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ORNL-2069
Isotope Separation

THE ANCO SYSTEM FOR BORON ISOTOPE ENRICHMENT

R. M. Healy
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THE ANCO SYSTEM FOR BORON ISOTOPE ENRICHMENT

SUMMARY

A new gas-liquid countercurrent system (the ANCO system from ANisole-COmplex) for the enrichment of boron isotopes has been developed. It is believed that use of this system will result in a considerably lower unit cost for enriched boron-10 than was previously possible.

The system utilizes the exchange reaction between BF_3(gas) and BF_3·anisole(liquid) to concentrate boron-10 in the liquid phase. The single stage isotopic separation factor for this system has been found to vary from 1.039 at 0°C to 1.029 at 30°C. The isotopic exchange reaction has been shown to be rapid. Vapor pressures of the complex as a function of temperature have been measured and the heat of formation of the complex determined. Laboratory experiments show that quantitative removal of the BF_3 from the complex can be accomplished by heating.

A complete minature ANCO plant was constructed and operated in the laboratory to test the feasibility of the system. The system was found to operate efficiently with a minimum of attention, and to enrich the isotopes of boron as expected.

Based upon the experience obtained with the laboratory ANCO unit, a pilot plant large enough to utilize a 6-inch diameter exchange column was designed. The design calculations of the major pieces of equipment are presented.

INTRODUCTION

Natural boron consists of two isotopes, boron-10 and boron-11. Boron-10, which has an abundance of 18.8% , is a desirable nuclear material because of its high thermal neutron absorption cross section. Methods of boron isotope concentration were considered at Columbia University in 1943.[1] As a result of this early study a method of boron isotope enrichment was conceived and developed. In this method of separation, BF_3·dimethyl ether complex was distilled at sub-atmospheric pressure. Boron-11 concentrated at the top of the column and boron-10 in the still pot. The effective single stage isotopic separation factor obtained in the distillation was 1.016.

Since the early efforts led to success so quickly, several areas of investigation were not studied extensively in the laboratory. This was especially true to the gas-liquid chemical exchange type of system where higher separation factors and through-puts can be attained. With this in mind, members of the Materials Chemistry Division of Oak Ridge National Laboratory began a systematic investigation of systems of this type. Although this search is not yet complete, it has resulted in development of a promising system for boron isotope enrichment, the ANCO system[2]. It is believed that this system offers several advantages over the BF_3·dimethyl ether system, and that with it, concentrated boron-10 can be produced at a

considerably lower unit cost. Furthermore, it is believed that a minimum of new equipment would be needed if a conversion of the present plant to the ANCO system were contemplated.

DESCRIPTION OF THE SYSTEM

In the ANCO system, BF_3 gas passes countercurrent to BF_3·anisole complex. Boron-10 is concentrated in the liquid phase. Reflux is accomplished at the boron-10 end by dissociating the complex with heat, and at the boron-11 end by absorbing the BF_3 in anisole. This is shown schematically in Fig. 1. Heat must be supplied to the decomposer and removed from the recombiner.

LABORATORY RESULTS

Separation Factor

Experimental determinations were made of the isotopic separation factor as a function of temperature. This data is summarized in Fig. 2. Details of this work can be found in Appendix A. The single stage separation factor was found to vary from 1.039 at $0^{o}C$ to 1.029 at $30^{o}C$. As with the BF_3·dimethyl ether system, the boron-11 was found to concentrate in the gaseous phase. The gas phase of the ANCO system, in contrast to the BF_3·dimethyl ether system, contains very little undissociated complex, and this contributes to the increased separation factor. The effective enrichment factor

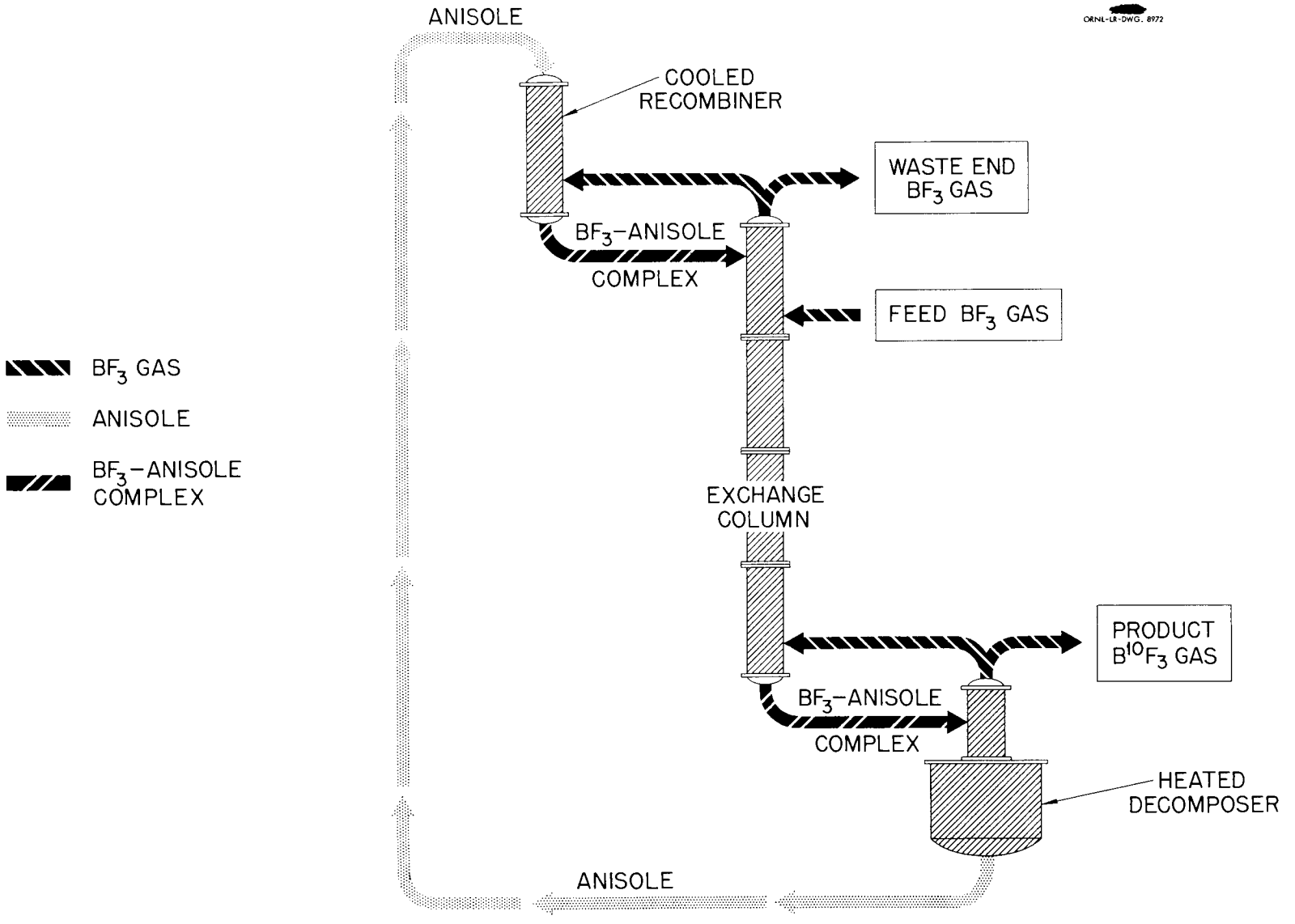

Fig. 1. ANCO System for Boron-10 Enrichment.

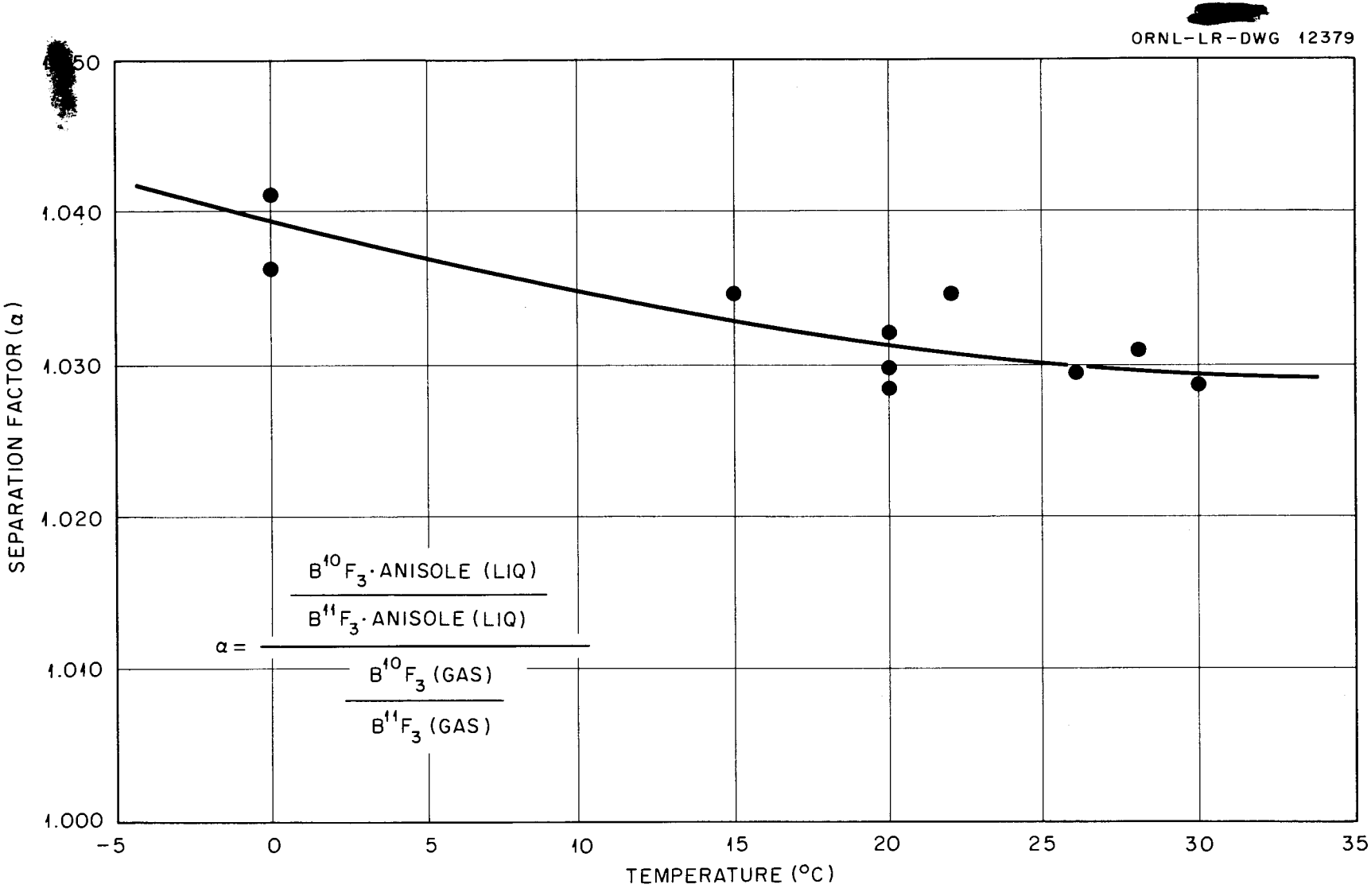

Fig. 2. Separation Factor as a Function of Temperature.

(separation factor -1) for the ANCO system is approximately twice that of the BF_3·dimethyl ether system. The high enrichment factor, the higher throughput which results from higher pressures, and the facility with which BF_3 product may be withdrawn, are believed to be important advantages over the dimethyl ether system.

Rate of Isotopic Exchange

If a chemical exchange system is to be efficient, it is necessary that rapid exchange occur between the isotopic species in each phase. The rate of exchange of the boron species in the ANCO system was studied under laboratory conditions through the use of enriched BF_3 gas and normal BF_3·anisole complex. Details of these experiments are given in Appendix B. The exchange was found to be complete after a few seconds. This exchange rate is quite adequate for efficient use in countercurrent exchange columns.

Regeneration of BF_3 from Complex

In order to determine if BF_3 could be quantitatively removed from the BF_3·anisole complex, laboratory experiments were performed in which the complex was heated and the BF_3 allowed to escape. Samples were taken of the residual anisole, and it was found that at the boiling point of anisole the amount of BF_3 left in the anisole was reduced to an average of 56 ppm on a mole basis. Details of these experiments are given in Appendix C. The amount of BF_3 left in

the anisole was found to be essentially independent of the BF_3 pressure over the complex in the range studied. This was apparently due to the increased boiling temperature of the liquid under an increased head of BF_3. If, in plant operation, the BF_3 content of the recirculating anisole can be reduced to this order of magnitude, operation of the reflux should be satisfactory since this would constitute a very small percent of the total product drawoff.

Vapor Pressure of BF_3·Anisole Complex

In conjunction with the measurements of the isotopic separation factor and the study of the decomposition of the BF_3·anisole complex, measurements of the vapor pressure of the complex were made. These measurements are summarized in Fig. 3. Details of the procedures used may be found in Appendix D. Using the integrated Clausius-Clapeyron equation with these data, an approximate value of $\Delta H = -12$ kcal/mole was estimated for the heat of formation of the complex as in the reaction:

$$BF_{3(g)} + \text{Anisole}_{(liq)} \rightleftharpoons BF_3 \text{ Anisole}_{(liq)}$$

Laboratory Scale ANCO Plant

In order to demonstrate the actual feasibility of the ANCO system, a small scale laboratory apparatus was built in which tests could be made of the complete cycle as visualized in an actual isotope separation plant. This apparatus is shown schematically in Fig. 4. It consisted of a bubble cap

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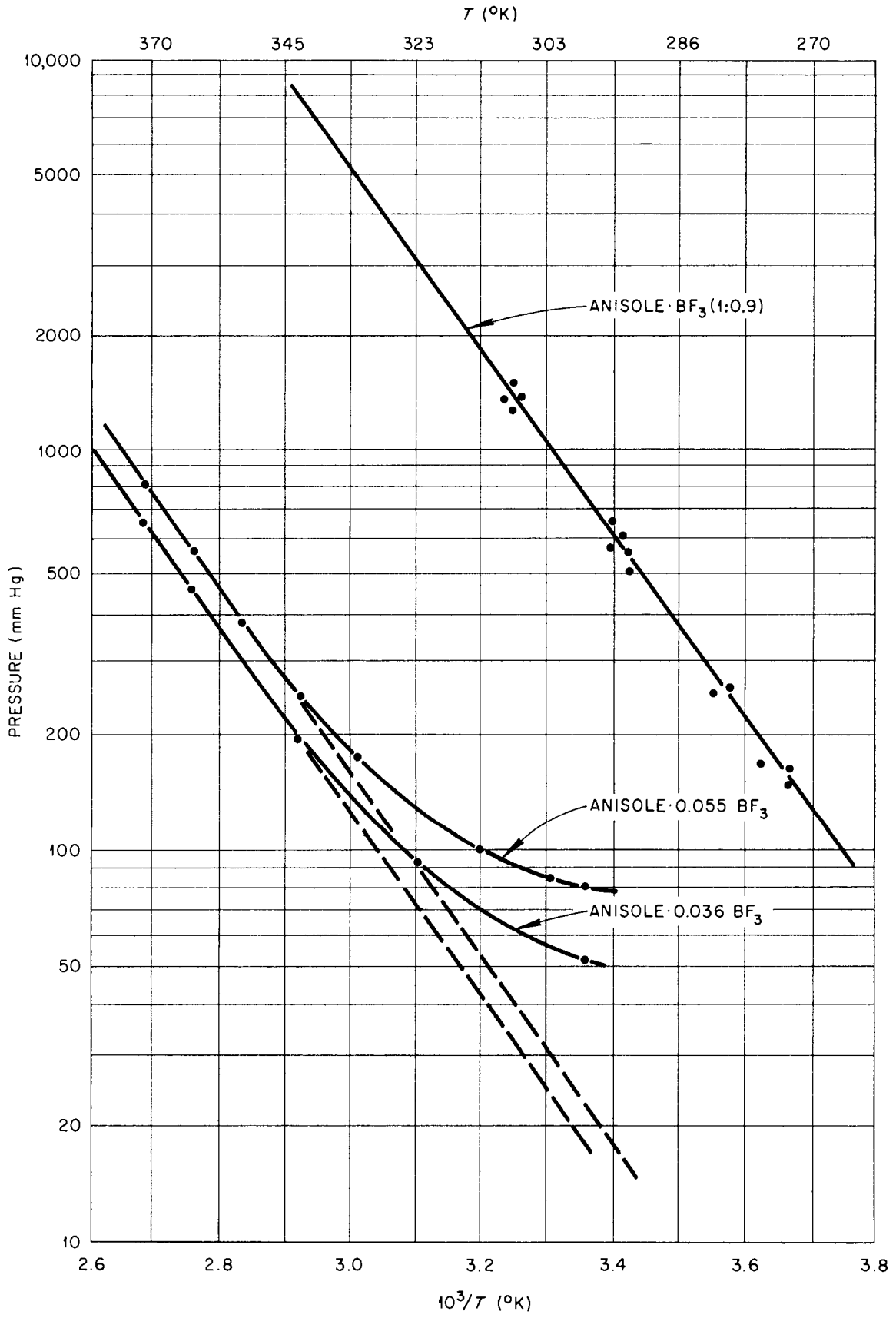

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Fig. 3. Vapor Pressure over Anisole–BF_3 Complex.

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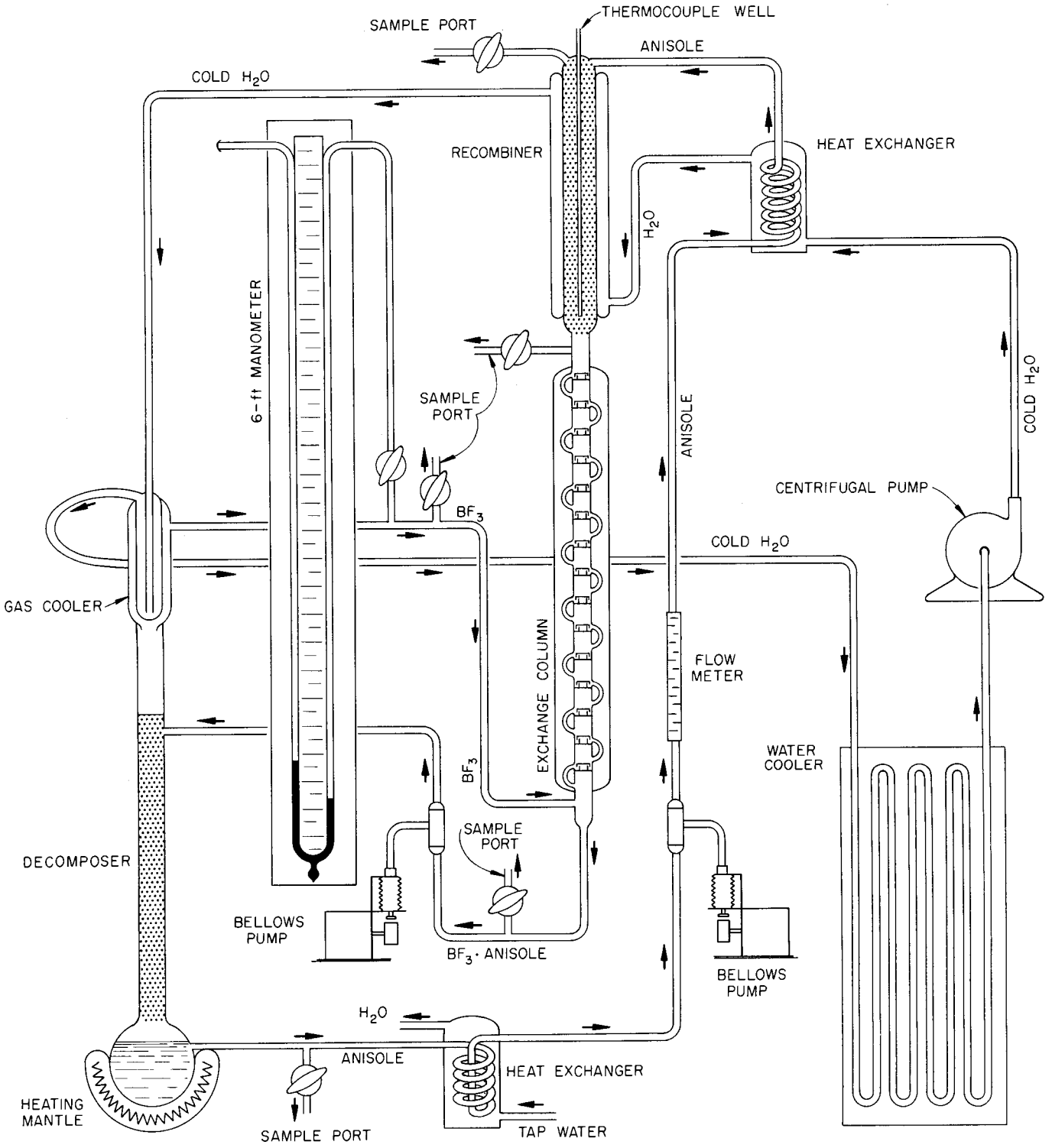

Fig. 4. Semi-Pilot Plant Apparatus used to Study the System $BF_{3\,(GAS)} \rightleftharpoons BF_3 \cdot ANISOLE_{(LIQ)}$.

exchange column, a decomposer with stripping column and condenser, and a packed recombiner with associated pumps and cooling equipment. The complete description of the apparatus can be found in Appendix D along with typical operating data. In general, it was found that operation was simple and easier to control than anticipated. Total isotopic fractionation showed a bubble cap efficiency of approximately 50%. Very little decomposition was apparent. Pressure increase was extremely slow after the initial equilibrium was established. The slow build up of boron decomposition products in the decomposer took place at a decreasing rate as time of operation increased. A red coloration appeared in the liquid phase of the recombiner. It is believed that this color results from the formation of a complex between an impurity and BF_3. The boron content of the stripped anisole was analyzed to be about 0.2 moles per 100 moles of anisole, which was considerably higher than the static tests. It is believed that this will be considerably less after anhydrous conditions are established, or that cleanup of a small fraction of the total anisole flow will substantially reduce this value. The stability and operating characteristics of the system were very satisfactory, and no difficulties are foreseen in larger scale operation.

PILOT PLANT DESIGN

The successful operation of the small laboratory ANCO

unit motivated the design of a larger pilot plant in which the ANCO system might be tested more fully. The design calculations were based on the use of a 6-inch diameter exchange column packed with Monel protuded packing. In addition to the exchange column, the following equipment was defined: the decomposer column, the decomposer reboiler, the anisole cooler, the BF_3 gas cooler, the recombiner, and the pumps. The characteristics of the equipment were based on the best information currently available. It is anticipated that some changes may be necessary in the design as additional characteristics of the system become apparent. Detailed specifications for the equipment were not determined,since it is intended that existing equipment will be utilized when available. The design criteria and calculations are shown in Appendix G.

APPENDIX A

Determination of the Isotopic Separation Factor[3,4]

The single stage separation factor for the ANCO system is the equilibrium constant for the reaction

$$B^{10}F_{3(g)} + C_6H_5OCH_3 \cdot B^{11}F_{3(liq)} \rightleftharpoons B^{11}F_{3(g)} + C_6H_5OCH_3 \cdot B^{10}F_{3(liq)}$$

The procedure used in measuring the single stage separation factor was as follows. A known amount of purified and distilled anisole (80-100 grams) was placed in a jacketed suction flask (see Fig. 5), containing a glass-encased stirring magnet. The flask was attached to the vacuum line, the anisole was frozen, and the apparatus was evacuated by means of the vacuum pump. The reaction flask was then isolated from the rest of the system, and boron trifluoride was admitted to the system from the BF_3 tank. The temperature and pressure of the gas were measured, and from a knowledge of the total volume of the system, the exact number of moles of BF_3 present were calculated. Enough BF_3 was admitted to the system so that approximately 150 cc (STP) of gas was present in excess of the amount required to prepare the 1:1 $C_6H_5OCH_3 \cdot BF_3$ complex. The BF_3 was purified by freezing it with liquid nitrogen, and evacuating the system to remove air or any other non-condensibles. Stopcock A was closed, and the gas was allowed to vaporize. Eight initial samples of gas were taken by sealing off the break-seal tubes.

The anisole was cooled to $0^{\circ}C$ by recirculating ice water

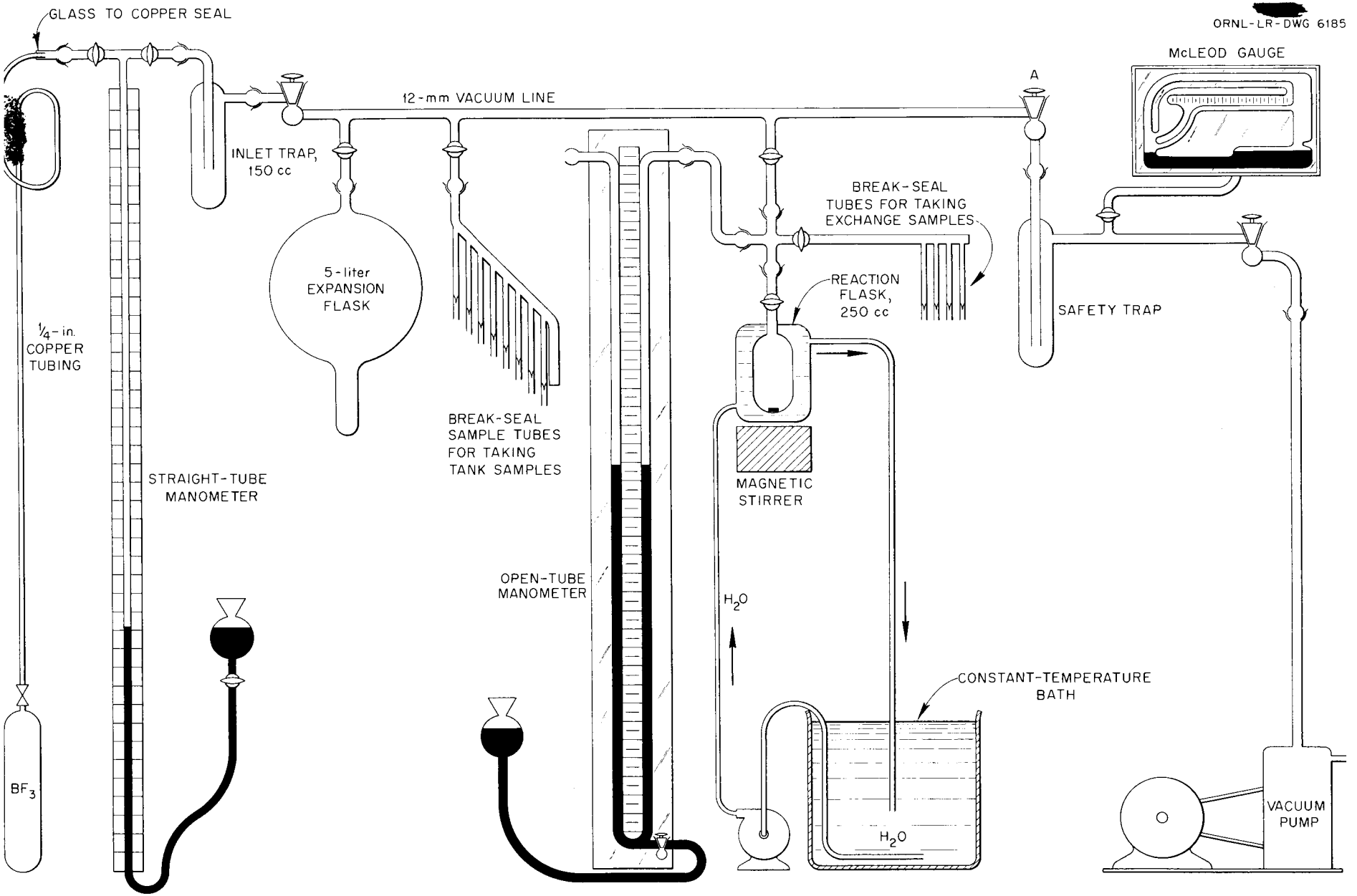

Fig. 5. Apparatus for Studying the System $BF_{3(GAS)} \rightleftharpoons BF_3 \cdot ANISOLE_{(LIQ)}$.

through the jacket of the reaction flask. The stopcock on the reaction flask was opened to the system to allow the BF_3 and the anisole to react. The reaction proceeded very smoothly at $0^{o}C$. When the reaction was complete, the residual BF_3 and the complex were frozen in the reaction flask, and the stopcock to the flask was closed. The system was warmed to operating temperature, and the liquid phase was stirred for 2 to 7 hours. After equilibrium was attained, the reaction flask was opened momentarily to allow a predetermined amount of BF_3 to escape to the exchange sampling system. This gas was frozen and was then distilled to free it from traces of $C_6H_5OCH_3 \cdot BF_3$ vapor. The B^{10}/B^{11} ratios of the initial and final samples were measured on a mass spectrometer.

It was unnecessary to sample the liquid phase because the anisole complex was present in so great an excess that its isotopic composition remained essentially unchanged throughout the experiment. The separation factor was calculated by taking the ratio of the B^{10}/B^{11} ratios in the initial and final samples. Results (see Fig. 2) are tabulated in Table 1.

TABLE 1. SEPARATION FACTOR AS A FUNCTION OF TEMPERATURE FOR THE ANCO SYSTEM

Run No.	Temperature (°C)	Separation Factor*
4	22	1.0345
8	20	1.0297**
9	20	1.0284**
10	0	1.0410
11	20	1.0280
12A	25	1.0346
12B	28	1.0307
13A	30	1.0288
13B	26	1.0295
14A	0	1.0364
14B	15	1.0344

* Separation Factor $= \dfrac{(B^{10}/B^{11})_{liquid}}{(B^{10}/B^{11})_{gas}}$

** Average of 3 analyses

APPENDIX B

The Rate of Exchange of Boron Between $BF_{3(gas)}$ and $BF_3 \cdot Anisole_{(liquid)}$[4]

To determine the rate of exchange between BF_3 gas and the anisole·BF_3 1:1 complex, the apparatus shown in Fig. 6 was used. This apparatus consisted of a 300 cc round bottom flask to which a 28/15 ball joint and a 3-way stopcock were attached. The flask was used as a gas-liquid contactor. The 28/15 ball joint was used to attach a thin-walled break tube that contained a known amount of BF_3·anisole complex. The 3-way stopcock was used to attach a set of sampling tubes, and also provided a means of evacuating the entire apparatus. Experiments with contacting times of the order of 4 seconds were possible.

The procedure for making a determination was as follows. After the apparatus had been cleaned and dried and a weighed amount of BF_3·anisole complex placed into the thin-walled break tube, it was assembled and attached to a vacuum manifold and evacuated. The break-seal gas sampling tubes were then isolated from the rest of the apparatus, and a known pressure of BF_3 gas was admitted to the 300 cc flask. The flask was closed and the apparatus was removed from the vacuum line. The 28/15 ball joint was then tilted until the thin-walled break tube was fractured, allowing the liquid complex to drop into the flask containing the BF_3 gas. The entire apparatus

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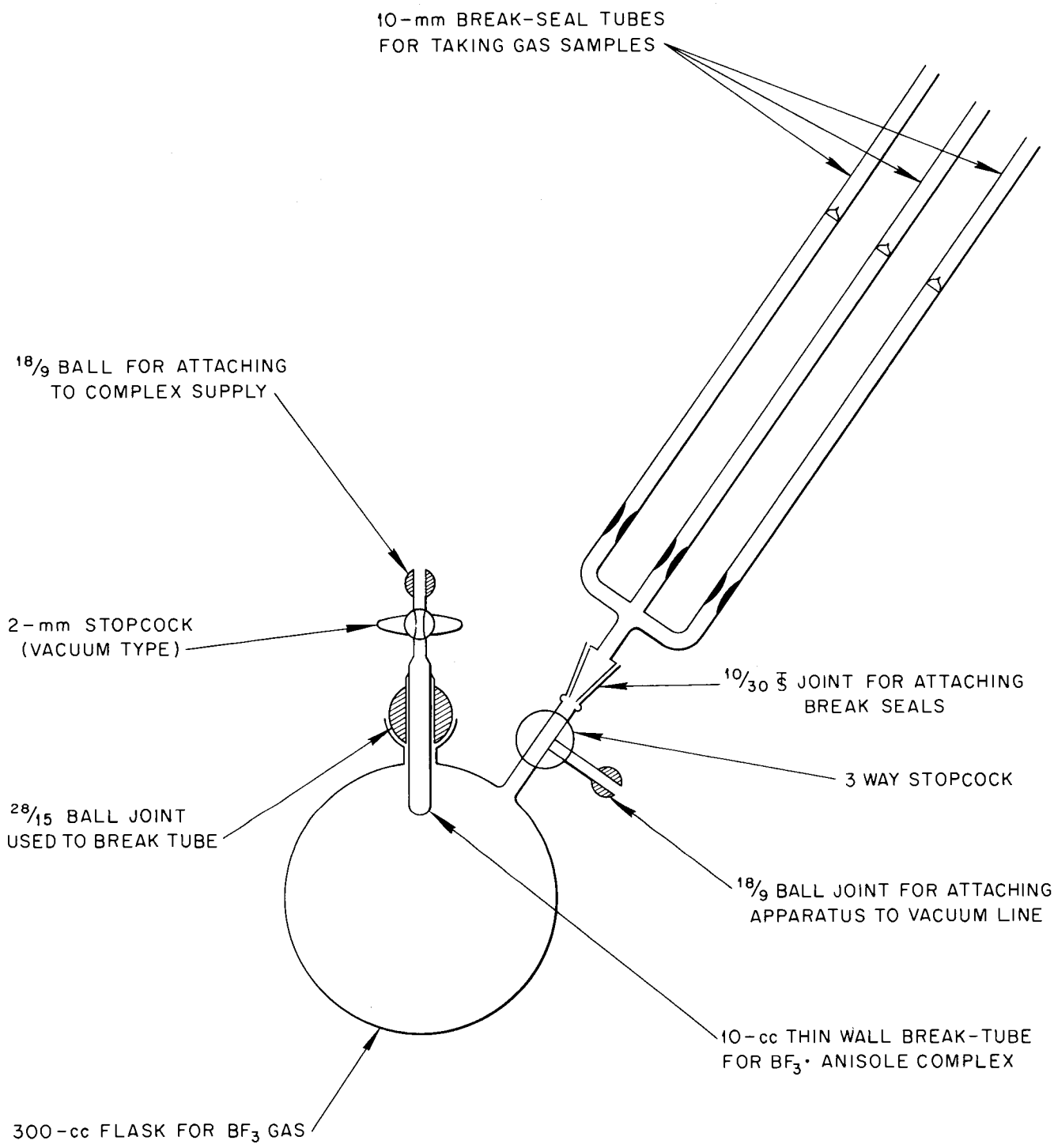

[redacted]. Apparatus Used to Study Exchange Rate for the System $BF_3(g) \rightleftharpoons$ Anisole $\cdot BF_3(l)$.

was then vigorously shaken by hand for the desired interval of time, after which the 3-way stopcock was momentarily opened allowing gas to enter the evacuated break-seal gas sampling tubes. The tubes were sealed off and the ratio of B^{10}/B^{11} determined by mass spectrometer analyses.

By knowing the total volume of the apparatus, the amounts of gas and liquid present, and the initial concentration of boron-10 in both phases, the concentration of boron-10 resulting from complete exchange could be calculated. From mass analyses of the gas phase before and after contact, the degree of exchange during the interval of contact could be determined.

Three separate runs were made and are shown in Table 2. The first run was made with normal BF_3 gas and normal BF_3·anisole complex, in order to check the operation of the equipment. The last two runs were made with 40% $B^{10}F_3$ gas and normal BF_3·anisole complex. The results show that exchange is quite rapid. With sufficient agitation, exchange was complete in less than seven seconds. The time measurement shown in the table is the total elapsed time for the experiment. Approximately 3 seconds were necessary for manipulating stopcocks, etc. Hence, contact time for the 7 second experiment was on the order of 4 seconds.

TABLE 2. RATE OF EXCHANGE

$$B^{10}F_3(g) + B^{11}F_3 \cdot C_6H_5OCH_3(liq) \rightleftharpoons B^{11}F_3(g) + B^{10}F_3 \cdot C_6H_5OCH_3(liq)$$

Wgt of Complex* (g)	Vol. BF_3 S.T.P. (cc)	Time	Measured % B^{10}		Equilibrium % B^{10}	
			Before	After	Calc.	% Exch.
9.04	170.6	2 min.	(1.034)**		-	-
10.523	224.5	15 sec.	40.71	23.05	23.2	~100
10.207	164.0	7 sec.	40.82	23.96	21.45	90

* Complex analyzed 35.2% BF_3 = 0.87 moles BF_3/mole anisole.

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

APPENDIX C

Regeneration of BF_3 from Complex[2]

Reflux at one end of the ANCO system is accomplished by heating the BF_3·anisole complex to regenerate BF_3. In the production of boron-10, this end is the product end, and the BF_3 must be separated quantitatively from the anisole.

The reflux was studied in the apparatus shown in Fig. 7. Anisole was introduced into the reaction vessel, air was removed, and complex was formed by the addition of BF_3. The blow-off manometer, which determined the pressure at which BF_3 escaped from the system, was connected. The reaction vessel was heated, and its temperature rose until the mixture in the reaction vessel reached its "boiling point" under the pressure chosen. Anisole did not pass the water condenser. When the BF_3 ceased to escape, the liquid in the reaction vessel was sampled. The results are given in Table 3.

TABLE 3. DECOMPOSITION OF BF_3·ANISOLE COMPLEX

T (°C)	Pressure BF_3 (cm of Hg)	Moles BF_3 Remaining per 10^6 Moles Anisole
157.0	80.0	69
159.8	87.5	60
163.2	93.7	42
165.0	99.9	54
166.2	106	59

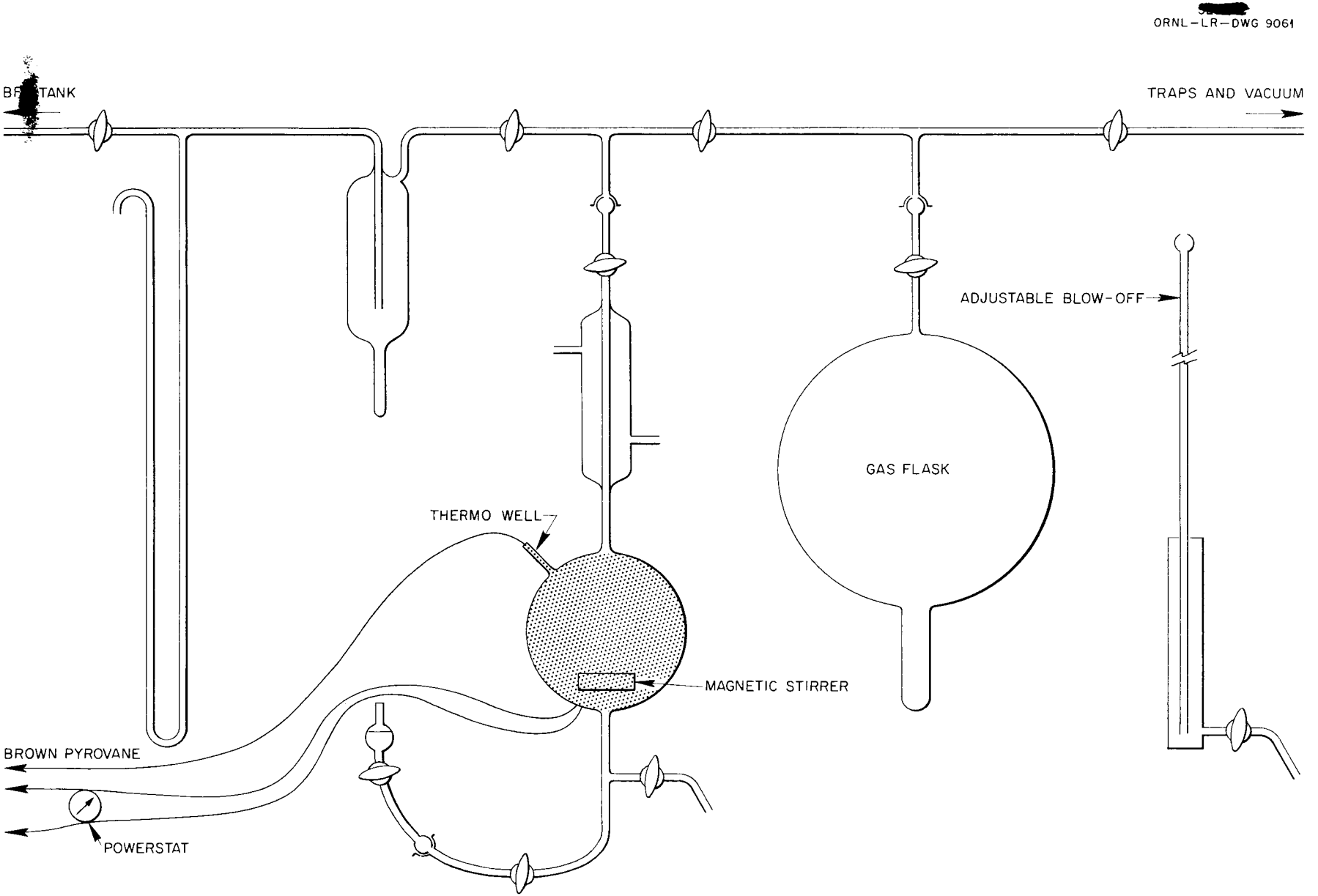

Fig. 7. Apparatus for Studying Reflux Reaction in the ANCO System.

APPENDIX D

Vapor Pressure of BF_3·Anisole Complex[4,5]

Vapor pressure measurements were made in the apparatus used to measure the isotopic separation factor (Fig. 5). After an α determination was completed, the complex in the reaction flask was frozen with a dry ice-acetone mixture, and any excess BF_3 was pumped off. Since the complex freezes at approximately $-12^{o}C$ and BF_3 gas freezes about $-101^{o}C$, dry ice acetone mixtures allowed excess BF_3 gas to be removed from the complex. There was no indication that BF_3 gas was soluble in the liquid complex.

After the excess gas was removed, the stopcocks on the apparatus were adjusted in such a manner that only the manometer was connected to the jacketed reaction flask. Water at a constant temperature was then circulated through the jacket, melting the complex and equilibrating the system at that specific temperature. After several readings were made to insure that equilibrium was attained, the temperature was changed and the process repeated. Readings were taken from several separate batches of complex from 0^{o} to $39^{o}C$. Since the volume of the thermostated part of the apparatus was large compared to the volume of the external system, and since pressure measurements were made at temperatures not too far removed from room temperature, no corrections were applied to these readings.

Vapor pressure measurements of BF_3·anisole complex containing much smaller amounts of BF_3 were made in the apparatus used to study the reflux reaction (Fig. 7). Both series of results are shown in Fig. 3. These results were combined to calculate the -12 kcal/mole heat of formation of the BF_3·anisole complex.

APPENDIX E

Laboratory Scale ANCO Plant

The semi-pilot apparatus was assembled to test the operation of the complete cycle of the ANCO system. The system is shown schematically in Fig. 4.

It consisted of an exchange column, a recombiner column, a decomposer and accessory equipment. The exchange column was a one inch O.D. pyrex, 30 plate bubble cap column, 36 inches high with a silvered vacuum jacket. The recombiner was a 22" section of 2" jacketed pyrex tubing packed with 1/8" pyrex helices. It had a thermocouple well down the center, and was attached directly to the top of the exchange column. The decomposer was a separate piece of apparatus consisting of a one liter, mantle-heated, boiler pot to which was attached a 2 ft section of 1-1/2" pyrex tubing packed with 1/8" glass beads. To the top of this tube was attached a Friedricks condenser. All pressure and sampling lines were 1/8" O.D. copper tubing. Water lines were 3/8" tygon tubing. Copper to glass connections were made by means of Kovar or Housekeeper seals. Microbellows stainless steel pumps transferred anisole and liquid complex, while a small centrifugal pump circulated refrigerated water. All valves used were either 1/4" stainless steel Crane replaceable copper bellows valves with D-29 seats or 1/4" Kerotest stainless steel diaphragm valves. The two heat exchangers were made from 1/4" copper tubing coiled inside a 2 liter

stainless steel jacket through which 8°C water was circulated. A standard office-type Westinghouse water cooler was used to refrigerate cooling water. The manometer was 7 feet high, and was capable of registering 2,000 mm Hg absolute pressure. Temperatures at various points throughout the system were recorded with a Brown Electronic recorder.

Several preliminary runs were made with this apparatus to determine operating procedures and flow rates. The apparatus was cleaned, dried, and evacuated, and enough clean, dry, distilled anisole was admitted to the decomposer pot to fill the pot plus the two feed pump bellows, the transfer lines, and the chambers of the bubble cap exchange column. This required about 700 cc of anisole. The inlet valve was then closed, and the feed and cooling water pumps were started. Heat was applied to the decomposer pot until the anisole began to boil. This temperature was about 42°C. Purified BF_3 gas was then admitted slowly to the bottom of the exchange column through the gas sampling port. As the gas was added, the pressure began to rise causing the boiling temperature of the anisole in the decomposer pot to increase. Addition of gas was continued until the pressure on the system was at one atmosphere. By this time, the boiling temperature in the decomposer had risen to 154°C. Approximately one mole of BF_3 gas was added to attain these conditions. Introduction of BF_3 was then stopped, and the system was allowed to come to chemical and isotopic equilibrium before samples were taken.

In operation, BF_3·anisole complex from the exchange column was pumped to the top of the reflux column. Here, it was decomposed by heat into BF_3 gas and anisole. The BF_3 gas passed upward through the cooling condenser, thence, up through the bubble cap tower and on into the recombiner. The anisole meanwhile flowed downward through the pot boiler and into the lower heat exchanger where it was cooled to 20°C. From here it was pumped through the second heat exchanger (where the temperature was lowered to 8°C) to the top of the recombiner. In the recombiner the anisole moving downward, and the BF_3 moving upward reacted to form the BF_3·anisole complex, which moved downward into the exchange column. In the exchange column, the countercurrent passage of gas and liquid caused the $B^{11}F_3$ to concentrate in the gaseous phase while the $B^{10}F_3$ concentrated in the liquid phase. From the bottom of the exchange column, the complex was pumped into the decomposer, and the cycle repeated. Several runs were made with this apparatus and are shown in Tables 4 and 5. The flow rate was essentially constant for this series at 300 cc anisole/hr. This corresponds to 2.776 moles BF_3 being refluxed per hour or 62.2 liters S.T.P. of BF_3 gas/hr passing up the exchange column. Approximately 22 liters of gas were charged into the system. Hence, there was a complete turnover of BF_3 three times per hour.

TABLE 4. OPERATING TEMPERATURES AND FLOWS FOR RUNS 3-6

COUNTERCURRENT EXCHANGE $BF_{3(g)}$ vs $BF_3 \cdot ANISOLE_{(liq)}$

Anisole flow	300 cc/hr	Cooling water	8 °C
BF_3 flow	62.2 l gas/hr	Operating pressure	800 mm Hg
Free volume of apparatus	1 liter	Effluent from rec.	12 °C
Pot temperature	155 °C	Effluent from exc. column	33 °C
Peak recombiner temperature	52 °C	Gas into exch. col.	24 °C

TABLE 5. COUNTERCURRENT EXCHANGE RUNS

$BF_{3(g)}$ vs $ANISOLE \cdot BF_{3(liq)}$

Run No.	Peak Pot T. (°C)	Peak Press. (mm Hg)	Length of run (hrs.)	Average Assay (B^{10}/B^{11}) Top	Bottom	Total*** Separation	Residual Moles B per 100 Moles Anisole
3	152	865	6	0.2860	*	-	0.147
4	155	950	5	0.2836	0.1997	1.420	0.163
5	162	1150	6	0.2837	0.1970	1.440	0.220
6	146	680**	6	0.3170	0.2080	1.525	-

* Gas sample lost.

** Flow rate during this run was cut to 175 cc/hr anisole which resulted in a larger total separation.

*** $\dfrac{(B^{10}/B^{11})_{top}}{(B^{10}/B^{11})_{bottom}}$

During this series of runs a red color developed in the liquid phase. The color intensity was apparently associated with some type of BF_3 complex, since no color was present in the decomposer pot, and since it appeared in the recombiner at the gas liquid interface. Decomposition as a whole in the system seemed to be slight. A small amount of insoluble material was collected in the decomposer, and slight pressure buildups of what appeared to be SiF_4 were noticed. These were apparently due to traces of water in the system. The time lapse between Run 1 and 6 was about 2 weeks.

APPENDIX F

Physical Properties BF_3 [6,7]

Molecular Weight	67.82
Boiling Point (760 mm)	$-101^{\circ}C$
Melting Point	$-127^{\circ}C$
Critical Temperature	$-12.25^{\circ}C$
Critical Pressure	49.2 atmospheres
Density at $0^{\circ}C$	3.07666 g/l
Specific Gravity of Gas (Air = 1)	2.394
Specific Gravity of Liquid at $-100^{\circ}C$	1.59 g/cc
Specific Gravity of Solid (Approx.)	1.87 g/cc
Cubic Feet of gas per lb.	5.173 at $32^{\circ}F$
Dielectric Constant ($0^{\circ}C$ - 760 mm)	1.119 esu
Dipole Moment	0.0
Specific Heat ($278^{\circ}K$)(Cp)	11.7 (cal/deg mole)
Vapor Pressure between 10 and 50 atmospheres (P in atmospheres, T in $^{\circ}K$)	$\log_{10} P = 5.1009 - \frac{(889.6)}{T}$
Flammability	None
Toxicity	Forms white pungent fumes in air which are difficult to breathe. At high concentrations will cause burns on the skin similar to HF. First aid measures are: washing with large amounts of cold water, dressing with a paste consisting of magnesium oxide, magnesium sulfate glycerine and procaine hydrochloride, then seeing a physician.

Anisole ($C_6H_5OCH_3$)[8,9]

Molecular Weight		108.13
Boiling Point		153.8°C
Melting Point		-37.3°C
Critical Temperature		384°C
Critical Pressure		38.8 atmospheres
Specific Gravity, 18°/4°C		0.996
Dielectric Constant (20°C)		4.41 esu
Dipole Moment		1.23 Debye Units
Specific Heat -	0°C	0.405 cal/gm
	24°C	0.422 " "
	31.6°C	0.462 " "
Vapor Pressure -	40°C	8.4 mm Hg
	60°C	25 " "
	80°C	63 " "
	100°C	140 " "
	120°C	275 " "
Heat of Vaporization (at 153.8°C)		8.8 kcal/mole
Refractive Index (20°C)		1.5165
Viscosity -	2°C	1.508 centipoises
	20°C	1.086 "
	40°C	0.805 "
	100°C	0.419 "
Solubility of H_2O in Anisole -	30°C	0.22%
	70°C	0.36%
Solubility of Anisole in H_2O -	30°C	0.01%
	70°C	0.09%
Anisole - H_2O Azeotrope -		
	Boiling Point	95.5°C
	Wt. % Anisole	59.5%

Surface Tension -	10°C	36.41 dynes/cm
	20°C	35.22 " "
	40°C	32.81 " "
	80°C	28.02 " "
	125°C	22.70 " "

Flash Point (Cleveland Open Cup) 125°F

Toxicity The acute toxicity of anisole by mouth, by inhalation, and by skin absorption is relatively low. The approximate lethal dose (oral) for rats is 5,000 mg/Kg.

BF_3 Anisole[10,11]

Molecular Weight	175.94
Melting Point	-12 to -13°C
Density of 1:1 complex (20°C)	1.2 g/ml
Vapor Pressure	See Fig. 3
Heat of Formation (Kcal/mole)	-12 (Calculated)

APPENDIX G

Design Criteria and Calculations for Pilot Plant

6" EXCHANGE COLUMN

(0.24" x 0.24" Cannon Packing)

Determination of flooding rate:

$G = 270\ (\rho_l)^{0.58}\ (\rho_g)^{0.42}$ *

G = Mass vapor velocity - lbs/hr sq ft

ρ_l = Density of liquid phase - lbs/cu ft

ρ_g = Density of vapor phase - lbs/cu ft

Operation at 25°C Sp Gr = 1.2

ρ_l = (1.2)(62.37 lbs/cu ft) = 74.84 lbs/cu ft

ρ_g = (3.0766 g/l at 0°C)(0.06237)$(\frac{273}{298})$

= (3.0766)(0.06237)(0.916)

= 0.176 lbs/ cu ft

$G = 270\ (74.84 \text{ lbs/cu ft})^{0.58}\ (0.176)^{0.42}$

G = (270)(12.2)(0.482)

= 1587.7 lbs/hr sq ft

6" ID Column

Area = $\pi r^2 = \frac{\pi (3)^2}{144}$ = 0.1963 sq ft

0.24" x 0.24" Cannon Packing has 96% free area.

(0.1963 sq ft) (0.96) = 0.1885 sq ft

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* Distillation Packing and Columns - Bulletin 12, Scientific Development Co., State College, Penn.

Flooding rate:

Gas Flow:

(1587.7 lbs/hr sq ft)(0.1885 sq ft) = 299.3 lbs/hr

$$\frac{(299.3 \text{ lbs/hr})(453.59 \text{ g/lb})}{67.82 \text{ g/mole}} = 2001.8 \text{ moles/hr}$$

$$\frac{2001.8 \text{ moles/hr} \times 22.4 \text{ l/mole}}{28.3 \text{ l/cu ft}} = 1584.5 \text{ cu ft/hr}$$

26.4 cu ft/min

0.44 cu ft/sec

Vapor velocity at flooding:

$$\frac{0.44 \text{ cu ft/sec}}{0.1885 \text{ sq ft}} = 2.33 \text{ ft/sec}$$

70% Flooding

2.33 ft/sec x 0.70 = 1.63 ft/sec

Flow rates - 70% flooding

Vapor:

2001.8 moles/hr x 0.70 = 1401 moles/hr

$$\frac{1401 \text{ moles/hr} \times 22.4 \text{ l/mole}}{28.3 \text{ l/cu ft}} = 1109 \text{ cu ft/hr}$$

18.48 cu ft/min

0.308 cu ft/sec

Liquid:

Assume 1:1 complex - Therefore the liquid flow will be equal to vapor flow mole to mole.

Complex Flow:

$$\frac{1401 \text{ moles/hr} \times 175.95 \text{ g/mole}}{453.59 \text{ g/lbs}} = 543.5 \text{ lbs/hr}$$

$$\frac{543.5 \text{ lbs/hr}}{(1.2)(8.34 \text{ lbs/gal})} = 54.3 \text{ gal/hr}$$

Anisole Flow:

$$\frac{1401 \text{ moles/hr} \times 108.13 \text{ g/mole}}{453.59 \text{ g/lbs}} = 334.5 \text{ lbs/hr}$$

$$\frac{334.5 \text{ lbs/hr}}{(0.9726)(8.34 \text{ lbs/gal})} = 41.2 \text{ gal/hr}$$

The basis for the calculations for a 6" diameter exchange column will be a column vapor velocity of 1.63 ft/sec which is 70% flooding for 0.24" x 0.24" Cannon packing.

For the 1:1 molar complex, the flow rates will be:

Molar flow = 1401 moles/hr

Gas rate = 1109 cu ft/hr

Complex flow = 54.3 gal/hr

Anisole flow = 41.2 gal/hr

DECOMPOSER COLUMN

Duty: To provide surface area and vapor space for the decomposition of the anisole-BF_3 complex.

Selection:

Diameter: 12 in. (minimum)

Length: 10 ft

Material of Construction: Monel or stainless steel.

Packing: Cannon Packing (0.24" x 0.24")

Feed inlet to be 2 ft from the top of the column. Two temperature control points to be located 2 ft apart in the center of the column.

Check on column loading using Cannon packing 0.24" x 0.24". Flooding rate - 1587.7 lbs/hr sq ft.

12" ID Column

$$\text{Area} = \pi r^2 = \frac{(\pi)(36)}{144} = 0.785 \text{ sq ft}$$

Packing has 96% free area: 0.785 sq ft x 0.96 = 0.753

Flooding rate:

1587.7 lbs/hr sq ft x 0.753 = 1195 lbs/hr

$$\frac{904 \text{ lbs/hr}}{1195 \text{ lbs/hr}} = 75.6\% \text{ column loading}$$

DECOMPOSER REBOILER

Duty: To supply sufficient heat to:

1. Heat to the boiling point (308.8°F)
   41.2 gph anisole.
2. Make up column heat losses.
3. Supply heat of decomposition for 1401 moles of complex per hour.

Calculations

λ = heat of vaporization anisole = 146 Btu/lb

C_p(anisole) = 0.422 Btu/lb °F

U (reboiler) = 100 Btu/hr sq ft °F

Use 85 psig steam at 327.6°F

U (column) = 2 Btu/hr sq ft °F

C_p(gas) = 0.1725 Btu/lb °F

Heat of decomposition of complex = 56 Btu/mole (measured)

M = 41.2 gph x 8.34 lb/gal x 0.9726 = 334.5 lbs/hr

Q(heating liquid) = $C_p \times M \times \Delta T$

= (0.422)(334.5)(308.8 - 77)

= 32,690 Btu/hr

Heat loss from column

12" diameter pipe 10 ft long

Area = 3.383 sq ft/ft

= (3.383)(10)

= 33.83 sq ft

Column temperature: $308.8^{o}F$

Room temperature: $77^{o}F$

ΔT $231.8^{o}F$

$Q_{(column\ losses)} = UA\Delta T$

$= (2)(33.83)(231.8)$

$= 22,450$ Btu/hr

$Q_{(decomposition)} = (M)(C_p)$

$= (1401$ moles/hr$)(56$ Btu/mole$)$

$= 78,456$ Btu/hr

$Q_{(heating\ gas)} = (C_p)(M)(\Delta T)$

$= (0.1725)(1109$ cu ft/hr$)(0.176$ lb/cu ft$)$

$= (308.8 - 77)$

$= 7,800$ Btu/hr

$Q_{(total)} = (32,690)(22,450)(78,456)(7,800)$

$= 141,400$ Btu/hr

Amount of anisole necessary to be vaporized.

$$\text{Amount} = \frac{Q}{\lambda}$$

$$\text{Amount} = \frac{141,400 \text{ Btu/hr}}{146 \text{ Btu/lb}} = 968 \text{ lbs/hr}$$

$$\frac{968 \text{ lbs/hr}}{(8.34 \text{ lbs/gal})(0.9726)} = 119.4 \text{ gal/hr}$$

$$A = \frac{Q}{U\Delta T} = \frac{141,400}{(100)(327.6 - 308.8)} = 75.2 \text{ sq ft area}$$

To allow for quick heat-up and flexibility of operation:

75.2 x 1.5 = 112.8 sq ft of heating area necessary.

Selection:

Reboiler

Capacity: 75 to 100 gallons liquid

Material of Construction: Monel or stainless steel

Heating coil:

Tube length:

1/2" tubing = 860 ft

1" tubing = 431 ft

1-1/2" tubing = 287 ft

2" tubing = 215 ft

Steam Consumption:

Steam pressure: 85 psig

Latent heat of evaporation: 888.2 Btu

$$\text{Steam rate} = \frac{141{,}400 \text{ Btu/hr}}{888.2 \text{ Btu/lb}}$$

$$= 159 \text{ lbs/hr}$$

ANISOLE COOLER

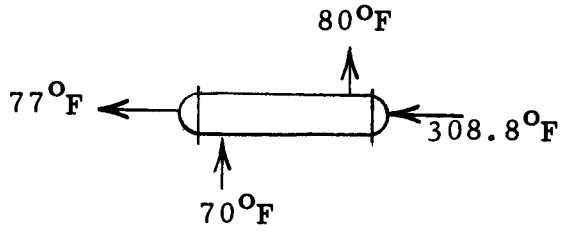
Duty: Cool from 308.8°F to 77°F 41.2 gal/hr (334.5 lbs/hr) of anisole. The anisole flows from the decomposer reboiler to the recombiner.

Calculations:

$U_{(cooler)}$ = 75 Btu/hr sq ft °F

C_p = 0.422 Btu/lb

Use cooling water into cooler at 70°F, out at 80°F



$\Delta t_1 = 308.8 - 80 = 238.8$

$\Delta t_2 = 77 - 70 = 7$°F

$\Delta t_{LM} = 65.7$

$Q = (C_p)(M)(\Delta T)$

$= (0.422)(334.5)(308.8 - 77)$

$= 32{,}700$ Btu/hr

$$A = \frac{Q}{(U)(\Delta T_{LM})} = \frac{32{,}700}{(75)(65.7)} = 6.6 \text{ sq ft area}$$

Safety factor = 1.5 x 6.6 = 9.9 sq ft

Selection:

Tube and shell heat exchanger

Material: Stainless steel or Monel

Tube length

3/8" tubing = 107 ft

1/2" tubing = 75.5 ft

3/4" tubing = 50.4 ft

1" tubing = 37.8 ft

Cooling water consumption

$$\frac{32{,}690 \text{ Btu/hr}}{(1)(80 - 70)(8.34 \text{ lbs/gal})} = 392 \text{ gal/hr}$$

BF_3 GAS COOLER

Duty: To cool 1109 cu ft/hr of BF_3 gas from 308.8°F to 77°F.

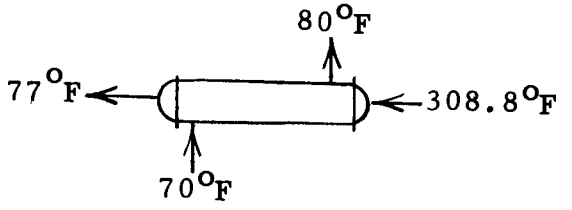
Calculations:

$C_{p(gas)}$ = 0.1725 Btu/lb°F

$U_{(gas\ to\ water)}$ = 5 Btu/hr sq ft°F

Cooling water in at 70°F, out at 80°F

Density = 0.176 lbs/cu ft



Δt_1 = 308.8 - 80 = 238.8

Δt_2 = 77 - 70 = 7

Δt_{LM} = 65.7

$Q = (C_p)(M)(\Delta T)$

= (0.1725)(1109 cu ft x 0.176 lbs/cu ft)(308.8 - 77)

= 7,800 Btu/hr

$$A = \frac{Q}{U(\Delta T_{LM})} = \frac{7,800}{(5)(65.7)} = 23.7 \text{ sq ft area}$$

Safety factor = 1.5 x 23.7 = 35.5 sq ft cooling area necessary.

Selection:

Shell and tube heat exchanger

Material: Monel or Stainless steel

Tube length

1/2" tubing = 271 ft

3/4" tubing = 181 ft

1" tubing = 136 ft

An entrainment separator or packed section should be included in the cooler to prevent carryover of liquid into exchange section.

Cooling water consumption

$$\frac{7{,}800 \text{ Btu/hr}}{(1)(80 - 70)(8.34)} = 93.5 \text{ gal/hr of water required}$$

RECOMBINER

Duty: To remove the heat of reaction of the formation of the anisole·BF_3 complex, and act as gas absorber.

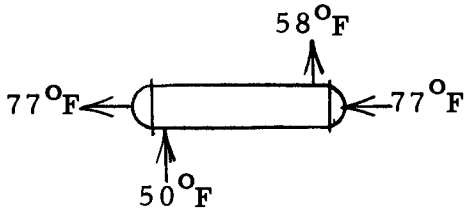
Calculations:

Heat of reaction = 56 Btu/mole (measured)

1401 moles/hr of complex formed

$U_{(\text{liquid phase continuous})}$ = 75 Btu/hr sq ft ^{o}F

Use chilled water in at 50 ^{o}F, out at 58 ^{o}F



$\Delta t_1 = 77 - 50 = 27$

$\Delta t_2 = 77 - 58 = 19$

$\Delta t_{LM} = 22.8$

$Q = (M)(C_p)$

$= (1401 \text{ moles/hr})(56 \text{ Btu/mole})$

$= 78{,}500 \text{ Btu/hr}$

$$A = \frac{Q}{U\Delta T_{LM}} = \frac{78{,}500}{(75)(22.8)} = 45.9 \text{ sq ft area needed}$$

Selection:

1st choice: Bubble cap column each tray cooled.

2nd choice: Packed vessel with cooling coils.

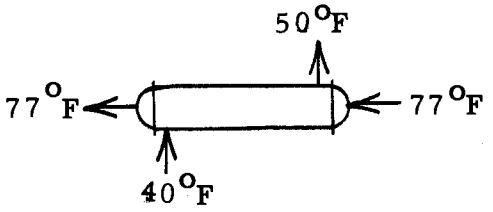
3rd choice: Agitated vessels with cooling coils.

4th choice: Packed heat exchanger.

$$\text{Water rate} = \frac{78{,}500}{(1)(8.34)(8)} = \begin{matrix} 1{,}177 \text{ gph} \\ 19.6 \text{ gpm} \end{matrix}$$

Alternate:

Use cooling water in at $40^{o}F$, out at $50^{o}F$



$\Delta t_1 = 77 - 50 = 27$

$\Delta t_2 = 77 - 40 = 37$

$\Delta t_{LM} = 32$

$$A = \frac{78,500}{(75)(32)} = 32.7 \text{ sq ft of cooling area needed}$$

Water consumption

$$\frac{78,500}{(1)(8.34)(50 - 40)} = 941 \text{ gph}$$

Water chilling unit

Capacity necessary

Cooling = 78,500 x 1.5 = 117,750 Btu/hr

Water rate = 19.6 x 1.5 = 29.3 gpm

Water in at $58^{o}F$, out at $50^{o}F$ or water in at $50^{o}F$, out at $40^{o}F$

Selection:

Packaged Liquid Chiller

Compressor hp = 10

Cooling capacity = 125,000 Btu/hr

Water rate (max.) = 31 gph

Acme Flow Cold Unit RC - 118D

Heat-X-Changer Co. Unit PC - 1000

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