



Separation of boron isotopes by gas phase membrane permeation of BF_3
by Ronald Scott Herbst

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

The separation of boron isotopes by selective permeation of BF_3 through a number of commercial and fabricated membranes was investigated.

The commercial films demonstrated little or no ability to fractionate boron isotopes, with calculated separation factors ranging between $\alpha = 1.000$ to $\alpha = 1.010$. The commercial films were studied at a pressure of 200 psig on the high pressure side of the membrane and at temperatures which gave a suitable permeation flux.

The fabricated membranes incorporated phenyl ether modifiers immobilized in a polyvinylidene fluoride support. With these fabricated membranes, enhanced selectivity for the mass 10 boron constituent of BF_3 was observed. Separation factors of $\alpha = 1.020$ to $\alpha = 1.090$ were determined, depending on the ether incorporated in the membrane. Operating conditions were 200 psig on the upstream side of the membrane and a temperature of 120°C .

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BY GAS PHASE MEMBRANE

PERMEATION OF BF_3

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APPROVAL

of a thesis submitted by

Ronald Scott Herbst

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

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ABSTRACT

The separation of boron isotopes by selective permeation of BF_3 through a number of commercial and fabricated membranes was investigated.

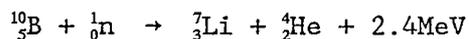
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The fabricated membranes incorporated phenyl ether modifiers immobilized in a polyvinylidene fluoride support. With these fabricated membranes, enhanced selectivity for the mass 10 boron constituent of BF_3 was observed. Separation factors of $\alpha = 1.020$ to $\alpha = 1.090$ were determined, depending on the ether incorporated in the membrane. Operating conditions were 200 psig on the upstream side of the membrane and a temperature of 120°C .

INTRODUCTION

With man's capability to harness the energy of the atom and the subsequent advent of the "Atomic Age" came the need for new and different technologies. Prevalent was the need for an effective method for the containment or capture of neutrons, the relatively energetic subatomic particles generated in nuclear reactions. Among elements, boron absorbs neutrons readily. Interest in the separation of boron isotopes evolved largely from the contrasting difference in thermal neutron absorption cross-sections of these isotopes. Hence, there has been sustained interest in the separation of boron isotopes since shortly after the discovery of atomic fission.

Boron occurs naturally in two stable isotopic forms, one of mass 10 (^{10}B) and the other of mass 11 (^{11}B). Boron 10 constitutes 19.7 atom percent of natural boron and has a thermal neutron absorption cross-section of 3,837 barns [1]. Boron 11, which constitutes the remaining 80.3% of the total, has a thermal neutron absorption cross-section of only 0.005 barn [1]. The nuclear reaction:



yields no secondary radiation effects since the lithium is stable and the alpha particles are easily stopped. Consequently, ^{10}B is particularly valuable as a neutron capture material. It is useful for neutron shielding, reactor control rods and as a neutron flux moderator or

neutron "poison." ^{10}B is 20 times more effective than lead and nearly 500 times more effective than concrete as a neutron shield for a given thickness [2, p. 1]. Based on this comparison, it is of little wonder that the nuclear industry thought the separation of boron isotopes to be imperative.

Historical Background

Prior to 1943, efforts to separate boron isotopes were confined primarily to thermal diffusion and mass spectroscopic techniques [3]. In 1943, during the early stages of the Manhattan Project, a group was established at Columbia University to study the separation of boron isotopes. Aside from one method based on thermal diffusion of BF_3 , research was directed toward the distillation of various boron compounds, mainly BF_3 -ether complexes. This work has been reported elsewhere in detail [3]. Isotopic distillation of the BF_3 -dimethyl ether complex, $(\text{CH}_3)_2\text{O}-\text{BF}_3$, was selected for production-scale boron isotope separation. Accordingly, laboratory scale development was conducted at Columbia and pilot plant testing was performed by Standard Oil of Indiana from 1944 to 1946. In 1953, a production scale plant was constructed and operated by Hooker Electrochemical Company in Model City, New York. This plant was successfully operated from 1954-1958, with a total production of several hundred kilograms of 90-95% ^{10}B metal. This relatively low product output over a four year span testifies to the difficulties and problems associated with the isotopic distillation process. Complete details of these ventures are reported elsewhere [4,5].

In the early 1950's, the United States Atomic Energy Commission desired to have available separation methods of any or all of the isotopes of the lighter elements in the periodic table up through calcium. Partially in the wake of this desire and partly due to the need for a more efficient and less cumbersome method of boron isotope separation, Oak Ridge National Laboratory began evaluating potentially useful systems for the fractionation of boron isotopes in the mid-1950's. During the ten year course of that study, thirty molecular addition compounds of BF_3 were examined, ten of these in detail. Results of that study are reported elsewhere [2] and provide a great deal of insight into boron isotope chemistry.

Currently, Eagle-Pitcher Industries, Inc. operates the only boron isotope enrichment process in the United States. This facility, located in Quapaw, Oklahoma, still utilizes the isotopic distillation of BF_3 and the BF_3 -dimethyl ether complex. Multiple distillations are effected in a series of 39 foot monel towers. The reported single-stage ideal separation factor in this distillation process is quite low at 1.016 [2]. The distillation is carried out at reduced pressure and recovery of the product is extremely difficult. Hence, the ^{10}B enriched product is relatively expensive. The most recent available figure for a 75% enriched ^{10}B sample is \$5.00 per gram of ^{10}B [6]. The major final product, ^{10}B enriched boric acid (H_3BO_3), is sold primarily to the Department of Energy for the weapons program.

Purpose and Scope of Investigation

This study was conceived for the sole purpose of investigating boron isotope separation by selective membrane permeation. The success of such an approach could ultimately spawn an improved, efficient and economical boron isotope separation method. Regardless of any ultimate success or failure, this study constitutes, to the best of the author's knowledge, the first recorded attempt to separate the isotopes of boron by selective permeation techniques.

Clearly, such a general study in so unexplored an area presents a number of avenues from which to approach the problem. The scope of this investigation was therefore limited to a few primary objectives. Consequently, this study was concerned with determining if and which commercially available polymeric films were non-reactive with and permeable to BF_3 gas. Potentially useful films were then examined to determine if any isotopic separation occurred during the permeation process. Thus, the commercial materials were studied to examine the possibility that boron isotopes exhibited different mass transport rates through these polymeric thin films. Preliminary results were also obtained for several thin films fabricated from polymer resins. These fabricated membranes were studied to deduce the plausibility of isotopic exchange reactions occurring interior to the membrane and resulting in enhanced separation during the permeation process.

THEORETICAL BACKGROUND

Chemical separation processes are generally based on differences in a physical property of the species to be separated. Membrane-based separations are no exception. The physical properties typically exploited in membrane separations are differences in solubilities and diffusion coefficients of a feed species in the membrane construction material. For the purposes of this discussion, a membrane will be defined as a thin, non-porous, polymeric barrier to dynamic flow which separates a volume into two distinct regions or compartments.

This study concerns binary component (two boron isotopes), gas phase permeation through non-porous polymeric membranes. Consequently, diffusional processes due to concentration or pressure gradients across the membrane are the primary mode of transport. The following discussion reflects these concerns by examining only gaseous permeation by a sorption-diffusion mechanism.

Nature of the Permeation Process

Permeation can be defined as the phenomenon in which chemical species are being transported across a membrane by diffusion. Thus, a membrane may be considered a region of discontinuity in a flow regime. As such, the flow regime may be characterized by five resistances to mass transport:

- (1) Diffusion of the gas species from the high pressure bulk phase to the gas-membrane interface.
- (2) Solution of the permeating species at the membrane surface.
- (3) Diffusion of the species through the membrane.
- (4) Desorption of the permeant species from the opposite membrane surface.
- (5) Transport of the permeant from the membrane surface to the low pressure bulk phase.

The concentration profile across the entire permeation flow regime is represented graphically in Figure 1. The general shape of the concentration profile when all five of the above transport resistances are operative is represented in Figure 1(a).

In gas phase permeation, the diffusivity of the permeants through the membrane is generally quite low, typically 10^{-7} to 10^{-10} cm²/sec [7, p. 509]. Gas phase diffusivities are generally orders of magnitude larger, typically 10^{-1} to 10^{-3} cm²/sec [8, p. 3-256]. Consequently, perfect mixing throughout the bulk gaseous phases is a valid assumption and resistances (1) and (5) are usually negligible.

Further simplification of the transport mechanism is affected if partition equilibrium of the permeant species is maintained at the membrane interfaces. This assures that the free energy barriers opposing entry and release of the permeant species are negligible [9, p. 10]. Under these conditions, resistances (2) and (4) may also be neglected. The resulting steady state concentration profile for the case of a strictly diffusional process is represented in Figure 1(b).

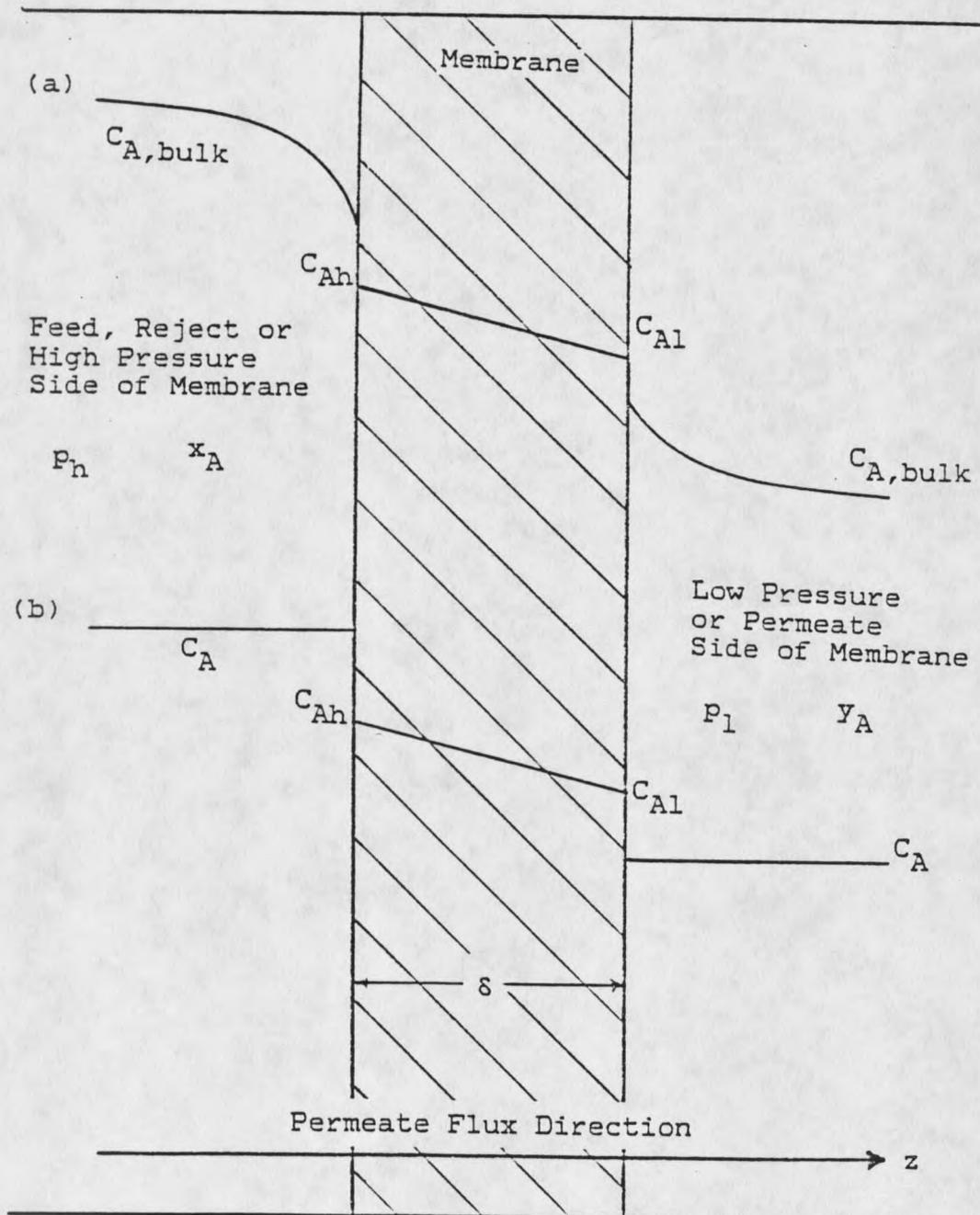


Figure 1. Concentration gradient through a gaseous permeation system. (a) With all transport resistances; (b) with only sorption/diffusion transport resistances.

In view of the above arguments, diffusion of the gaseous species through the membrane is the major transport resistance. Hence, gas phase permeation can generally be dealt with in terms of diffusion of a permeant species through a polymeric membrane. This simplified approach provides a very useful description for the nature of gas permeation.

Diffusive Transport Through a Membrane

Diffusion of gases through polymeric membranes greatly depends on whether the polymer is "glassy" or "rubbery." Rubbery polymers are characterized by a high degree of chain mobility, whereas in a glassy polymer chain mobility is greatly reduced. These two concepts are somewhat interrelated by the existence of a characteristic glass transition temperature, where the chain mobility and hence polymer state, is affected. The following discussion is restricted to gas diffusion through rubbery polymeric membranes.

The single component permeation flux of species A is adequately represented by Fick's first Law [10, p. 21]:

$$N_A = -D \frac{dC_A}{dz} \quad (1)$$

where D is the diffusion coefficient and C_A is the concentration of the permeating species in the membrane. Equation (1) reflects the following assumptions:

- (1) The diffusivity is constant and independent of direction.
- (2) Concentration is a function of only direction, thus whole derivatives are appropriate in equation (1).

The boundary conditions required for the solution of equation (1) are:

$$C_A = C_{Ah} \text{ at } z = 0$$

$$C_A = C_{Al} \text{ at } z = \delta$$

where δ is the membrane thickness. C_{Ah} and C_{Al} are the concentrations just inside the respective membrane interface. With these boundary conditions, equation (1) is readily integrated. Whence, upon rearrangement:

$$N_A = \frac{D_A}{\delta} (C_{Ah} - C_{Al}) \quad (2)$$

Equation (2) indicates that given membrane thickness, experimentally determined bulk concentrations and permeation flux, the overall diffusivity coefficient, D , can be calculated. The overall diffusivity obtained in this manner reflects not only the diffusivity of the permeant species, but the effect of the membrane on the permeation flux as well.

In the cases of gaseous systems, it is often convenient to express concentrations in terms of the partial pressures of the components. The concentrations and pressures of the permeant species in the membrane are generally quite low. Thus, it is appropriate to assume Henry's Law is a valid description of the permeant equilibrium at the membrane interfaces:

$$C_{Ah} = S_h p_h x_A \quad (3)$$

$$C_{Al} = S_l p_l y_A \quad (4)$$

The Henry's Law constant, S , is defined as the solubility of the gas species in the polymer. If the solubility coefficient is a function of

temperature only, and both sides of the membrane are maintained at the same temperature, then

$$S_h = S_1 = S \quad (5)$$

Upon substitution of equations (3), (4) and (5), equation (2) can be rearranged to give the permeation flux as

$$N_A = \frac{SD}{\delta} (P_h x_A - P_l y_A) \quad (6)$$

This result indicates that the permeation flux is dependent upon the solubility and diffusivity of the permeant gas in the polymer membrane material. From this standpoint, the more soluble and/or diffusive components can be separated from a feed stream if the proper polymeric material is selected for membrane construction.

It is often convenient to define a mean permeability coefficient P^* as

$$P^* = SD \quad (7)$$

P^* is often reported in the literature in units of barrers, where

$$1 \text{ barrer} = 10^{-10} \frac{\text{cm} \cdot \text{cm}^3 (\text{STP})}{\text{cm}^2 \cdot \text{cmHg} \cdot \text{sec}}$$

This unit was named after R. M. Barrer, an early pioneer in membrane studies [11, p. 233].

Combination of equations (6) and (7) yields

$$N_A = \frac{P^*}{\delta} (P_h x_A - P_l y_A) \quad (8)$$

Equation (8) is the commonly encountered expression relating permeation flux to composition for gas phase permeation through rubbery polymers.

Temperature and Pressure Effects on Transport

For many gases above their critical temperatures, the Arrhenius type relations:

$$D = D_o \exp(-E_D/RT) \quad (9)$$

$$S = S_o \exp(-\Delta H_s/RT) \quad (10)$$

provide valid descriptions of the temperature effects on the diffusivity and solubility coefficients D and S , respectively [8, p. 15-17]. Increased temperatures therefore cause a corresponding exponential increase in the permeability coefficient defined by equation (7). Thus, according to equation (8), increased temperatures cause a corresponding increase in permeation flux.

Equation (2) was founded on the basis that a concentration gradient was the driving force for mass transport. For dilute gaseous systems, pressure is related to concentration through Henry's Law, equations (3) and (4). Thus, the permeation flux through a membrane is generally increased by increasing the pressure drop across the film.

Binary Component Permeation: The Separation Factor

It is often convenient to express equation (8) in terms of the molar flow rate of permeate, L :

$$L = \frac{A P_A^m}{\delta} (p_h x_A - p_l y_A) \quad (11)$$

Equation (11) was obtained by multiplication of equation (8) by the area perpendicular to the direction of flux, A , and the molar density. Hence P^m is the molar permeability of the species in the polymer.

For a binary component permeation process where species A and B are permeating simultaneously and non-interactively through the film, the following relationships hold:

$$y_A L = \frac{A P_A^m}{\delta} (p_h x_A - p_l y_A) \quad (12)$$

$$(1-y_A) L = \frac{A P_B^m}{\delta} [p_h (1-x_A) - p_l (1-y_A)] \quad (13)$$

Equations (12) and (13) are obtained by combination of binary component material balances with equation (11). Taking the ratio of equations (12) to (13) and cancelling like terms, the following relationship is obtained:

$$\frac{y_A}{(1-y_A)} = \frac{P_A^m}{P_B^m} \frac{[p_h x_A - p_l y_A]}{[p_h (1-x_A) - p_l (1-y_A)]} \quad (14)$$

Further simplification of (14) is effected by defining an overall separation factor α , and the pressure ratio p_r such that

$$\alpha \equiv \frac{y_A (1 - x_A)}{x_A (1 - y_A)} \quad (15)$$

$$p_r = p_l / p_h \quad (16)$$

Combination of equations (14), (15) and (16) with appropriate rearrangement yields the following relationship:

$$\alpha = \frac{P_A^m}{P_B^m} \frac{(1 - x_A)/(1 - y_A)}{[(1 - x_A)/(1 - y_A)] + P_r [(P_A^m/P_B^m) - 1]} \quad (17)$$

The overall separation factor, α , defined by equation (15) is a convenient measure of the degree of separation through a membrane. Equation (17) indicates α depends only on the ratio of the molar permeabilities, the reject mole fraction (x_A), the permeate mole fraction (y_A) and the pressure ratio across the membrane.

The ratio of permeabilities is defined as the ideal separation factor, α^* :

$$\alpha^* = P_A^m / P_B^m \quad (18)$$

The ideal separation factor depends only on temperature and the nature of the gas-membrane system. In gas phase permeation, the pressure ratio across the membrane is generally quite small, $p_r \ll 1$. Equation (17) indicates that as $P_r \rightarrow 0$, the overall separation factor reduces to the ideal separation factor ($\alpha = \alpha^*$).

In this study, the analysis of a successful separation was determined by equation (15). The steady state mole fractions of ^{10}B were determined in the reject and permeate streams for each tested membrane. The overall separation factor, α , was then calculated by equation (15). A membrane exhibiting an overall separation factor significantly greater than unity ($\alpha > 1$) could be potentially useful in a permeation technique for boron isotope fractionation.

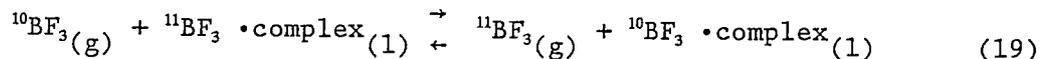
Complex Transport

Due to the similarities in the chemical and physical properties of the boron isotopes, fractionation based on a strict sorption/diffusion permeation mechanism may not be plausible. However, it may be possible to enhance the selectivity of a polymeric film for boron isotope separation by incorporating a chemical agent which selectively interacts with one of the isotopes. In this research, several fabricated membranes were prepared in this laboratory to explore such a mechanism, defined as complex transport.

Complex transport results through a mechanism where a chemical reagent or carrier incorporated in the membrane reacts reversibly with a species in the feed mixture. The reaction product or chemical complex preferentially captures and transports one species across the membrane. Thus, the carrier must undergo a reversible complexation reaction with one species in the permeate selectively with respect to the other permeate components.

The idea of carrier mediated transport for the membrane separation of the boron isotopes evolved largely from the review of literature pertinent to the isotopic distillation process [2,3]. This process involved the chemical fractionation of boron isotopes between BF_3 gas and liquid molecular addition compounds or complexes of BF_3 . Thus, the isotopic distillation was effected by passage of BF_3 gas flowing counter

currently to the liquid complex through a packed column. The distillation process is represented by the equilibrium reaction:



The ^{10}B therefore concentrates in the descending liquid phase while the ^{11}B is concentrated in the upflowing vapor phase.

A number of BF_3 complexes were studied or screened by previous researchers for potential use in the isotopic distillation scheme [2]. Among the more potentially useful candidates for this system were the BF_3 complexes formed from the phenyl ethers: anisole ($\text{C}_6\text{H}_5\text{OCH}_3$), phenetole ($\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$) and diphenyl ether ($\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$). Consequently, these phenyl ethers were selected as carriers for the preliminary studies of complex membrane transport.

In the membranes fabricated for this study, the liquid phenyl ether or BF_3 -ether complex was immobilized in a polyvinylidene fluoride (PVDF) membrane. The theory behind these fixed-site carrier, complex transport membranes was that the isotopic exchange reaction as given by equation (19) would occur within the membrane, a thermodynamic reaction equilibrium would be established throughout the film and thereby selectively transport the ^{10}B constituent of the feed across the membrane.

The ethers were effectively immobilized in the interstices of the PVDF lattice, or perhaps even covalently bonded to the lattice. Thus, the carrier ether was thought to occupy fixed sites in the membrane. The reversible complexation reaction was then envisioned as occurring continuously throughout the thickness of the thin film.

Theoretically, a purely diffusive flux of both isotopic constituents of BF_3 would exist through the PVDF lattice of the membrane. The fixed site carrier would provide an alternative route for the transport of $^{10}\text{BF}_3$. Hence, the mass 10 boron trifluoride molecules could effectively "jump" between carrier sites. This mechanism would result in enhancement of the $^{10}\text{BF}_3$ transport and an isotopic enrichment in the permeate stream. Under these conditions, the separation factor, α , was determined as given by equation (15):

$$\alpha = \frac{y_A (1-x_A)}{x_A (1-y_A)} \quad (15)$$

Note that the complex transport mechanism is not necessarily restricted to enhanced $^{10}\text{BF}_3$ permeation. With the ether carriers, ^{10}B selectivity is the expected or postulated result. Other compounds, when used as carriers, could just as well show ^{11}B selectivity by the same mechanism. The overall separation factors for the two components of a binary system are related by:

$$\alpha (^{10}\text{B}) = \frac{1}{\alpha (^{11}\text{B})} \quad (20)$$

The relationship shown in equation (20) merely assures that the reported separation factors are greater than unity ($\alpha > 1$), which is the accepted convention.

EXPERIMENTAL MATERIALS, EQUIPMENT AND PROCEDURES

Reagents and Materials

Boron trifluoride, BF_3 , sometimes referred to as boron fluoride, was the selected feed gas for the boron isotope separation studies. A cylinder containing five pounds of this material at 1300 psig was obtained from the Matheson Gas Company, Inc. The BF_3 gas was of chemical purity (c.p.) grade, with a minimum reported purity of 99.5% BF_3 . This material was used directly as feed stock for all permeation experiments with no attempt at further purification.

A cylinder of helium was obtained from the Alphagaz Company. This material was of ultra high purity (UHP) grade, with a minimum reported purity of 99.999% helium. The helium was used primarily to purge the experimental system prior to each permeation test. Such a high degree of purity was required by the mass spectral analysis procedure, since lesser purity helium was found to contain enough residual air to be detected by the mass spectrometer.

Polyvinylidene fluoride (PVDF) resin (Kynar®), Grade 301, was obtained from the Pennwalt Corp., Philadelphia, PA. This material was utilized as the polymer base in a number of "fabricated" membranes manufactured in this laboratory. The manufacturer lists the chemical structure of the PVDF resin as $(-\text{CH}_2-\text{CF}_2-)_n$.

Dimethyl formamide (DMF, $\text{HCON}(\text{CH}_3)_2$), reagent grade, was obtained from Baker Chemical Co., Phillipsburg, PA. This material was used as the solvent for the PVDF resin.

Anisole ($\text{C}_6\text{H}_5\text{-O-CH}_3$), phenetole ($\text{C}_6\text{H}_5\text{-O-C}_2\text{H}_5$), and diphenyl ether ($\text{C}_6\text{H}_5\text{-O-C}_6\text{H}_5$) were all obtained from the Aldrich Chemical Co., Milwaukee, WI, in I.R. grade purity. These phenyl ethers were used as "modifiers" or additives in the PVDF membranes.

A number of commercially available polymeric plastics were used as membranes. In the list of these materials that follows, all films were manufactured by E. I. Dupont De Nemours Co., Inc., Wilmington, DE, unless otherwise noted.

Teflon® (FEP) fluorocarbon film, type 200A, obtained in 2 mil thickness.

Tedlar® polyvinylfluoride (PVF) film.

Cellulose acetate, type 100CA43, 2 mil thickness.

Mylar® polyester film, type S, 50 gauge (0.5 mil thickness)

Kapton® polyimide film, type 100H, 1 mil thickness.

Cellophane type PD150 film, 1.3 mil thickness.

Glysar P® polyolefin (polypropylene) type P-1A3 film, 0.85 mil thickness.

Polyethylene type A, 1.25 mil thickness.

Polyethersulfone (PES) film, manufactured by Westlake Plastics Co., Lenni, PA.

Polysulfone, 5 mil thickness, obtained from Union Carbide.

Capran® 77C nylon film, manufactured by Allied Chemical Co., 1 mil thickness.

Trycite® polystyrene film, 1 mil thickness, Dow Chemical, Midland, MI.

Saran® polyvinylidene chloride, polyvinyl chloride copolymer, Dow Chemical, Midland, MI.

Equipment and Apparatus

The experimental permeation system is shown schematically in Figure 2. The major system components include: (1) permeation cell; (2) feed supply; (3) sample capture and flow measurement equipment; (4) constant temperature enclosure; and (5) helium purge gas system. The entire experimental apparatus was assembled in a fume hood to prevent accidental human exposure to the BF_3 gas. The major system components are described separately below.

Permeation Cell

The "heart" of the experimental system is the permeation cell. This device supports and houses the thin polymeric membrane and separates the experimental system into regions of high and low pressure. An exploded schematic indicating the permeation cell construction arrangement is shown in Figure 3. The cell body consists of two stainless steel flanges, 6.5 centimeters in diameter, which are held together by a large compression nut. A porous monel or stainless steel disc fits snugly into the cavity of the low pressure flange. This disc provides the necessary membrane support while allowing unrestricted flow of the permeant gas.

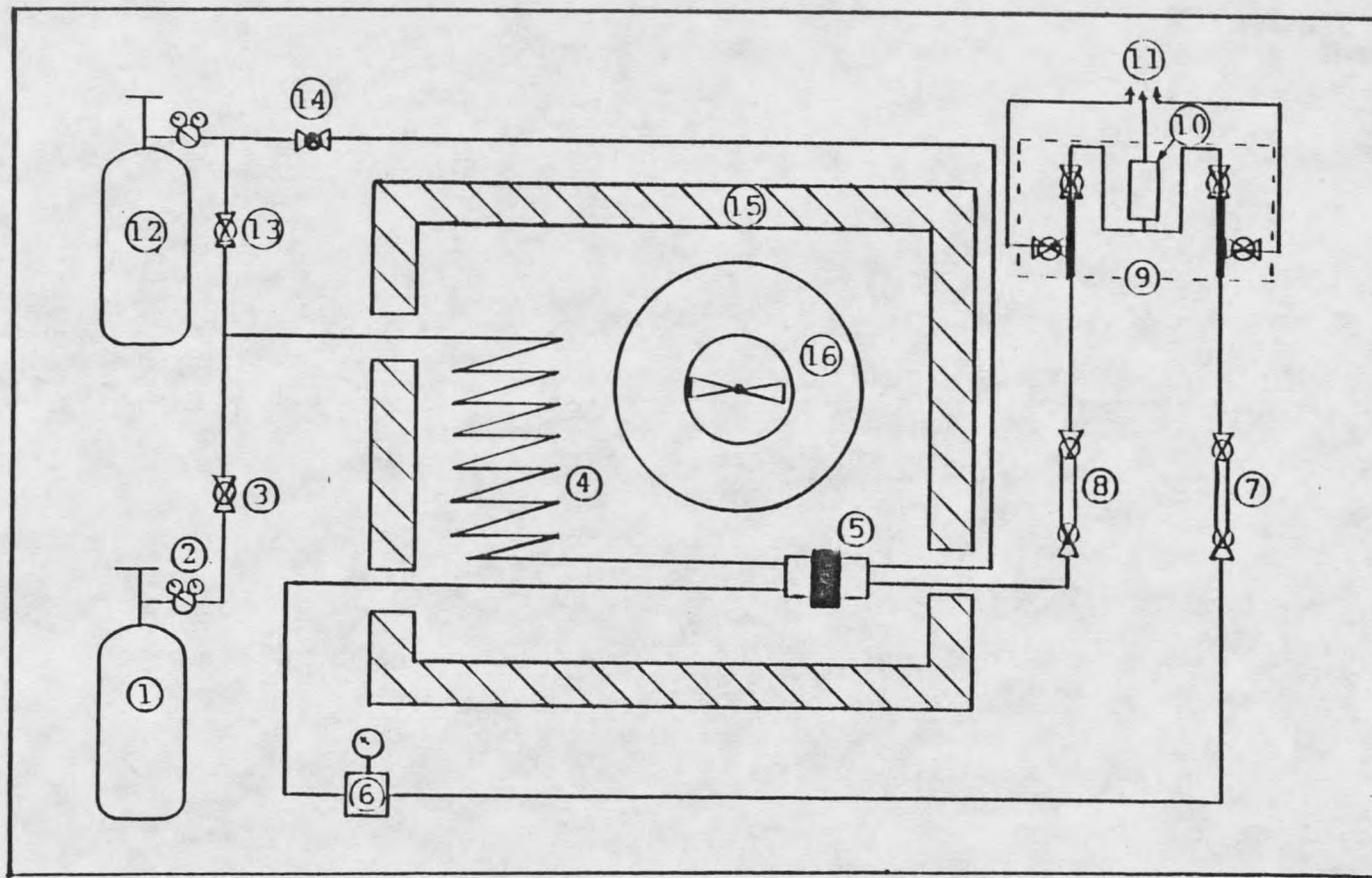


Figure 2. Permeation equipment diagram. (1) Feed gas, (2) pressure regulator, (3) feed control valve, (4) heat exchanger coil, (5) permeation cell, (6) back pressure regulator, (7) reject sample capture reservoir, (8) permeate sample capture reservoir, (9) flow measurement manifold, (10) flow transducer, (11) vent, (12) purge gas, (13) high pressure purge control valve, (14) permeate purge control needle valve, (15) constant temperature enclosure, (16) fan and heater assembly.

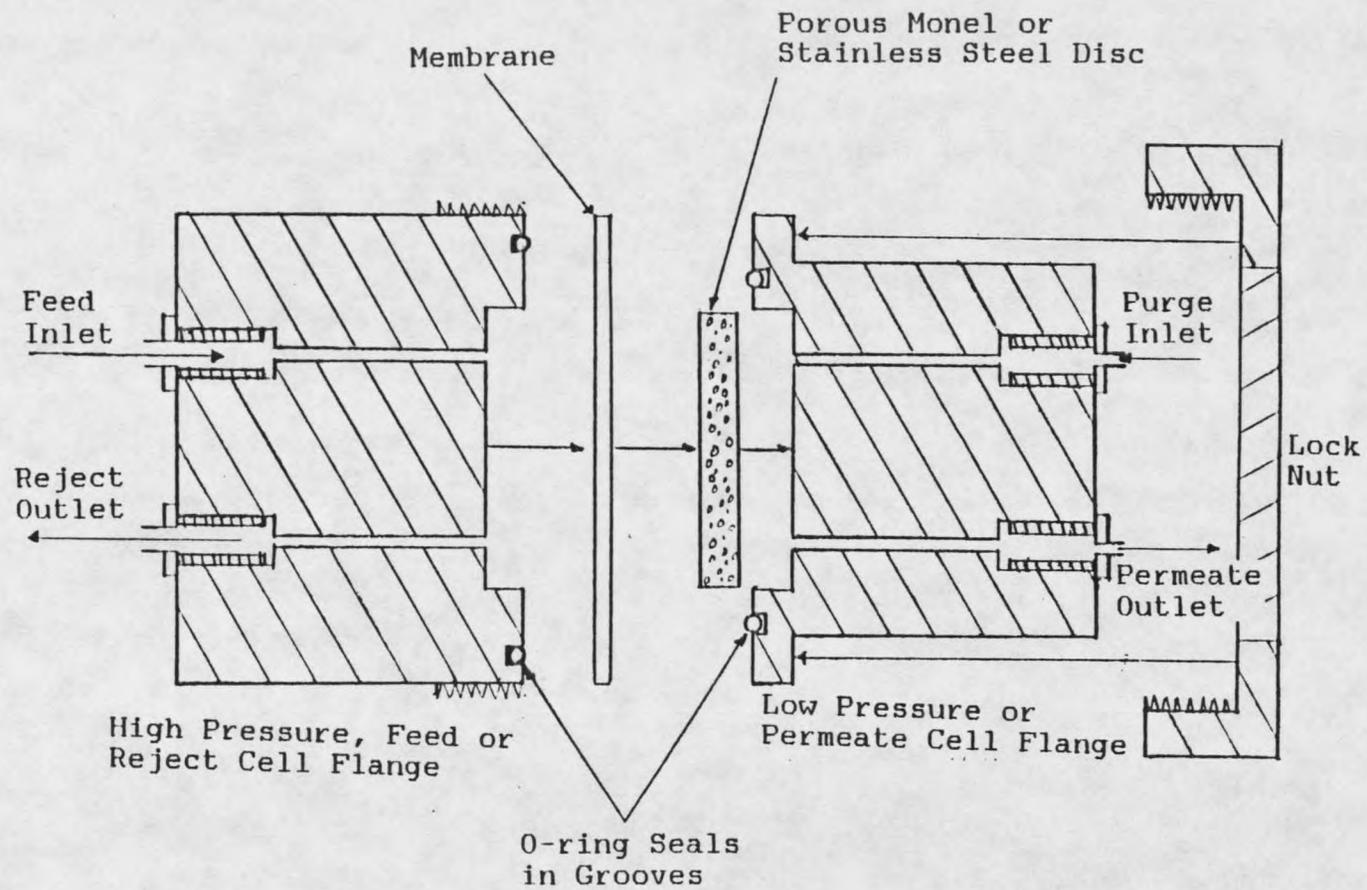


Figure 3. Exploded view of the permeation cell.

A thin porous teflon filter disc placed between the membrane and the metal support buffers the membrane from surface discontinuities around the support/flange perimeter. This teflon filter helped eliminate membrane failure under high pressure loads. With this arrangement, there is approximately 17 cm² of membrane area available for permeation. Two o-rings, one in either half of the cell, are placed in machined grooves to provide the necessary seals from the atmosphere and between the two sides of the membrane. The high pressure half of the cell includes a feed inlet, reject outlet and thermocouple well. The inlet on the low pressure side of the cell was connected to the purge gas system, while the low pressure outlet allowed purge gas or permeate to exit the cell.

Feed Gas Supply and Control

A cylinder of BF₃ gas equipped with a Matheson pressure regulator supplied the pressurized feed to the high pressure side of the membrane. The desired operating pressure on the feed side of the membrane was maintained and controlled by a Grove back pressure regulator. A pressure gauge in the reject line was utilized to monitor the feed side pressure. A coil of excess tubing in the feed supply line was placed in the constant temperature enclosure to help insure constant feed gas temperature. All tubing utilized in the feed gas system was constructed of 0.125 inch O.D. stainless steel. All valves in contact with the high pressure BF₃ feed gas had teflon stem seals.

Sample Reservoirs and Flow Measurement

Two sample capture reservoirs, one for each of the permeate and reject gas samples, were constructed from a 6 inch length of 0.25 inch

O.D. stainless steel tubing. Each length of tubing was valved at either end. These capture reservoirs were connected to the respective permeate or reject streams from the permeation cell. When a sample of one or both streams was required, the valves were closed and a "plug" of sample was captured for transport and analysis.

During experimental runs, the outlets of the sample capture reservoirs were connected to a flow measurement manifold. The manifold allowed measurements of the stream flow rates independently with only one flow meter and insured the two outlet streams were never in contact. Flow of the stream being measured was directed through the flow transducer of a Matheson model 8160 mass flow meter, while the other stream vented to the atmosphere. Transfer lines from the sample reservoirs to the manifold and the manifold vent lines were 0.125 inch O.D. teflon tubing. The teflon tubing was used since there were no high pressure requirements and the flexibility facilitated easy connection.

Constant Temperature Enclosure

The permeation test cell was placed in a constant temperature enclosure equipped with an electrical resistance heater and a circulating fan. This enclosure provided the heat source and temperature control for permeation tests at elevated temperatures. The temperature was controlled by a Powerstat variable transformer connected to the resistance heater. Temperature measurement was effected by a Fluke digital thermometer connected to a thermocouple located in the thermowell of the test cell. With this arrangement, the temperature in the enclosure could be controlled and monitored to within 1°C.

Purge System

The purge gas supply system consisted of a cylinder of ultra high purity (UHP) helium connected to a Matheson pressure regulator. Purge gas to the high pressure side of the cell was fed through a valve into the BF_3 supply line just below the BF_3 regulator (refer to Figure 2). A second line was used to supply purge gas through a needle valve to the permeate side of the membrane. This arrangement allowed the entire experimental system to be purged prior to a permeation testing, thus eliminating air and possible contaminants from the system. Furthermore, either the high or low pressure side of the cell could be purged independently.

Experimental Procedures

Permeation Test Procedure

A properly sized membrane was cut from the material to be tested using a permeation cell flange as a template. The membrane was then loaded and sealed in the test cell. The integrity of the membrane and cell seals was tested by pressurizing the high pressure side of the cell with UHP helium. By monitoring any gas flow from the permeate outlet with a beaker of water, undesirable leaks in the membrane could be detected prior to mounting the cell in the test system. The same procedure could have been effected with the purge gas system of the experimental apparatus, but it was less cumbersome when conducted outside of the fume hood.

The pressure-tested permeation cell was mounted in the constant temperature enclosure and the corresponding supply or exit lines were

connected. With all lines connected and the sample reservoirs in place, the purge gas supply valve to the high pressure side of the cell was opened. The purge gas pressure was maintained at approximately 200 psig on the high pressure side of the membrane using the back pressure regulator. Purge gas flow rate was adjusted with the helium tank regulator by increasing helium pressure to just above the pressure maintained by the back pressure regulator. The needle valve controlling purge gas flow to the permeate side of the cell was opened and used to adjust the purge gas flow rate through the low pressure side of the experimental system. It was necessary to maintain the high pressure on the unsupported side of the membrane while adjusting the purge gas flow, since the membrane could easily be ruptured by a pressure surge from the permeate side of the cell. The system was allowed to purge for 10 to 24 hours prior to commencement of a test run.

After suitably purging the system, the purge gas supply valves were closed and the BF_3 supply valve opened, initiating the permeation test. The system was brought up to the desired temperature and the reject flow rate and high pressure were adjusted. The permeate flow was monitored continuously with the mass flow meter. Reject flow was set by simply watching the gas flow being vented to the atmosphere. The permeate flow rate was manually monitored and recorded until a steady state permeation rate was achieved. In order to facilitate representative samples, the system was allowed to operate for several hours after attaining steady state. The reject flow rate was then monitored and recorded. At that point, the sample capture reservoir valves were closed and the samples were ready for analysis. Due to the complex nature of the mass spectral

analysis procedure, a thorough discussion of this topic is delayed to a subsequent section.

Membrane Fabrication

In order to study isotopic separation by the complex transport mechanism, several membranes were fabricated incorporating BF_3 -ether complexes of either anisole or phenetole. In other cases, modified membranes were prepared by adding an ether directly. The BF_3 complexes were prepared by bubbling BF_3 feed gas through the respective ether for several hours. Complex formation was accompanied by a color change from the clear ether to a brown/orange color of the complex. In the case of diphenyl ether, complex formation was not attempted although such a complex is certain to exist. Hence, the diphenyl ether was added directly as a membrane modifier.

The fabricated membranes were prepared by dissolving 4 to 5 grams of polyvinylidene fluoride (PVDF) in 5.7 ml of dimethyl formamide (DMF) per gram of PVDF. A predetermined, weighed amount of the ether or BF_3 -ether complex was then added to this solution for a 10% mixture on a dry weight PVDF basis. The mixture was heated at 100°C with constant stirring for several hours to insure complete solution, then covered and allowed to stir for 24 to 48 hours at ambient temperature.

The membrane solution was then poured or cast onto a clean glass plate with raised edges. The height of the edges on the mold controlled the membrane thickness, usually about 0.005 inches (5 mil). Once cast onto the glass, the solution was smoothed with a clean glass rod and placed in an oven at 100°C for about 1 hour. The baking process drove

off the DMF solvent, leaving a solid, uniformly thick membrane which was easily removed from the glass plate.

Mass Spectral Analysis

The development of a reliable mass spectral procedure for determination of boron isotopic ratios in BF_3 samples provided a number of unique challenges. Obstacles such as the systematic isolation and elimination of components constructed from materials which reacted with BF_3 and produced unwanted species had to be considered accordingly. It was necessary to determine a number of optimum instrument operating parameters to insure consistent day-to-day analysis of the boron isotopic ratio in BF_3 samples. Considerations such as the choice of mass spectral signals used for isotopic analysis, corrections to these signals for interfering ions, the effect of memory and the isotopic abundance of boron in the BF_3 feed gas were also taken into account. Obviously, the determination of boron isotopic content was neither a straightforward nor simple measurement. Due to the highly non-routine nature of the isotopic abundance analysis, the following discussion is included for completeness.

The mass spectrometer utilized in all analyses was a VG Scientific MM16F located in the chemistry department at Montana State University. This magnetic sector instrument was operated in electron impact ionization (EI) mode with positive ion detection. A data collection system using a Digital PDP8/A hard drive incorporated the necessary software and interfaces for data collection and processing as well as automation and control of many mass spectrometer functions. Consistent analyses were obtained with an amplifier gain (VG Scientific, FA3) of 10^{-6} amps and

