For example, in distillation of non-azeotropic mixtures a constant recycle ratio is typically used for all stages in the cascade and the minimum recycle condition occurs at the feed stage. Minimum recycle results when the operating lines for the enriching and stripping sections meet the equilibrium line. The result is an *invariant zone* or *pinch point* where an infinite number of stages are required to reach the composition at which the operating and equilibrium lines intersect.

For a reflux ratio approaching the minimum value, separation ceases at some point in the cascade and the desired separation cannot be obtained irregardless of the number of ideal stages used. A condition of minimum reflux for any stage i is expressed mathematically as:

$$Y_{i+1} = Y_i \quad (45)$$

The minimum recycle ratio for a given stage in the enriching section, up to and including the feed stage is:

$$(R_i)_{\min} = \frac{Y_P(\alpha x_i + 1 - x_i) - \alpha x_i}{(\alpha - 1)x_i(1 - x_i)} \quad (i = 1, 2, 3, \dots, n_P) \quad (46)$$

Likewise, in the stripping section, the minimum reflux ratio for any stage above the feed stage is:

$$(R_i)_{\min} = \frac{W(Y_i - x_W)}{P(\alpha - 1)x_i(1 - Y_i)} \quad (i = n_{P+1}, n_{P+2}, n_{P+3}, \dots, n_{T-1}) \quad (47)$$

Minimum reflux is impractical since no separation is obtained irregardless of the number of ideal stages used in the cascade. A knowledge of the minimum reflux for stages in the enriching or stripping sections as given by equations (46) and (47) is necessary to insure that actual values of reflux are greater than the minimum at a given stage. This insures that fractionation actually occurs in the cascade.

A salient feature of the minimum recycle ratio is that it increases as the composition departs more and more from the product or waste compositions. Thus, the maximum requirements for reflux occurs at the feed stage and these requirements decrease steadily as the ends of the cascade are approached.

Providing Recycle in the Cascade

Two types of process equipment are required to provide recycle or alter the exiting recycle ratio at various stages in a cascade based on the isotope exchange reaction. A *decomposer* is required to convert the liquid complex to gaseous BF_3 and liquid donor. Thus, a decomposer provides the gaseous BF_3 recycle and is required at all points in the enriching section of a cascade where recycle is required or the recycle ratio is altered. A *recombiner* combines gaseous BF_3 with the donor material to produce the liquid BF_3 -donor complex. Consequently, the recombiner provides liquid recycle and is associated with the stripping section of the cascade.

A minimum of one recombiner and one decomposer is required for the operation of any cascade (this minimum corresponds to the constant recycle case described subsequently). Referring to Figure 9, a recombiner is necessary at the waste end of the cascade to provide liquid recycle. A decomposer is required at the product end of the cascade to provide gaseous recycle.

The design of decomposer and recombiner systems used in actual cascades requires thermodynamic data for the BF_3 /donor formation reaction. This data was not available from the experimental work for the various systems studied, but was recommended for future study as previously discussed.

Number of Separation Stages

In general, the number of ideal stages required to effect a specified separation cannot be determined directly for a practical cascade. A stagewise computational scheme or graphical method must usually be employed to determine the number of stages needed to effect the required separation. The computer models utilized in this study were designed to determine stage requirements, as well as other design parameters, for the various cascade configurations. Again, it must be emphasized that the lack of stage efficiency data limits this portion of the study to the evaluation of *ideal* (equilibrium) stage requirements.

The number of actual stages in a cascade is a basic design parameter since column cost is generally based on the unit cost of a single stage. For example, based on the previously calculated stage requirements for a cascade operating at total reflux (refer to Table 4), the currently used dimethyl ether system would require 424 ideal stages while the nitromethane system would require 77 ideal stages to perform the same separation. Assuming the cost of a single stage to be independent of the donor used and that stage size or volume remained constant, the cost of the column associated with the dimethyl ether system would be $(424/77)$ or approximately 5.5 times greater than for the column associated with the nitromethane system. Consequently, a knowledge of the stage requirements for a given donor system provides a rough comparison of capital cost associated with columns utilizing different donors.

Total Interstage Flow

The total interstage flow rate through a cascade is the total amount of material, both heads and tails, processed by the collective stages in the cascade to produce the desired quantity and purity of product. Consequently, the total interstage flow rate is a measure of the size of the separation plant required to perform a specified separation. For example, the total volume of column internals is proportional to the total interplate vapor flow rate through a distillation column.

The stagewise modelling process was used to determine the total interstage flow rates associated with the various cascade configurations and donor systems studied. The flow rate of each heads and tails stream exiting each stage in the cascade was calculated. These rates were summed over all stages to determine the total interstage flow rate.

For the constant recycle cascade modelled with the dimethyl ether system (*vide infra*) the total interstage flow rate was approximately 3.42×10^5 mols/hr. This means that 342,000 moles of material must be processed through the cascade per hour to produce 2 moles/hour of ^{10}B product enriched to 95%. In isotope separation plants, a substantial amount of the unit production cost is derived from the enormous size of the process equipment in terms of ideal stage requirements and the inventory of process materials available in the cascade as holdup. The volume of column internals will depend on the total interstage flow through the cascade. Therefore, the total interstage flow rate, in conjunction with the ideal stage requirements, provides a useful measure of the size of various cascade configurations operated with different donor systems.

Practical Recycle Ratio

For a practical separation plant, the foregoing discussions clearly indicate that the recycle ratio in a cascade must lie between the minimum value and total reflux. At total reflux, the required number of ideal stages will be a minimum while the total interstage flow is infinite. At the minimum recycle ratio, the cascade just ceases to separate and the number of ideal stages and total interstage flow are both infinite. This suggests that the total interstage flow for a given cascade performing a specified separation goes through a minimum at some finite value of the recycle ratio between the two extremes of minimum and total reflux. For the value of the recycle ratio where total interstage flow is minimized, the number of ideal stages will be somewhere between the minimum required and an infinite number. It is of interest to examine the effect reflux has on the total interstage flow and ideal stage requirements as an aid in determining a "practical" recycle ratio for isotope separation cascades based on the chemical exchange systems of interest in this study.

It is common to express the recycle ratio in a cascade as a function of the minimum reflux for a stage as given by equation (46) for the enriching section. The functional relationship between the practical and minimum recycle ratio is simplest when related by a multiplication factor:

$$R_1 = A \cdot (R_1)_{\min} = A \cdot \frac{y_p(\alpha x_1 + 1 - x_1) - \alpha x_1}{(\alpha - 1)x_1(1 - x_1)} \quad (48)$$

The recycle multiplication factor, A , in equation (48) may take on any value from $A = 1$ to $A = \infty$. Note that for $A = 1$, $R_1 = (R_1)_{\min}$ and as $A \rightarrow \infty$, $R_1 \rightarrow \infty$ corresponding to total or infinite reflux. Therefore, the actual

or practical recycle ratio expressed by equation (48), as well as the minimum recycle ratio, is dependent upon the separation factor, α , and the tails stream composition exiting stage i , x_i . Furthermore, the practical recycle ratio is greatest at the feed stage in a countercurrent recycle cascade. Since the separation factor is close to unity ($\alpha = 1.027$ to $\alpha = 1.067$ @ 30°C) for the boron exchange systems under consideration, x_i at the feed point is expected to approximate the feed composition, z_F . As a first approximation, equation (48) can be rewritten in terms of the feed composition:

$$R_1 = A^*(R_1)_{\min} = A^* \frac{y_F(\alpha z_F + 1 - z_F) - \alpha z_F}{(\alpha - 1)z_F(1 - z_F)} \quad (49)$$

It is important to note that the practical recycle ratio as expressed by equation (49) is strictly valid only in the limit as $\alpha \rightarrow 1$.

Total interstage flow and the required number of ideal stages are plotted as a function of $1/A$ for $\alpha = 1.027$ in Figure 10. Similarly, the same results for $\alpha = 1.067$ are shown in Figure 11. The results indicated in these figures are based on the constant recycle cascade model developed and discussed in subsequent sections (*vide infra*). The selection of inverse multiplication factor, $1/A$, as the independent variable provides a convenient method for normalizing the x-axis. Note that $1/A \rightarrow 0$ as $A \rightarrow \infty$, or total reflux, and the number of ideal stages for $1/A = 0$ corresponds to the minimum as given by equation (23), the Fenske equation. Similarly, as $1/A \rightarrow 1$, the number of stages becomes infinite in accord with the condition of minimum recycle as previously discussed.

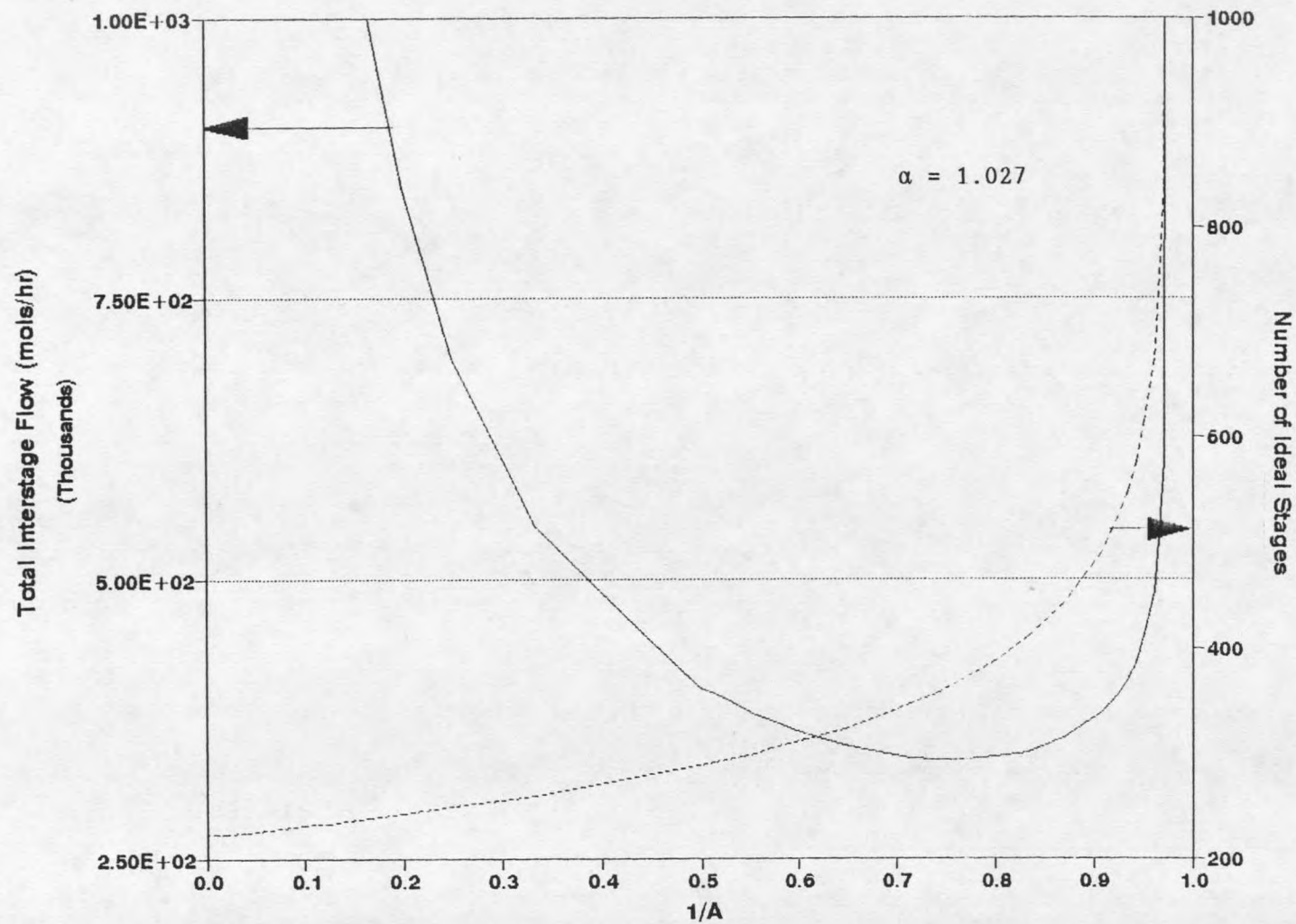


Figure 10. Inverse multiplication factor vs. total interstage flow and number of ideal stages for the dimethyl ether/ BF_3 system.

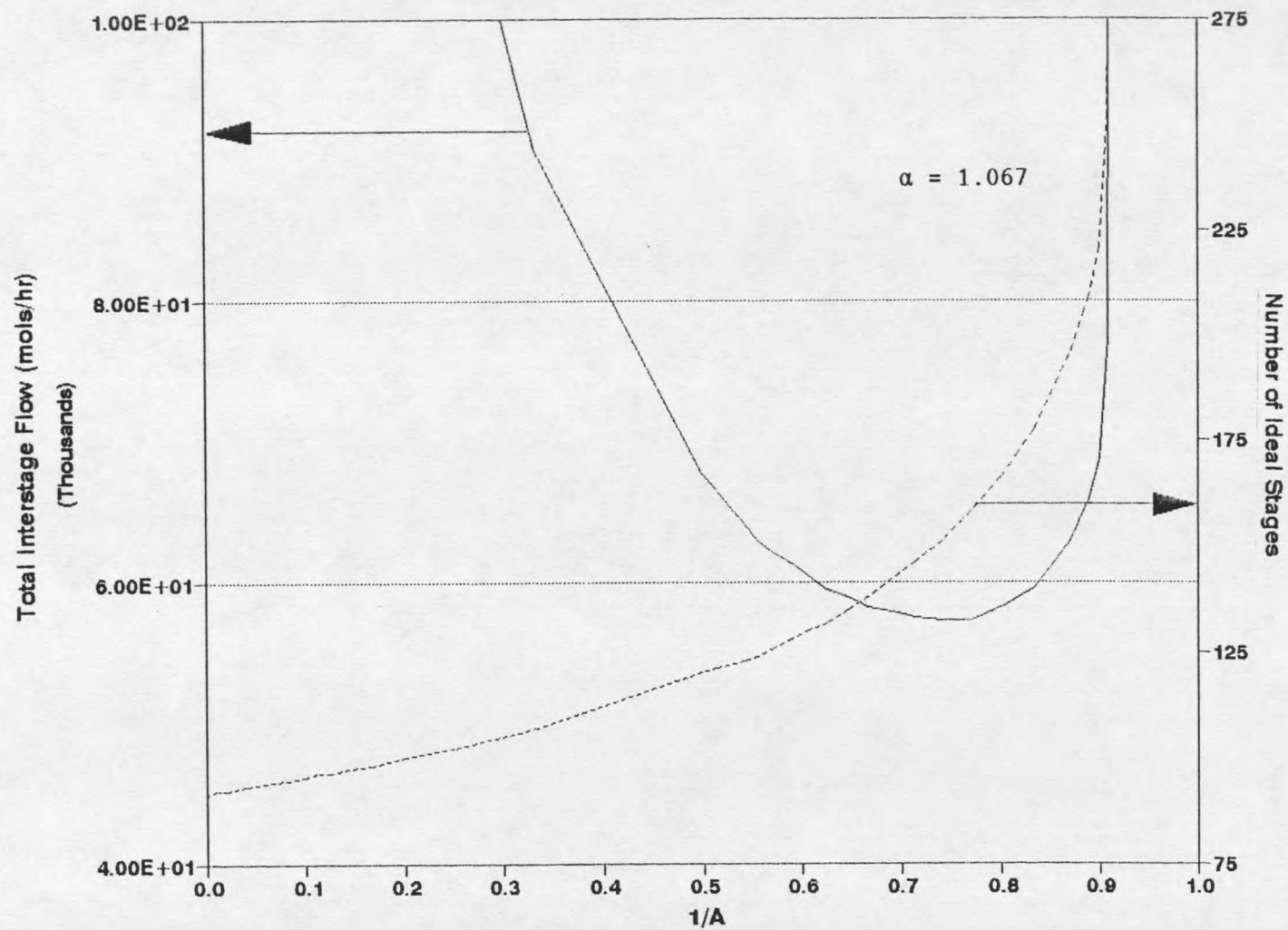


Figure 11. Inverse multiplication factor vs. total interstage flow and number of ideal stages for the nitromethane/ BF_3 system.

Figures 10 and 11 indicate that total interstage flow indeed goes through a minimum in the vicinity of $1/A \approx 0.75$, corresponding to a recycle ratio of $R_1 = 1.33 \cdot (R_1)_{\min}$. Comparison of these figures indicates that the minimum total interstage flow is consistent over the range of separation factors associated with the BF_3 /donor systems pertinent to this study. However, the required number of ideal stages begins to increase rather sharply in the vicinity of minimum total interstage flow. As a result, a slight increase in recycle ratio would substantially reduce the number of ideal stages without a dramatic increase in the total interstage flow. It is apparent from Figures 10 and 11 that the practical recycle ratio should lie somewhere in the range of $1/A \approx 0.6$ to 0.8 , corresponding to $R_1 \approx 1.25$ to 1.7 times the minimum, respectively, in order that the total interstage flow remain in the vicinity of the minimum. However, the practical recycle ratio must be as large as possible, i.e. near 1.7 times the minimum, in order to keep the ideal stage requirements as low as possible.

Obviously, a great deal of latitude exists in the selection the practical recycle ratio, and this selection is an important design and economic factor for a practical separation plant. The determination of an appropriate recycle ratio is typically dependant on the specific system, and hence separation factor, α , used to effect the given separation. Depending on the system, values of 1.05 to 5 times the minimum recycle ratio are commonly encountered in literature sources [4,39] in accord with the above results. In fact, the selection of the practical recycle ratio will ultimately require an in depth economic analysis for a particular separation problem and is outside the scope of this project.

For isotopic separations, recycle ratios of 1.5 to 1.8 times the minimum are typically reported [4,41]. For the purposes of this study, recycle ratios, where required to be specified, were set at 1.45 times the minimum. Although this value may not be the optimum for the systems under consideration, it approximates the values commonly reported for isotope separations and is likely to approximate the recycle ratio used in the design of actual boron isotope separation systems.

Cascade Models

Three different types of cascades were modelled in this study: the ideal cascade, the constant recycle cascade, and different squared off cascade configurations. With the ideal cascade, inefficiencies are removed and the total interstage flow rate is minimized. For a specified practical recycle ratio, the constant recycle cascade (a distillation column is a typical example) requires the minimum number of stages of all recycle cascade configurations. The ideal and constant recycle cascades are limiting cases for the actual design of isotope separation cascades; the constant recycle case minimizes stage requirements while the ideal cascade minimizes total interstage flow. Although a detailed economic analysis is ultimately required, it is probable that both types of cascades are impractical for the boron isotope separation problem and a balance between the two systems must be devised; such is the purpose of the squared off cascade. A squared off cascade can be designed to approach minimum interstage flow requirements associated with the ideal cascade while the number of separation stages in the squared off cascade approaches those of a constant recycle cascade.

If a viable comparison of total interstage flows and stage requirements for the various types of cascades operating with different donor systems is to be made, each cascade must be performing *the same separation*. Consequently, the external variables specified for each type of cascade in all models were as follows:

$y_P \geq 0.950$ = mol fraction ^{10}B in the product stream

$z_F = 0.198$ = mol fraction ^{10}B in the feed stream

$x_W \leq 0.050$ = mol fraction ^{10}B in the waste stream

$P = 2.00$ mol/hr = product stream flow rate

α = the single stage separation factor for a particular donor

With these external variables specified, the feed rate, F , and the waste rate, W , are fixed as specified by equations (36) and (37), respectively. These variables were selected to approximate production rates and purities associated with the currently used dimethyl ether plant as reported in the literature [2,3,4,36].

Notice that a stripping section was required to produce a waste stream composition substantially lower than the composition of the feed stream. Recall that the stripping section is that portion of the cascade operating between the composition range z_F and x_W . The need for a stripping section in the design of an actual plant would require an in-depth economic analysis involving the cost of providing fresh BF_3 feed and disposal of the ^{10}B depleted waste stream.

Ideal Cascade

An important type of cascade that is easy to treat theoretically, minimizes total interstage flow, and is generally approximated by all isotope separation plants designed for minimum equipment costs is the *ideal cascade*. An ideal cascade is characterized by the following properties:

1. The compositions of the heads and tails streams forming the feed to a stage are the same, expressed mathematically:

$$y_{i+1} = x_{i-1} = z_i \quad (i = 2, 3, 4, \dots, n_T - 1) \quad (50)$$

2. The heads separation factor β is constant and equal to the square root of α :

$$\beta = \alpha^{0.5} = \gamma \quad (51)$$

The first condition, corresponding to equation (50), is often termed the *no-mix criteria*. The mixing of streams of different isotopic compositions to form the feed to a separation stage obviously constitutes an inefficiency since it is precisely the reverse of this process that is desired and takes place within the stage itself. The no-mix criteria is a key property of the ideal cascade which fixes the recycle ratio as a function of stage number. This results in minimum equipment size (stage volume) to separate the isotopic mixture.

Heads Separation Factor

The ramifications of the second condition, expressed by equation (51), are not intuitively obvious. This condition is necessary to insure minimum total interstage flow, as indicated by the following development.

First, assume that the stage separation factor α is constant for each stage in the cascade. For an ideal cascade, the no-mix criteria, equation (50), may also be expressed in terms of mole ratios:

$$\epsilon_{i-1} = \eta_{i+1} = \zeta_i \quad (52)$$

Figure 12 shows three stages of an ideal cascade for which this condition holds. First, consider the relationship between the heads separation factors for every other stage in the cascade, e.g. stages $i-1$ and $i+1$ in Figure 12. From the definition of β , equation (29), it follows that:

$$\beta_{i-1} \equiv \frac{\eta_{i-1}}{\zeta_{i-1}} \quad (53)$$

and

$$\beta_{i+1} \equiv \frac{\eta_{i+1}}{\zeta_{i+1}} \quad (54)$$

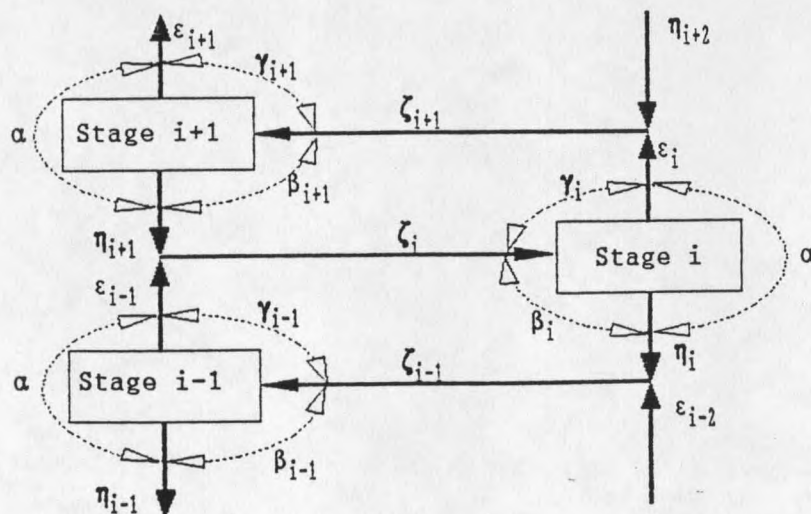


Figure 12. Mole ratios in a section of an ideal cascade.

Since the cascade is ideal,

$$\zeta_{i-1} = \eta_i \quad (55)$$

and $\zeta_{i+1} = \epsilon_i \quad (56)$

Substituting these relations into equations (53) and (54):

$$\beta_{i-1} = \frac{\eta_{i-1}}{\eta_i} \quad (57)$$

$$\beta_{i+1} = \frac{\eta_{i+1}}{\epsilon_i} \quad (58)$$

Dividing equation (58) by equation (57):

$$\frac{\beta_{i+1}}{\beta_{i-1}} = \frac{\eta_{i+1}}{\epsilon_i} \frac{\eta_i}{\eta_{i-1}} \quad (59)$$

From equation (52) and the definition of α , equation (28), the right hand side of (59) is simply α/α or 1, thus:

$$\beta_{i+1} = \beta_{i-1} \quad (i = 2, 3, 4, \dots, n_T - 1) \quad (60)$$

Equation (60) indicates that for constant α , the heads separation factor β is fixed and constant for at least every other stage in the cascade.

Next consider the relationship between the heads separation factors on adjacent stages in a section of the cascade shown in Figure 12, i.e. stages i and $i-1$. Equation (57) is still valid:

$$\beta_{i-1} \equiv \frac{\eta_{i-1}}{\eta_i} \quad (57)$$

and

$$\beta_i \equiv \frac{\eta_i}{\zeta_i} = \frac{\eta_i}{\epsilon_{i-1}} \quad (61)$$

The right hand side of (61) is a result of equation (52) for an ideal

cascade. Solving equations (57) and (61) for η_i , equating and rearranging:

$$\beta_i \beta_{i-1} = \frac{\eta_{i-1}}{\epsilon_{i-1}} \equiv \alpha \quad (62)$$

Equation (62) provides the key result that for an ideal cascade with constant α , the product of the heads separation factors on adjacent stages of the cascade are equal to the stage separation factor α . Expressed mathematically:

$$\beta_i \beta_{i-1} = \alpha \quad (i = 2, 3, 4, \dots, n_T) \quad (63)$$

Equations (60) and (63) suggest that it may be convenient to relate α and β through the relationship:

$$\beta = \alpha^q \quad \text{where} \quad 0 < q < 1 \quad (64)$$

The exponential factor q must lie in the prescribed range since it is easily shown that for $q = 1$ or $q = 0$, no fractionation occurs and the cascade ceases to separate. Note that for the case of $q = 0.5$, equation (64) is identical to equation (51).

It is of practical interest to examine the effect q has on a plot of recycle ratio versus stage number in the ideal cascade. Such a plot is shown in Figure 13, derived from the ideal cascade computer model (*vide infra*) for $\alpha = 1.05$. It is apparent from Figure 13 that for $q = 0.5$ the recycle ratio increases monotonically from either end of the cascade up to the feed stage. For $q = 0.4$ the curve is becoming unstable and appears more as a band than a smooth curve. As the value of q departs further from the central value of 0.5, the curve will exhibit wider oscillations.

The behavior of the cascade exhibited in Figure 13 for different values of q in equation (64) can be envisioned as follows. For $q = 0.5$,

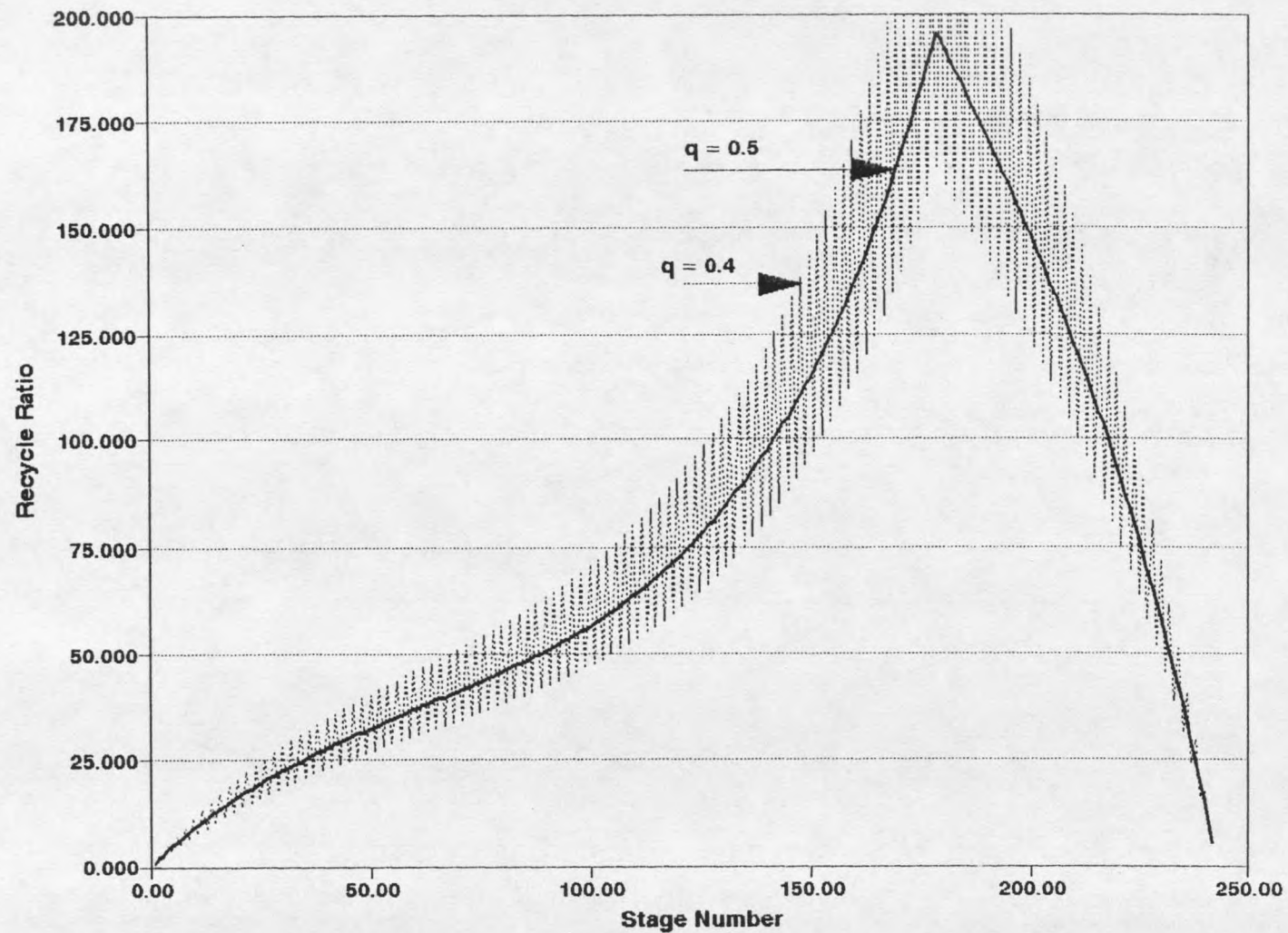


Figure 13. Effect of the exponential factor, q , on the recycle ratio versus stage number curve for the ideal cascade.

the amount of material and hence the volume or size of each stage in the cascade decreases smoothly from the feed point toward the waste and product ends of the cascade. Thus the stage volume in an ideal cascade changes monotonically in *one dimension* for $q = 0.5$. For values of $q \neq 0.5$, the stage volume decreases smoothly for either adjacent or opposite stages in the cascade from the feed point to the ends of the cascade as well as from stage to stage. Consequently, stage volume varies in *two dimensions* for values of $q \neq 0.5$. This indicates that for $q \neq 0.5$, half of the cascade, consisting of every other stage, is processing more material than the remaining half and the work of performing the desired separation is not distributed equally between the two halves.

Finally, it is advantageous to discern the effect q has on the total interstage flow rate through an ideal cascade. Using the model for the ideal cascade discussed subsequently, the total interstage flow rate was determined for a variety of q values with $\alpha = 1.05$. The results are plotted in Figure 14. The important feature indicated by Figure 14 is that the total interstage flow is a minimum at $q = 0.5$. Furthermore, as q approaches the limiting values of 0 and 1, the total interstage flow becomes infinite. This indicates that as q approaches 0 or 1 as limits, infinite interstage flow is required to perform the separation.

Thus, an ideal cascade is one in which no mixing of streams with different compositions occurs ($y_{i+1} = z_i = x_{i-1}$ or $\eta_{i+1} = \xi_i = \epsilon_{i-1}$) and the heads separation factor is constant with $\beta = \alpha^{0.5}$. These two conditions insure a cascade with minimum interstage flow, an ideal cascade by definition.

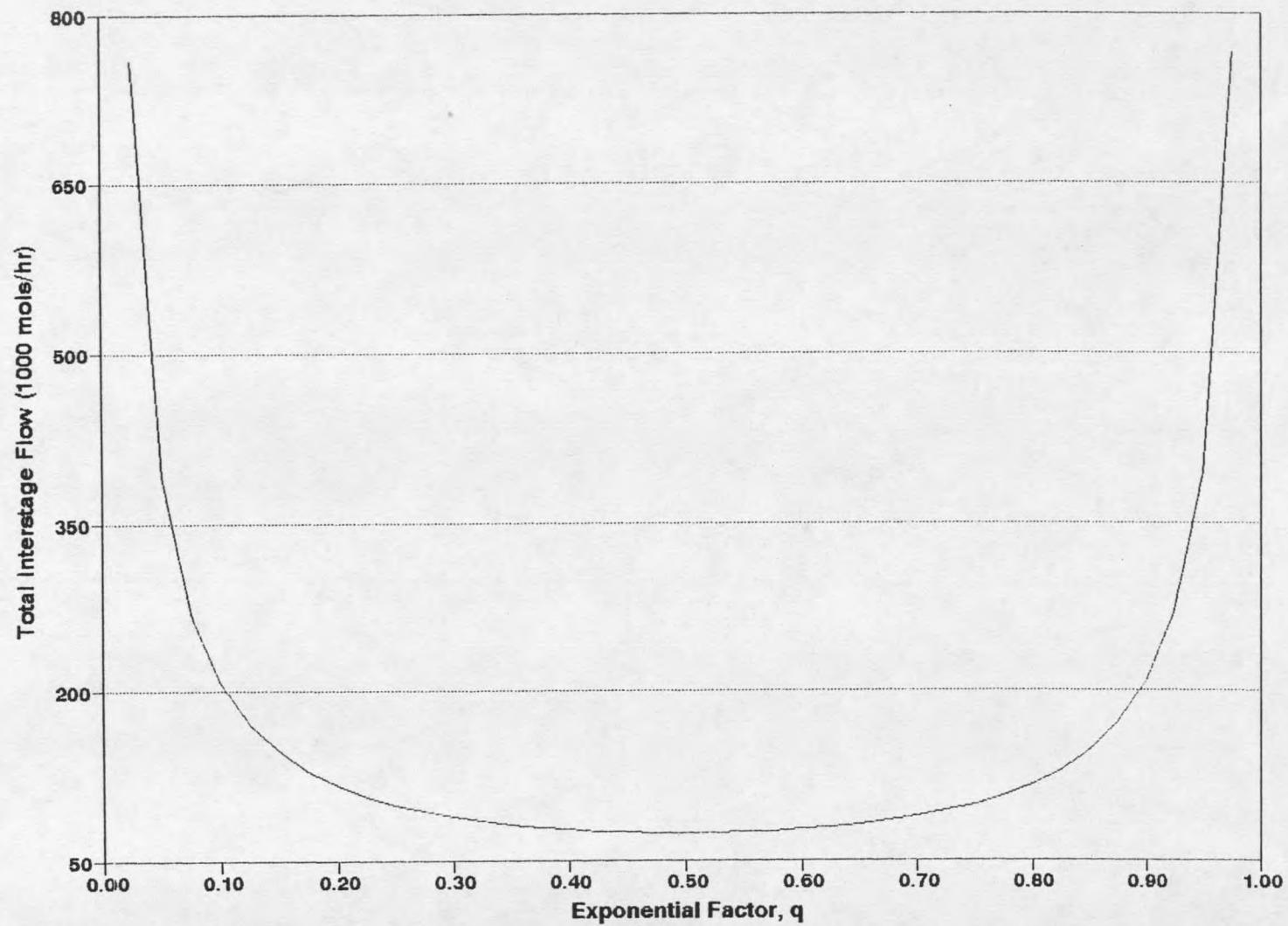


Figure 14. Effect of the exponential factor, q , on total interstage flow rate in the ideal cascade.

The Ideal Cascade Model

The ideal cascade was the simplest to model since the composition of all streams was fixed and easily determined once the composition of a single stream at any point in the cascade was specified. With reference to Figure 9, the logical starting point for the ideal cascade is the feed stage, denoted n_F . The fresh feed composition, z_F , was specified as the natural isotopic abundance of boron ($z_F = 0.198$). With z_F fixed, the no-mix criteria fixes the composition of the heads stream from the next higher stage y_{n_F+1} and the tails composition of the next lower stage x_{n_F-1} . Since α was known from experiment and assumed constant for a particular BF_3 /donor system and $\beta = \alpha^{0.5}$ in an ideal cascade, the composition of the heads stream exiting the feed stage was fixed according to equation (31). The composition of the tails stream exiting the feed stage, x_{n_F} , was then determined by the equilibrium expression given by equation (32).

With the compositions about the feed point known, the compositions for each stream in the enriching section was determined by successive application of the no-mix criteria, equation (50), and the equilibrium expression, equation (31). Once the heads composition, y_i , of a stage was greater than or equal to the desired product purity ($y_F \geq 0.95$), the product stage was located.

A similar method was employed to determine the compositions of streams above the feed stage in the stripping section. Successive use of the no-mix criteria and equation (32) in a stagewise manner provided the compositions of all streams in the stripping section. When the tails stream composition exiting a stage (x_i) was less than or equal to the specified waste composition ($x_w \leq 0.05$), the waste stage was located.

In the above manner, the composition of each stream and the total number of stages in the ideal cascade were determined. With compositions known, the recycle ratio for each stage required to bring about condition (50), the no-mix criteria, in the enriching section of the cascade is given by:

$$R_1 = \frac{1}{(\beta-1)} \left[\frac{y_P}{x_1} - \frac{\beta(1-y_P)}{1-x_1} \right] \quad (65)$$

Similarly, the necessary recycle ratio required in the stripping section for any stage above the feed point is given by:

$$R_1 = \frac{(W/P)(x_{1-1} - x_w)}{(x_{1-1} - x_1)} \quad (66)$$

The recycle ratio for each stage in the ideal cascade is calculated from equations (65) and (66) in the appropriate section. From the definition of recycle ratio, equation (44), the flow rate of the tails stream leaving each stage is simply the recycle ratio for the stage multiplied by the flow rate of the product stream. The heads flow rate leaving each stage is easily determined from material balance equations, (38) and (41) for stages in the enriching and stripping sections, respectively. The total interstage flow rate is the summation of all stream flows exiting the various stages throughout the cascade.

The above model provided values for all the important variables throughout the ideal cascade for a given BF_3 /donor system. A number of these variables were then used to compare the different donor systems studied with the ideal cascade and eventually compare the performance of the other types of cascades modelled.

Results and Discussion of the Ideal Cascade Calculations

The important process variables from the ideal cascade models with the different donor systems studied experimentally are listed in Table 5. The currently used dimethyl ether system was also modelled based on the separation factor reported in the literature (see Table 1). The dimethyl ether system was used as a reference to compare the consequences of selecting one of the other donor systems studied experimentally for fractionation of boron isotopes.

The first column of Table 5 indicates the BF_3 /donor system along with the appropriate separation factor, α . In order to make a viable comparison, the separation factors associated with each system were for a temperature of 30°C. Thus, isothermal operation of the separation column at this temperature was assumed.

The total number of ideal stages, N_t , the number of stages in the enriching section, N_s , and the number of stages in the stripping section, N_b , are also indicated in Table 5. There is a dramatic increase in the required number of stages as the separation factor is decreased from $\alpha = 1.067$ for nitromethane to $\alpha = 1.027$ for dimethyl ether. This trend is expected in view of the previous discussion involving the Fenske equation (refer to equation (23) and Table 4). For the ideal cascade, stage requirements decrease by nearly 60% for nitromethane as compared to dimethyl ether. Stage requirements for acetone are approximately 30% less than for dimethyl ether. The total number of stages is an indication of the size or height of the column required to perform the desired separation. Note that N_b is the feed stage number as counted from the product end of the cascade.

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

System	N_1	N_2	N_3	Total Interstage Flow (mols/hr)	External Process Variables
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	181	134	47	41,900	$y_F = 0.9501$ $x_H = 0.0495$ $F = 12.128$ mols/hr $W = 10.128$ mols/hr
DIBK $\alpha(30^\circ) = 1.043$	280	207	73	99,700	$y_F = 0.9507$ $x_H = 0.0494$ $F = 12.132$ mols/hr $W = 10.132$ mols/hr
MIBK $\alpha(30^\circ) = 1.039$	308	228	80	120,500	$y_F = 0.9509$ $x_H = 0.0498$ $F = 12.161$ mols/hr $W = 10.161$ mols/hr
Acetone $\alpha(30^\circ) = 1.038$	315	233	82	126,400	$y_F = 0.9501$ $x_H = 0.0499$ $F = 12.156$ mols/hr $W = 10.156$ mols/hr
Dimethyl Ether $\alpha(30^\circ) = 1.027$	443	327	116	248,800	$y_F = 0.9506$ $x_H = 0.0494$ $F = 12.128$ mols/hr $W = 10.128$ mols/hr

The total interstage flows through the ideal cascades are also tabulated. The reduction of interstage flow with increasing separation factor is even more dramatic than the stage requirements. Interstage flow requirements for the nitromethane system are about 83% less than for the dimethyl ether system, decreasing by a factor of nearly six. Even for acetone, the interstage flow requirements are substantially reduced by a factor of two or roughly 50%. The interstage flows indicated are the minimum amounts required for each donor system in any possible type of recycle cascade arrangement performing the specified separation.

The last column of Table 5 shows the values of the external variables y_p , x_w , and the feed and waste flow rates determined from the models. These are the values necessary to satisfy external material balances, equations (34) and (35), for the particular BF_3 /donor systems in the ideal case. Comparison of the external variables indicates that they are close enough to insure each cascade is performing essentially the same separation.

The recycle ratio as a function of stage number is depicted graphically in Figure 15 for the ideal cascade with each of the different donors. The conical shape of each curve is typical of the ideal cascade. The "peak" or largest value of recycle coincides with the feed stage for each case. As the separation factor increases from that of dimethyl ether to nitromethane, the required number of ideal stages is observed to decrease. Furthermore, the area under the curve is proportional to the total interstage flow through the cascade and this area also decreases with increasing separation factor. These observations are consistent with the previous discussion of the ideal cascade.

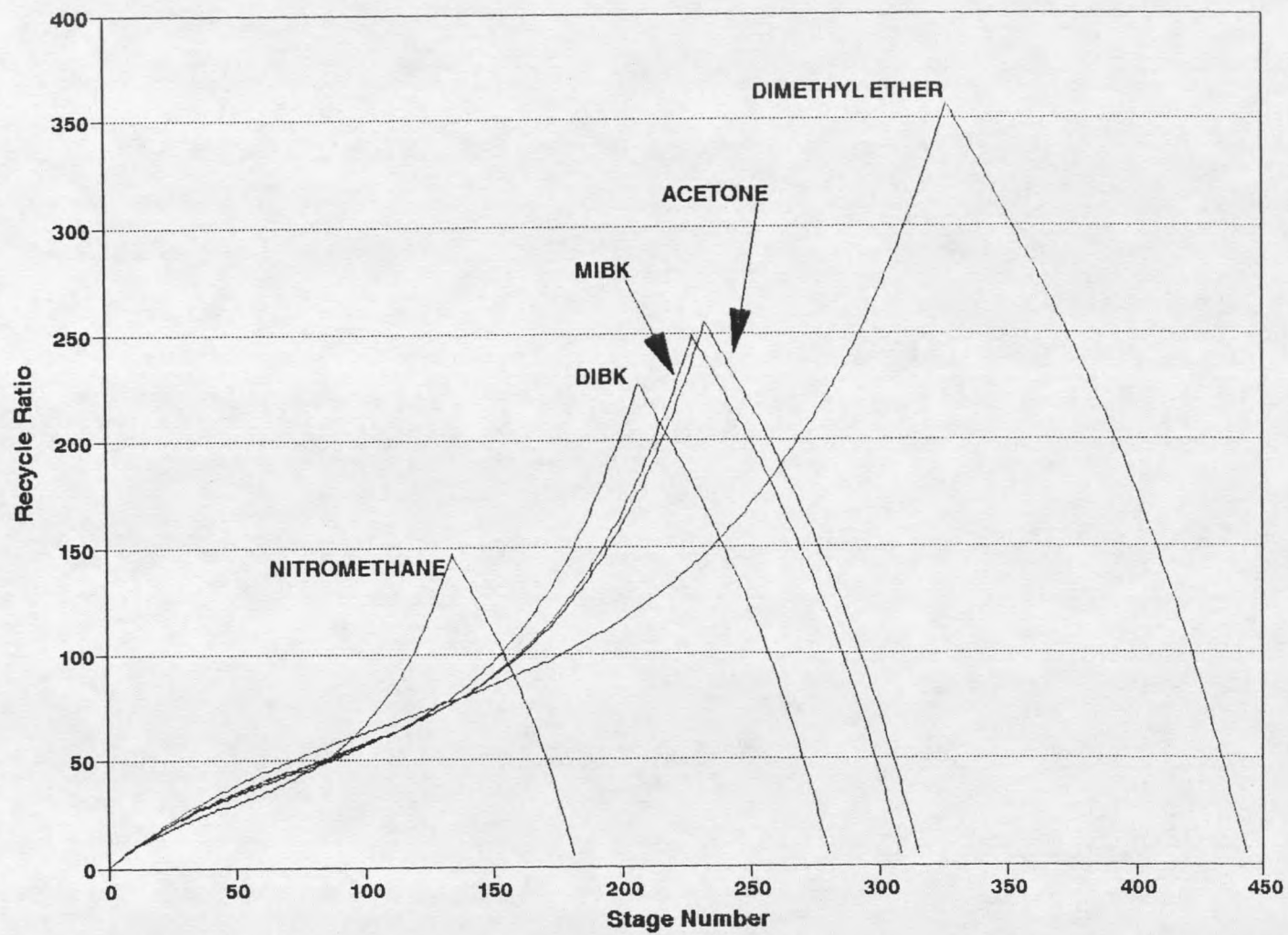


Figure 15. Recycle ratio versus stage number for the ideal cascade with the different donors.

Figure 15 indicates that the recycle ratio is greatest at the feed stage and decreases sharply as the ends of the cascade are approached. The amount of material processed by each stage, and hence the stage volume or size, increases from the product stage up to the feed point and then decreases from the feed point to the waste end of the cascade. Therefore, each stage is of a different size and the recycle ratio must be changed at each stage in the ideal cascade. In order to alter the recycle ratio, each stage in the enriching section requires a decomposer to convert the liquid complex to BF_3 gas. Similarly, each stage in the stripping section must include a recombiner to convert BF_3 gas into liquid complex and alter the recycle ratio. In the ideal cascade, not only is each stage of a different size, but each must incorporate either a decomposer or recombiner for the system to operate properly.

Clearly, the interconnection of stages and the operation of the ideal cascade would be extremely complex. Furthermore, the manufacturing and construction costs associated with such a system would probably be enormous. In general, the actual use of an ideal cascade would probably not be economically feasible.

The importance of the ideal cascade lies in the fact that it is theoretically the most efficient design (from the standpoint of minimum equipment size) available to perform the desired separation. This is a result of the no-mix criteria and minimum total interstage flow. For this reason, the ideal cascade provides a convenient basis for comparing the efficiency of other appropriate cascade designs and indicates the direction such designs must take to increase separation efficiency.

Constant Recycle Cascade

The simplest type of recycle scheme is the *constant recycle cascade* (CRC). The recycle ratio, R_1 , is specified and constant for every stage in the CRC. For the specified recycle ratio, the constant recycle design provides the minimum number of stages to perform the desired separation for any cascade arrangement. On the other hand, total interstage flow and therefore total cascade size, is greatest in the CRC than for other cascade designs. A typical distillation column is the classical example of a constant recycle cascade.

The Constant Recycle Model

The general method used for modelling the constant recycle cascade was a straight forward, double iterative procedure. The product composition, y_P , product flow rate, P , waste composition, x_W , and feed composition, z_F , were specified. The recycle ratio was also specified. In the constant recycle cascade, minimum recycle occurs at the feed point in accord with the pinch point previously described. In accord with the previous discussion of practical recycle ratio, equation (49) was used with a value of $A = 1.45$ to specify the value of R_1 at the feed point. With the external variables specified, the feed rate, F , and waste rate, W , were fixed and calculated from equations (36) and (37), respectively. The value of the separation factor, α , was fixed for a specific donor system and was assumed constant for every stage in the cascade.

Referring to Figure 9, the calculation process started at the product stage, defined as stage number 1 in this study. The tails stream composition exiting the first stage, x_1 , was calculated from equation (32), the equilibrium expression. The material balance relation for the

enriching section, equation (40), was used to determine the composition of the heads stream exiting stage 2, y_2 . Equation (32) was then reapplied to stage number 2, and the calculation process repeated. By successive application of the equilibrium and material balance relations in a stepwise iterative process, the number of ideal stages in the enriching section of the cascade were determined.

When the composition difference between the tails stream leaving a stage (x_{nF-1} in Figure 9) and the fresh feed composition, z_F , was minimized, the feed stage was located. Once feed stage location was determined, the stripping section material balance, equation (43), was required in the stagewise calculation procedure for all stages above the feed point. The equilibrium expression remained the same for the stripping section stages.

When the tails composition exiting a stripping section stage was less than or equal to the specified waste purity, x_W , the waste stage was located, all internal material balances were satisfied and the number of ideal stages was determined. However, since each stage is a discrete equilibrium step, the calculated waste composition was seldom equal to the specified value and the conditions of the overall material balances were not met. A second iterative loop around the external variables was therefore required. With the value of x_W determined from the first iteration, new feed and waste flow rates were calculated from equations (36) and (37). The other external variables (y_F , z_F , P and α) and the recycle ratio remained fixed at their previous values. The entire stagewise iterative process was repeated, beginning at the product stage, until the calculated waste stream composition, x_W , satisfied external as well as internal material balances.

From the definition of recycle ratio, equation (44), the tails stream flow rate exiting each stage was fixed once the recycle ratio was specified. The heads stream flow rate exiting each stage was then determined by rearranging the appropriate material balance, equation (38) or (41) for the enriching or stripping section, respectively. The flow rates of the heads and tails streams for each stage was fixed and the total interstage flow rate was the summation of the individual stage flows over the entire cascade.

The CRC model provided information regarding the required number of ideal stages, waste stream flow rate and composition, feed stream flow rate, and the total interstage flow rate for the specified separation and donor system.

Results and Discussion of the CRC Calculations

The important design parameters obtained from the constant recycle cascade models with the various BF_3 /donor systems studied are listed in Table 6. The separation factor associated with each donor was for a temperature of 30°C and isothermal column operation was assumed. The recycle ratio indicated in Table 6 was specified for each donor at 1.45 times the minimum requirements at the feed stage in accord with the previous discussion of practical recycle ratio.

It is apparent that the total number of required stages, N_t , increases as the separation factor decreases. This is also true for the stage requirements of the enriching section, N_e , and the stripping section, N_s . The nitromethane system requires 58% or 195 fewer ideal stages while the acetone system requires 28% or 95 fewer stages than the dimethyl ether

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

System	Recycle Ratio	N_t	N_e	N_s	Total Interstage Flow (mols/hr)	External Process Variables	n_{dist} Fenske Eq.
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	102	142	94	48	57,900	$x_W = 0.0483$ $F = 12.044$ mols/hr $W = 10.044$ mols/hr	91
DIBK $\alpha(30^\circ) = 1.043$	160	215	144	71	136,800	$x_W = 0.0429$ $F = 12.114$ mols/hr $W = 10.114$ mols/hr	141
MIBK $\alpha(30^\circ) = 1.039$	176	236	159	77	165,700	$x_W = 0.0494$ $F = 12.120$ mols/hr $W = 10.120$ mols/hr	155
Acetone $\alpha(30^\circ) = 1.038$	181	242	163	79	174,400	$x_W = 0.0496$ $F = 12.118$ mols/hr $W = 10.118$ mols/hr	159
Dimethyl Ether $\alpha(30^\circ) = 1.027$	254	337	227	110	342,000	$x_W = 0.0494$ $F = 12.119$ mols/hr $W = 10.119$ mols/hr	222

system to perform the specified separation. Note that for each donor system, the constant recycle cascade requires far fewer stages than the corresponding ideal case (refer to Table 5). Comparison of Table 6 with Table 5 indicates that column height is substantially reduced in the constant recycle case for donor systems with larger separation factors. However, the size or volume of each ideal stage in the CRC must be greater to accommodate the larger overall interstage flow.

The total interstage flow also decreases as the separation factor is increased. Nitromethane requires approximately 83% less total interstage flow while acetone requires nearly 50% less than for the dimethyl ether system. The total interstage flow of each system in the constant recycle case is considerably more than for the corresponding ideal cascade (refer to Table 5). As a result, the total internal volume and holdup of process materials, i.e. the size of the cascade, is substantially greater for the CRC than for the ideal cascade.

The absolute minimum number of ideal stages required to perform the desired separation is given by equation (23), the Fenske equation, previously discussed. This minimum stage requirement, $N_{\min}$, obtained from equation (23) for the various donor systems is tabulated in the final column of Table 6. Note that for each donor system with the specified recycle ratio of $1.45 \cdot (R_1)_{\min}$, approximately 52% more ideal stages than the absolute minimum are required. Larger recycle ratios would result from increasing the recycle multiplication factor, A , in equation (49) causing a decrease in total ideal stage requirements while increasing the total interstage flow. Conversely, lowering the recycle ratio would increase stage requirements with a concomitant decrease in the total interstage

flow. In a detailed economic evaluation, an optimum recycle ratio would be determined. This optimum is expected to be in accord with the specified recycle ratio of $1.45 \cdot (R_1)_{\min}$ as previously discussed.

The external variables as determined from the models for the different donor systems are also indicated in Table 6. The CRC process variables are in excellent agreement with the external process variables for the ideal cascade (Table 5). Consequently, each cascade accomplished essentially the same degree of separation and the comparison is valid.

A plot of recycle ratio as a function of stage number for the CRC models with the different donor systems is shown in Figure 16. As indicated, the plot for each donor is rectangular as a result of using a constant recycle ratio. This rectangular shape is characteristic of the CRC. As the separation factor increases from that of the dimethyl ether system to that for nitromethane, both the number of ideal stages and the practical recycle ratio decreases. This results in a reduction of the area under each curve in Figure 16. This area is directly proportional to the total interstage flow through the CRC. Consequently, both the total interstage flow and the number of ideal stages, i.e. the size of the CRC, decreases as the separation factor increases. These observations are consistent with the foregoing results and discussion of the constant recycle cascade.

The construction and operation of a constant recycle cascade for the fractionation of boron isotopes is conceivable. It is the simplest device that can be used to achieve the desired separation, although it may not be the best from an economic standpoint. Distillation columns containing 100 actual stages are not uncommon. The CRC would perform the prescribed

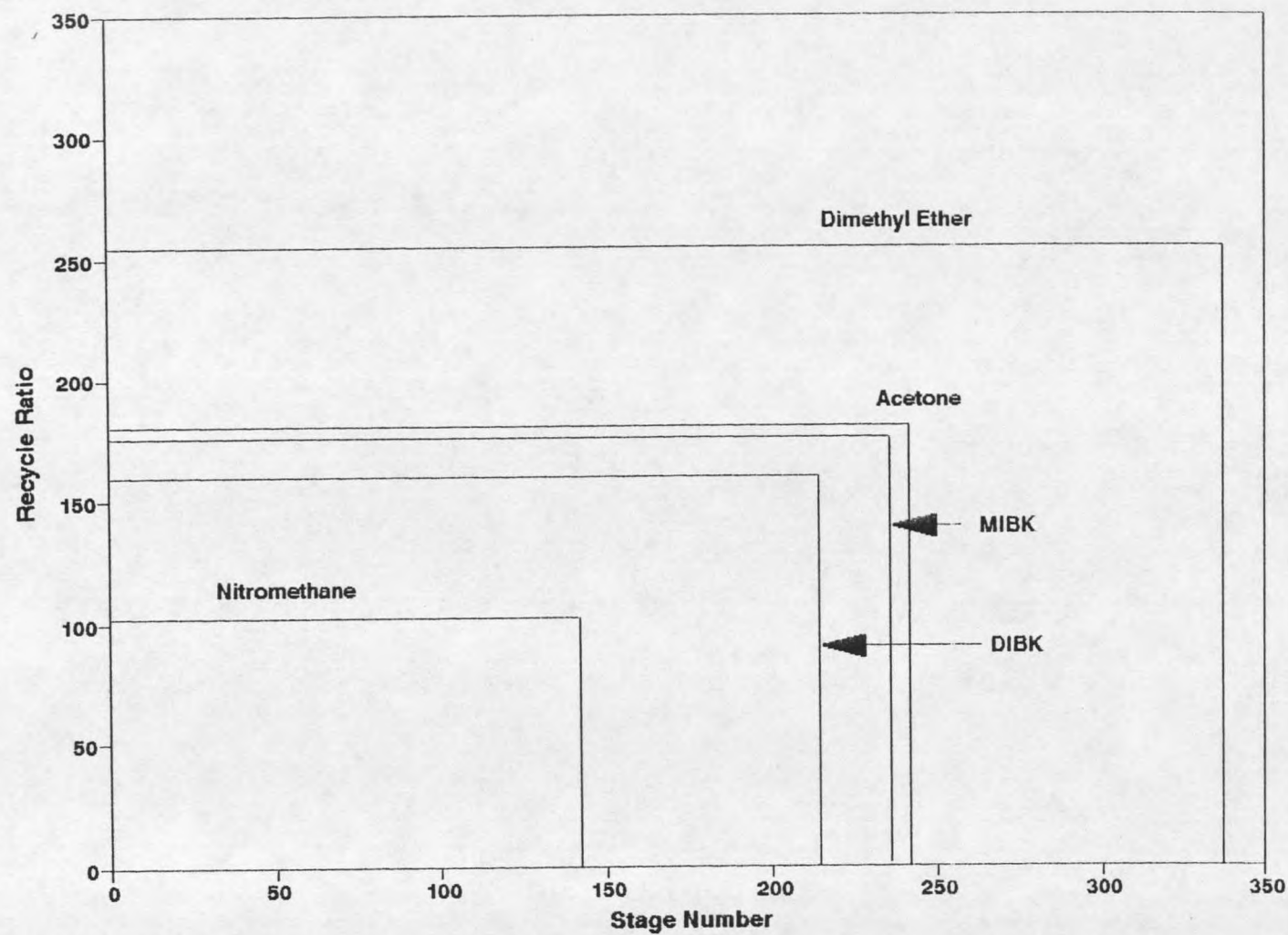


Figure 16. Recycle ratio versus stage number for the constant recycle cascade with the different donors.

separation with the minimum number of stages for a specified practical recycle ratio. This property of constant recycle cascades provides a convenient basis for stage requirement comparisons between different cascade designs. The CRC is less efficient, in terms of total interstage flow rate, than the ideal case. A compromise between minimum total interstage flow and minimum stage requirements may ultimately result in a more efficient and practical fractionation system.

Squared Off Cascade

The total interstage flow is minimized in the ideal cascade while the stage requirements are minimized for the constant recycle cascade operated at a specified recycle ratio and performing the same degree of separation. A realistic approach to the design of an efficient separation system is to find a compromise between these two minimums. Such is the function of the *squared off cascade (SOC)*. "Squaring off" a section of the cascade is a result of utilizing a constant recycle ratio over a consecutive group of stages to perform a portion of the desired overall separation. A "square section" is therefore a portion of the cascade composed of identical stages, that is, a consecutive group of stages with the same separation factor, α , operating with the same (constant) recycle ratio. As such, a square section is typically regarded as an independent separation column which can be treated as a constant recycle cascade, but performs only a fraction of the desired overall separation.

A great deal of latitude exists for specifying the number of square sections used in the SOC. Squaring off the entire cascade with a single section results in the constant recycle case. Squaring off each stage in

the cascade essentially results in the ideal case. Consequently, minimum stage requirements are approached as fewer squared sections are used while minimum interstage flow requirements are approached as the number of square sections increases. The design of an efficient SOC requires a compromise between these two opposing minimums.

The Squared Off Model

The purpose of the SOC is to approximate the shape of the ideal cascade without the complexity of having each stage a different size. The number of possible squared off configurations capable of performing the desired separation are virtually limitless. How closely a particular SOC design approximates ideal behavior will depend on a number of design parameters. The important design variables includes the number of square sections and the number of ideal stages per square section.

The CRC previously discussed utilized a specified and constant recycle ratio (fixed by the feed and product compositions) over each stage in the cascade. As such, the CRC can be considered a squared off cascade utilizing a single square section. Various SOC configurations result by altering the CRC such that two or more constant recycle ratios are utilized. The recycle ratio in the vicinity of the feed stage of an SOC must remain fixed in accord with equation (49) to avoid a pinch point. However, the recycle ratio can be reduced towards the product or waste stages in accord with the ideal cascade concept. Changing the recycle ratio at various points between the feed and the waste or product stages is equivalent to adding square sections to the CRC. Consequently, it is convenient to view the SOC models as propagating from the addition of one or more square sections to the CRC model. As a limiting case, the recycle

ratio can be altered at every stage in a cascade, when specified in accord with the no-mix criteria and constant β , the result is the ideal case.

As indicated in previous discussions, the enriching section is that portion of the cascade from the product stage up to and including the feed stage. The stripping section is then defined as the remainder of the cascade from the waste stage up to but not including the feed stage. The feed stage is therefore the dividing line between these two portions of any cascade. Furthermore, the largest minimum recycle ratio necessary to avoid a pinch point in a counter-current cascade will occur at the feed stage. As a matter of practicality in this regard, square sections added adjacent to the feed stage in either the enriching or stripping section of the SOC will require approximately the same constant recycle ratio, which is fixed at the feed stage by the feed composition. Therefore, it is possible to add any number of square sections to the enriching portion of the SOC while utilizing a single square section to span a portion of the enricher (near the feed stage) and the entire stripping section. Conversely, several square sections can be added to the stripping portion of a SOC while including the entire enriching segment and a portion of the stripper in a single square section. Finally, square sections could be incorporated simultaneously into the enriching and stripping segments.

In accord with previous discussions, a larger recycle ratio is required on either side of the feed stage than in any other portion of the cascade. Obviously, a great deal of latitude exists in specifying the recycle ratio in a square section and how the square sections are added to the SOC. For simplicity, square sections were added only in the enriching segment of the SOC's for the initial modelling studies. In subsequent

models and discussions (*vide infra*), squared sections were added to the stripping portion of the SOC while maintaining a constant number (two) in the enricher. Consequently, the effects of adding square sections to the different segments of the SOC were examined independently.

By altering the number of squared sections added in the enricher of the SOC models, the impact on cascade size in terms of both ideal stage requirements and total interstage flow was examined. To this end, square cascades composed of 2, 3, 4, and 5 square sections were modelled in this part of the study. The stripping segment in these SOC were composed of a single square section that utilized the same constant recycle ratio as the adjacent squared off enriching section and the feed stage.

The method for specifying the number of ideal stages and hence size of each square section in the SOC models is less apparent. Every square section can be treated mathematically as a constant recycle cascade. In accordance with the CRC models, the recycle ratio must be specified for each squared off section and the number of stages per section depends on the selected value of the recycle ratio. Thus, ideal stage requirements and recycle ratio for a square section are directly related and were specified by the composition range spanned by each square section.

The method used in all the SOC models for specifying the range over which each square section operated was to divide the enriching section composition range, as specified by the product and feed stream mole fractions, by the desired number of squared sections. The composition range covered by any square section was specified by the relation:

$$\text{Composition range} = \frac{Y_P - Z_P}{\# \text{ of sections}} = \frac{0.95 - 0.198}{\# \text{ of sects.}} = \frac{0.752}{\# \text{ of sects.}} \quad (67)$$

Thus, for the SOC model with two squared off sections, each section spanned the composition range of $0.752/2 = 0.376$. The first section operated between mole fractions of $y_P = 0.95$ and $x_1 = 0.95 - 0.376 = 0.574$. The second section covered the remaining composition range of $x_1 = 0.574$ to $z_P = 0.198$. The use of equation (67) results in equivalent composition ranges over each square section in the enriching segment of the cascade.

The recycle ratio used in a square section of the SOC was required to be greater than the minimum, $(R_1)_{\min}$, for that particular section. In accord with equation (49), the practical recycle ratio used in a square section of the enricher was given by:

$$R_1 = A \cdot (R_1)_{\min} = A \cdot \frac{y_P(\alpha x_1 + 1 - x_1) - \alpha x_1}{(\alpha - 1)x_1(1 - x_1)} \quad (68)$$

Minimum recycle was determined for each square section as per equation (68) with a multiplication factor of $A = 1.45$. The composition of the tails stream exiting a square section, x_1 , i.e. the composition numerically closest to the feed composition, was used in equation (68) to determine the recycle ratio in that particular section.

Since each square section in the SOC is itself a constant recycle cascade, the iterative methods previously discussed in accord with the CRC model were applicable to the individual sections. Using a similar stage-wise iterative procedure, stream compositions and flow rates were determined for each stage in a square section. Hence, the SOC models required specifying the number of squared sections, the composition range over which each square section operated, and the recycle ratio used in each section of the cascade in accord with the above methods.

Note that the above SOC models, based on the specification of equivalent composition ranges and recycle ratios of 1.45 times the minimum for each square section, does not necessarily insure the best SOC approximation with regards to the ideal cascade. Different combinations of recycle ratios and/or composition ranges could conceivably result in SOCs which would more closely approximate ideal cascade behavior. Ultimately, an optimization procedure based on detailed system design for a specific BF_3 /donor system is necessary. However, the above models are suitable to establish the appropriate equipment configuration on a comparative or relative basis as opposed to absolute column design.

For the specified number of squared sections, the above model provided the required number of ideal stages and the total interstage flow rate through each SOC. These results were then compared for the different donor systems and ultimately, with the other types of cascades modelled.

Results and Discussion of the SOC Calculations

Results from the squared off cascade models containing 2, 3, 4, and 5 sections are listed in Table 7 for the different BF_3 /donor systems studied. The tabulated results were obtained based on the experimental separation factors at 30°C . Isothermal column operation at that temperature was assumed. For comparative purposes, the results from the CRC (one square section) and the ideal cascade calculations (maximum number of square sections) are included in Table 7.

The required number of total stages, N_t , and enriching section stages, N_e , as well as the total interstage flow rate increased as the separation factor decreased for the respective donor systems. This trend

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

System	# of Square Sections	N_1	N_2	N_3	Total Interstage Flow (mols/hr)	x_1	Feed Rate (mols/hr)	Waste Rate (mols/hr)
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	CRC(1)	142	94	48	57,900	0.0483	12.044	10.044
	2	166	119	47	48,100	0.0495	12.127	10.127
	3	185	138	47	47,200	0.0485	12.058	10.058
	4	191	144	47	46,800	0.0485	12.062	10.062
	5	198	151	47	46,700	0.0489	12.088	10.088
	†IC(181)	181	134	47	41,900	0.0494	12.183	10.128
DIBK $\alpha(30^\circ) = 1.043$	CRC(1)	215	144	71	136,800	0.0429	12.113	10.114
	2	253	182	71	114,100	0.0490	12.093	10.093
	3	274	203	71	111,000	0.0490	12.097	10.097
	4	289	218	71	110,300	0.0489	12.087	10.087
	5	301	230	71	110,000	0.0495	12.125	10.125
	†IC(280)	280	207	73	99,700	0.0494	12.132	10.132
MIBK $\alpha(30^\circ) = 1.039$	CRC(1)	236	159	77	165,700	0.0494	12.120	10.120
	2	278	200	78	138,200	0.0489	12.088	10.088
	3	301	223	78	134,200	0.0482	12.106	10.106
	4	317	239	78	133,100	0.0493	12.117	10.117
	5	329	252	77	132,900	0.0495	12.128	10.128
	†IC(308)	308	228	80	120,500	0.0498	12.161	10.161
Acetone $\alpha(30^\circ) = 1.038$	CRC(1)	242	163	79	174,400	0.0496	12.119	10.119
	2	285	205	80	145,400	0.0489	12.087	10.087
	3	309	229	80	141,500	0.0488	12.083	10.083
	4	325	246	79	140,100	0.0493	12.114	10.114
	5	338	258	80	140,200	0.0492	12.107	10.107
	†IC(315)	315	233	82	126,400	0.0499	12.156	10.156
Dimethyl Ether $\alpha(30^\circ) = 1.027$	CRC(1)	337	227	110	342,000	0.0494	12.119	10.119
	2	396	286	110	283,900	0.0494	12.121	10.121
	3	429	319	110	276,200	0.0492	12.109	10.109
	4	452	342	110	273,900	0.0495	12.125	10.125
	5	469	359	110	273,400	0.0496	12.133	10.133
	†IC(443)	443	327	116	248,800	0.0494	12.128	10.128

† IC(n) $\equiv$ Ideal Cascade with n square sections where $n = N_1$, the number of ideal stages.

is expected based on results from the previously discussed models, and is due to the prescribed separation becoming more difficult as the separation factor decreases.

For a given donor (constant α), the total and enriching section stage requirements increased with the number of squared sections. As the number of squared sections increased, the composition range over which each section operates is reduced. This results in a reduction of minimum recycle requirements in accord with equation (68) (recall actual recycle was set at $1.45 \cdot (R_1)_{\min}$ for each section). A reduction in recycle ratio results in a concomitant increase in the number of ideal stages. The fact that the total number of stages increases as the number of squared sections increases is a salient feature of the squared off cascade.

A comparison of the ideal stage requirements between the SOC and ideal cascade models in Table 7 indicates an interesting phenomenon. The three section SOC requires approximately the same number of stages as the ideal cascade for a particular donor system, while the four and five section SOCs require more ideal stages than the corresponding ideal cascade. This anomaly is a result of the method by which the practical recycle ratio was specified in the SOC cascades as given by equation (68). By specifying a larger recycle, i.e. a larger value of A in equation (68), fewer ideal stages would be required in the various SOC models. At some point, the increased recycle ratio would result in all SOCs requiring fewer ideal stages than the ideal cascades. Note, however, that in all cases, the SOCs require substantially more total interstage flow than the corresponding ideal case. Any further increase in recycle ratio would increase the total interstage flow in each SOC model.

The waste stream composition, x_w , and the fresh feed and waste stream flow rates required to satisfy the external material balances are listed in the last three columns of Table 7. The slight variations in the external variables are unavoidable in the stagewise models since each stage is a discrete equilibrium step. The agreement is sufficient to insure each cascade performs essentially the same degree of overall separation.

The number of stripping section stages, N_s , remained constant for a given donor system as the number of squared sections changed. This is a result of adding square sections only to the enricher. Note that the total interstage flow would decrease and the ideal stage requirements would increase in the same manner indicated by Table 7 if one or more square sections had been incorporated into the stripping segment concomitantly with the enriching section. By adding square sections not only to the enriching segment, but also the stripping section, the SOC's would more closely approach the performance of the ideal cascade. The effect of adding squared off sections to the stripping portion in the SOC model is examined in detail in a subsequent section.

The recycle ratio is plotted as a function of stage number for the SOC's with 2, 3, 4 and 5 sections for each of the five different donors in Figures 17 through 21. Regardless of the particular donor, the shape of each curve is a "staircase" with the number of "steps" corresponding directly to the number of squared sections. Consequently, the five section SOC has five "steps" between the product and waste ends of the cascade, the four section model has four steps, etc. The staircase shape of the recycle ratio versus stage number curve is typical of the SOC where

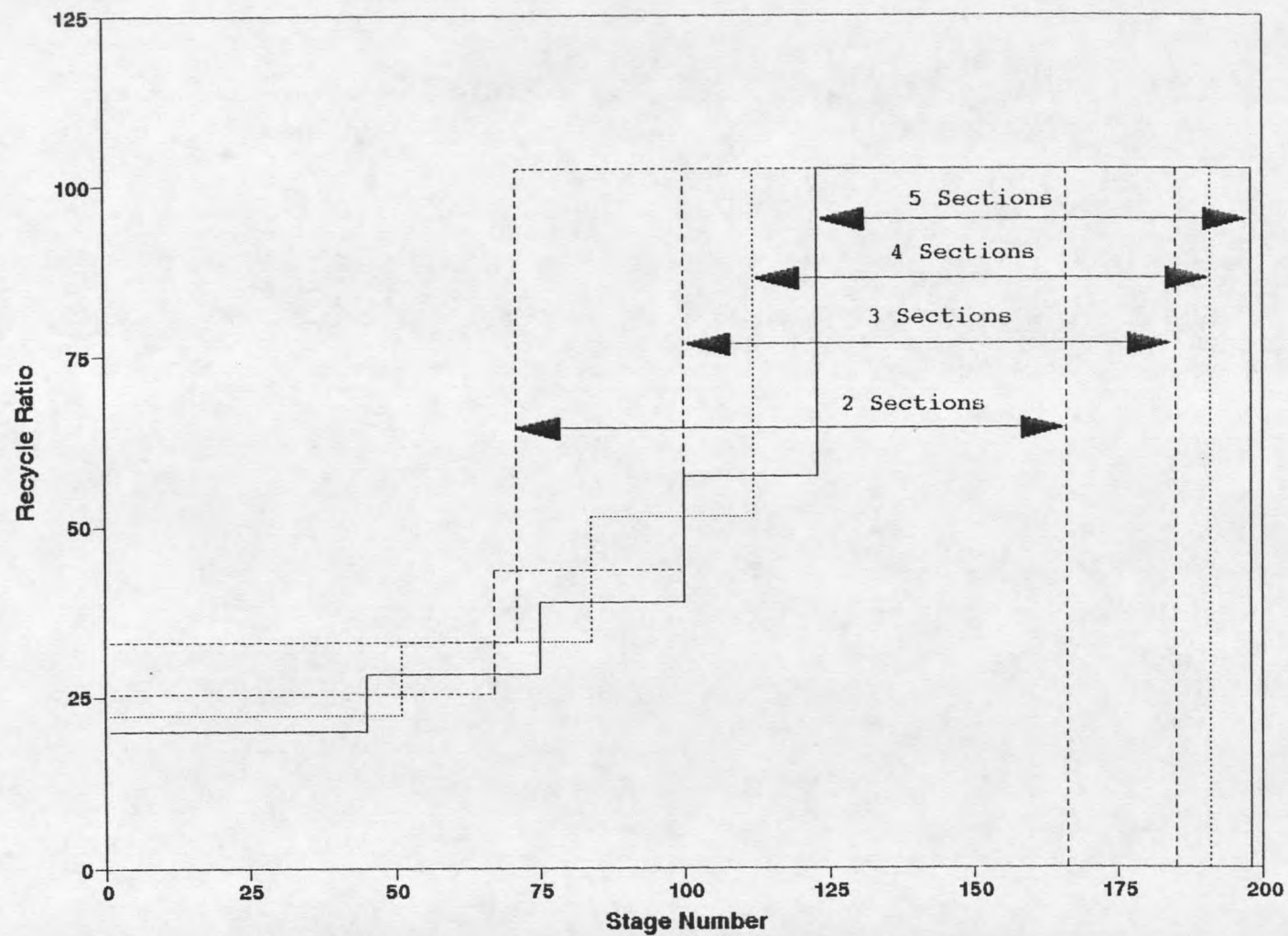


Figure 17. Recycle ratio versus stage number for the SOC with the nitromethane/ BF_3 donor system.

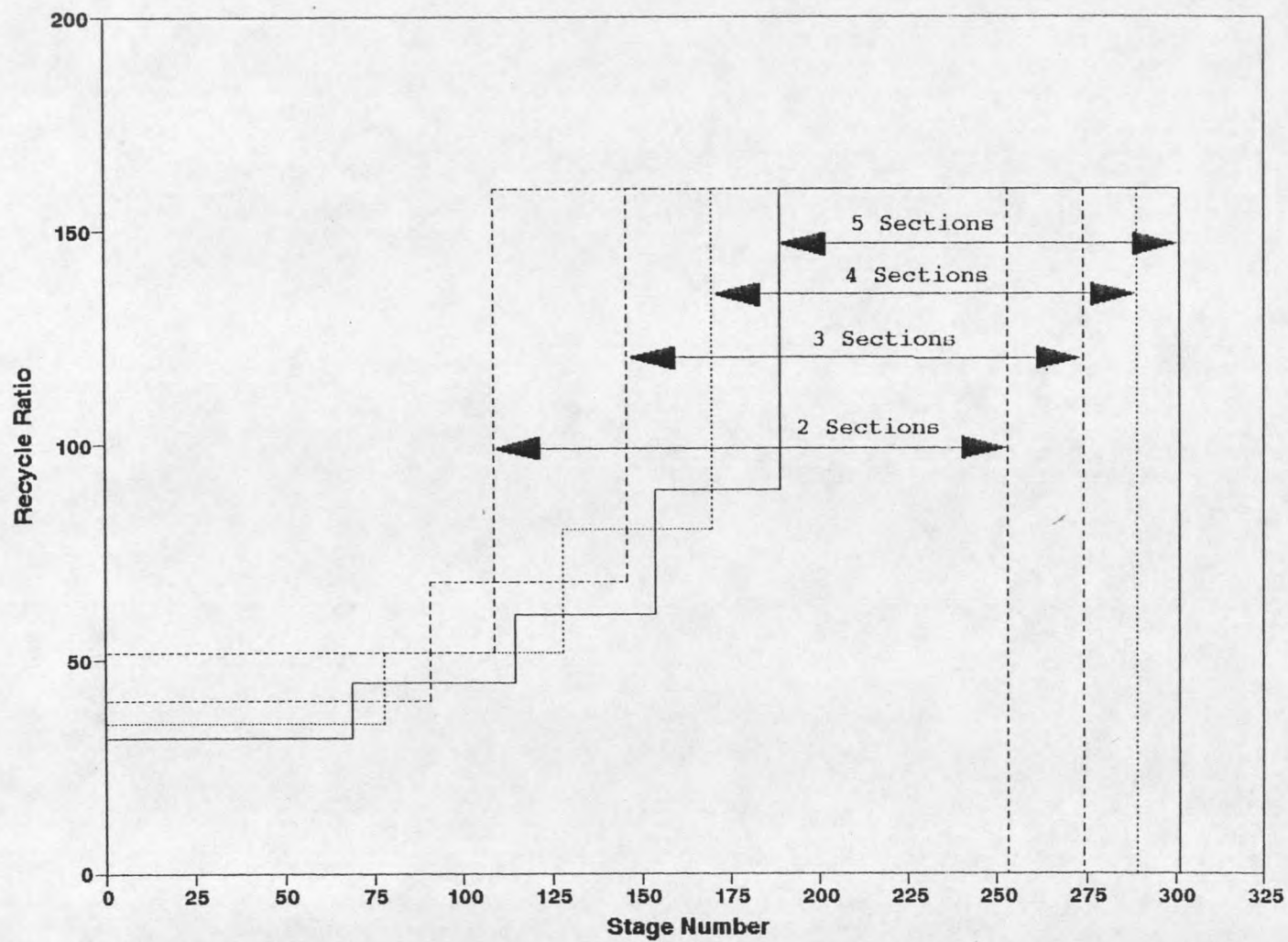


Figure 18. Recycle ratio versus stage number for the SOC with the DIBK/BF₃ donor system.

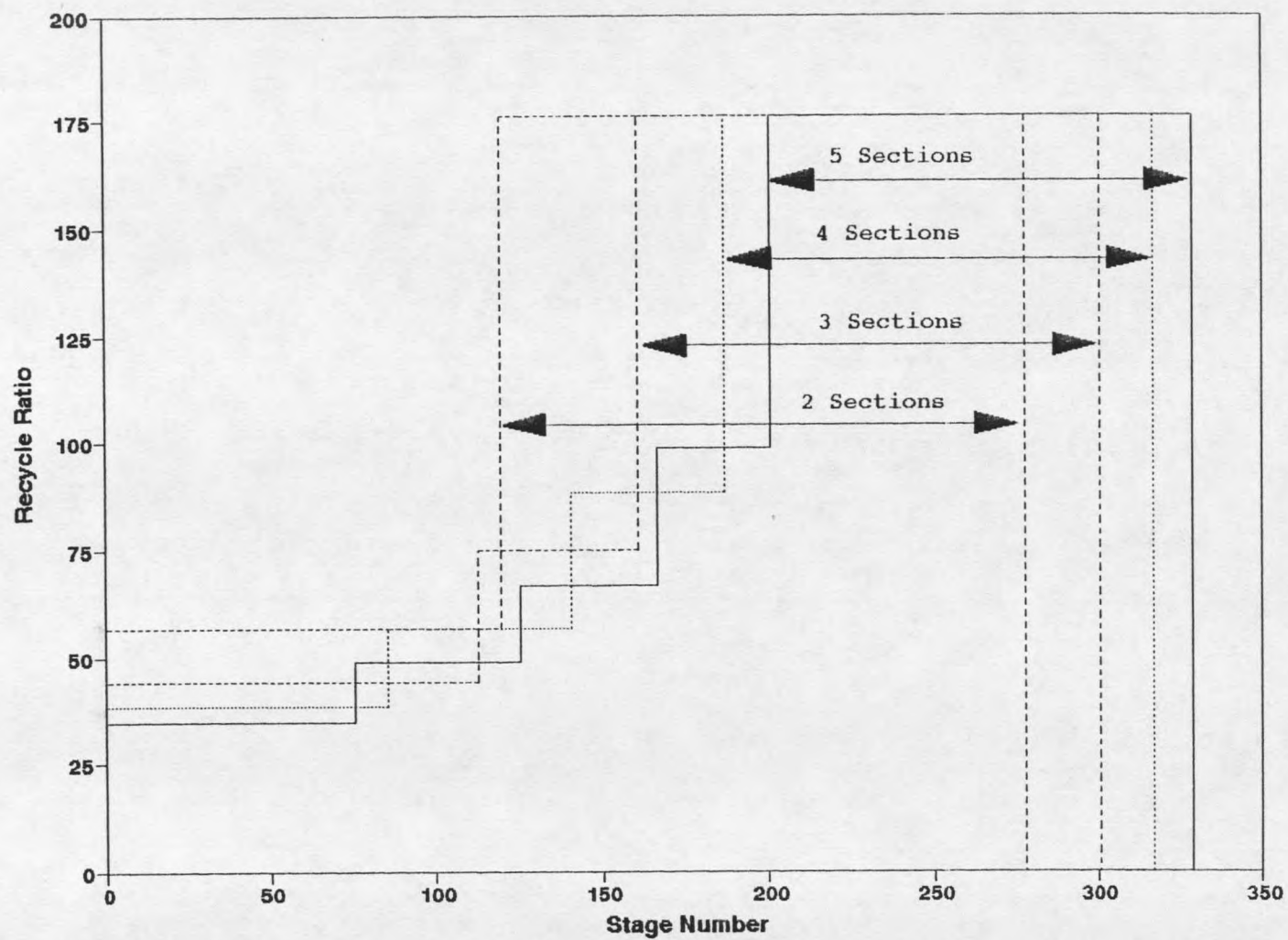


Figure 19. Recycle ratio versus stage number for the SOC with the MIBK/BF₃ donor system.

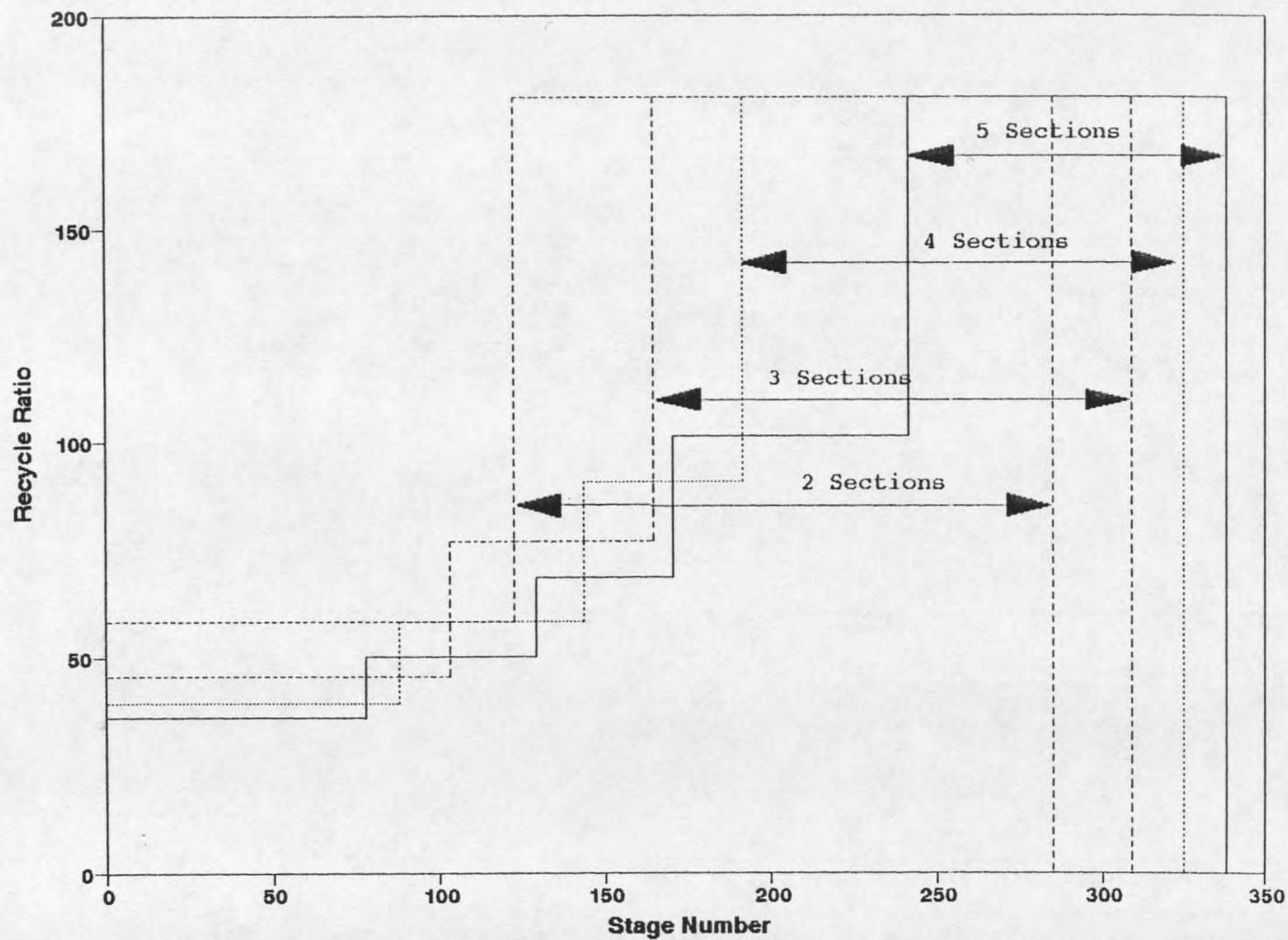


Figure 20. Recycle ratio versus stage number for the SOC with the acetone/BF₃ donor system.

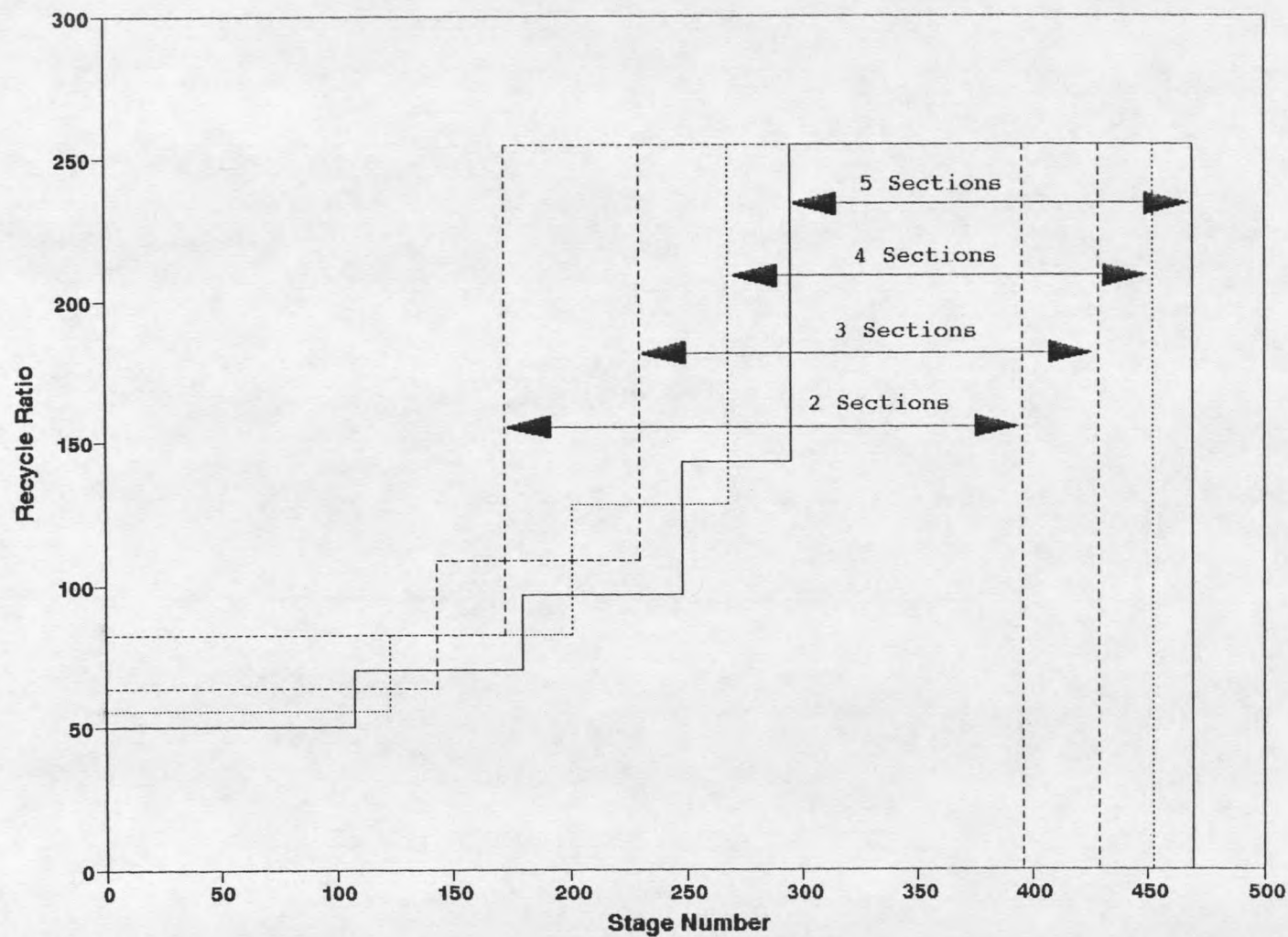


Figure 21. Recycle ratio versus stage number for the SOC with the dimethyl ether/ BF_3 donor system.

the horizontal regions correspond to the constant recycle over a number of stages, i.e. a square section. These figures provide a graphical representation of where the square sections are located, the recycle ratio used in each square section and the number of ideal stages per section for the SOC models with the donor systems.

Table 7 and the area under the curves in Figures 17 through 21 indicate that for a given donor, the total interstage flow decreased as the number of squared sections increased. As the number of sections increases, the amount of material processed by a particular enriching section stage decreases due to a reduction in recycle ratio. This results in reduced volume for each stage in the enriching section and a concomitant decrease in the total interstage flow requirements. The reduction of total interstage flow with an increased number of squared sections is a key property of the squared off cascade. An efficient system must compromise the opposing conditions of minimum stage requirements versus minimum interstage flow. The above results indicate the squared off cascade is adaptable and well suited to this purpose.

Comparison of Cascade Models

The total interstage flow rate and the number of ideal stages required for a particular cascade configuration are a measure of the size of the necessary process equipment. The results for the three different cascade configurations modelled are reiterated for convenience in Table 8. The total interstage flow rates are between those of the CRC and ideal cascades for each donor. The ideal stage requirements are a minimum for the constant recycle cascade.

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

Cascade Model	Ideal		Constant Recycle		Squared Off		
System	N_1	Total Interstage Flow (mols/hr)	N_1	Total Interstage Flow (mols/hr)	# of Sects.	N_1	Total Interstage Flow (mols/hr)
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	181	41,900	142	57,900	2	166	48,100
					3	185	47,200
					4	191	46,800
					5	198	46,700
DIBK $\alpha(30^\circ) = 1.043$	280	99,700	215	136,800	2	253	114,100
					3	274	111,000
					4	289	110,300
					5	301	110,000
MIBK $\alpha(30^\circ) = 1.039$	308	120,500	236	165,700	2	278	138,200
					3	301	134,200
					4	317	133,100
					5	329	132,900
Acetone $\alpha(30^\circ) = 1.038$	315	126,400	242	174,400	2	285	145,400
					3	309	141,500
					4	325	140,100
					5	338	140,200
Dimethyl Ether $\alpha(30^\circ) = 1.027$	443	248,800	337	342,000	2	396	283,900
					3	429	276,200
					4	452	273,900
					5	469	273,400

Consider the nitromethane/ BF_3 donor system. With two squared sections, the SOC requires only 24 or 17% more stages than the minimum requirement of 142 stages for the CRC model. On the other hand, the total interstage flow for the two section SOC is 48,100 mols/hr or about 15% greater than the minimum requirement of 41,900 mols/hr for the ideal cascade model. With three sections, 30% more stages are required than for the CRC model and 13% more interstage flow than the ideal case is required. The four section SOC requires 35% more stages and 12% more interstage flow than the respective minimums. Finally, with five square sections, 39% more stages and 11% more interstage flow is required. It is apparent that the greatest change in the ideal stage and total interstage flow requirements in the SOC, as compared to the constant recycle and ideal cascade minimums, respectively, occurs when two squared sections are used. Addition of the third, fourth, or fifth sections reduces the total interstage flow requirements only slightly while dramatically increasing the ideal stage requirements for the nitromethane system. For the design of a SOC operating at 10% to 15% more interstage flow than the ideal cascade, the use of two squared off sections is the logical choice.

A similar comparison for each of the other donor systems listed in Table 8 indicates analogous behavior. In each case, two square sections results in a 12% to 13% increase in the minimum total interstage flow as compared to the ideal cascade or a 16% to 17% decrease as compared to the CRC. The total number of stages is 17% to 18% greater than the minimum ideal stage requirements fixed by the constant recycle model.

It is instructive to compare the recycle ratio versus stage number curves for the ideal, CRC and SOC models for a given donor system. Figure

22 shows such a plot for the nitromethane/ BF_3 system with squared off cascades incorporating 3 & 4 square sections. Figure 23 presents this information for the dimethyl ether/ BF_3 system with the 2 and 5 square section SOC. These plots are representative of any of the donor systems with the different cascade configurations and a varying number of squared sections in the SOC model.

The x-axis, indicating stage number, is altered in Figures 22 and 23 from the convention adopted in previous figures representing recycle versus stage number curves. Previously, stages have been numbered consecutively from stage 1 at the product end of the cascade up through the waste stage. In Figures 22 and 23, the feed stage is counted as stage number zero; enriching section stages are numbered consecutively beginning at the feed point (stage n_F is counted as stage 0) up to the product stage. The stripping section stages are numbered consecutively with negative numbers beginning with the first stage in the stripping section (stage n_{F-1} is counted as stage number -1) to the waste end of the cascade. With this convention, the number of ideal stages required in either the enriching or stripping sections of the different cascade configurations are indicated relative to the feed stage in the recycle ratio versus stage number plots. Thus, the feed stage for each cascade coincides with the vertical line indicated in these figures; enriching section stages lie to the right of the vertical "feed stage" line, all stripping section stages are in the region to the left.

Figures 22 and 23 indicate an important aspect of the SOC models developed in this study. As previously discussed, the specification of recycle ratio at 1.45 times the minimum for each square section and the

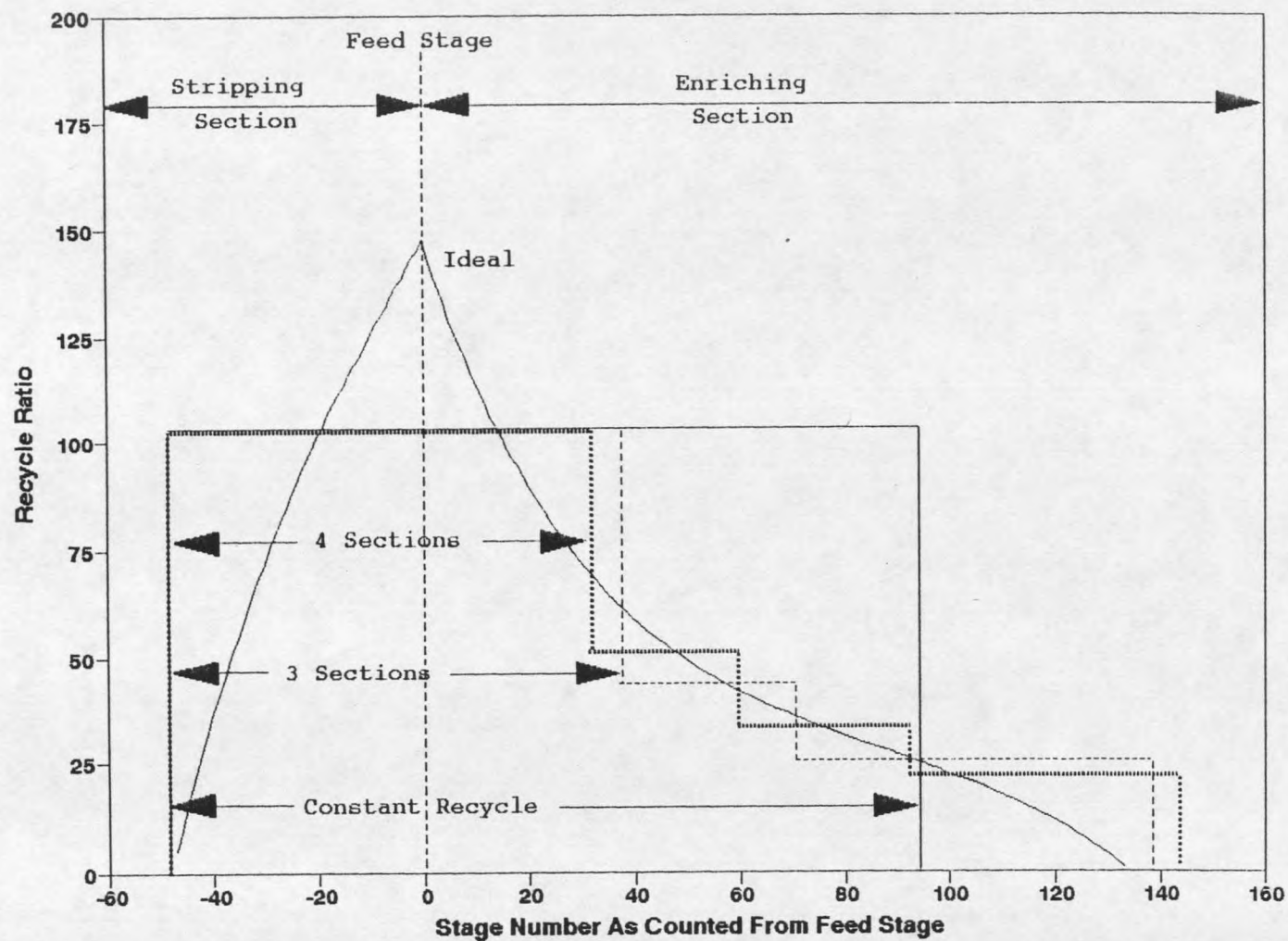


Figure 22. Comparison of recycle ratio versus stage number for the nitromethane/ BF_3 donor system with the ideal, CRC, and 3 & 4 section SOC models.

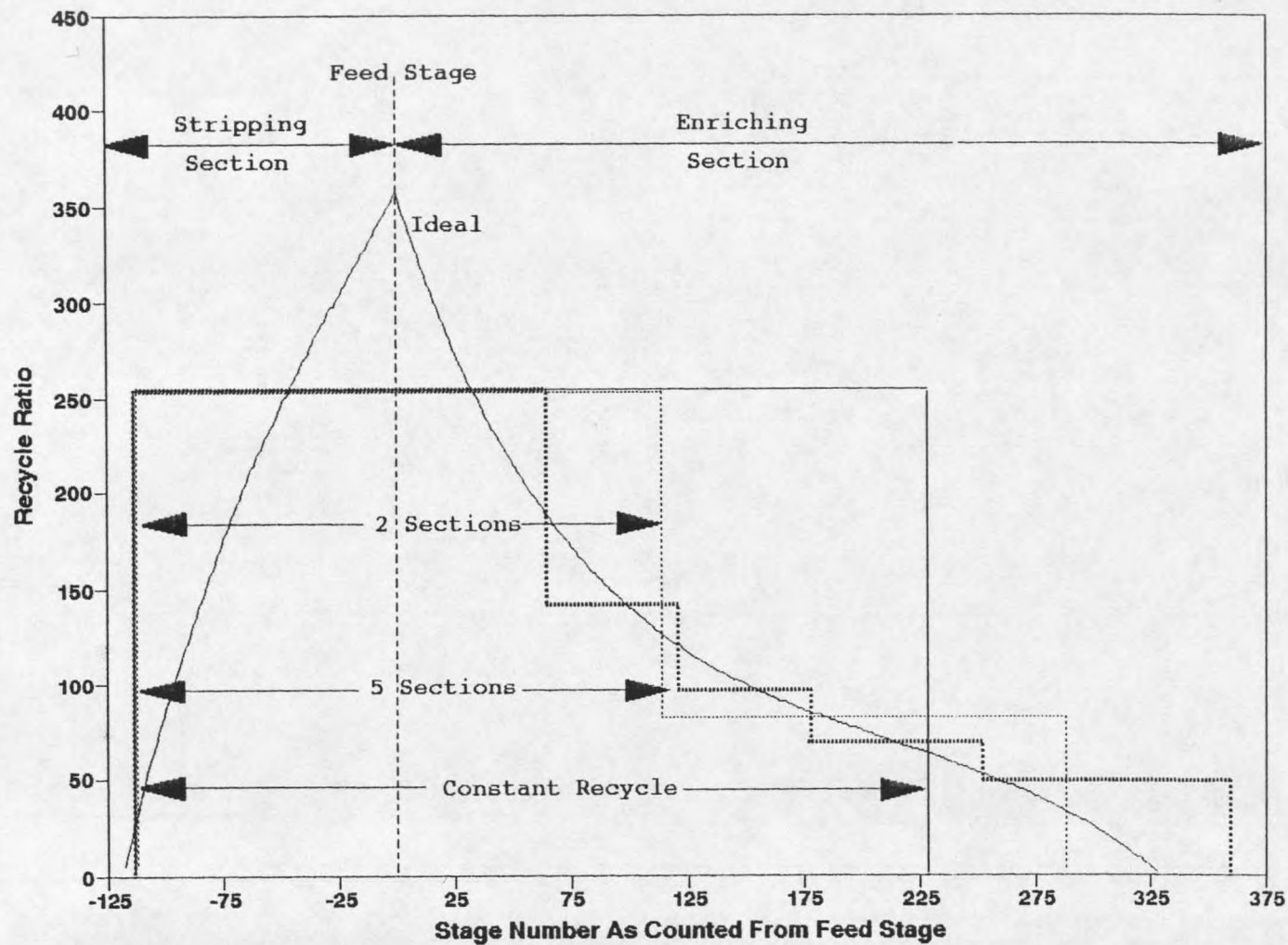


Figure 23. Comparison of recycle ratio versus stage number for the dimethyl ether/ BF_3 donor system with the ideal, CRC, and 2 & 5 section SOC models.

use of equal composition ranges across which each square section operates, results in SOC's which adequately approximate the taper of the ideal cascade. This is not to imply these models are the "best" approximation of ideal behavior; rather, that they are reasonable approximations of ideal behavior.

It is apparent from Figures 22 and 23 that the ideal stage requirements for the CRC are at a minimum while the area under the curve (total interstage flow) is at a maximum as compared with the other configurations. As the number of square sections used in the SOC model increases, the stage requirements increase and the total interstage flow (area) decreases. Finally, in the case of the ideal cascade, the total interstage flow is minimized. These graphical presentations visually indicate the effect of using an increased number of square sections to approximate ideal cascade behavior in accord with the ideas propagated in previous discussions.

The above comparison provides general guidelines for the design of fractionating columns based on the isotope exchange reaction associated with boron isotope separation. In general, for the specified recycle ratio of 1.45 times the minimum, two squared sections in the SOC arrangement will result in a cascade operating with 14% to 15% more total interstage flow than the corresponding ideal cascade. The same SOC requires 17% to 18% more ideal stages than the constant recycle cascade. This appears to be the most logical design based on the specified parameters since the addition of a third column would reduce the total interstage flow by only an additional 2% to 3%, while ideal stage requirements would increase by approximately 12% to 13%.

Effect of the Stripping Section

The discussion to this point has focussed on the impact adding square sections to the enriching segment has on SOC design. As was indicated, the function of the SOC is to approximate the shape of the ideal cascade without the complexity of having each stage a different size. It is intuitively obvious from Figures 22 and 23 that incorporating two (or more) squared off sections in the stripping segment would result in an SOC design more closely approximating the ideal "taper". On the other hand, the optimum tails composition, which could in fact differ from the specified value of $x_w = 0.05$, must ultimately come from detailed design work outside the scope of this study. For this reason, the waste composition, and therefore the requirements of the stripping section, are uncertain. In some instances it could be economically advantageous to completely eliminate the stripping section. In light of these uncertainties, the purpose of this section is twofold. First, it is of interest to examine the impact additional squared off sections in the stripping segment has on SOC design. Secondly, it is appropriate to consider the impact complete elimination of the stripping section would have on the design, and specifically the size, of a squared off cascade.

Addition of Square Sections to the Stripper

It was indicated in conjunction with Figures 22 and 23 that the shape and size of the ideal cascade would be more closely approximated if additional square sections were utilized in the stripping segment of the SOC. In the previous models, the stripping section was completely incorporated into a single, large square section which included the feed

stage and a portion of the enricher. Based on the results previously presented, adding several squared off sections to the stripper was expected to reduce total interstage flow and increase ideal stage requirements as more square sections were incorporated into the stripping section. If the purpose of the SOC is to approximate ideal behavior, these effects must, at least briefly, be examined.

The two section SOC model developed and discussed previously was taken as the base case or starting point for the squared off stripping section SOC calculations. The external variables, i.e. the external compositions and flow rates, were specified at their previous values.

The composition range over which each square enriching section operated was determined as per equation (67). A similar relationship was applied to the composition ranges for each square section in the stripper:

$$\text{Composition range} = \frac{z_F - x_W}{\# \text{ of sections}} = \frac{0.198 - 0.05}{\# \text{ of sects.}} = \frac{0.148}{\# \text{ of sects.}} \quad (69)$$

Equation (69) implies equivalent composition ranges over each square stripping section, just as equation (67) resulted in equivalent composition ranges in each (squared off) enriching section. Thus, by using two square sections in the stripping portion of the cascade, each section spanned the composition range of $0.148/2 = 0.074$. The first square section operated between the feed composition, $z_F = 0.198$, and a waste composition of $x_1 = 0.198 - 0.074 = 0.124$. This square section actually included the feed stage and a portion of the enriching segment. The second square section covered the remaining composition range between $x_1 = 0.124$ and the mole fraction of the waste stream, $x_W = 0.05$.

The recycle ratio in a square section of the stripper was specified by reasoning similar to the arguments which led to equation (68) for the enriching section. Thus, the recycle ratio was specified by a linear combination of $(R_1)_{\min}$ for a square stripping section, equation (47), and the recycle multiplication factor, A , whence:

$$(R_1)_{\text{stripping}} = A * \frac{W(x_1 - x_w)}{P(\alpha - 1)x_1(1 - x_1)} \quad (70)$$

The recycle multiplication factor in equation (70) was specified at the previously defined value of $A = 1.45$. The value of the tails stream, x_1 , is defined as that value numerically closest to the waste composition in a square section. Using the modifications introduced in accord with the above relationships, the calculational procedures were the same as those discussed in conjunction with the earlier SOC models.

The results from the SOC containing additional square sections in the stripper are presented in Table 9. The CRC and ideal cascade results previously tabulated and discussed are reiterated in Table 9 for comparison.

The nomenclature of Table 9, adopted for SOCs containing additional square sections in the stripper, is rather confusing and warrants further explanation. The two section SOC results are precisely the same as those presented earlier and are included in Table 9 for comparative purposes. Thus, the two square section SOC is equivalent to using a single square section in the stripping portion of the cascade. The three and four square section SOC results presented in Table 9 are not to be confused with those of the earlier models based on increasing the number of square sections in the enricher. The three section SOC includes the first square

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

System	# of Square Sections	N_1	N_2	N_3	Total Interstage Flow (mols/hr)	x_w	Feed Rate (mols/hr)	Waste Rate (mols/hr)
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	CRC(1)	142	94	48	57,900	0.0483	12.044	10.044
	2	166	119	47	48,100	0.0495	12.127	10.127
	3	174	119	55	47,900	0.0487	12.077	10.027
	4	179	119	60	47,800	0.0490	12.096	10.096
	$^t\text{IC}(181)$	181	134	47	41,900	0.0494	12.183	10.128
DIBK $\alpha(30^\circ) = 1.043$	CRC(1)	215	144	71	136,800	0.0429	12.113	10.114
	2	253	182	71	114,100	0.0490	12.093	10.093
	3	264	182	82	113,200	0.0487	12.075	10.075
	4	269	182	87	112,400	0.0497	12.096	10.141
	$^t\text{IC}(280)$	280	207	73	99,700	0.0494	12.132	10.132
MIBK $\alpha(30^\circ) = 1.039$	CRC(1)	236	159	77	165,700	0.0494	12.120	10.120
	2	278	200	78	138,200	0.0489	12.088	10.088
	3	289	200	89	136,500	0.0487	12.094	10.094
	4	296	200	96	136,200	0.0495	12.129	10.141
	$^t\text{IC}(308)$	308	228	80	120,500	0.0498	12.161	10.161
Acetone $\alpha(30^\circ) = 1.038$	CRC(1)	242	163	79	174,400	0.0496	12.119	10.119
	2	285	205	80	145,400	0.0489	12.087	10.087
	3	296	205	91	143,500	0.0492	12.105	10.105
	4	303	205	98	143,200	0.0496	12.136	10.136
	$^t\text{IC}(315)$	315	233	82	126,400	0.0499	12.156	10.156
Dimethyl Ether $\alpha(30^\circ) = 1.027$	CRC(1)	337	227	110	342,000	0.0494	12.119	10.119
	2	396	286	110	283,900	0.0494	12.121	10.121
	3	412	286	126	280,600	0.0493	12.112	10.112
	4	422	286	136	280,200	0.0494	12.123	10.123
	$^t\text{IC}(443)$	443	327	116	248,800	0.0494	12.128	10.128

$^t\text{IC}(n)$ = Ideal Cascade with n square sections where $n = N_1$, the number of ideal stages.

section covering a portion of the enricher; a second section which includes the remainder of the enricher, the feed stage, and a portion of the stripping section; and a final or third square section which includes the remainder of the stripper. The four section SOC is defined in the same manner as the three section SOC, but includes an additional or fourth square section as part of the stripper.

As expected from previous results and indicated in Table 9, the total number of ideal stages, N_t , and the total number of ideal stripping stages, N_s , increases as more square sections are added to the SOC. Note that the number of ideal enriching stages, N_e , remains constant for the two, three, and four section SOC models. This is a consequence of using identically squared enriching sections in each of the models and varying only the number of squared sections utilized in the stripper.

Table 9 indicates that the addition of a third or fourth section in the stripping portion of the cascade decreases the total interstage flow rate. Consequently, these SOC models more closely approximate the behavior of their ideal cascade counterparts. The greatest decrease in total interstage flow, as compared to the two section SOC, occurs when an additional square section is added to the stripping portion of the cascade. As a result, the three section SOC typically requires only 12% to 13% more total interstage flow than the ideal cascade. For the two section SOC, the total interstage flow is approximately 37% to 38% greater than for the ideal cascade, depending on the particular donor. At the same time, ideal stage requirements increase by approximately 3% to 4% for the three section SOC as compared with the two section SOC. The additional square stripping section in the four section SOC decreases

total interstage flow by less than 1% while increasing ideal stage requirements by nearly 4% as compared with the three section SOC.

A comparison of the results in Table 9 with those in Table 8 for SOCs where square sections were added to the enricher, indicates that virtually the same results could have been obtained by using three square sections in the enricher. Consequently, for the design basis of this study, the additional complication of using additional square sections in the stripping portion of the SOC is not easily justified. Furthermore, the specified waste composition of $x_w = 0.05$ may not be the best choice from an economic standpoint. Again, it is important to note that the selected design criteria (recycle ratios and composition ranges) may not be the optimum conditions for reducing equipment size.

It is instructive to compare the recycle ratio versus stage number curves for several different SOC configurations with the ideal cascade. Figure 24 is such a plot for the nitromethane/BF₃ system. Figure 25 presents the corresponding results for dimethyl ether/BF₃ system. These plots are typical for each of the different donors examined. Adopting the convention discussed earlier, the x-axis in these figures is scaled such that the feed stages for the different cascade configurations coincide with the vertical "feed stage" line. As with the previous SOC models, each vertical region of constant recycle, or "step" represents a square section in the cascade. In accord with the above discussion, these figures indicate the enriching section was unaltered in the different models. Furthermore, the difference between the two and three section SOCs with squared stripping sections and those without squared stripping sections (refer to Figures 22 and 23) can be visually emphasized.

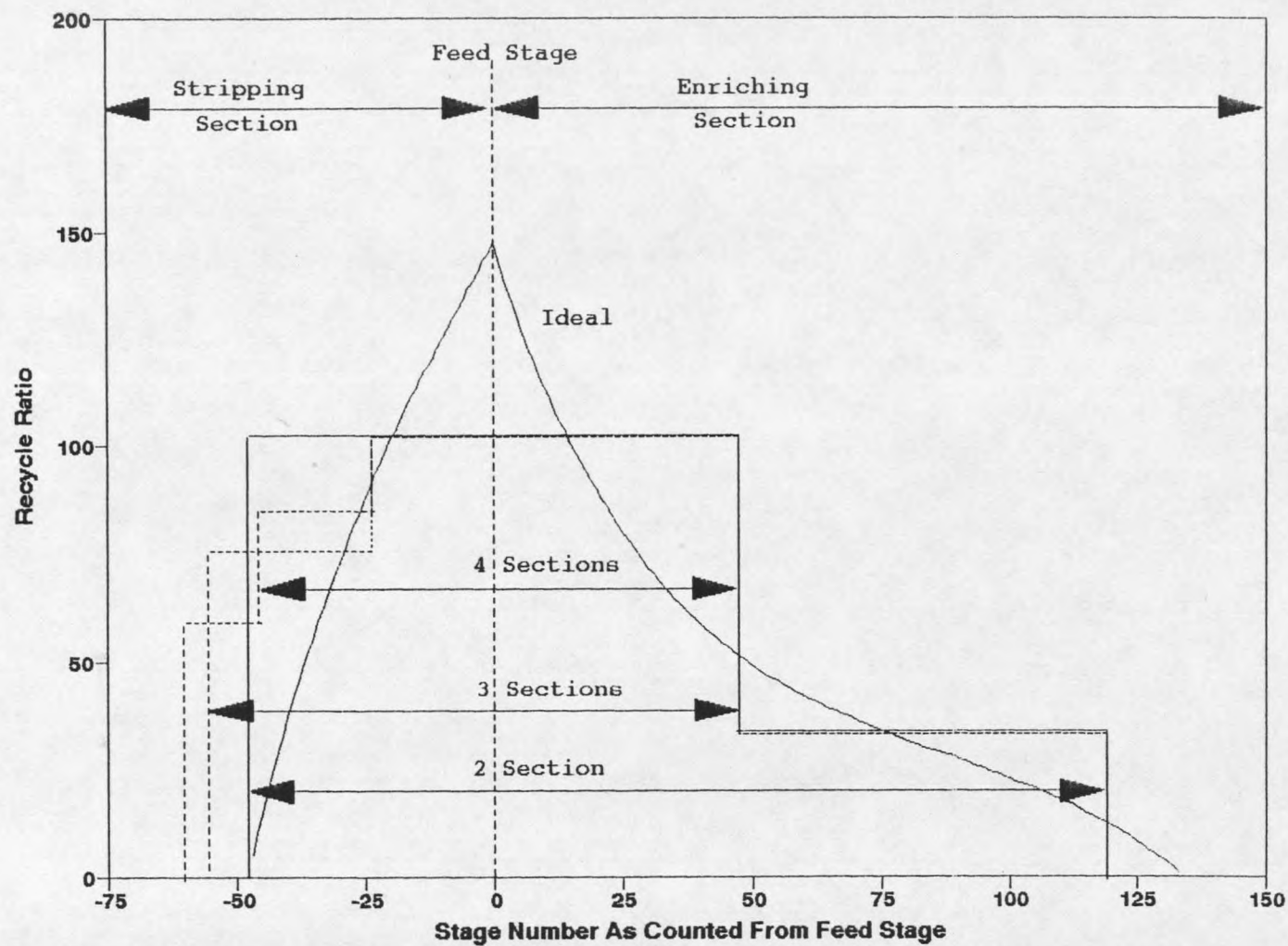


Figure 24. Effect of adding square sections to the stripping portion of the nitromethane/BF₃ SOC.

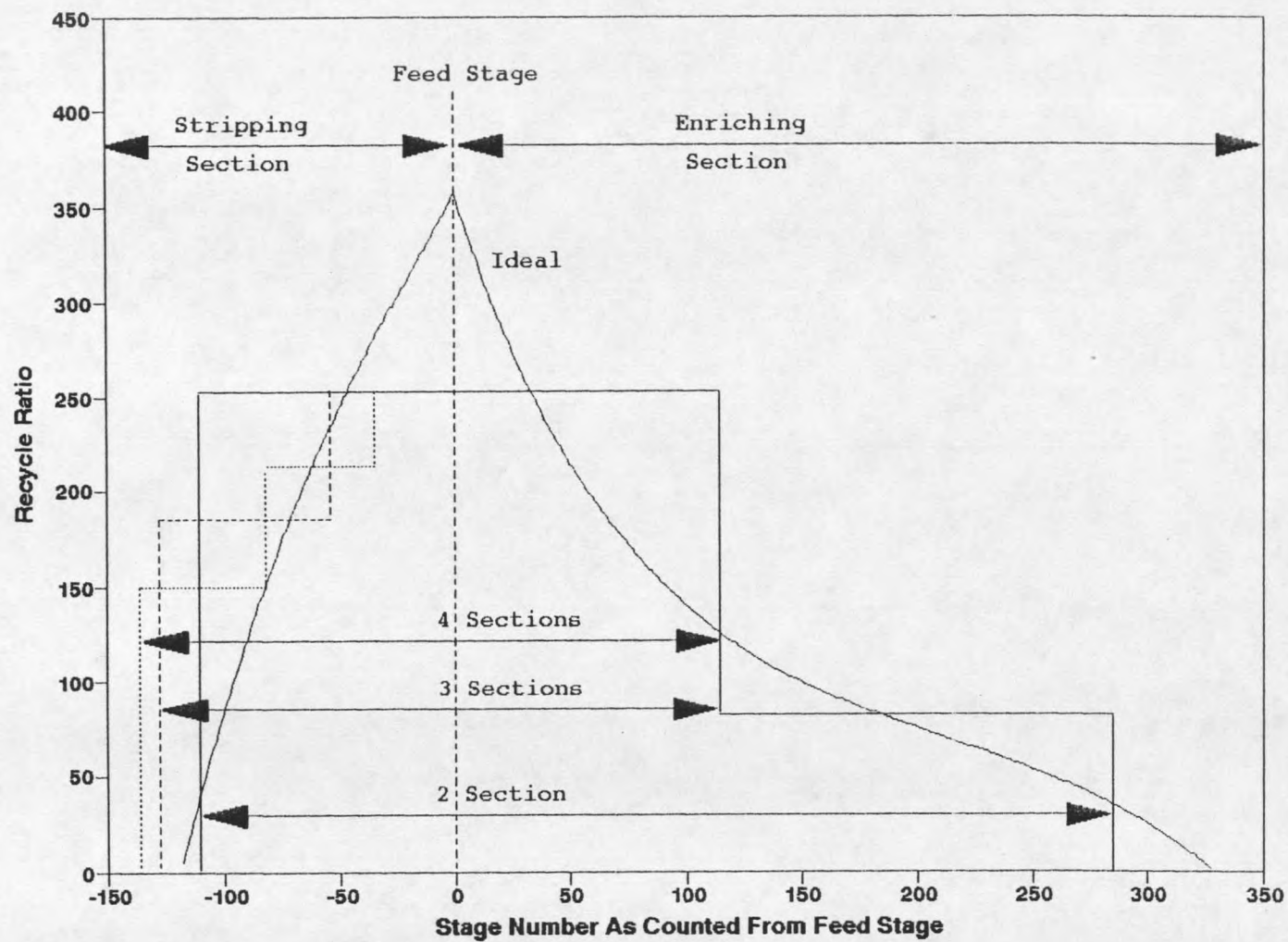


Figure 25. Effect of adding square sections to the stripping portion of the dimethyl ether/ BF_3 SOC.

Figures 24 and 25 indicate the SOC model more closely approximates the shape of the ideal cascade as the number of square sections used in the stripper of the cascade is increased. The area under the curve decreases as more square sections are incorporated, resulting in decreased total interstage flow through the SOC. However, the number of ideal stripping section stages is larger for both SOC designs than for the ideal cascade. This feature results from the method the recycle ratio was specified in the squared sections. If larger recycle ratios were used, i.e. larger values of A in equation (70), fewer ideal stages would be required both for a given squared off section, and for the entire SOC.

In conjunction with Figures 24 and 25, the results in Table 9 clearly indicate the effect using additional square sections in the stripper has on the SOC design. As with the previous results, the total interstage flow is reduced while the ideal stage requirements are increased as more square sections are added to the stripper in the SOC. For the comparative purposes of this study, i.e. in terms of equipment size, the same effect could be realized by adding more square sections to the enricher as opposed to the stripper. To be truly meaningful, the number and location of squared sections in a realistic SOC design would require a detailed economic evaluation and optimization procedure which is outside the scope of this study.

Elimination of the Stripping Section

It is of interest to examine the impact that complete elimination of the stripping section would have on the ideal stage and total interstage flow requirements (plant size) in the different cascade configurations.

Recall that the stripping section is not required to produce isotopically enriched material of the desired purity. However, stripping is necessary to reduce the amount of fresh feed required by the cascade and results in a concomitant decrease in the amount of waste, or isotopically depleted material, which is produced. Intuitively, the economic optimum is expected to be somewhere between stripping to a waste composition of 5% and no stripping at all.

The decision to incorporate or eliminate the stripping section in the actual design of an isotope separation facility must ultimately rely on a detailed economic evaluation of a particular system and is outside the scope of this study. Rather, the purpose here is to explore the reduction in plant size in terms of the total interstage flow and number of ideal stages in the absence of the stripping section in the different cascade configurations. The additional fresh feed requirements and waste production rates are also emphasized for cascades operated without a stripping section.

In the absence of the stripping section, the feed stage of the cascade is also the waste stage. Thus, the isotopically depleted gas stream exiting the feed stage (x_{nF} in Figure 9) is the gaseous waste stream of composition x_w . Consequently, the modelling procedures and enriching section equations for the different cascades discussed previously are applicable with the exception that once the feed stage is located, the waste composition is then known and the stripping section material balances are not required. Except for the waste composition, which was obviously specified as approximately the feed composition, the other external variables were specified at their previous values for each of the

different cascade models. Specifying the same feed and ^{10}B enriched product compositions with the same ^{10}B enriched product rate in each case, both with and without stripping, insured a valid comparison since each cascade would produce approximately the same final purity of enriched material ($y_F \approx 0.95$) for a given feed composition ($z_F = 0.198$). As before, only ideal stages were considered in the comparison.

The Ideal Cascade Without Stripping

The results from the ideal cascade models without stripping sections are listed in Table 10 for the different BF_3 /donor systems. As before, the results are based on values of α at a temperature of 30°C for each of the donor systems. In accord with previous results, the total ideal stage requirements and total interstage flow are observed to decrease for each donor as the separation factor is increased. A comparison of the product composition, y_F , and the waste composition, x_W , for each of the donor systems in the ideal cascade indicates that approximately the same degree of separation was obtained in each case.

A comparison of Table 5 and Table 10 for the ideal cascades with and without stripping sections, respectively, indicates that approximately 26% or over one quarter of the total ideal stage requirements are associated with the stripping section irregardless of the donor system. Furthermore, the stripping section consistently accounts for about 38% of the total interstage flow through the ideal cascade. It is apparent from this comparison that elimination of the stripping section results in an ideal cascade requiring substantially fewer ideal stages with a concomitant decrease in total interstage flow. Consequently, the total size of the separation plant can be greatly reduced if a stripping section is not

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

System	N_t	Total Interstage Flow (mols/hr)	y_F	x_H	Feed Flow Rate (mols/hr)	Waste Flow Rate (mols/hr)
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	134	26,100	0.950	0.193	297	295
DIBK $\alpha(30^\circ) = 1.043$	207	61,700	0.951	0.195	455	453
MIBK $\alpha(30^\circ) = 1.039$	228	74,800	0.951	0.195	501	499
Acetone $\alpha(30^\circ) = 1.038$	233	78,400	0.950	0.195	513	511
Dimethyl Ether $\alpha(30^\circ) = 1.027$	327	153,700	0.951	0.196	716	714

incorporated. An important consideration in the design of an actual separation system would include the equipment cost associated with providing a stripping section.

Comparison of Table 5 with Table 10 for the ideal cascades with and without stripping sections, respectively, indicates that the feed and waste flow rates are approximately 25 to 60 times greater, depending on the donor, for the ideal cascade without stripping. This is a result of eliminating that portion of the cascade above the feed point (the stripping section) which recovers or strips the desired isotope from the waste stream. Consequently, a dramatic increase in fresh feed is required to supply the necessary amount of the desired isotope to meet product purity and flow specifications in accord with previous discussions. An important consideration in eliminating the stripping section would be the increased operating costs associated with supplying much larger quantities of fresh BF_3 feed and disposing of larger amounts of slightly isotopically depleted BF_3 gas from the waste end of the plant. This of course, assumes that the waste stream has no value, or the same value as the feed.

The CRC Without Stripping

The modelling results from the constant recycle cascade without a stripping section are shown in Table 11. As previously described, the recycle ratio used in these models was 1.45 times the minimum required at the feed point. As expected, the ideal stage requirements and total interstage flow rates decrease upon substitution of donors with successively larger separation factors. The waste stream compositions of $x_w = 0.194$ to $x_w = 0.196$ are close enough to insure that each CRC is performing approximately the same amount of isotopic fractionation.

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

System	Recycle Ratio	N_t	Total Interstage Flow (mols/hr)	x_w	Feed Flow Rate (mols/hr)	Waste Flow Rate (mols/hr)
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	102	94	38,100	0.194	369	367
DIBK $\alpha(30^\circ) = 1.043$	160	144	91,300	0.195	538	536
MIBK $\alpha(30^\circ) = 1.039$	176	159	111,200	0.194	397	395
Acetone $\alpha(30^\circ) = 1.038$	181	163	117,000	0.194	415	413
Dimethyl Ether $\alpha(30^\circ) = 1.027$	254	227	231,300	0.196	661	659

Comparison of Table 6 for the CRC with stripping and Table 11 for the CRC without stripping indicates that approximately 33% to 34% of the ideal stage requirements are a result of the stripping section. This figure appears to be independent of the donor. Furthermore, about 33% of the total interstage flow through the CRC occurs in the stripping section. As with the ideal case, the feed and waste flow rates vary from donor to donor and are roughly 30 to 55 times greater than for the constant recycle cascade that includes a stripping section. Again, comparison of the CRC's with and without stripping indicates that the size of the fractionation plant is greatly reduced if the stripping section is eliminated, but more fresh feed is required and a greater volume of waste is produced.

The SOC Without Stripping

The modelling results for the squared off cascade with 2, 3, 4, and 5 square sections without stripping sections are tabulated in Table 12 for the different BF_3 /donor systems. The recycle ratio in each section of the different square cascades was 1.45 times the minimum required for that section as was discussed in conjunction with the earlier SOC models. As with all previous cases, the ideal stage requirements and total interstage flow through the square cascades with a given number of square sections increases as the separation factor decreases for the different donor systems. Thus, for the two square section SOC, nitromethane requires fewer ideal stages and less total interstage flow than for any of the other donor systems utilizing two square sections.

As with the earlier SOC models, the ideal stage requirements are observed to increase as the number of square sections increased. Likewise, the total interstage flow decreases as more sections are

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

System	# of Square Sections	N_t	Total Interstage Flow (mols/hr)	x_p	Feed Rate (mols/hr)	Waste Rate (mols/hr)
Nitromethane $\alpha(30^\circ\text{C}) = 1.067$	CRC(1)	94	38,100	0.194	369	367
	2	119	29,300	0.193	336	334
	3	134	28,300	0.191	230	228
	4	144	28,000	0.192	248	238
	5	151	27,900	0.192	272	270
	$\dagger\text{IC}(134)$	134	26,100	0.193	297	295
DIBK $\alpha(30^\circ) = 1.043$	CRC(1)	144	91,300	0.195	540	538
	2	182	69,500	0.195	445	443
	3	203	66,300	0.195	460	458
	4	218	65,700	0.194	424	422
	5	230	65,900	0.194	350	348
	$\dagger\text{IC}(207)$	207	61,700	0.195	455	453
MIBK $\alpha(30^\circ) = 1.039$	CRC(1)	159	111,200	0.194	397	395
	2	200	84,100	0.195	503	501
	3	223	80,100	0.196	604	602
	4	239	79,000	0.196	699	697
	5	252	79,500	0.194	422	420
	$\dagger\text{IC}(228)$	228	74,800	0.195	501	499
Acetone $\alpha(30^\circ) = 1.038$	CRC(1)	163	117,000	0.194	415	413
	2	205	88,400	0.195	527	525
	3	229	84,500	0.195	507	505
	4	246	83,800	0.194	400	398
	5	258	83,200	0.196	655	653
	$\dagger\text{IC}(223)$	223	78,400	0.195	513	511
Dimethyl Ether $\alpha(30^\circ) = 1.027$	CRC(1)	227	231,300	0.196	661	659
	2	286	173,200	0.196	672	670
	3	319	165,500	0.195	585	583
	4	342	163,100	0.196	696	694
	5	359	162,700	0.196	803	801
	$\dagger\text{IC}(327)$	327	153,700	0.196	716	714

$\dagger\text{IC}(n) \equiv$ Ideal Cascade with n square sections where $n = N_t$, the number of ideal stages.

utilized in the cascade. These observations are expected based on the earlier results and discussion of the previous models incorporating stripping sections.

Comparing the results of the SOC models with stripping sections listed in Table 7 to those without stripping sections in Table 12 indicates the relative effect the stripping section has on the squared off cascade. With the nitromethane system and the two section SOC, the stripping section requires approximately 28% more ideal stages than the same cascade without stripping. For the same donor but with three square sections, about 26% more ideal stages are required with the use of a stripping section. The four square section cascade with stripping requires about 25% more stages and the five section cascade requires approximately 24% more ideal stages than if stripping were eliminated. This trend is consistent when donors other than nitromethane are compared between the different SOC models. For the donors considered, it is apparent that the stripping section accounts for just under 30% of the total ideal stage requirements.

The same type of comparison with total flow requirements indicates that roughly 40% of the total interstage flow occurs in the stripping section of the square cascade. Consequently, the elimination of the stripping section in the SOC reduces the total interstage flow through the cascade by approximately 40% while ideal stage requirements are reduced by nearly 30%. It is obvious that the stripping section can contribute substantially to the overall cost of a separation facility.

While the size of the SOC is greatly reduced by eliminating the stripping section, Table 12 indicates that the fresh feed and waste flow

rates are dramatically increased. Depending upon the donor, the SOC without stripping requires anywhere from about 20 to 70 times more fresh feed and produces that much more waste material than the same SOC which incorporates a stripping section. Again, it is intuitively obvious that the economic optimum would occur somewhere between stripping to a waste composition of 5% and no stripping at all. For example, in the case of the nitromethane/BF₃ two section SOC, it makes little sense to feed 336 moles/hr of feed with a composition of $x_F = 0.198$ and produce 334 moles/hr of waste with a composition of $x_W = 0.193$.

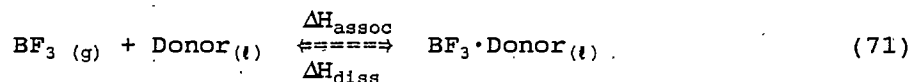
The cost associated with purchasing the additional BF₃ feed and disposing of the increased amount of waste must be balanced by the additional equipment and operation costs associated with providing and supporting a stripping section. It is of course possible to specify the waste composition, x_W , at any value less than the feed composition, x_F . In this manner, the size of the stripping section can be adjusted to any number of ideal stages and total interstage flow. For the purposes of this study only two possibilities were considered: no stripping and stripping to a waste composition of $x_W = 0.05$. Finally, once an optimum x_W is determined, squaring off the stripping section may become an alternative. In the final analysis, a detailed economic study is required to determine the optimum between the expenses associated with incorporating and operating a stripping section and the opposing costs of providing increased amounts of fresh feed and the production of increased amounts of isotopically depleted waste. Such an analysis is outside the scope of this project, but is necessary in the design of practical full scale isotope separation facilities.

Energy Requirements

It is appropriate at this point to inquire about the energy input necessary to perform the desired separation of boron isotopes in the chemical exchange cascades under discussion. All separation processes require an input of energy in order to perform the desired fractionation, and the boron isotope separation systems are no exception. Energy is utilized in the system to maintain the required flow rates of process streams through the entire cascade, to overcome frictional losses in the column and associated piping, and to balance enthalpy changes associated with mixing, chemical reactions, etc. Finally, the overall effect of the isotope exchange system is to *unmix the isotopic components in the feed stream to form relatively pure isotopic product streams, hence the entropy of the feed stream must decrease*. Since the separation or unmixing process is not spontaneous and the work expended within a cascade to effect a prescribed separation typically increases with the difficulty of separation, isotopic separations are inherently energy intensive processes. The energy requirements for providing and maintaining the necessary reflux through a cascade is readily performed by an analysis developed in accord with the first law of thermodynamics. Similarly, the energy requirements associated with the stagewise separation process are amenable to analysis in accord with the second law. In the absence of all effects which reduce system efficiency, e.g., for a thermodynamically reversible or "ideal" system, the energy necessary to support the separation is the sum of these two contributions. It is from this standpoint that energy requirements for the three different cascade configurations were developed in this portion of the study.

Energy Requirements for Providing
Recycle in the Cascade

Reflux in the cascades under consideration is supplied by the formation reaction previously discussed:



The formation reaction is assumed completely reversible simply by the addition or removal of heat. The energy removed from the system for equation (71) to proceed in the forward direction as written is given by the molar enthalpy of association, ΔH_{assoc} . The energy required to decompose the complex into BF_3 gas and the liquid donor, the reverse of reaction (71), is the molar enthalpy of dissociation, ΔH_{diss} . Complete reversibility of equation (71) is implied by assuming:

$$\Delta H_{\text{rxn}} = \Delta H_{\text{diss}} = -\Delta H_{\text{assoc}} \quad (72)$$

For the systems studied experimentally, ΔH_{rxn} is unknown (reaction enthalpy data does not exist) but is constant for a particular BF_3 /donor system. For the dimethyl ether/ BF_3 system, the association enthalpy is reported [6] to be $\Delta H_{\text{assoc}} = -13.8$ kcal/mol, indicating that the formation reaction is indeed exothermic.

In the enriching section, recycle in the cascade is provided by dissociation of the complex in one or more decomposers. The energy input, δQ_{decomp} , to a single decomposer is simply:

$$\delta Q_{\text{decomp.}} = D * \Delta H_{\text{diss}} \quad (73)$$

where D is the molar flow rate of material being decomposed and has the same units as the process streams in the cascade or moles/hour. The total

energy input in the enriching section, ΔQ_{enrich} , is the sum of the energy required by the individual decomposers:

$$\Delta Q_{\text{enrich}} = \Sigma(\delta Q_{\text{decomp}}) \quad (74)$$

Similarly, for the stripping section, where recycle is provided by formation of the liquid complex in recombiners:

$$\delta Q_{\text{recomb}} = C * \Delta H_{\text{assoc}} \quad (75)$$

$$\Delta Q_{\text{strip}} = \Sigma(\delta Q_{\text{recomb}}) \quad (76)$$

Thus, the energy input requirements for providing recycle in the different sections of the cascade are directly proportional to the total amounts of material that must be decomposed or recombined in the appropriate process equipment.

In conjunction with the appropriate cascade models, it can be shown mathematically that the total amount of material, ΔD , which must be decomposed in the enriching section of any counter current recycle cascade based on chemical exchange (refer to Figure 9) is given by:

$$\Delta D = \Sigma(D) = (R_{\text{NF}} + 1) * P \quad (77)$$

where R_{NF} is the recycle ratio at the feed stage in the cascade and P is the product flow rate. Furthermore, the total amount of material which must be decomposed in the stripping section of any counter current recycle cascade based on chemical exchange is:

$$\Delta C = \Sigma(C) = (R_{\text{NF}}) * P - W \quad (78)$$

where W is the waste stream flow rate in mols/hr.

Combining equations (77), (73) and (74), the total energy input to all decomposers in the enriching section is given by:

$$\Delta Q_{\text{enrich}} = \Delta H_{\text{diss}} * (R_{\text{NF}} + 1)P \quad (79)$$

Similarly, in the stripping section, the total energy requirements are given by:

$$\Delta Q_{\text{strip}} = \Delta H_{\text{assoc}} * (R_{\text{NF}} * P - W) \quad (80)$$

Equations (79) and (80) are valid measures of the total energy required to provide recycle, independent of the number of decomposers or recombiners incorporated into the enriching or stripping sections of a countercurrent recycle cascade. Furthermore, the recycle ratio can be altered between any two consecutive stages, but a minimum of one decomposer and one recombiner is required at the waste and product ends of the cascade.

The total work expended by the cascade to produce and maintain the necessary reflux are fixed once the recycle ratio at the feed stage, R_{NF} , and the waste and product compositions are specified. As a consequence of this rather extraordinary result, *the energy requirements for providing reflux in any countercurrent chemical exchange isotope separation recycle cascade are fixed and remain constant once the recycle ratio at the feed point is specified, regardless of the number of points where the recycle ratio is altered.* Expressed alternatively: the amount of material decomposed and recombined to provide the specified reflux at the feed point is constant, whether produced entirely at the ends of the cascade, or at numerous points between the feed stage and the two ends.

The above analysis leads to an interesting conclusion. The energy supplied to the CRC and different SOC configurations is the same for the specified recycle ratio of $1.45 * (R_1)_{\text{min}}$ at the feed point for a particular BF_3 /donor system. Recall however, that the recycle ratio at each stage in the ideal cascade is fixed by the no-mix criteria. Mathematically it has

been shown [4] that the recycle ratio at the feed point in an ideal cascade is approximately twice the minimum, or $2*(R_1)_{\min}$. As a consequence, the energy associated with providing recycle in the ideal cascade cannot be altered, but rather is fixed by the no-mix criteria. Therefore, by specifying smaller recycle ratios than $2*(R_1)_{\min}$ at the feed point for the CRC and SOCs, *these cascades are more economical than the ideal cascade in terms of the energy required by the decomposers and recombiners to provide recycle.* This result is contrary to the fundamental concept that the ideal cascade is the most efficient design for performing a given separation. In this regard, it is apparent that the above analysis does not account for everything that is occurring within the cascade and further consideration must be given to energy requirements of the various cascade configurations.

For the models developed in this study, the size and holdup of the process equipment was substantially reduced by successively increasing the number of points where the recycle ratio was altered in the cascade. While this "tapering" action reduced overall equipment size, the energy requirements associated with providing recycle where unaltered provided the specified recycle ratio at the feed point remains constant. As a result, the energy requirements for each of the different models with a particular BF_3 /donor system and constant recycle ratio at the feed stage were essentially constant. This result is consistent with literature discussions of the energy requirements for hydrogen and nitrogen isotope separation [43,44] based on chemical exchange recycle cascades.

Energy Requirements for Stagewise
Separation of Components

While the foregoing analysis examined the energy requirements associated with providing recycle in the decomposers and recombiners, it also indicated that a CRC or SOC could be operated more economically than the corresponding ideal cascade. This result is a contradiction of the basic premise behind the ideal cascade and does not completely account for the separation process that is occurring within the system. Therefore, it is of interest to examine the stagewise separation process that is occurring as a result of "unmixing", or separating, the isotopic mixture.

Consider a typical separation stage in a countercurrent recycle cascade, such as stage i shown in Figure 26. For the SOC or CRC, streams of different compositions from the stages immediately above and below are mixed to form the feed for stage i . This process is associated with the mixing point indicated in Figure 26. For the ideal cascade, the composition of the streams entering and exiting the mixing point are equivalent due to the no-mix criteria. It is precisely the opposite of this process which is occurring within the stage. Consequently, for the SOC and CRC, the stage must overcome the effect of re-mixing streams of different compositions at the mixing point and provide a fraction of the desired overall separation. In the ideal cascade however, the inefficiency associated with the mixing point is removed and the energy required for the unmixing or separation process will be a minimum. This condition of minimum energy input is a primary basis upon which the ideal cascade concept is based.

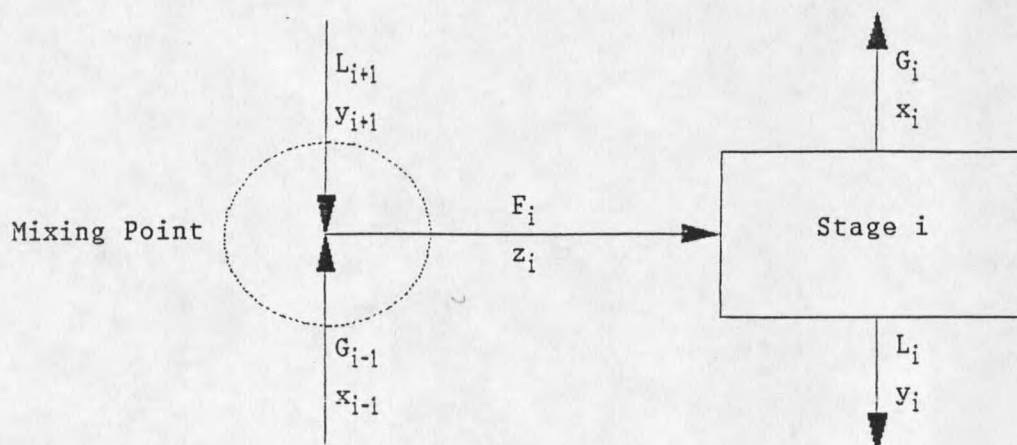


Figure 26. Typical stage from a countercurrent recycle cascade.

It is advantageous to consider the mixing point and stage as shown in Figure 26 independently for an energy analysis of the stagewise separation process. The logical starting point for such an evaluation is the Gibbs Function for the mixing process:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} \quad (81)$$

The subscripts in the above equation indicate the respective thermodynamic quantities are considered only for mixing of streams with different isotopic compositions. The enthalpy of mixing, ΔH_{mix} , is unknown for the BF_3 /donor systems under consideration. However, isotopic species are often considered to form the proverbial "ideal" gas or liquid mixtures, e.g., the enthalpy of mixing for gaseous $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$ is approximately zero. Therefore, ΔH_{mix} is anticipated to be relatively small and is assumed to be identically zero for the systems being studied.

The entropy of mixing in equation (81) can be expressed as:

$$\Delta S_{\text{mix}} = -R \sum_i [(x_i \ln x_i)_{\text{feed}} - (x_i \ln x_i)_{\text{products}}] \quad (82)$$

The mole fractions are those entering or leaving in the feed and product streams for either the mixing point or stage. Using the nomenclature of Figure 26, expanding equation (82), and combining with equation (81) provides the key relation for energy requirements *about the mixing point*:

$$\begin{aligned} \Delta G_{\text{mix pt}} = RT\{ & G_{i-1}[x_{i-1} \ln x_{i-1} + (1-x_{i-1}) \ln (1-x_{i-1})] \\ & + L_{i+1}[y_{i+1} \ln y_{i+1} + (1-y_{i+1}) \ln (1-y_{i+1})] \\ & - F_i[z_i \ln z_i + (1-z_i) \ln (1-z_i)] \} \end{aligned} \quad (83)$$

The respective flow rates (L, G, and Z) are incorporated in equation (83) to convert ΔG from a molar basis to that of energy consumption, or kJ/hr. With the understanding that the above relation was derived only for mixing of ideal gases or liquids, the "mix" subscript has also been dropped. In a similar fashion, the energy requirements for the separation process *occurring within the stage* can be derived:

$$\begin{aligned} \Delta G_{\text{stage}} = RT\{ & F_i[z_i \ln z_i + (1-z_i) \ln (1-z_i)] - L_i[y_i \ln y_i + (1-y_i) \ln (1-y_i)] \\ & - G_i[x_i \ln x_i + (1-x_i) \ln (1-x_i)] \} \end{aligned} \quad (84)$$

Note that the above equations derived for both the mixing point and stage are valid only for a general stage as shown in Figure 26. These equations are not valid for the feed stage nor for the waste or product stages, and must be appropriately altered when applied at these points in the cascade. Furthermore, for the ideal cascade, mole fractions of the feed streams entering at the mixing point, x_{i-1} and y_{i+1} , are equal to the composition exiting the mixing point, z_i . Consequently, equation (83) is identically zero at every stage in the ideal cascade.

Equations (83) and (84) were derived and used to evaluate the work expended in the isotope separation process at a given stage in the cascade based on the second law of thermodynamics. In conjunction with the cascade models, the total work required by a cascade to perform the prescribed separation was determined by summing the individual energy terms about the mixing points or individual stages across the entire cascade:

$$E_{\text{mix}} = \sum_i \Delta G_{\text{mix pt}, i} \quad (85)$$

$$E_{\text{stage}} = \sum_i \Delta G_{\text{stage}, i} \quad (86)$$

It is important to understand the significance of each work term as established by equations (85) and (86). The total work of mixing, E_{mix} , as given by equation (85) can be interpreted as *lost work* due to the generation of entropy associated with the mixing process. Consequently, the numerical value of E_{mix} is *negative*, which implies ΔS_{mix} is *positive* about the individual mixing points. This concurs with the accepted sign convention that a (spontaneous) mixing process results in an increase in entropy. In the same manner, the sum of the work terms associated with the separation process within the individual stages, E_{stage} , is a measure of the actual *separative work* performed in the cascade and is therefore positive. Consequently, ΔS_{mix} as given by equation (82) is *negative* for the individual stages in accord with the concept that separation or unmixing *decreases* the entropy of the isotopic mixture. It is therefore possible to define and evaluate the *ideal or thermodynamic minimum work*, E_{ideal} , required by the cascade to accomplish the desired separation:

$$E_{\text{ideal}} = E_{\text{stage}} + E_{\text{mix}} \quad (87)$$

Table 13. Comparison of different types of energy input and total interstage flow for the various cascade configurations with the nitromethane/BF₃ donor system.

# of Sections	E_{stage} (kJ/hr)	E_{mix} (kJ/hr)	E_{ideal} (kJ/hr)	Recycle Energy (kJ/hr)	Total Interstage Flow (kJ/hr)
1 (CRC)	11.939	-2.729	9.210	$258 * \Delta H_{diss}$	57,900
2	10.709	-1.521	9.188	$258 * \Delta H_{diss}$	48,100
3	10.081	-0.888	9.193	$258 * \Delta H_{diss}$	47,200
4	9.856	-0.642	9.215	$258 * \Delta H_{diss}$	46,800
5	9.721	-0.530	9.192	$258 * \Delta H_{diss}$	46,700
Ideal	9.183	-----	9.183	$297 * \Delta H_{diss}$	41,900

Results of calculations involving the different cascade models incorporating the above energy considerations are shown in Table 13. The calculations were performed only for the BF₃/nitromethane system. Each of the other donor systems are expected to parallel these trends by analogy with previous modelling results. The total separative work, E_{stage} , lost work, E_{mix} , and the thermodynamic minimum or ideal work, E_{ideal} are indicated in Table 13. These quantities were determined on a stage wise basis from the appropriate model and summed across the entire cascade in accord with the previous discussion. Table 13 indicates that the total separative energy, E_{stage} , is a maximum for the constant recycle cascade and decreases as progressively more square sections are to the SOC. For the ideal cascade, E_{stage} corresponds to the thermodynamic minimum since the lost energy term, resulting from mixing streams of different compositions, is identically zero.

The lost work, E_{mix} , is greatest (more negative) for the CRC, decreases as more square sections are incorporated into the SOC, and is identically zero for the ideal cascade. This is a direct consequence of removing inefficiencies associated with the mixing point as more square sections are incorporated into the SOC design. The use of additional square sections in the SOC reduces inefficiencies associated with the mixing points. Consequently, the thermodynamic minimum energy defined by the ideal cascade is approached as more sections are utilized in the SOC.

The thermodynamic minimum work, E_{ideal} , is approximately the same for all cascade configurations when effects of the mixing process are removed. Slight differences in E_{ideal} for the different designs are due to small differences in waste stream compositions and flow rates in the various cascades. (Recall that the waste composition and flow rate varies slightly for the different cascade configurations due to the use of discrete equilibrium stages in the modelling process.)

The ramifications of the above results are apparent when the ideal cascade is considered. Due to the no-mix criteria, E_{mix} is identically zero for the ideal cascade and equation (87) indicates that $E_{\text{ideal}} = E_{\text{stage}}$. In conjunction with the above discussions, it is intuitively obvious that *the ideal cascade has the potential to perform the desired separation with the minimum thermodynamic energy input for all possible countercurrent recycle cascade designs as a result of eliminating the inefficiencies of mixing.* Alternatively, the CRC consumes the greatest amount of energy, and any degree of compromise between these limiting cases defined by the CRC and ideal cascade can be achieved with SOC configurations. These results were derived and are consistent with the second law of thermodynamics.

Another interesting aspect in the energy analysis of recycle cascades evolves from an examination of energy requirements as a function of recycle ratio for a given cascade configuration. For the CRC and BF_3 /nitromethane system, energy requirements (E_{stage} and E_{ideal}) were determined as a function of inverse recycle factor, $1/A$. A similar type of analysis was previously used by defining the recycle factor, A , to establish minimum total interstage flow. Separative and ideal work are plotted as a function of $1/A$ in Figure 27 for the CRC with nitromethane as the donor. As expected the minimum or ideal energy of separation, E_{ideal} , indicated by the dotted line in Figure 27, is essentially constant and independent of recycle factor. However, as the recycle ratio decreases from total reflux ($1/A \rightarrow 0$), the total energy requirements of the cascade decreases. The total separative work, E_{stage} , goes through a minimum in the vicinity of $1/A = 0.75$, corresponding to a recycle ratio of $R_{\text{NF}} = 1.34 \cdot (R_1)_{\text{min}}$, and then increases as minimum reflux ($1/A = 1$) is approached. For comparison, total interstage flow is also indicated in Figure 27 as a function of $1/A$. The interesting point is that the energy requirements of the CRC parallel the total interstage flow requirements as the recycle ratio varies. In fact, the two quantities go through a minimum at the same "optimum" recycle ratio of approximately $1.35 \cdot (R_1)_{\text{min}}$. This result lends further credibility to the selection of recycle ratio in the CRC and SOC models at $1.45 \cdot (R_1)_{\text{min}}$.

Up to this point, two contributions to the energy requirements of the separation cascades under consideration have been examined: that associated with providing reflux in the decomposer/recombiner systems and that of providing the separative work within the individual stages. In

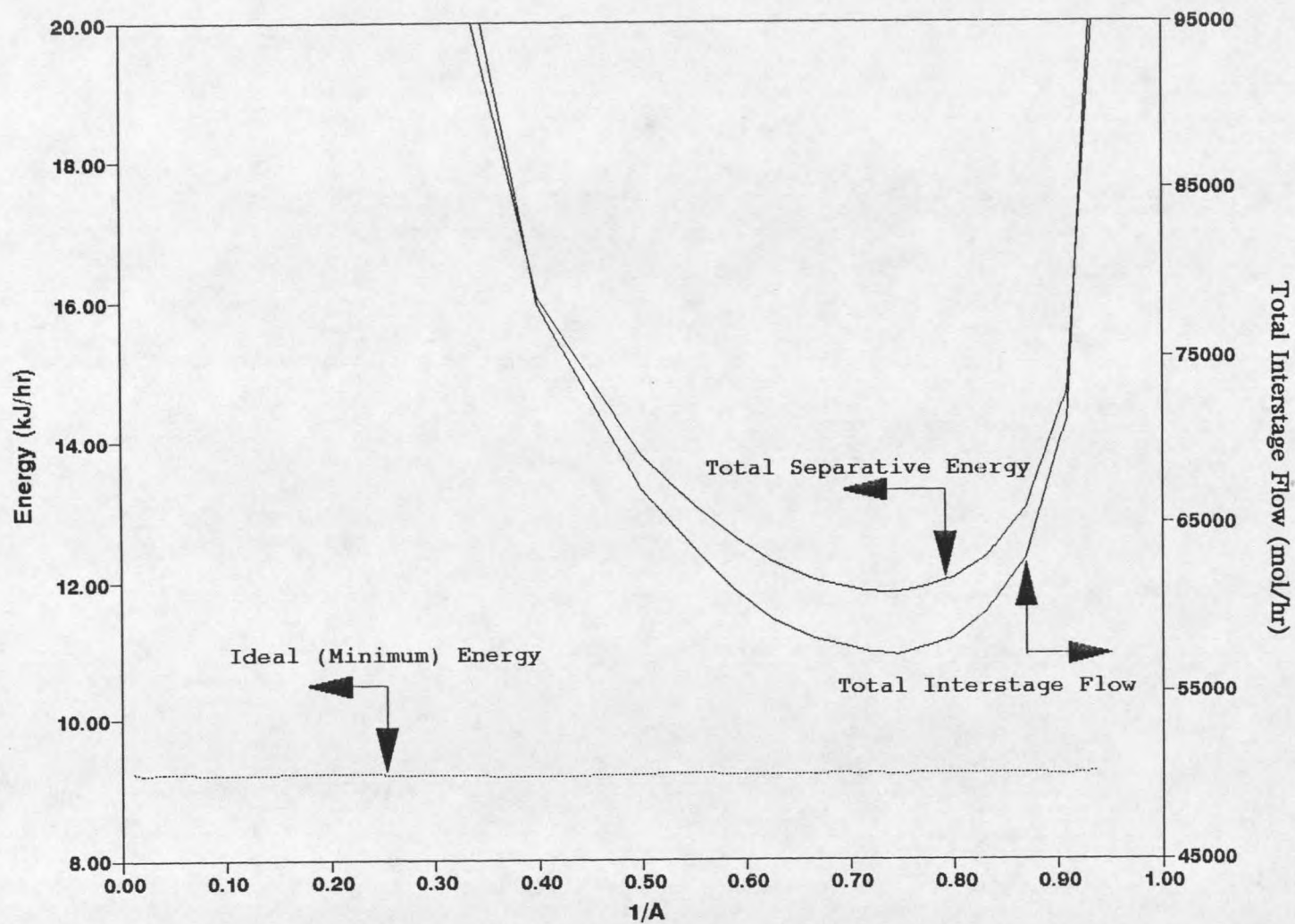


Figure 27. Ideal energy, separative energy and total interstage flow as a function of inverse recycle factor ($1/A$) for the CRC with the nitromethane/ BF_3 donor system.

reality, both types of energy must be provided for the cascade to function in the designed manner. Furthermore, the utilization of energy within the systems is not as efficient as the above discussion indicates and additional energy to support non-idealities in the actual process are required. As a minimum, the combination of recycle and separative energy must be provided for each of the cascade configurations to support the desired fractionation. Figure 28 shows each type of energy requirement as a function of recycle ratio for the CRC with the nitromethane/BF₃ donor system.

The recycle energy indicated in Figure 28 is based on equation (79) which was derived only for the decomposer. The derivation of this equation was based on the fact that ΔH_{diss} was unknown but constant for the nitromethane/BF₃ system. Note that the recycle energy is a linear function of recycle ratio, as expected from equation (79). It is apparent that the minimum work for recycle is associated with minimum reflux, while maximum recycle energy is required at total reflux. Consequently, it is economical to operate the cascade with the lowest possible recycle ratio at the feed stage.

The work required to support the stagewise separation process in the cascade, E_{stage} , previously discussed is also indicated in Figure 28. The important point to be emphasized in Figure 28 is the required amount of energy supplied to the CRC operating at a specified recycle ratio and given donor is the sum of the two discussed contributions. For the optimum recycle ratio of $1.34 \cdot (R_1)_{min}$ with the nitromethane/BF₃ donor system, 11.8 kJ/hr must be provided to overcome the mixing process and separate the isotopic mixture. At the same time, roughly $190 \cdot \Delta H_{diss}$ kJ/hr

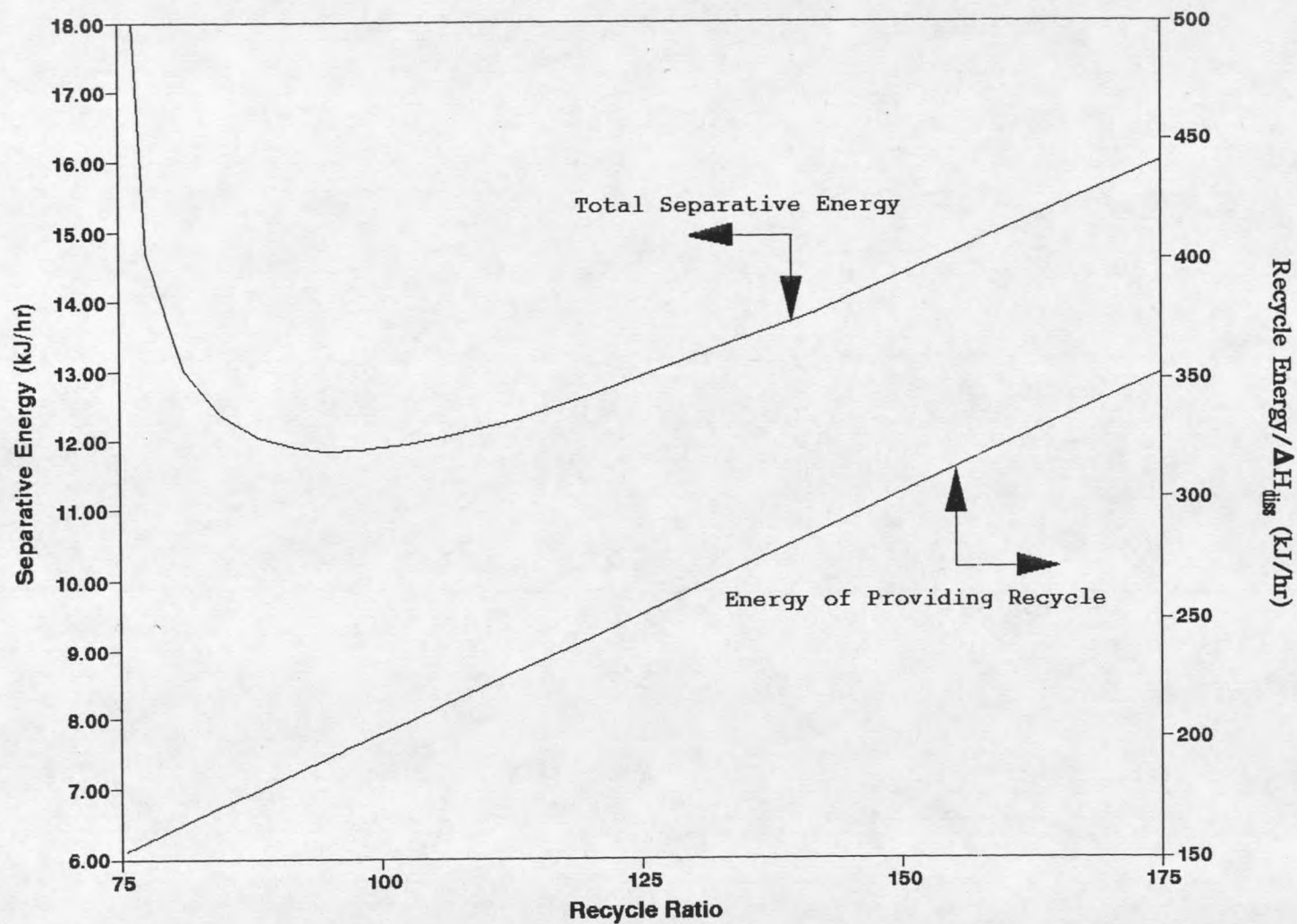


Figure 28. Recycle and separative energy as a function of recycle ratio for the CRC with the nitromethane\BF₃ donor system.

must be provided in the decomposer to maintain the necessary recycle ratio in the enriching section of the cascade. If ΔH_{diss} is assumed to be 10 kJ/mol (similar to the dimethyl ether/BF₃ system), the total energy input requirements for the system would be:

$$\Delta E_{total} = 11.8 + 190 \times 10 = 1912 \text{ kJ/hr} \quad (88)$$

It is apparent from equation (88) that the greatest contribution to the energy requirements of the CRC result from providing the necessary recycle. As noted earlier, this energy is constant for the different cascade configurations for a constant recycle ratio at the feed stage.

The above analysis and results cannot incorporate quantitative measures for estimating all possible energy contributions in the recycle cascades under consideration. The necessary directions cascade design must take to minimize the energy requirements are apparent from the above analysis. First, the recycle ratio at the feed stage must be maintained as close as possible to the "optimum" value. Recall that consideration must be given to the required number of ideal stages to insure an inordinate number is not necessary. This criteria insures that the energy requirements of providing recycle is as low as possible. Secondly, by incorporating a number of squared off sections, the energy requirements necessary to provide separative work to the cascade will more closely approximate the thermodynamic minimum associated with the ideal case. Finally, the above analysis provides a thermodynamic basis establishing how and why the ideal cascade is potentially the most energy efficient type of cascade for a specified separation. Such an analysis has not been reported in the literature for separations based on chemical exchange reactions.

CONCEPTUAL BORON ISOTOPE ENRICHMENT PLANT

The ultimate goal of research in the area of boron isotope separation would be to devise a large scale method economically competitive or superior to the currently used dimethyl ether/BF₃ system. The experimental portion of this study was directed at examining several different donors with the concept that any one could prove potentially useful in a large scale fractionation scheme. Based on the magnitude of the separation factor, α , the nitromethane/BF₃ isotope exchange system indicates the greatest potential for achieving the desired goal. The modelling and analysis studies were conceived to examine the benefits of utilizing the various donor systems in terms of large scale plant design and to indicate the configuration of a suitable separation process. Within the confines of the specific designs considered in this study, the two section SOC, used in conjunction with nitromethane as the donor, is an appropriate system for the large scale fractionation of the isotopes of boron.

A conceptual process flow schematic for the two square section cascade utilizing the nitromethane/BF₃ donor system is shown in Figure 29. This process is based entirely on the modelling and analysis results. Each column corresponds to a square section of the cascade and contains the appropriate number of identical ideal stages to perform the specified amount of separation for that section.

The first section, denoted as column #1, contains the feed stage, a portion of the enriching section, and the entire stripping section. This

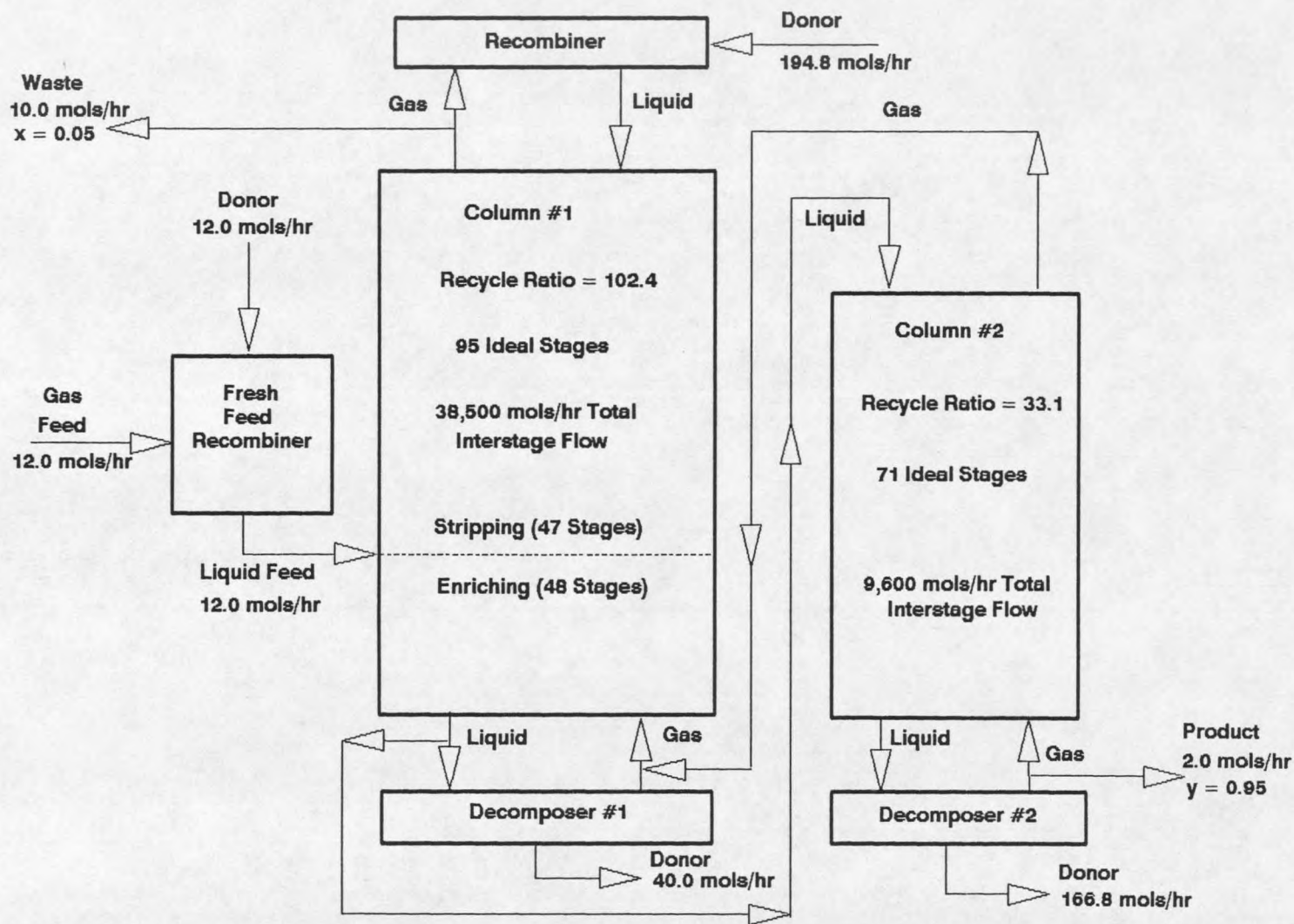


Figure 29. Process flow schematic for the two section SOC with the nitromethane/BF₃ donor system.

is the largest of the two sections. A fraction of the isotopically depleted BF_3 gas is cut from the stream exiting the top of this column (corresponding to the stripping section) as the gaseous waste. The remainder of this gas stream is passed to a recombiner where it is reacted with an equimolar amount of the pure nitromethane donor to form the liquid complex. The nitromethane/ BF_3 complex formed in the recombiner is returned to the top of the column as liquid recycle.

A fraction of the liquid complex exiting the bottom of the first section flows to a decomposer where it is completely dissociated (thermal reversal of the formation reaction) into equimolar amounts gaseous BF_3 and the liquid donor. The remainder of this stream forms the liquid feed to the top of column #2, the second square section. The BF_3 gas generated from the complex in decomposer #1 is combined with the gas stream exiting the top of the second column and returned to the bottom of the first column as gaseous recycle. The donor recovered from the decomposer would, if necessary, be purified in a separate system and stored for reuse in the recombiners.

The second square section, corresponding to column #2, is the smaller of the two columns and produces the final product of the specified composition. The entire liquid stream exiting the base of this section flows to decomposer #2 where it is thermally decomposed to gaseous BF_3 and nitromethane. The donor is reclaimed for reuse and a fraction of the gas stream exiting the decomposer is taken as the isotopically enriched BF_3 product. The remainder is returned to the bottom of column #2 as gaseous recycle.

Note that the total amount of donor exiting the decomposers is equivalent to the amount of nitromethane required in the recombiners. This is a result of assuming that the formation reaction is completely reversible; the donor is neither consumed nor replaced in the exchange system. Consequently, the donor is continuously recycled and reused in the separation system. In the event of irreversible decomposition of the nitromethane/BF₃ complex, the appropriate donor purification system would be incorporated into the actual plant design.

The first and largest column in the cascade includes the entire stripping section. Of the 95 ideal stages included in this column, 47 of these stages located above the feed stage in the upper portion of the column, form the stripping section. The balance, or 48 ideal stages, located from the bottom of the column up to and including the feed stage, are a portion of the enriching section. In accord with previous discussions, the size of the stripping section could be reduced or even eliminated entirely, depending on the desired waste composition. If stripping were completely eliminated, the first section would contain only 48 ideal stages with a total interstage flow rate of 19,900 mols/hr through the column. Therefore, even in the absence of stripping, column #1 would still be the largest in terms of total interstage flow. Note that the recycle ratio for this section of the cascade would be the same if the size of the stripping section were reduced or even eliminated. This is a consequence of the fact that the specified recycle ratio (1.45 times the minimum) is fixed by the feed and product compositions in accord with equation (49). This specified recycle ratio through the column also fixes the energy requirements to the cascade.

The total interstage flow through the individual columns is greatest in the first section or column, which includes the feed stage, a portion of the enriching section, and the entire stripping section, and smallest in the final, or product, column. Recall that the total interstage flow through the two section SOC, as determined from the model, was 48,100 mols/hr (Table 7). Of this, 38,500 mols/hr or 80% of the total interstage flow occurs in the first section. The balance, 9,600 mols/hr or roughly 20% of the total interstage flow through the system, occurs in the final (and smallest) section. This is a consequence of decreasing the recycle ratio in the different sections as the product end of the cascade is approached. These trends are expected and consistent with previous discussions. In fact, the desired objective of the SOC design is a reduction in total interstage flow with a concomitant decrease in column size as the product end of the cascade is approached.

It is of interest to compare the above conceptual design of the proposed nitromethane/BF₃ two section SOC with the actual large scale facility using the dimethyl ether/BF₃ system. The appropriate literature sources [2,3,36] are somewhat vague regarding the necessary operating variables (i.e. recycle ratios, actual stages, etc.) of the commercial plant to develop a detailed model. However, the actual plant is reported to perform the same separation in terms of the external compositions and flow rates as the conceptual system. The commercial facility reportedly operates with two columns [36]. Consequently, the two section SOC model for the dimethyl ether/BF₃ system developed in this study was used to approximate actual plant behavior. A process flow schematic for the two section SOC based on the dimethyl ether/BF₃ system is shown in Figure 30.

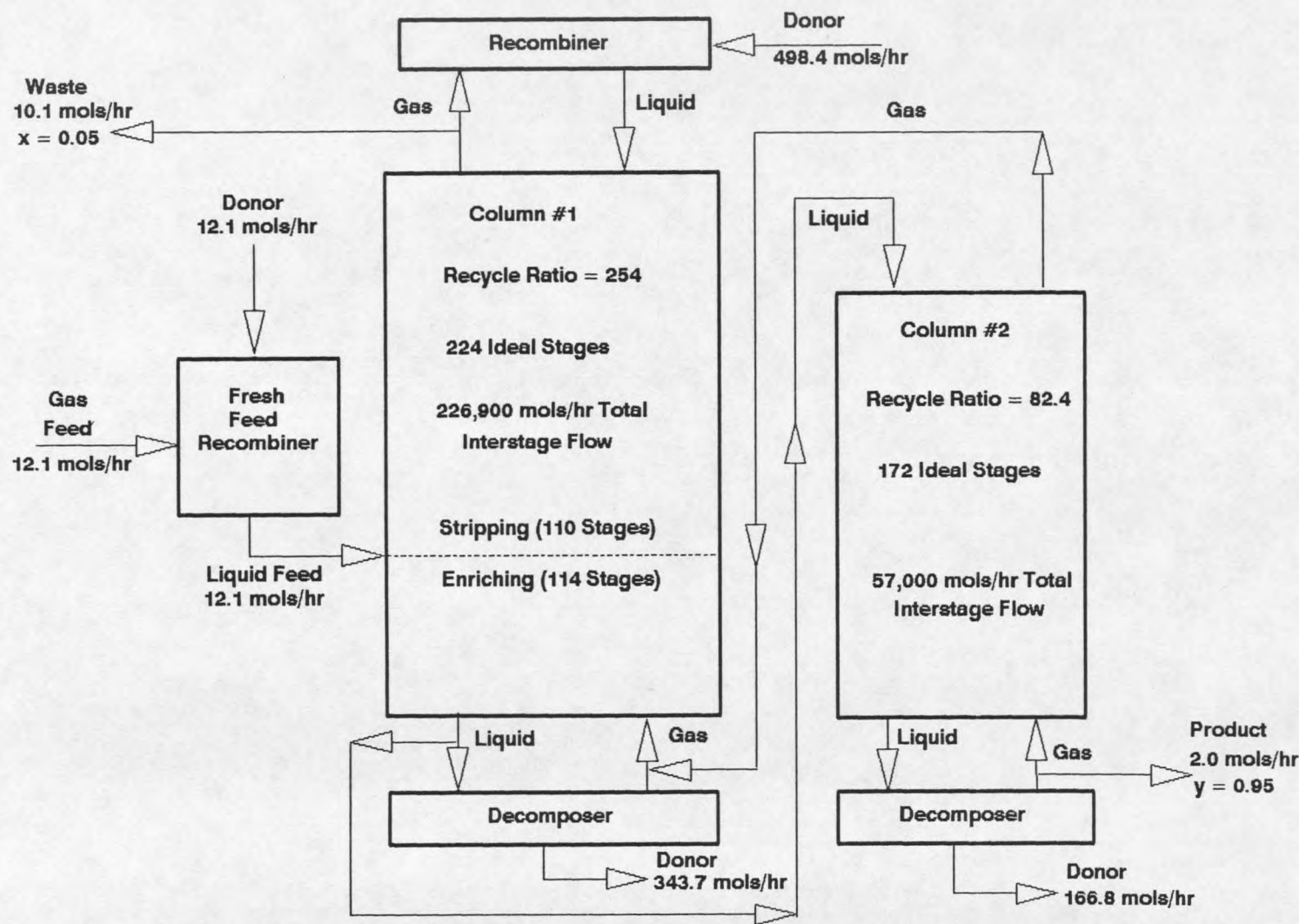


Figure 30. Process flow schematic for the two section SOC with the dimethyl ether/ BF_3 donor system.

The operation of the two separation schemes is essentially the same. The waste, product, and feed compositions and flow rates, or the external variables, are approximately equal for both systems. The first section, column #1 in Figure 30, contains a portion of the enriching section, including the feed stage, and the entire stripping section. The decomposer at the base of this column serves to alter the recycle ratio between the two sections. Column #1 contains 224 ideal stages with a total interstage flow rate of 226,900 mols/hr. Consequently, this is the largest section of the cascade, providing roughly 80% of the total interstage flow through the entire system.

The second column contains 172 ideal enriching section stages and produces the isotopically enriched gaseous product. This is the smallest section with a total interstage flow of 57,000 mols/hr through the column. This interstage flow accounts for the remainder or 20% of the total interstage flow through the cascade. As with the conceptual nitromethane process, the two section dimethyl ether SOC is designed with a smaller column at the product end of the system in order to the approximate behavior of an ideal cascade.

A comparison of the two different conceptual designs indicates both the number of ideal stages and total interstage flow is significantly reduced with the nitromethane donor system. For two square sections with the nitromethane system, 166 ideal stages are required to perform the specified separation as compared to 396 ideal stages for the dimethyl ether design. Thus, the nitromethane/BF₃ system requires 230 or 58% fewer stages than the dimethyl ether system. Furthermore, the total interstage flow is 235,800 mols/hr or 83% less for the nitromethane/BF₃ system than

for the dimethyl ether SOC performing the same amount of isotopic fractionation.

Note that for the dimethyl ether system, the decomposers process a total of 511 mols/hr as compared to 207 mols/hr for the nitromethane system. Consequently, the size of the decomposer and recombiner systems are substantially smaller when nitromethane is used as the donor. From the above discussion, it is obvious that a major benefit of incorporating nitromethane in the large scale separation system would be the immense reduction in the required size of the separation cascade.

The experimental and modelling portions of this study ultimately resulted in defining the above conceptual process design for the two section SOC with the nitromethane/ BF_3 donor system. The major benefit (a reduction in overall cascade size) of such a design relative to the currently used dimethyl ether system was explored. In reality, the design of an actual optimum boron isotope separation plant would be quite complex. A detailed design would relate equipment size, performance and costs to several related process variables such as stream compositions, flow rates, number of stages, recycle ratios and total interstage flow rates for the different cascade designs. The main isotope fractionation system would consist of a large number of separating units or stages with the associated pumps and compressors, heat exchange equipment, connecting piping, and control systems. The entire system would require feed and withdrawal facilities, auxiliary systems, and support and operating personnel. It would probably be enclosed in a suitable structure and be surrounded by the appropriate type of land. The sizes and costs of these, and other, important items must be related to the process variables. For

a given design with a specified set of process variables, the associated costs can in principle be defined. Therefore, for a given design it is possible to select many different sets of values for the process variables and solve for the optimum or minimum cost design by a trial and error procedure.

Prior to embarking on a detailed and labor intensive design and economic analysis, feasibility studies similar to the procedures of this work are generally required. A complete feasibility study would include extensions of the experimental and modelling results propagated in this study. The existence and effects of irreversible decomposition of the liquid complex must be established. The reversibility and thermodynamics of the BF_3 /donor formation reaction must be determined. Furthermore, the kinetics of the isotope exchange reaction with each potential donor should be established. While the physical properties, such as viscosity and density of BF_3 gas are tabulated in the literature [42], such data is generally unavailable for the liquid complexes under consideration. The design of process equipment, such as pumps and columns, may rely on a knowledge of these physical properties. Bench scale or pilot plant studies are required to establish stage heights and efficiencies if the number of actual (as opposed to ideal) separation stages is to be determined. The above information would then be incorporated into the design calculations of the modelling and analysis section and a better estimation of feasibility established. The above considerations are necessary and recommended in future studies.

Despite the limitations imposed on a more detailed examination of production scale plant design, the results of this study indicate some

important directions such designs must take. Plant size is strongly dependent on the magnitude of the separation factor. Potential donors, such as nitromethane or any of the ketones examined, could substantially reduce the size of a separation facility. The cascade configuration also plays an important role regarding plant size. The constant recycle cascade minimized ideal stage requirements while maximizing total interstage flow. The ideal cascade required an increased number of ideal stages but minimized total interstage flow. A number of squared off cascade designs were propagated as a compromise between the performance of the CRC and ideal cascades. Based on these results, the most logical design was the two section SOC configuration used in conjunction with the nitromethane/ BF_3 exchange system.

CONCLUSIONS

- (1) Acetone, MIBK, DIBK and nitromethane are suitable donors and form relatively stable liquid complexes with BF_3 .
- (2) Each of these four donors exhibits larger values of separation factor than dimethyl ether in the boron isotope exchange reaction. In this regard, each is more amenable to large scale fractionation than the dimethyl ether/ BF_3 system.
- (3) Nitromethane exhibits separation factors substantially higher than those predicted theoretically or for any known system in boron isotope chemical exchange reactions. This anomaly is postulated to be due to a dual site exchange mechanism. An understanding for the cause of this anomaly could provide valuable insight into the isotope exchange process and donor selection.
- (4) The constant recycle cascade minimizes total ideal stage requirements and maximizes total interstage flow. The ideal cascade minimizes total interstage flow with increased ideal stage requirements. Any degree of compromise between these opposing effects can be obtained in a squared off cascade by altering the number of squared sections.
- (5) A logical compromise between total interstage flow and ideal stage requirements in the squared off cascade can be obtained by using two square sections.

- (6) A reduction in total interstage flow and ideal stage requirements could be achieved by reducing the size of the stripping section. A reduction in stripping section size would result in an increase in the amounts of fresh feed required and waste produced.
- (7) The energy requirements of providing reflux in any countercurrent recycle cascade depends only on the recycle ratio at the feed stage. Therefore, if the recycle ratio at the feed stage is equivalent in the CRC, SOC, and ideal cascade, the energy requirements of maintaining the necessary reflux for each of the different cascades will be equal. This condition holds only if each different cascade is performing the same overall separation. As a result of this unique property, CRCs and SOC can be designed to be more efficient than the ideal cascade in terms of the work expended to provide and maintain the necessary recycle ratio.
- (8) From the standpoint of re-mixing and separating internal streams with different isotopic compositions, the ideal cascade is potentially the most energy efficient system. This is a result of the no-mix criteria upon which the ideal cascade is founded. In this regard, the CRC is the least energy efficient of the recycle cascade configurations examined.

RECOMMENDATIONS FOR FURTHER STUDY

- (1) Further study with the liquid complexes formed between BF_3 gas and the different donors (acetone, MIBK, DIBK and nitromethane) is necessary to establish rates of irreversible decomposition, reversibility of the formation reaction and physical properties such as viscosity and densities associated with these complexes.
- (2) Studies into the mechanism of the boron isotope exchange reaction between BF_3 and the nitromethane/ BF_3 complex are strongly suggested. These studies should examine the phenomenon responsible for the large separation factors associated with this system. The suggested starting point would be to use spectroscopic techniques, such as proton or fluorine NMR or perhaps UV-VIS spectroscopy to examine the molecular addition compound. With these techniques, it may be possible to determine the number and arrangement of BF_3 molecules associated or bound to a nitromethane molecule in the liquid complex. A knowledge of the bonding arrangement in the complex could help support the dual site exchange mechanism proposed in this study.
- (3) Bench scale and/or pilot plant studies are required to establish the stage efficiencies and kinetics of isotope exchange with each of the four different donor compounds. Potential bench scale experimental systems readily adapted to examine these parameters have been reported in the literature [24].

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