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CHEMICAL SEPARATION OF ISOTOPES SECTION
SEMIANNUAL PROGRESS REPORT
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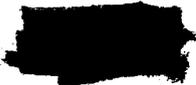
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CHEMICAL SEPARATION OF ISOTOPES SECTION
SEMIANNUAL PROGRESS REPORT
For Period Ending December 31, 1955

J. S. Drury, Supervisor

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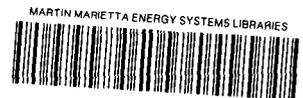
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CHEMICAL SEPARATION OF ISOTOPES SECTION

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SUMMARY

Vapor pressure data were obtained for several mixtures of BF_3 and anisole. An equation relating the composition, temperature, and pressure was derived. The melting point of the anisole- BF_3 complex was found to be between 1 and 2°C, which is 14°C higher than the literature value. The heat of reaction between BF_3 and anisole to form the BF_3 -anisole complex was measured calorimetrically and found to be 20 kcal/mole at 30°C.

The laboratory scale ANCO system was operated to check various aspects and components of the process. The apparatus has been completely redesigned and rebuilt with special attention given to flexibility, corrosion resistance, sturdiness, and automatic control. Isotopic equilibrium time is less than eight hours at design flows and temperatures. Chemical decomposition in the system is slight, and decomposer effluents containing less than 10 ppm boron, on a weight basis, are possible. A reflux test facility was constructed for use in a detailed study of the method of reflux in the ANCO system.

The field of BCl_3 complexes was surveyed. Separation factors for boron isotopes were determined for the most likely systems involving these complexes. No BCl_3 system was found to be competitive with the ANCO system. A new compound, diphenyl ether- BCl_3 , is reported and characterized.

Nuclear magnetic resonance shift measurements were made for a number of BF_3 -organic complexes. There appears to be a correlation between the magnitude of the shift observed and the separation factor for boron isotopes between BF_3 and the BF_3 -organic complexes.

Properties of platinum metal catalysts for catalysis of the hydrogen-water exchange have been studied and exchange rates determined. The effect of ultraviolet radiation of HCl on the catalysis of the hydrogen-water exchange has been found to be too slow to be practical for isotope enrichments.

A simple versatile method was developed for the determination of deuterium in hydrogen compounds. Hydrogen was obtained from hydrogen-containing compounds by passing them over uranium metal

turnings at 500°C. The rate of effusion of the gas through a small orifice was measured by means of a matched pair of thermistors. Deuterium can be determined to $\pm 1\%$. A few hundredths of a milliliter of gas at standard conditions is sufficient to make a determination.

The rate of isotopic exchange of nitrogen between HNO_3 solutions and the gaseous oxides of nitrogen was found to depend on gas composition. Exchange was considerably faster at 4 M HNO_3 , where the equilibrium amount of NO_2 was greater than at 1 M HNO_3 .

The equilibrium constant for the isotopic exchange of nitrogen between NO and NO_2 has been determined by direct mass spectroscopic measurements to be 1.028 ± 0.002 (95% C.I.) at 23°C. Nitrogen-15 concentrates in the NO_2 molecule. The theoretical values for this equilibrium constant calculated from recent spectral data is 1.035 at 25°C.

A 15-mm exchange column for the enrichment of N^{15} by the Nitrox process was operated automatically and continuously for nine days. An over-all enrichment greater than fiftyfold, or 16% N^{15} , was realized. The equilibrium time for the system was 200 hr for an HNO_3 flow rate of 360 ml/hr. Stage heights as low as 1.0 in. were experienced.

The fractionation of nitrogen isotopes between aqueous NH_4OH and metal ammonia complexes absorbed on Dowex 50 resin was studied. Separation factors were measured for complexes of Ni, Cu, Zn, Cd, and Ag.

The effect of the temperature of the ion exchange column on the total separation achieved in the Ames ammonium resin-ammonium hydroxide system was investigated. Except in the case of very rapid rates of band travel, there is no need to cool the column.

An acidic solution of $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$ equilibrated with gaseous CO enriched the O^{18} content of the CO in the liquid phase. The separation factor $(\text{O}^{16}/\text{O}^{18})_{\text{gas}}/(\text{O}^{16}/\text{O}^{18})_{\text{liq}}$ was 1.041. When O_2 was substituted for CO, no isotopic enrichment was observed.

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Gaseous O_2 equilibrated with O_2 absorbed on cobalt di(salicyl)ethylenediamine enriched O^{18} in the gas phase. A separation factor $(O^{18}/O^{16})_{gas}/(O^{18}/O^{16})_{solid}$ of 1.013 was determined.

The single stage separation factor between O^{16} and O^{18} in the methyl ether(g)-methyl ether· $BF_3(l)$ system was found to be 1.017 ± 0.005 (95% C.I.) at room temperature. The heavy isotope concentrated in the liquid complex.

SEPARATION OF BORON ISOTOPES

THE ANCO SYSTEM FOR BORON ISOTOPE ENRICHMENT

The ANCO (anisole-complex) system utilizes the exchange reaction between BF_3 gas and the liquid $\text{BF}_3 \cdot \text{anisole}$ complex to concentrate B^{11} in the gas phase and B^{10} in the liquid phase. A previous report¹ discusses the determination of the isotopic separation factor, rate of isotopic exchange, and the quantitative decomposition of the complex.

Vapor Pressure of Anisole $\cdot \text{BF}_3$ Complex

R. M. Healy

Optimization of recombiner operation in the ANCO system requires vapor pressure-temperature-composition data for anisole- BF_3 mixtures. The materials used in this work were carefully purified, and the compositions of the mixtures used were accurately determined gravimetrically. The results are summarized in the log pressure vs reciprocal temperature plot of Fig. 1. Curves B and C were obtained by using the apparatus of Fig. 2. This apparatus is similar to that described by L. L.

¹R. M. Healy and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955, ORNL-2005, p 2.*

Brown² in a previous report. Compared to the liquid volume, the amount of gas space in this apparatus was not quite small enough to be disregarded. Slight corrections were made to curves B and C because of the loss of BF_3 from the liquid phase as the mixtures were heated. The other curves were obtained by using data from an apparatus in which the gas space was negligible. In the latter apparatus agitation was achieved with a built-in magnetic stirrer.

By making some simplifying approximations the data in the range of most interest can be fitted to a simple equation. The method used was as follows: from a pressure-reciprocal temperature plot, composition points along the 100-cm isobar were fitted by least squares to a parabolic curve. It was assumed that the vapor pressure vs reciprocal temperature curves of Fig. 1 were straight lines all having the same slope. Thus, they could be fitted to the expression $\log P = A - B/T$, where B is the same for all curves. The value A differs for each composition and is obtained from the temperature-composition parabolic curve. Combining the two equations gives for the vapor pressure of anisole $\cdot x\text{BF}_3$:

$$\log P = 10.07 - 3.69x + 3.76x^2 - \frac{2380}{T},$$

where P is in cm, x is the mole ratio $\text{BF}_3/\text{anisole}$, and T is the absolute temperature in degrees Kelvin. The equation is useful for operation and design purposes for $x = 0.5$ to 1.0 and for P from 60 cm up to at least 200 cm.

In the course of the work, an approximate melting point, between 1 and 2°C, for the 1:1 complex was observed. This may be compared with the literature value of -12 to -13°C.

Heat of Reaction of Anisole with BF_3

L. Landau

In order to determine the cooling requirements for the recombiner in the ANCO system, the heat of reaction for anisole + $\text{BF}_3 \rightarrow \text{anisole} \cdot \text{BF}_3$ complex was measured.

²L. L. Brown, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955, ORNL-2005, p 20.*

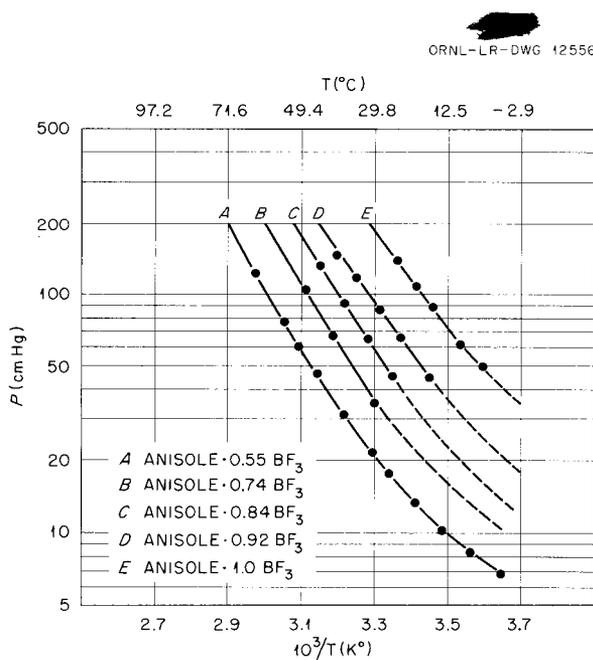


Fig. 1. Vapor Pressure of Anisole $\cdot \text{BF}_3$ Complex.

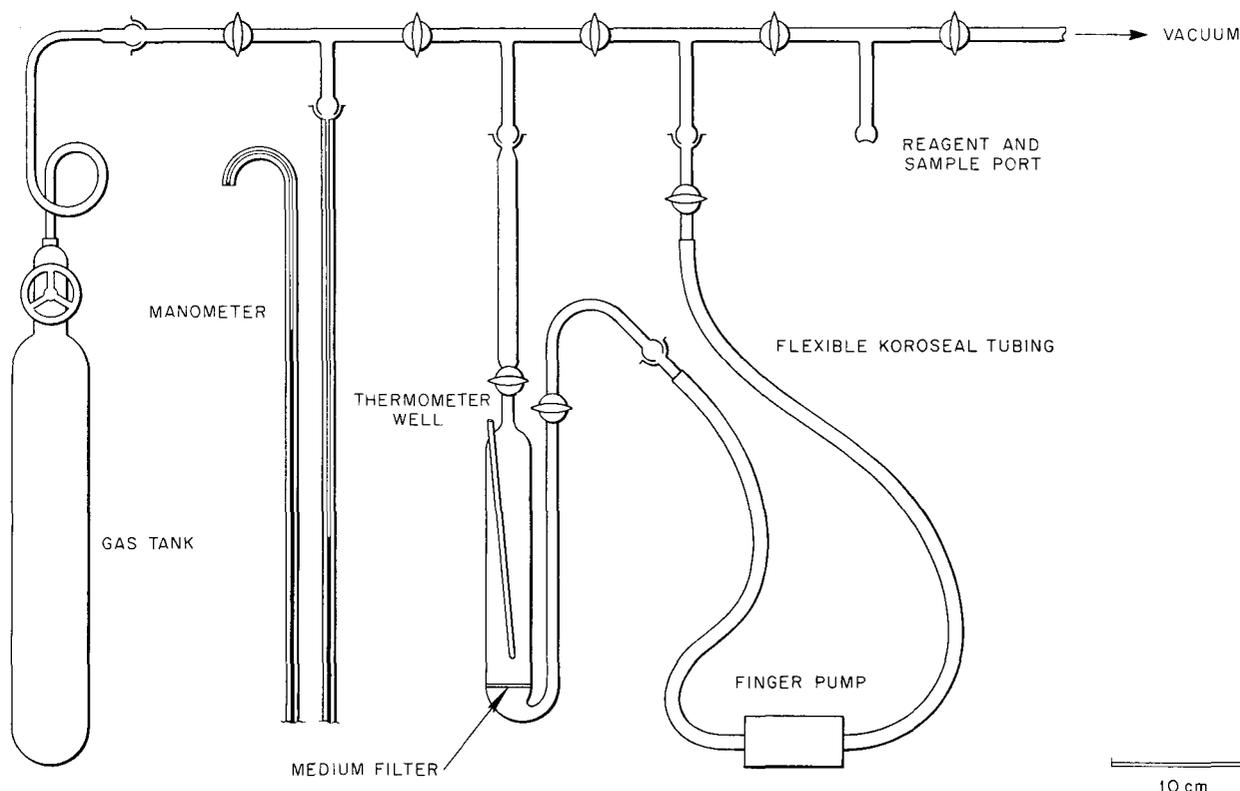
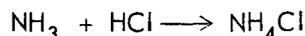


Fig. 2. Apparatus for Obtaining Separation Factors and Vapor Pressures.

The apparatus used in this study is pictured in Fig. 3. The pressure of BF_3 in flask B (volume 2170 ml) was measured, and the BF_3 was allowed to flow through the capillary tubing into the vacuum-jacketed calorimeter. The calorimeter was shaken vigorously, and the temperature rise was followed by means of thermocouples in the thermocouple well of the calorimeter and on the inside wall of the Dewar flask acting as the calorimeter jacket. The heat losses to the calorimeter were determined by measuring the temperature rise for the known reaction:



The heat capacity of the anisole· BF_3 complex was measured by passing a known amount of current through a coil immersed in the complex,

and measuring the rise in temperature. A similar experiment was performed, using pure anisole, to determine the heat losses to the calorimeter. A value of 0.462 cal/g/°C at 31.6°C was used as the heat capacity of anisole. Using anisole·0.95 BF_3 in place of the pure anisole, a value of 0.87 cal/g/°C was obtained for the heat capacity of the complex at ~40°C.

Table 1 shows the data obtained for the addition of 10 increments of BF_3 to 137.7 mmoles of anisole, giving a final composition of anisole·0.93 BF_3 . The last column shows the heat of reaction for that particular addition. In Fig. 4 these values for the heats of reaction are plotted against the mean temperature and a marked temperature dependence is noted, with a value of 20 kcal/mole at 30°C. Figure 5 shows a plot of the heat of reaction, corrected to 30°C, against the total

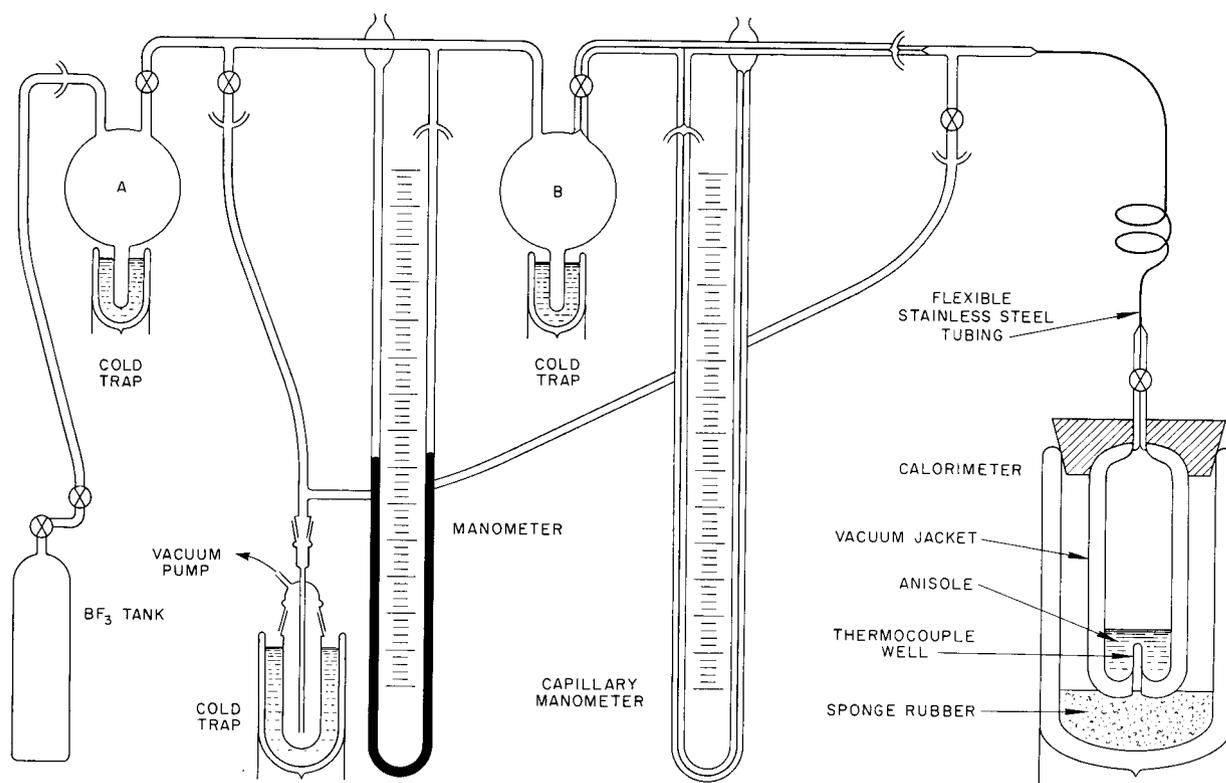


Fig. 3. Apparatus for Measuring Heat of Formation of the Anisole·BF₃ Complex.

TABLE 1. HEAT EVOLVED ON ADDING BF₃ TO ANISOLE

Increment Number	BF ₃ Added (mmoles)	Cumulative BF ₃ Added (mmoles)	ΔT (°C)	Mean Temperature (°C)	$-\Delta H$ (kcal/mole)
1	14.77	14.77	16.5 ₈	38.4	16.1
2	16.82	31.59	17.1 ₃	48.1	16.3
3	17.89	49.48	13.0 ₁	50.6	13.0
4	23.78	73.26	21.0 ₈	38.5	18.0
5	10.62	83.88	7.9 ₃	42.2	16.0
6	15.26	99.14	14.9	15.3	22.4
7	8.66	107.8	8.4 ₄	20.8	23.3
8	2.59	110.4	2.2 ₉	20.9	21.3
9	11.56	123.0	11.9 ₅	15.7	26.3
10	5.40	128.4	5.3 ₆	19.9	25.7

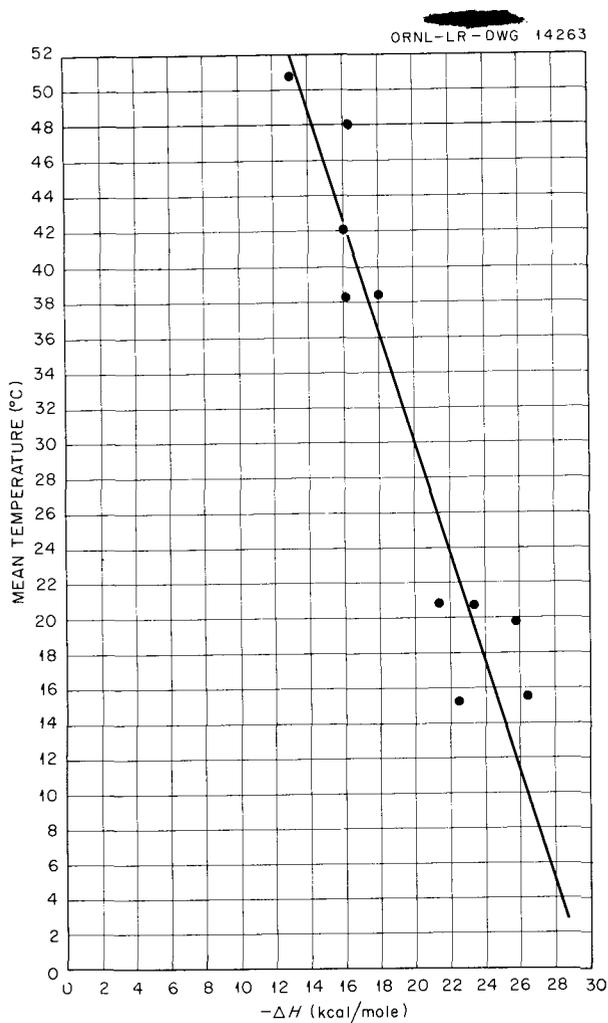


Fig. 4. Heat of Reaction of Anisole + BF₃ as a Function of Temperature.

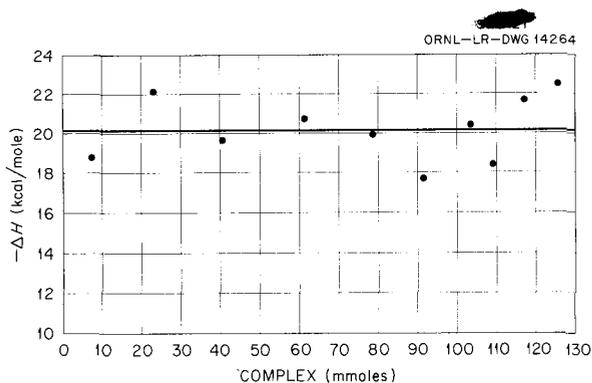


Fig. 5. Heat of Reaction of Anisole + BF₃ at 30°C as a Function of Composition.

amount of BF₃ added. This plot shows no slope, indicating a constant heat of reaction over this composition range.

Laboratory Scale ANCO System

A. A. Palko

Initial studies of the ANCO system on a semi-pilot-plant scale, along with a description of the apparatus and operating procedures were presented in a previous report.³ Runs 7 through 20 described in this report are a continuation of this work.

Runs 7-12 were made in order to determine rate and amount of buildup of boron in the decomposer effluent. Isotopic equilibrium time, decomposition of solvent, and formation of insoluble products in the system were also investigated. These six runs, covering a period of 8 days, were made on the old apparatus and showed that boron concentration increased quite rapidly with time. However, later runs on the redesigned apparatus gave much lower concentrations of boron in the recycle anisole stream. Some typical operating conditions for runs 7-12 follow:

Flow rate BF ₃ , moles/hr	2.78
Flow rate anisole, cc/hr	300
Pressure, mm Hg	~850
Recombiner temperature, °C	8
Exchange column temperature, °C	~28
Decomposer temperature, °C	~155

Table 2 shows analysis of the effluent stream for boron, copper, and iron. Figure 6 shows the total separation with respect to time for run 8.

Total reflux time indicated in Table 2 was the total time the system was at equilibrium with the decomposer at operating temperature. Total contact time was the total time that BF₃ was in the system, whether the system was operating or not. During these runs, it was noticed that a slight precipitate began to form in the decomposer boiler; hence, effluent samples, both filtered and unfiltered, from runs 9-12 were analyzed to determine what portion of the boron was contained in the precipitate. The analysis revealed that most of the boron in the effluent stream was associated with the

³R. M. Healy and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep.* June 30, 1955, ORNL-2005, p 7.

TABLE 2. METAL CONTENT OF DECOMPOSER EFFLUENT

Run No.	Reflux Time (hr)	Contact Time (hr)	Weight of Metal (ppm)			
			B ^a	B ^b	Cu	Fe
7	3.5	3.5		95		
	4.75	4.75		167		
8	9.75	27.75		240		
	14	32		280		
9	22	56	40	350	1640	60
10	30	128	50	480	3000	70
11	38	152	110	620	2900	130
12	46	176	335			

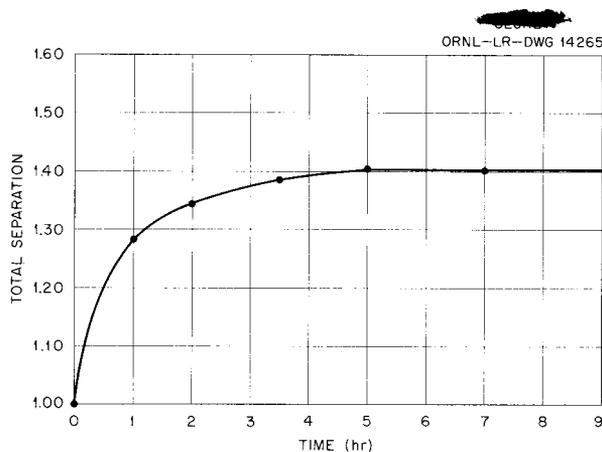
^aEffluent filtrate.^bUnfiltered effluent.

Fig. 6. Total Separation as a Function of Time for Run 8.

precipitate. Copper concentration was quite high because of leaching of the copper transfer lines. Examination of the decomposer after run 12 showed that the glass bead packing in the hot portion was becoming corroded. The corrosion of the glass packing, rather than decomposition within the chemical system, could account for the high concentration of boron in the effluent stream even though no silica was found in the effluent. Analysis of the gas stream at the top of the recombiner showed small quantities of SiF_4 .

At the conclusion of this series of experiments the entire system was redesigned and rebuilt with special attention given to flexibility, corrosion

resistance, sturdiness, and automatic control. The major changes made in the apparatus were replacement of glass packing with Podbielniak nickel Heli-Pak, substitution of flanged glass pipe joints for the fragile Kovar glass-to-metal seals, replacement of all copper transfer lines with nickel lines, and the addition of an anisole cleanup system. Columns, pumps, transfer lines, and valves of the same size were used. The bubble-cap exchange column, however, was replaced by a 3-ft section of 1-in. jacketed column in order that closer control of exchange temperature could be obtained. Microbellows pumps and $\frac{1}{4}$ -in. monel valves of either the diaphragm or bellows type were retained. Whenever possible, metal connections were made with stainless steel Crawford or Parker tubing fittings. Glass-to-metal connections were made with flanged glass pipe joints and full-faced Teflon-gasketed nickel flanges, to which were silver-soldered transfer lines, valves, dip tubes, etc. Little difficulty was experienced in making the system pressure- and vacuum-tight. Teflon gaskets were satisfactory for all gasketed joints even in the hot portion of the system. Other gasket materials tried were P-10, Koroseal, rubber, Silastic, asbestos, and Teflon-covered Koroseal and asbestos. Rubber and Koroseal are softened by anisole to such an extent that they are useless. Silastic and P-10 react with BF_3 , and the binder is leached from Garlock asbestos. However, Teflon-covered Koroseal and asbestos gaskets are satisfactory for pipe joints 1 in. or larger. Teflon O and U

rings are especially useful for sealing full-face metal flanges to $\frac{1}{2}$ - or $\frac{1}{4}$ -in. glass pipe.

A sketch of the redesigned apparatus is shown in Fig. 7. On the right of the drawing is shown the anisole cleanup system. The volume of the recombiner was 400 ml. Under operating conditions it contained about 300 ml of complex, which is equivalent to 71 liters of BF_3 gas at STP. The volume of the exchange column was approximately 420 ml, and liquid holdup was between 40–75 ml of complex depending on the flow rate. Total volume of the decomposer system was 2000 ml, and holdup of anisole was about 800 ml. Complex pump No. 1 was used as the control pump, and all other pumps were adjusted accordingly. On No. 2 and No. 3 pumps, the valving and piping arrangement was such that anisole could be pumped directly from the decomposer to the recombiner by one or both pumps, or it could be pumped by the No. 3 pump to the anisole cleanup still. The No. 2 pump then pumped purified anisole back into the system. On automatic control both pumps were

used to pump anisole from the decomposer to the recombiner. One pump operated continuously, while the other operated intermittently. Automatic control was achieved by taking advantage of pressure fluctuations within the system. When there was a deficiency of anisole in the recombiner, the excess BF_3 caused the pressure in the system to rise. An excess of anisole in the recombiner caused the pressure of the system to fall. By inserting two contacts into the outside leg of the manometer, a relay-type controller could be actuated. The relay, in turn, controlled either the No. 2 or No. 3 pump. When the system was operating on automatic, one pump operated continuously at a rate which caused a deficiency of anisole in the recombiner. When the pressure in the system reached a preset value the relay mechanism turned on the other pump. As soon as the pressure fell, the pump was turned off. By carefully adjusting the pumps, pressure fluctuations of $<\pm 0.5$ cm could be maintained in the system, and very smooth operation resulted.

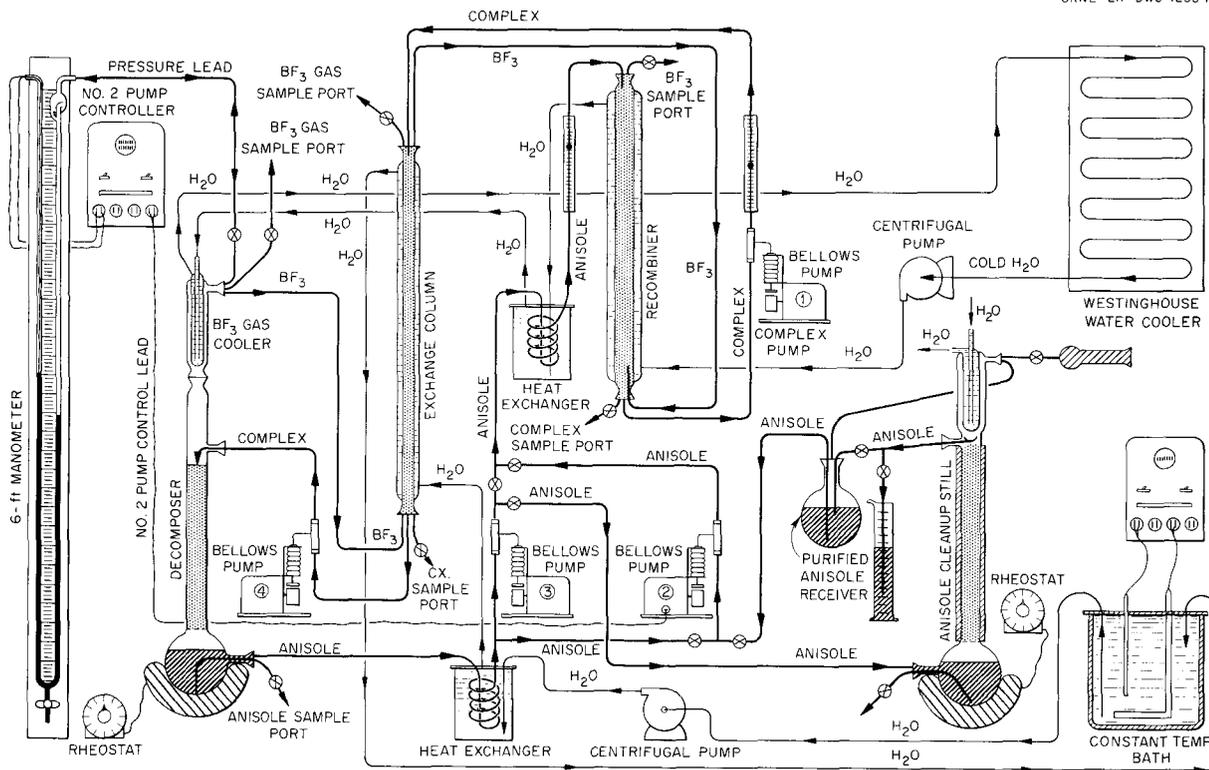


Fig. 7. Laboratory-Scale ANCO System.

After the apparatus was assembled, leak-tested, and calibrated, it was charged with clean, dry anisole, and BF_3 was admitted until the system was at 1 atm pressure under operating conditions. Several runs were made in order to establish operating conditions, chemical and isotopic equilibrium times, efficiency of the recombiner at 7 and 20°C, boron concentration in the decomposer effluent,

and separation as a function of time and flow rate.

Table 3 shows the operating conditions for runs 13 through 20. The total amount of BF_3 in the system was approximately 3 moles.

Several runs were made to study the effect on the total separation of varying the flow rate. Figure 8 shows total separation as a function of

TABLE 3. OPERATING CONDITIONS FOR RUNS 13-20

Run No.	Pressure (mm Hg, ± 25)	Temperature ($^{\circ}\text{C}$)				Total BF_3 in System (moles)	Anisole Flow Rate (cc/hr)	BF_3 Flow Rate (moles/hr)
		Recombiner Exit	Exchange Column	Decomposer Maximum	Recombiner Maximum			
13	740	6	24	158	37	2.9	307	3.4
14	740	6	22	162	41	2.9	530	4.9
15	850	6	27	163	48	2.9	650	6.2
16	900	7	28	166	42	3.05	650	6.2
17	900	7	28	165	53	3.17	530	4.9
18	830	6	27	160	53	3.17	530	4.9
19	850	5	28	160	45	3.17		8
20	825	20	27	154	58	3.17	1400	13

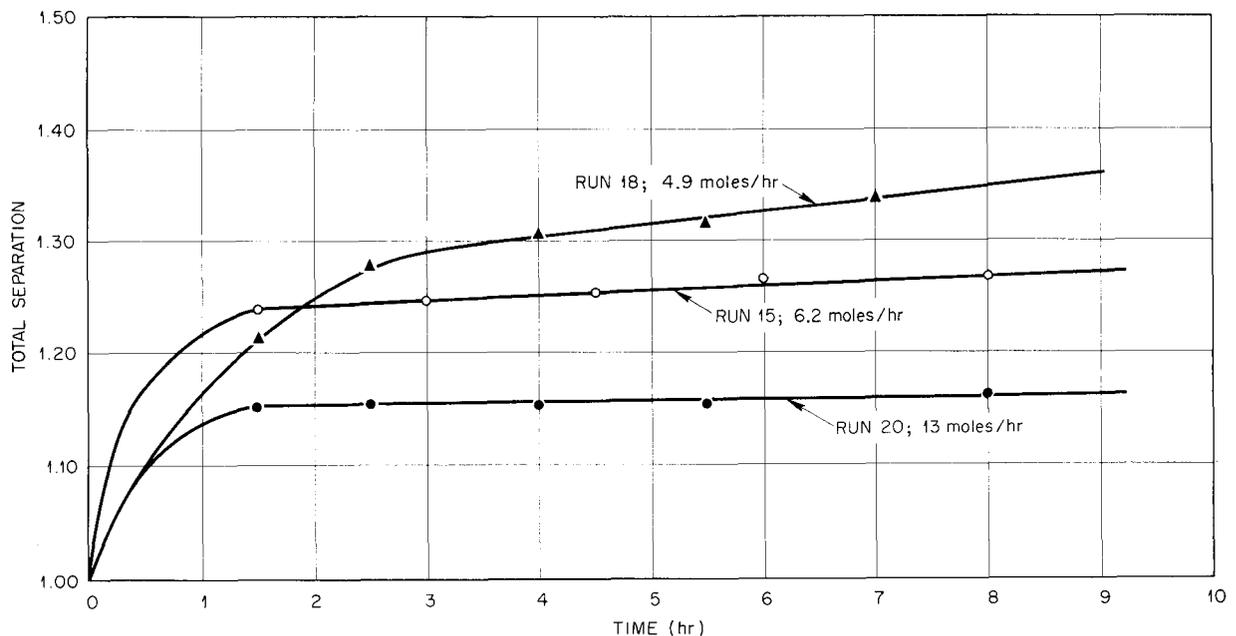


Fig. 8. Total Separation-Time Study of ANCO System.

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time for runs 15, 18, and 20. During run 20, the column showed signs of flooding.

Three runs were made to determine the ratio of BF_3 to anisole in the complex leaving the recombiner. The apparatus was run for at least 4 hr at equilibrium before the recombiner was sampled. Approximately 30 ml of sample was taken in each case. Runs 16 and 17 were duplicates with recombiner exit temperature at 7°C , while run 20 was made with recombiner exit temperature at 20°C . The results are shown in Table 4.

TABLE 4. RECOMBINER STUDY - ANCO SYSTEM

Run No.	Ratio $\text{BF}_3/\text{Anisole}$	Exit Temperature ($^\circ\text{C}$)	Pressure (mm Hg)
16	1.07	7	850
17	1.06	7	950
20	0.92	20	875

Three studies of the variation of boron concentration with operating time were made on the decomposer system. The first covered 30 hr, after which time the anisole cleanup system was run for 2 days to purify the anisole; the second covered 78 hr total contact time, after which the system was thoroughly cleaned and automatic controls were installed; the third study covered 56 hr total contact time and operating flow rates of 13 moles of BF_3 per hour with the recombiner at 20°C . The results are shown in Table 5. At the high flow rates of run 20, the decomposer heater was operating at near capacity. This could account for the higher concentration of boron in the effluent; also, at high flow rates, the residence time in the decomposer pot is cut to a minimum.

Since some difficulty was experienced in synchronizing the pumps, flows, temperature, etc. throughout the apparatus during this series of runs, several small changes were made in order that the system could be run automatically for extended periods of time. By using the pressure-actuated pump control, the system operated very smoothly. However, the recombiner had to be operated at 20°C in order to minimize gassing in the complex pump.

TABLE 5. DECOMPOSER EFFLUENT ANALYSIS - ANCO SYSTEM

Run No.	Time (hr)		Total Boron (ppm)
	Actual Operating	Contact	
First Study			
15-16	14	30	9.9
Second Study			
17	5	26.5	7.0
	1.5	1.5	4.5
18	7		6.7
	0.5	26	6.1
19	8	24	9.2
	Total	22	78
Third Study			
20	16	56	31.5

ANCO Reflux Test Facility

E. F. Joseph

A reflux test facility was designed and constructed to permit a more detailed study of the method of refluxing the ANCO system and to make possible further improvements in the process. Shown in Fig. 9 is a flow diagram of the system.

The basis for the design of the system was a 4-in.-ID exchange column. This column consisted of an 8-ft-long pyrex glass pipe packed with 0.24×0.24 in. Cannon protruded monel packing. Sample ports were located at 2-ft intervals along the column. In the upper 4-ft section was placed a cooling coil, 40 ft long, of $\frac{3}{8}$ -in. stainless steel tubing, which had 9.2 ft^2 of area.

The recombiner, decomposer, and accessory plant equipment were sized to handle the maximum flow through the exchange column.

For the recombiner a jacketed finger-type cooler, constructed of stainless steel and packed with protruded metal packing, was used. The recombiner had 16.9 ft^2 of area; cooling water for the unit was supplied by a Heat-X-changer Co. packaged water chiller with a cooling capacity equivalent to 5 tons of refrigeration.

The decomposer section consisted of a re-boiler tank with an external heat exchanger, a

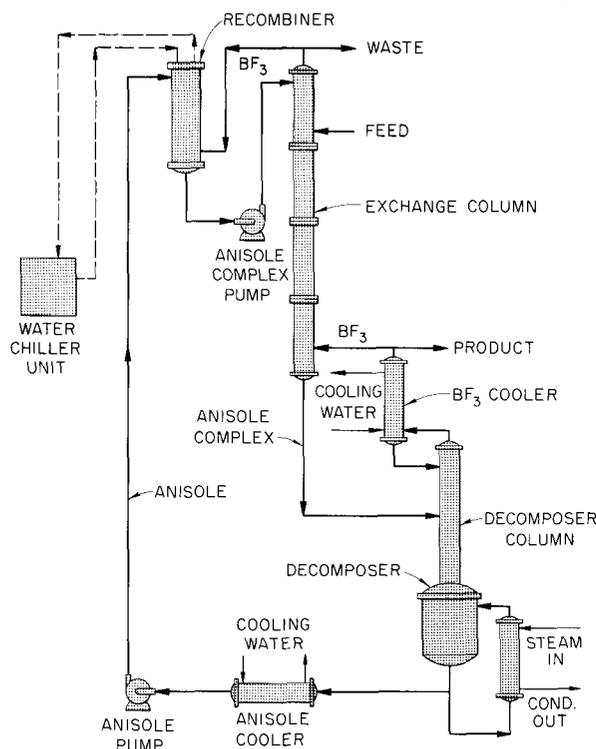


Fig. 9. Flow Diagram of the ANCO System.

gas cooler, and an anisole cooler. The reboiler tank was constructed of stainless steel and had a capacity of 10 gal. Also constructed of stainless steel was the heat exchanger, a 116-tube single-pass unit with 34 ft² of heating area. The decomposer column was a section of 6-in.-ID pyrex glass pipe 24 in. long, packed with 1-in. pyrex glass rings. Used as a cooler for the BF₃ gas stream was a finger-type cooler, similar to the recombiner unit, packed with stainless steel Yorkmesh demister material. A 70-ft coil of 1/2-in. stainless steel tubing with 9.2 ft² of area submerged in a tank of running water was used to cool the anisole going to the recombiner. Two Lapp Pulsafeeder pumps, model CPS-2 with master Speedranger drives, were used for transferring the anisole and liquid complex.

A safety rupture disk of 0.001-in.-thick silver sheet, in a special holder, was installed in the gas line between the gas cooler and the exchange column. This type of rupture disk was tested and found to hold pressures up to 11 psig. Thermocouples were placed throughout the system and the

temperatures were recorded on three 12-point recorders.

All connections in the system were either welded, flanged, or had compression-tubing fittings. Teflon gasket material was used in the flanged connections. Valves used in the system were 1/2-in. Fulton Syphon packless valves and 1/4-in. Teflon-packed Hoke needle valves.

The anisole for use in the process was dried by batchwise distillation through a 2-in.-ID column, 5 ft high, packed with 1/2-in. Intalox saddles. Capacity of the drying still was 8 gal per batch. It was found that the small trace of water (0.02%) in the anisole could not be effectively removed in this large equipment because of the water adhering to the walls of the condenser and in the reflux lines. The method of drying the anisole was revised to use 22-liter flasks and heating mantles. Columns consisting of 1-in.-ID glass tubing 3 ft long were packed with 1/4-in. stainless steel Lessing rings. The anisole was allowed to reflux until the water content of the overhead material was reduced to 75 to 100 ppm water. Then the reflux head on the column was replaced with a straight distillation head and the anisole coming over at 153°C was collected and stored in dried, stoppered bottles.

The system was cleaned and dried by distilling and circulating hot anisole through the equipment.

To start up the system, the decomposer reboiler and the recombiner were filled with freshly distilled anisole. Total holdup of the system was 66 liters of anisole. After the decomposer was brought up to temperature, anisole was allowed to reflux in the decomposer column. The anisole and anisole-complex pumps were started, and anisole was circulated throughout the system until the flow rates and tank levels remained constant, at which time BF₃ gas was fed into the base section of the exchange column. When sufficient complex was formed and the pressure in the recombiner started to rise, the gas flow was stopped.

During operation, the anisole-BF₃ complex from the exchange column flowed by gravity into the top of the decomposer column. Heat was supplied by boiling the anisole in the reboiler to decompose the complex into BF₃ gas and anisole. The BF₃ gas flowed through the gas cooler into the exchange column and then into the recombiner. Anisole from the reboiler passed through a heat exchanger and was cooled to room temperature;

it was then pumped into the top of the recombiner. In the recombiner the anisole was the continuous phase and flowed countercurrent to the BF_3 gas with which it reacted to form the complex. The complex was then metered into the exchange column where it flowed countercurrent to the BF_3 gas from the gas cooler. The B^{11}F_3 concentrated in the gas phase and the B^{10}F_3 concentrated in the liquid phase.

The equipment operated on a schedule of 8 hr per day. A startup procedure was developed which permitted the system to be in full operation within 12 min and completely shut down in 15 min. Tests are in progress to determine the actual heat requirements for the decomposer section and the cooling necessary for the recombiner section.

BCl_3 - BCl_3 COMPLEX SYSTEMS

R. M. Healy

Since BCl_3 forms complexes in a manner similar to BF_3 , the feasibility of using BCl_3 in a countercurrent system was considered. A system employing BCl_3 exhibits some attractive features. Boron trichloride can be readily liquefied at room temperature. Therefore, its use might make possible a high-throughput liquid-liquid system. Also, under some circumstances BCl_3 might be less costly than BF_3 .

The field of BCl_3 complexes was surveyed and found to be considerably more limited, especially for our purposes, than BF_3 -complex chemistry. However, several possible systems were devised. Separation factors for boron isotopes were determined in the more promising systems.

In a preliminary experiment, an attempt was made to measure the separation factor between BCl_3 and anisole· BCl_3 . The basic part of the apparatus consisted of a 100-ml flask with a large vacuum stopcock. Complex in the flask was equilibrated with gas in the stopcock. The gas phase could then be separated from the liquid phase by simply turning the stopcock. This avoided the possibility of drawing boron from the liquid into the gas sample. The method of freezing the complex was not considered feasible because of the relatively high boiling point of BCl_3 . The amount of gas was small compared with the amount of complex, so that the separation factor could be obtained by comparing the gas phase to the normal starting material.

The apparatus was first tested by measuring the known separation factor for the BF_3 -anisole· BF_3 system. Equilibration time was 4 hr. A value of 1.024 ± 0.0008 (95% C.I.) at 25°C was obtained, which is in fair agreement with an interpolated value of 1.030 from previous work.⁴

It was observed that a mole of anisole would absorb only one-half mole of BCl_3 to form the complex, anisole· $\frac{1}{2}\text{BCl}_3$. The compound was not stable, but decomposed over the period of equilibration. The BCl_3 was depleted from the gas phase so that a separation factor could not be determined.

Subsequent experiments on BCl_3 complexes were done in the apparatus shown in Fig. 2. The better contacting obtained with this technique shortened the time of complex formation and the gas-liquid equilibration time.

The separation factors found for the BCl_3 systems studied are shown in Table 6.

TABLE 6. SEPARATION FACTORS FOR BORON ISOTOPES IN BCl_3 - BCl_3 COMPLEX SYSTEMS

Complex	Separation Factor* (95% C.I.)	Temperature ($^\circ\text{C}$)
Acetylchloride· BCl_3	1.003 ± 0.01	-55
	1.014 ± 0.007	2
	1.004 ± 0.001	25
Ethylene oxide· BCl_3	1.022 ± 0.004	25
Diphenyl ether· BCl_3	0.998 ± 0.002	28
	0.999 ± 0.002	-1

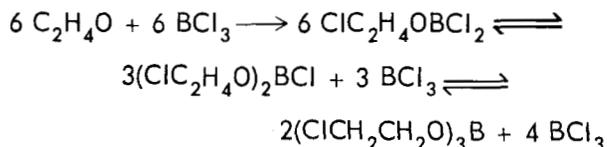
$$* \left(\frac{\text{B}^{10}}{\text{B}^{11}} \right)_{\text{BCl}_3 \text{ gas}} / \left(\frac{\text{B}^{10}}{\text{B}^{11}} \right)_{\text{liquid complex}}$$

The complex, ethylene oxide· BCl_3 , was reported⁵ in 1954. From the vapor pressure data of that paper $\Delta H = -8$ kcal/mole was calculated for the formation of the complex. However, a violently exothermic reaction between ethylene oxide and BCl_3 was observed, even at -78°C .

⁴R. M. Healy and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep.* June 30, 1955, ORNL-2005, p 3.

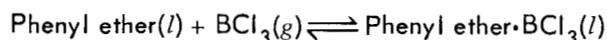
⁵J. Grimley and A. K. Holliday, *J. Chem. Soc.* 1954, 1212.

After separation factors for the system BCl_3 -ethylene oxide· BCl_3 were obtained, a new paper⁶ on the compound came to our attention. The authors of this paper claimed that the compound was not a simple addition compound and they presented cogent evidence in support of their contention that the ether ring is split by BCl_3 . The equilibria may be represented by the following reactions:



The first reaction is strongly exothermic, while the following equilibria explain the reversibility of vapor pressure with temperature. Since only two-thirds of the total boron in the liquid phase can be reconverted to BCl_3 by simple heating, the ethylene oxide complex would not be suitable for use in a thermally refluxed isotope separation system.

The phenyl ether complex is a new compound. The compound is of theoretical interest because BF_3 does not complex with phenyl ether.^{7,8} Phenyl ether· BCl_3 has a melting point between 3 and 4°C; it tends to supercool. Vapor pressure-temperature data for mixtures of phenyl ether- BCl_3 are shown in Fig. 10. By assuming that only BCl_3 exerts a significant vapor pressure over the liquid, the heat of the reaction can be calculated as:



A least-square treatment of the data yields

$$\Delta H = -5.2 \pm 0.3 \text{ (95\% C.I.) kcal/mole .}$$

The possibility that BCl_3 splits the rings of the ether instead of adding to it was eliminated by showing that the BCl_3 could be removed from the liquid by simple heating and pumping. Weight difference in the ether (before addition of and after removal of BCl_3) and chemical analysis gave results in excellent agreement, showing that only

⁶J. D. Edwards, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.* 1955, 1470.

⁷H. Bowls and J. A. Nieuwland, *J. Am. Chem. Soc.* 53, 3835 (1931).

⁸H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.* 134, 51 (1932).

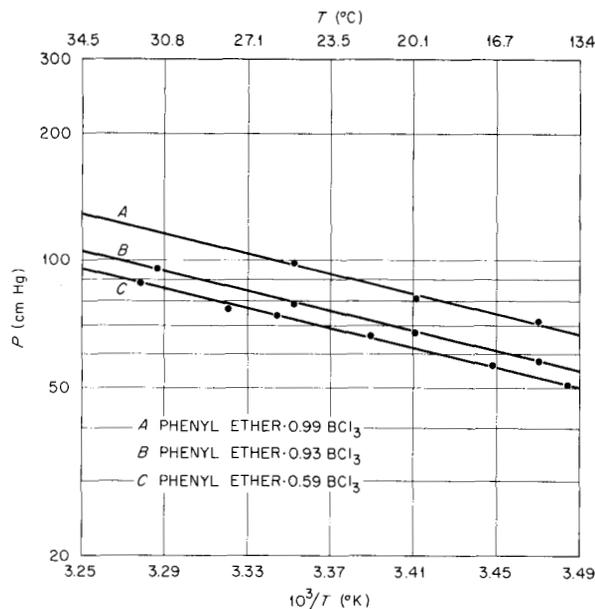


Fig. 10. Vapor Pressure of Phenyl Ether· BCl_3 Complex.

0.02% of the boron remained.

The claim that BF_3 does not form a complex with phenyl ether was confirmed in the following manner. Gaseous BF_3 at 1 atm pressure was pumped through phenyl ether for approximately 24 hr. The ether absorbed less than 0.2% of its weight of BF_3 . The small amount of BF_3 absorbed was readily removed by warming and pumping. Some of the gas absorption was probably due to impurities in the ether, since the liquid was pink while it contained the BF_3 .

Because of the small separation factors found, the reactive nature of BCl_3 , and recent promising developments in BF_3 reduction, it is felt that further research on BCl_3 complexes is not warranted at this time.

NUCLEAR MAGNETIC RESONANCE SHIFT MEASUREMENTS ON BF_3 -ORGANIC COMPLEXES

H. E. Walchli⁹

R. M. Healy

It is an experimentally known fact that the magnetic field at the nucleus of an atom is the sum of

⁹Stable Isotopes Division.

any externally applied magnetic field and the internal fields arising from the chemical state of the atom. One of the internal fields is determined by the nuclide's electronic structure, and another is caused by the effects of adjacent atoms or molecules which may be positioned near, due to physical state, or chemically bonded to the atom under investigation. It should then be possible to correlate, in some manner, the magnetic field at the center of the nucleus with the degree of bonding occurring in a particular compound or solution. Since the isotopic fractionation between chemical species at equilibrium is also a function of the bonding in those species, some correlation might be expected between the magnetic shifts observed when measuring a series of related compounds and the separation factor data for the same compounds.

If the nucleus of the atom is excited by a radio-frequency field while in a fixed magnetic field, it will undergo certain orientation changes (resonances) when the sum of the magnetic fields at the nucleus satisfies the relationship $\mu/I = f/0.76229 \times 10^3 H$, where f is frequency, H is magnetic field in gauss, μ is the nuclear moment, and I is the nuclear spin.

By using an oscillating field of constant frequency, changes in the internal magnetic field can be detected by observing the new value of the applied external field required to bring the nucleus into resonance. Thus, it is possible to detect slight changes in internal magnetic shielding effects by observing the small changes occurring in the applied field. In this experiment, attempts were made to determine the shifts in the resonances of boron when it was bonded with several organic compounds.

The resonance observations were made in the research laboratory of the Electro Metallurgical Company at Niagara Falls, N. Y., with the cooperation and assistance of T. J. Rowland of that company. The instrument used was a Varian nuclear magnetic resonance spectrometer, and the magnet was a Varian 12-in. adjustable electromagnet with regulated voltage and current supply. The field did not vary more than 0.03 gauss over the sample volume, and the combined radio-frequency and magnetic field stability was greater than 1 part in 500,000 (0.0002%). Measurements were made at a fixed frequency by sweeping the field slowly over the region of resonance at a rate of 1.2 gauss per minute. The resonances were recorded on two

time-driven charts by using a Leeds and Northrup Speedomax recorder. Shift measurements were made from the recordings; paper velocity was assumed to be constant.

The ethers used to prepare BF_3 complexes were dried over sodium, distilled in 3-ft packed columns, and transferred under vacuum into weighed 9-mm tubes. Phenol was handled similarly, but without being dried over sodium. Boron trifluoride was purified by the usual method.¹⁰ The amount of BF_3 needed to form 1:1 complexes was measured volumetrically and condensed on the organic compounds. The tubes were then sealed. These tubes were in the form of hooked canes. The heads served as reservoirs; the amount of material being examined at the opposite ends of the tubes could thus be varied at will.

Measurements were made relative to a sample of boric acid which was contained in a 15-mm test tube into which the sealed sample being investigated was placed. Attempts to obtain measurements on BF_3 gas as a reference were unsuccessful. Shifts between the various samples were recorded by simultaneously placing two of the sealed tubes in the spectrometer. The results of these measurements, together with some experimentally determined separation factors, are presented in Table 7.

There is an apparent correlation between the nuclear magnetic resonance shift of these compounds referred to boric acid and the separation factor for boron isotopes between BF_3 and the compounds. It cannot be stated at this time whether or not the correlation is fortuitous. No such simple relationship between the separation factor and resonance shift was observed when the nuclear magnetic data of Holder and Klein¹¹ were compared with literature values for separation factors involving these species. In the case of nitrogen, however, the oxidation state of the isotope varied in the different species. Attempts to measure similar nuclear magnetic resonance shifts in lithium were unsuccessful because of the extremely narrow natural line width of the lithium

¹⁰R. M. Healy and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep.* June 30, 1954, ORNL-1815, p 5.

¹¹B. E. Holder and M. P. Klein, *J. Chem. Phys.* **23**, 1956 (1955).

resonance. A high-resolution spinning technique with a very small sample would be necessary to resolve these resonances. The failure to resolve the resonances of lithium was due to a characteristic of the equipment, and does not eliminate the possibility of shifts of the same order of size as

for boron. With some further study, the nuclear magnetic resonance shift may prove to be a convenient guide for comparing a series of similar compounds and for getting an indication of which species are likely to yield the largest isotopic separation factors.

TABLE 7. NUCLEAR MAGNETIC RESONANCE SHIFTS AND SEPARATION FACTORS FOR BF_3 -ORGANIC COMPLEXES

Compound	Magnetic Shift ^a		α^c	Width of Resonance Line ^d (gauss)
	Arbitrary Chart Units ^b	Gauss		
Methyl ether· BF_3	48 ± 2.1	1.31	1.025	0.462
Ethyl ether· BF_3	47 ± 3.4	1.28	1.025	0.435
Phenol· BF_3	42 ± 1.4	1.14	1.027	1.006
Anisole· BF_3	41 ± 0.6	1.12	1.032	0.571
Butyl sulfide· BF_3	39 ± 2.8	1.06	1.033	0.489

^aThis shift is with respect to the resonance in boric acid which occurs at the lower value of applied external field.

^bOne arbitrary chart unit is equal to 0.0272 gauss and is 0.1 mm of chart travel. The deviations are the probable error of the total deviations observed as taken from 4 traces for each test. (Two observations were taken with increasing field and two with field decreasing.)

$$^c \frac{B^{10}/B^{11}(\text{complex})}{B^{10}/B^{11}(\text{BF}_3 \text{ gas})}$$

^dThe width of the line, in general, directly affects the accuracy of determination of the shift.

DEUTERIUM ENRICHMENT

D. A. Lee

PLATINUM METALS CATALYSIS OF THE HYDROGEN-WATER EXCHANGE REACTION

The molecular hydrogen-water exchange reaction¹⁻³ would be suitable for the production of deuterium if the hydrogen exchange were rapid between the two compounds at temperatures at which liquid water might be conveniently used. The reaction $\text{HD(g)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HDO(l)} + \text{H}_2\text{(g)}$ is extremely slow, and the aim of this work has been to catalyze the exchange with a liquid-transported catalyst.

Suspensions of rhodium catalysts on finely divided supports have been reported earlier³ as being the most effective of the catalysts tried. Additional experiments have been made with platinum metal catalysts. A comparison was made of rhodium and platinum on Alon C (0.02 μ particle size alumina) as exchange catalysts. The procedure³ for preparing these catalysts and the apparatus and procedure¹ for determining the exchange rate have been described previously. Each aqueous suspension contained 20 ml of water, 2 g of Alon C, and 0.02 g of metal. The pH of the suspensions was 4.0 and the exchange was measured at 73°C, with a stirring rate of 1200 rpm. The results are plotted in Fig. 11. The half time for the hydrogen-water exchange using the rhodium catalyst was 43 min. The initial half time for the exchange employing the platinum catalyst was 30 min; however, the rate decreased with time.

Rhodium catalysts have an initial fast start for the catalysis of the hydrogen-water exchange.³ An experiment was made to determine the shape of the rate curve at the beginning of the exchange. By using less catalyst, the rate should be slower and the shape of the curve more definite. However, using 10 mg of catalyst in 20 ml of water instead of 100 mg, the characteristic shape was the same and the initial fast start was still unexplained. The results are shown in Fig. 12.

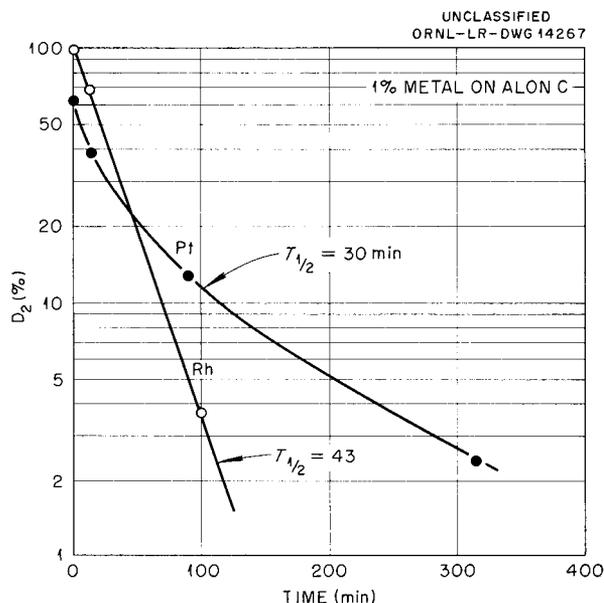


Fig. 11. Rate of D₂-H₂O Exchange, Platinum and Rhodium on Alon C.

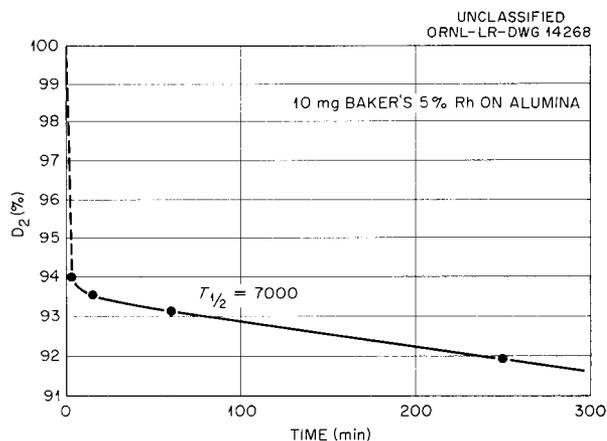


Fig. 12. Rate of D₂-H₂O Exchange, Rhodium on Alumina Catalyst.

It was observed during the exchange experiments using platinum metal oxide catalysts (from The American Platinum Works) that the oxides were reduced to the metal. A comparison of the catalysis by the oxide, and by the reduced oxides of rhodium, palladium, and platinum was made. The results are plotted in Figs. 13, 14, and 15, respectively. Rhodium metal was more effective as a catalyst than rhodium oxide; however, palla-

¹D. A. Lee, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1954*, ORNL-1815, p 13.

²D. A. Lee and L. Landau, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. Dec. 31, 1954*, ORNL-1874, p 7.

³D. A. Lee, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955*, ORNL-2005, p 13.

dium metal was less active than its oxide. Platinum metal had approximately the same catalytic activity as platinum oxide.

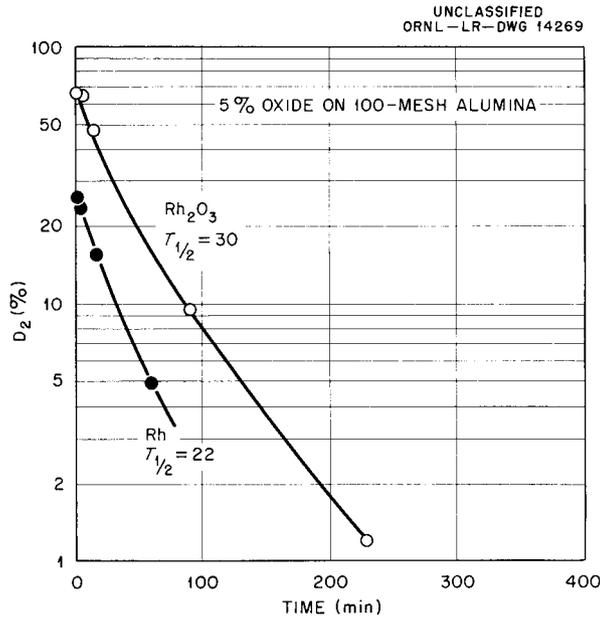


Fig. 13. Effect of Oxide on D₂-H₂O Exchange for Rhodium Catalysts.

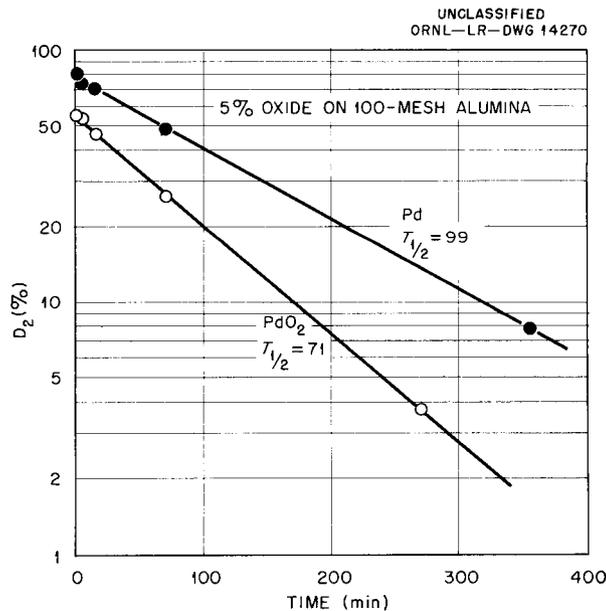


Fig. 14. Effect of Oxide on D₂-H₂O Exchange for Palladium Catalysts.

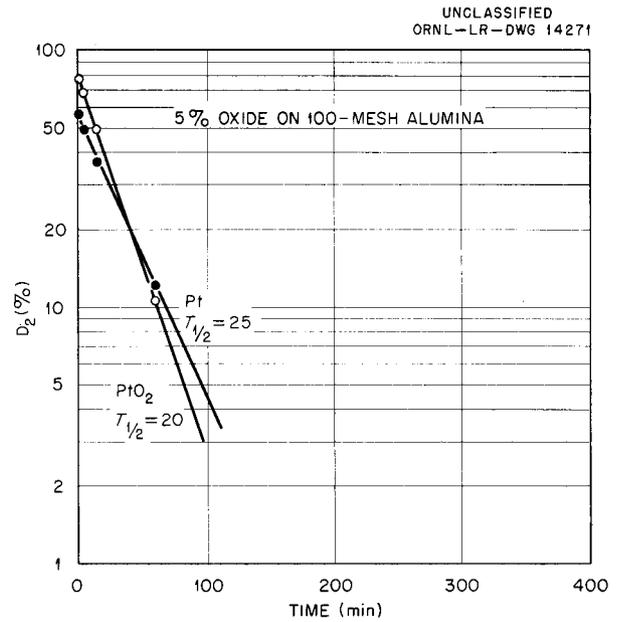
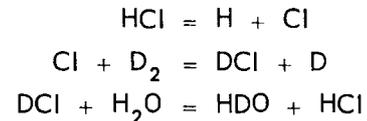


Fig. 15. Effect of Oxide on D₂-H₂O Exchange for Platinum Catalysts.

HCl CATALYSIS OF THE HYDROGEN-WATER EXCHANGE REACTION

It has been suggested by Harteck⁴ of Rensselaer Polytechnic Institute that the liquid water-hydrogen exchange reaction may be catalyzed by the presence of irradiated HCl in the gas phase. The energy required to dissociate HCl is⁵ 101.7 kcal per mole. Wavelengths of less than 2800 Å will furnish adequate energy to do this. The reaction may then proceed as follows:



The exchange was studied as follows: A 600-ml quartz vessel was equipped with a sealed stirrer, an appropriate gas inlet, and a sampling device. The stainless steel Wilson seal housing and stirrer were coated with Teflon to prevent acid reaction with the metal. A 25-ml 4.8 N HCl solution was equilibrated with about 1/2 atm of D₂ gas for 5 hr in the presence of ultraviolet light. The

⁴Private communication to G. H. Clewett.

⁵M. Barak and D. W. G. Style, *Nature* 135, 307 (1935).

lamp used was a mercury vapor lamp made by Hanovia Chemical & Mfg. Co. The light intensity in the cell at 2800 Å was estimated to be 10^{17} quanta/sec. The mercury tube was approximately 2 in. from the quartz cell. The temperature rose to 54°C during the experiment, because of heating from the lamp. Samples of the gas phase were taken at various time intervals. The water and HCl were trapped out of the samples by using liquid nitrogen. The deuterium samples were analyzed by mass spectrometry.

Another experiment was made, using 12 N instead of 4.8 N HCl. The conditions and procedure were identical to those described above. The Teflon coating failed and the stainless steel stirrer reacted with the HCl to produce H₂. Although the deuterium was diluted with hydrogen, evidence of exchange was still noted. Less than 1/2 atm of H₂ was produced by the HCl reduction.

The stirrer was then coated with Unichrome, and another experiment with 12 N HCl was made. No stainless steel attack was noted.

The results of the three experiments are shown in Fig. 16.

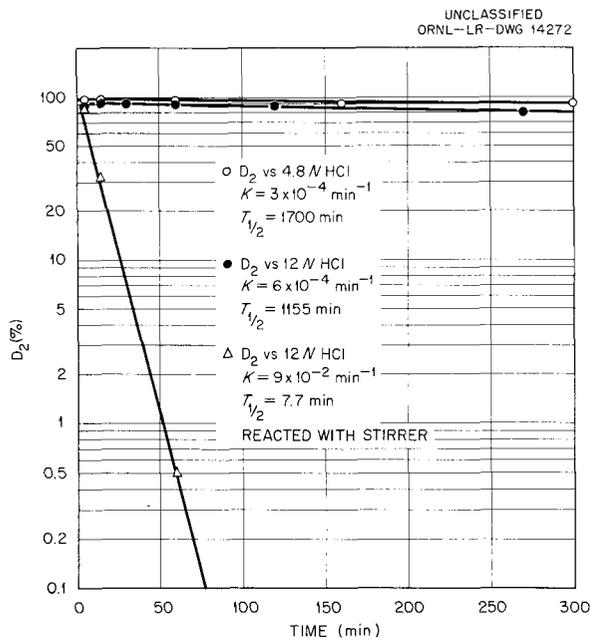


Fig. 16. Effect of Ultraviolet Light on D₂-HCl Exchange.

It can be concluded that irradiated HCl did catalyze the hydrogen-water exchange; however, the rate was still much too slow to be practical for isotope separation.

MICRODETERMINATION OF DEUTERIUM EFFUSIOMETRY

In order to facilitate the catalysis studies of the hydrogen-water exchange reaction, a simple and rapid method was developed for the determination of deuterium by effusiometry.

Molecular weights of pure gases have been determined by means of a low pressure microeffusimeter using matched thermistors as a pressure gauge.⁶ This method has been modified to apply

⁶P. D. Zeman, *Rev. Sci. Instr.* **23**, 176 (1952).

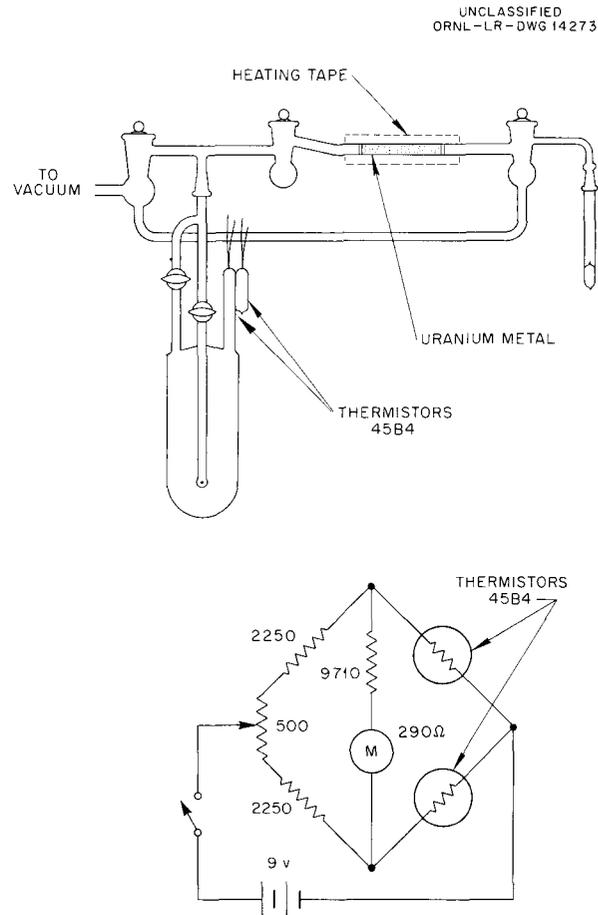


Fig. 17. Hydrogen-Deuterium Effusiometry Apparatus.

to hydrogen-deuterium analyses. Since hydrogen will effuse more rapidly than any other gas, all impurities must be removed from the hydrogen sample. This has been done effectively by passing the gas sample over uranium metal chips at 500°C.

The effusion orifice was made by blowing a thin glass bulb on the end of a 7-mm pyrex tube and sparking a hole through the glass⁷ with a high voltage Tesla coil. The hole is etched to the proper size with dilute HF.

The apparatus as shown in Fig. 17 was attached to a high vacuum system. The rate of effusion was determined by observing the change in pressure with time by utilizing a 45B4 thermistor.⁸

At pressures of 200 μ and less, a straight line was obtained when the log of the meter reading was plotted as a function of time. The slope of this line varies inversely as the square root of the molecular weight.

Briefly, the procedure consisted in passing the gas sample over the hot uranium metal into the evacuated effusimeter, pumping out the gas through the small orifice, and recording the time required to effuse between two preselected pressures as indicated on a microammeter. The per cent of deuterium in the sample was read from a plot of standard hydrogen-deuterium mixtures.

It was observed that the log of the pressure plotted against time was linear for all hydrogen-deuterium mixtures as shown in Fig. 18. The per cent of hydrogen in a mixture plotted against effusion time was found to be linear over all con-

⁷R. J. Munson, *Rev. Sci. Instr.* 26, 236 (1955).
⁸Victory Engineering Corp., Union, N. J.

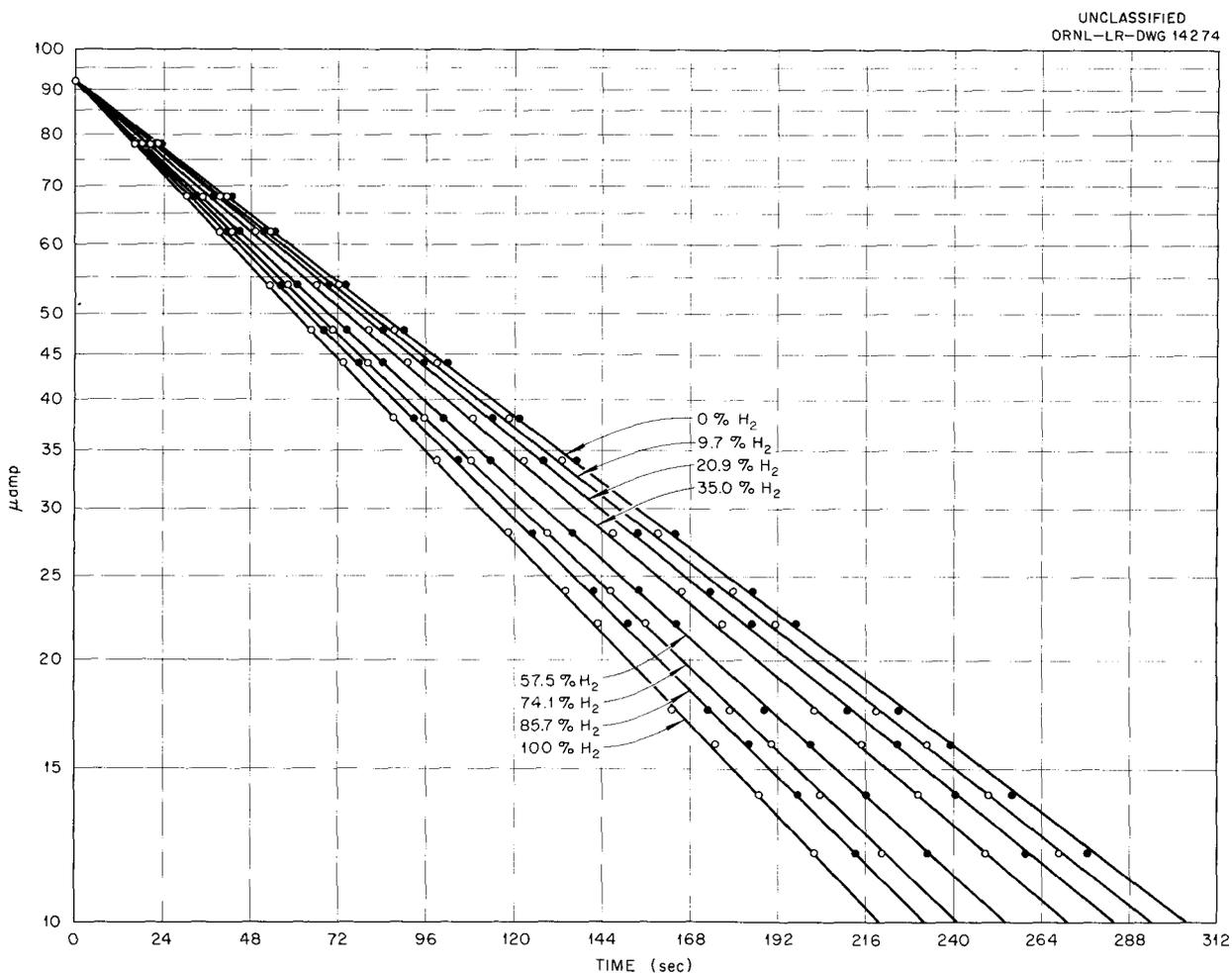


Fig. 18. Effusion Rate of Hydrogen-Deuterium Mixtures.

CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

centrations; this is shown in Fig. 19. The reproducibility of readings for succeeding aliquots of hydrogen-deuterium gas samples is shown in Table 8.

By using hot uranium metal chips, air can be removed from hydrogen samples, and hydrogen-containing compounds can be analyzed directly for deuterium content. The uranium converts the compounds quantitatively to hydrogen.^{9,10} Compounds that were analyzed directly were water, ammonia, and hydrogen sulfide. A calibration curve for water samples is shown in Fig. 20.

⁹A. S. Newton, *The Purification of Some Laboratory Gases*, MDDC-724 (Declassified Jan. 1947).

¹⁰J. Bigeleisen, M. L. Pearlman, and H. C. Prosser, *Anal. Chem.* 24, 1356-1357 (1952).

This device may also be useful in the determination of mixtures of noble gases.

TABLE 8. REPRODUCIBILITY OF EFFUSION TIME FOR H-D MIXTURES

Sample No.	Time (sec)		
	1	254.4	254.3
2	242.2	241.7	242.8
3	232.1	232.4	231.6
4	204.4	203.9	204.1
5	204.7	204.3	204.2
6	202.2	202.3	203.6

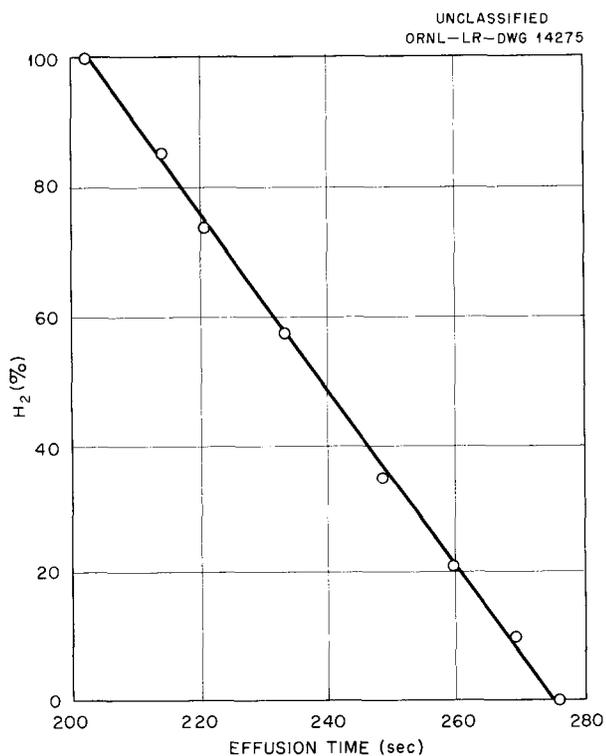


Fig. 19. Calibration Curve for Hydrogen-Deuterium Mixtures.

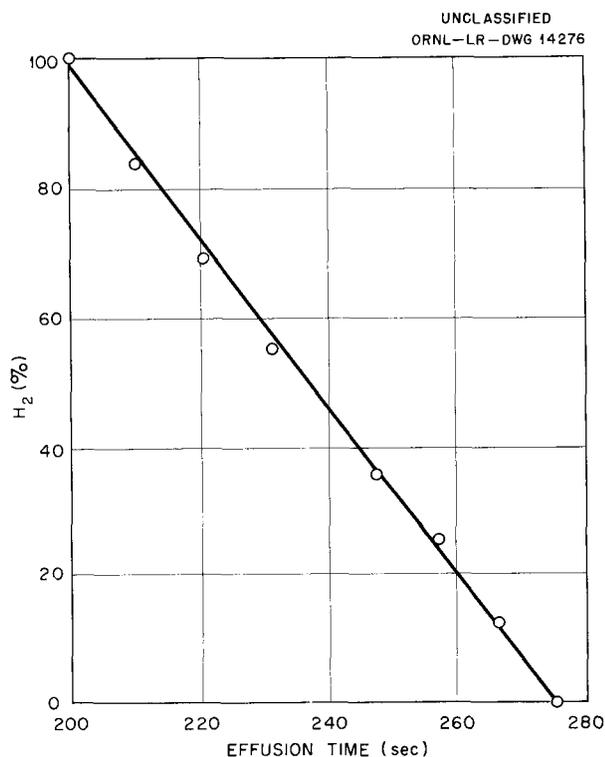


Fig. 20. Calibration Curve for Water Containing Hydrogen-Deuterium.

CONCENTRATION OF N¹⁵THE NITROX SYSTEM FOR NITROGEN
ISOTOPE ENRICHMENT

Rate-of-Exchange Studies

L. L. Brown

A study of the various experimental data related to the Nitrox system suggested that the rate of isotopic exchange is not constant at all acid concentrations. Spindel and Taylor¹ observed a maximum total separation at 10 M HNO₃ in their column studies. Data from this laboratory² showed a decrease in the single-stage separation factor with increasing acid molarity. It is known that the composition of the gas phase varies with acid concentration in such a way that below 6 M HNO₃ there is little NO₂ in the gas phase. Below 3 M HNO₃, the gas is colorless. A comparison of gas composition and separations achieved suggested that NO₂ is necessary for rapid exchange to occur.

The experimental measurement of the rate of isotopic exchange was complicated by the simultaneous establishment of chemical equilibrium. It was assumed that up to 4 M HNO₃ the amount of NO₂ in the gas phase was so small that it could be ignored and that chemical equilibrium occurred between NO and HNO₃ only. This assumption permitted following the isotopic change in the gas phase to measure the rate of exchange. A second simplifying assumption was made; namely, that taking a small portion of the gas for an isotopic sample at intervals did not appreciably disturb the equilibrium of the system. This assumption was fairly safe, since NO is only slightly soluble, and any gas that came out of solution at decreased pressure would not isotopically affect the composition of the bulk gas phase.

A contactor similar to that previously described,² but having only 20 ml of liquid and about 100 ml of gas was used to equilibrate NO with HNO₃. The exact volumes of liquid and gas were measured, and the pump speed adjusted to recycle the entire gas phase 3 times every minute. A capillary tubing gas manifold was used to take gas samples at various intervals. The NO was

reduced with iron powder at 350°C to N₂, which was isotopically compared with a standard N₂ sample. Two runs were made with NO slightly enriched in N¹⁵.

The usual rate-study parameters of time and concentration have little meaning in this work and in their place two rather arbitrary units have been used. "Cycles" is the number of times the gas phase has been pumped through the liquid phase in its entirety. "Assay" is the ratio of N¹⁵/N¹⁴ for the gas sample divided by that ratio for a standard N₂ gas sample. The "assay" parameter decreased with time ("cycles"), since the isotopic fractionation favors N¹⁵ in the liquid phase. The slope of the curve obtained from plotting "assay vs cycles" was proportional to the rate of exchange.

Table 9 summarizes the data for the acid concentrations used; the final value listed is the equilibrium value. The values for 1 M HNO₃ and 3 cycles, and 2 M HNO₃ and 0 cycles, seem obviously in error (air contamination will account for the direction of error) and were ignored in calculating slopes. The 1 M acid work was repeated because of a possible ambiguity. The first run used normal material and depended on the large separation factor (1.065) to detect isotopic changes, but, due to the slow exchange, normal variations in the isotopic analysis obscured the trend of the data. A second experiment, in which enriched NO was used, gave a slope slightly less than for 2 M acid but of the same magnitude. The values at the two concentrations differ by about 10% of the average value, and experimental dif-

TABLE 9. GAS ASSAY* VALUES
FOR NITROX RATE STUDY

1 M HNO ₃		2 M HNO ₃		4 M HNO ₃	
Cycles	Assay	Cycles	Assay	Cycles	Assay
0	1.1291	0	1.0164	0	2.0072
3	1.0000	5	1.0169	6	1.5428
8	1.0115	10	1.0066	15	1.0855
17	0.9912	16	0.9971	32	1.0562
36	0.9906	120	0.9988		

$$* \text{Assay} = \left(\frac{N^{15}}{N^{14}} \right)_{\text{sample}} / \left(\frac{N^{15}}{N^{14}} \right)_{\text{std } N_2}$$

¹W. Spindel and T. I. Taylor, *J. Chem. Phys.* **23**, 981 (1955).

²L. L. Brown, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955*, ORNL-2005, p 19.

facilities of sampling are sufficient to account for this. Between 2 and 4 M HNO₃, the rate increased 3.5-fold, and the NO₂ content in the gas phase was 2.5 times greater. Gas composition at 1 M HNO₃ is so low in NO₂ that a fair comparison with rate is not possible. A greater absolute value of the slope indicates a faster rate of isotopic exchange. Table 9 shows the slopes calculated from data included in Table 10.

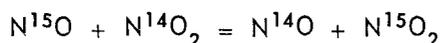
TABLE 10. RATE OF ISOTOPIC EXCHANGE AT DIFFERENT ACID MOLARITIES

Molarity	Slope	$\left(\frac{\text{NO}_2}{\text{NO}}\right)_{\text{gas}}$
1	-0.022	0.0006
2	-0.018	0.002
4	-0.068	0.005

Isotopic Fractionation Between NO and NO₂

G. M. Begun C. E. Melton³

In the course of isotopic analysis of some samples of NO and NO₂ which were enriched in N¹⁵, it was found that an accurate and direct measurement of the equilibrium constant for the exchange reaction between NO and NO₂ could be made. The exchange reaction involved was



$$\text{where } \alpha = \frac{\text{N}^{15}\text{O}_2/\text{N}^{14}\text{O}_2}{\text{N}^{15}\text{O}/\text{N}^{14}\text{O}}$$

This equilibrium constant had been measured previously by Leifer⁴ and reported to be 1.04 ± 0.02. In view of the large uncertainty in this value and because of questions concerning the method used for separating the NO and NO₂, it was decided to attempt to determine a more accurate value.

The procedure used was as follows: Mixtures of NO and NO₂ containing about 15% N¹⁵ were admitted to the expansion chamber of a modified G-E 6-in.-radius, 60-deg-sector-type mass spectrometer. The pressure in the expansion chamber

was 0.05 to 0.1 mm Hg, and the temperature was 23°C. Low pressures were used to prevent formation of appreciable quantities of N₂O₃ or N₂O₄ molecules. After standing for 20 to 30 min, to ensure attainment of equilibrium, samples of the gaseous mixture were admitted to the mass spectrometer ion chamber. The N¹⁴/N¹⁵ ratio was determined by using mass peaks 30/31 and also mass peaks 46/47. These values were corrected for O¹⁷ by using the normal abundance ratio of 1/267 for O¹⁷. Since the N¹⁵ concentration in the samples was so much higher than the O¹⁷ concentration, fractionation of O¹⁷ would introduce a negligible error. The 46/47 ratio was taken as representative of the isotopic content of the NO₂. It was then necessary to correct the 30/31 ratio for the contribution of the NO₂ to the NO peak. The relative amount of NO was kept 10 to 20 times that of NO₂ to make this correction small. By measuring the amount of peak 30, produced when pure NO₂ was admitted to the mass spectrometer under similar conditions, it was determined that for NO₂ the number of NO⁺ ions was 1.4 times the number of NO₂⁺ ions produced, and this factor was used to correct the 30/31 ratio for the NO₂ contribution to the NO isotopic ratio.

Table 11 shows the results of these experiments. Two series of determinations were made at different N¹⁵ concentrations.

The equilibrium constant for the isotopic exchange reaction of nitrogen between NO and NO₂ was determined to be 1.028 ± 0.002 (95% C.I.).

It was still necessary to prove that the value of the N¹⁴/N¹⁵ ratio in pure NO₂ was the same whether determined from the 30/31 or 46/47 mass ratios. Schaeffer and Owen⁵ have found mass discrimination effects in the case of CO₂. In order to prove this point, pure NO₂ was introduced into the mass spectrometer and the 30/31 ratio was compared with the 46/47 ratio. The results are shown in Table 12.

The average of the quotients of the 30/31 ratios divided by the 46/47 ratios was found to be 1.0003 ± 0.002 (95% C.I.); thus, within the limits of error of the technique used, no nitrogen mass discrimination was found in the electron impact ionization of NO₂, and the separation factor results should be valid.

³Stable Isotopes Division.

⁴E. Leifer, *J. Chem. Phys.* 8, 301-303 (1940).

⁵O. A. Schaeffer and H. R. Owen, *J. Chem. Phys.* 23, 1305-1309 (1955).

TABLE 11. MASS ANALYSIS OF NO + NO₂ MIXTURES

Sample	Mass Ratios		30/31 46/47	N ¹⁵ O ₂ /N ¹⁴ O ₂ ^b N ¹⁵ O/N ¹⁴ O
	30/31 ^a	46/47 ^a		
A	5.432	5.332	1.019	1.022
A	5.418	5.303	1.022	1.025
A	5.434	5.319	1.022	1.026
A	5.532	5.392	1.026	1.031
A	5.509	5.364	1.027	1.031
B	7.324	7.125	1.028	1.031
B	7.139	6.961	1.026	1.028
B	7.115	6.936	1.026	1.029
B	7.115	6.942	1.025	1.028
B	7.117	6.946	1.025	1.027
B	7.109	6.934	1.025	1.028

^aEach number is the average of 10 scans of each mass peak and has been corrected for O¹⁷.

^bCorrected for the contribution of NO₂ to the 30/31 ratio.

TABLE 12. MASS ANALYSES OF PURE NO₂ SAMPLES

Sample	Mass Ratios		30/31 46/47
	30/31 ^a	46/47 ^a	
C	276.5	278.1	0.9941
C	279.8	281.1	0.9960
C	281.8	282.8	0.9950
D	7.116	7.086	1.004
E	5.660	5.642	1.003
E	5.614	5.618	0.9993
E	5.620	5.618	1.0002
E	5.610	5.607	1.0006
E	5.608	5.596	1.0021
E	5.601	5.587	1.0025

^aEach number is the average of 10 scans of each mass peak and has been corrected for O¹⁷.

Equilibrium isotopic separation factors can be calculated from spectroscopic data by using the methods described by Urey and Rittenberg.⁶ These have been developed further by Urey⁷ and by Bigeleisen and Mayer.⁸ Leifer⁴ has calculated the factor between NO and NO₂ to be 1.034 at 25°C. Spindel,⁹ using later spectral data, calculated the factor by using central-force assumptions of 1.021, and by using valence-force assumptions of 1.040 at 25°C. Since Spindel's calculations were made, new spectral data has been published¹⁰ on NO₂. This new data changes the assignment of the ω₂ frequency by over 100 cm⁻¹. For this reason, a new calculation of the separation factor was made by using the observed frequencies and the observed angle.^{10,11} For the NO₂ molecule the valence bond assumptions were used.¹² Table 13 gives the constants used in the calculation and the resulting isotopic frequencies.

Table 14 gives the partition function ratios calculated at various temperatures for the isotopic species by using the methods cited previously.^{7,8}

The calculated value for the equilibrium constant is 1.035 at 25°C, which is to be compared with the experimental value of 1.028 ± 0.002 (95% C.I.) at 23°C. The agreement, although good, is not entirely satisfactory and indicates that either the frequency assignments are still somewhat in error or the simple valence bond model gives a rather naïve approximation of the NO₂ molecule. Although the present calculated value is quite close to that obtained by Leifer, the spectral data used was considerably different and agreement is coincidental.

⁶H. C. Urey and D. Rittenberg, *J. Chem. Phys.* **1**, 137 (1933).

⁷H. C. Urey, *J. Chem. Soc.* **1947**, 562-581.

⁸J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.* **15**, 261-267 (1947).

⁹W. Spindel, *J. Chem. Phys.* **22**, 1271-1272 (1954).

¹⁰M. Brown and M. K. Wilson, *J. Chem. Phys.* **22**, 955 (1954).

¹¹G. E. Moore, *J. Opt. Soc. Amer.* **43**, 1045-1050 (1953).

¹²G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, 2d ed., Van Nostrand, New York, 1950.

TABLE 13. SPECTROSCOPIC DATA FOR NO AND NO₂

		$\omega_e(\text{cm}^{-1})$	$\omega_e X_e(\text{cm}^{-1})$	Reference		
NO						
	N ¹⁴ O ¹⁶	1904.03	13.97	a		
	N ¹⁵ O ¹⁶	1869.99	13.47	Calculated		
$\omega_1(\text{cm}^{-1})$	$\omega_2(\text{cm}^{-1})$	$\omega_3(\text{cm}^{-1})$	k_1	k/l^2	α	Reference
NO ₂						
N ¹⁴ O ₂ ¹⁶	1322.5	750.9	1616.0		67°	b, c
N ¹⁴ O ₂ ¹⁶	1303.5	744.1	1580.2	10.78	1.236	67° Calculated, d

^aSee ref. 12, p 558.

^bSee ref. 10.

^cSee ref. 11.

^dFor the valence forces see G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*, p 169, Van Nostrand, New York, 1945.

TABLE 14. PARTITION FUNCTION RATIOS

T(°K)	NO(Q ¹⁵ /Q ¹⁴)	NO ₂ (Q ¹⁵ /Q ¹⁴)	α^*
170	1.132 ₅	1.214 ₄	1.072
220	1.096 ₉	1.155 ₄	1.053
273.1	1.073 ₆	1.116 ₈	1.040
298.1	1.065 ₆	1.103 ₄	1.035
400	1.043 ₈	1.067 ₃	1.023
500	1.031 ₇	1.047 ₃	1.015
600	1.023 ₆	1.034 ₉	1.011

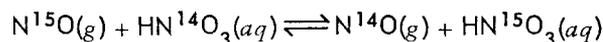
$$*\alpha = \frac{N^{15}O_2/N^{14}O_2}{N^{15}O/N^{14}O}$$

Column Experiments

L. B. Yeatts, Jr.

The enrichment of the N¹⁵ isotope by the Nitrox process consists in passing the gaseous oxides of nitrogen countercurrent to aqueous HNO₃. The exchange reaction, with N¹⁵ concentrating in the

aqueous phase, is given essentially by the reaction:



Sulfur dioxide is used to reduce the HNO₃ to NO and NO₂ for the product-end reflux, producing H₂SO₄ as a by-product. Nitric acid is re-formed at the waste-end reflux by reacting the NO with air and dissolving the NO₂ in water.

An apparatus (Fig. 21) for investigating operating conditions, rate of isotopic enrichment, equilibrium time for the column, stage height, and efficiency of the critical product reflux was assembled and operated. The 15-mm-ID water-cooled exchange column was 7 ft long and was packed with Podbielniak stainless steel Heli-Pak, 0.03 × 0.070 × 0.070 in. The product refluxer with internal and external cooling was packed with 3/32-in. glass helices for about 12 in. above the SO₂ inlet, in the case of the initial two column experiments. A short section at the bottom of this refluxer, serving to cool the hot H₂SO₄ effluent, was also packed with this material. The water-cooled waste-end refluxer was 3.5 ft long with an inside diameter of 1 in. and was packed with 3/32-in. glass helices. The exchange column and

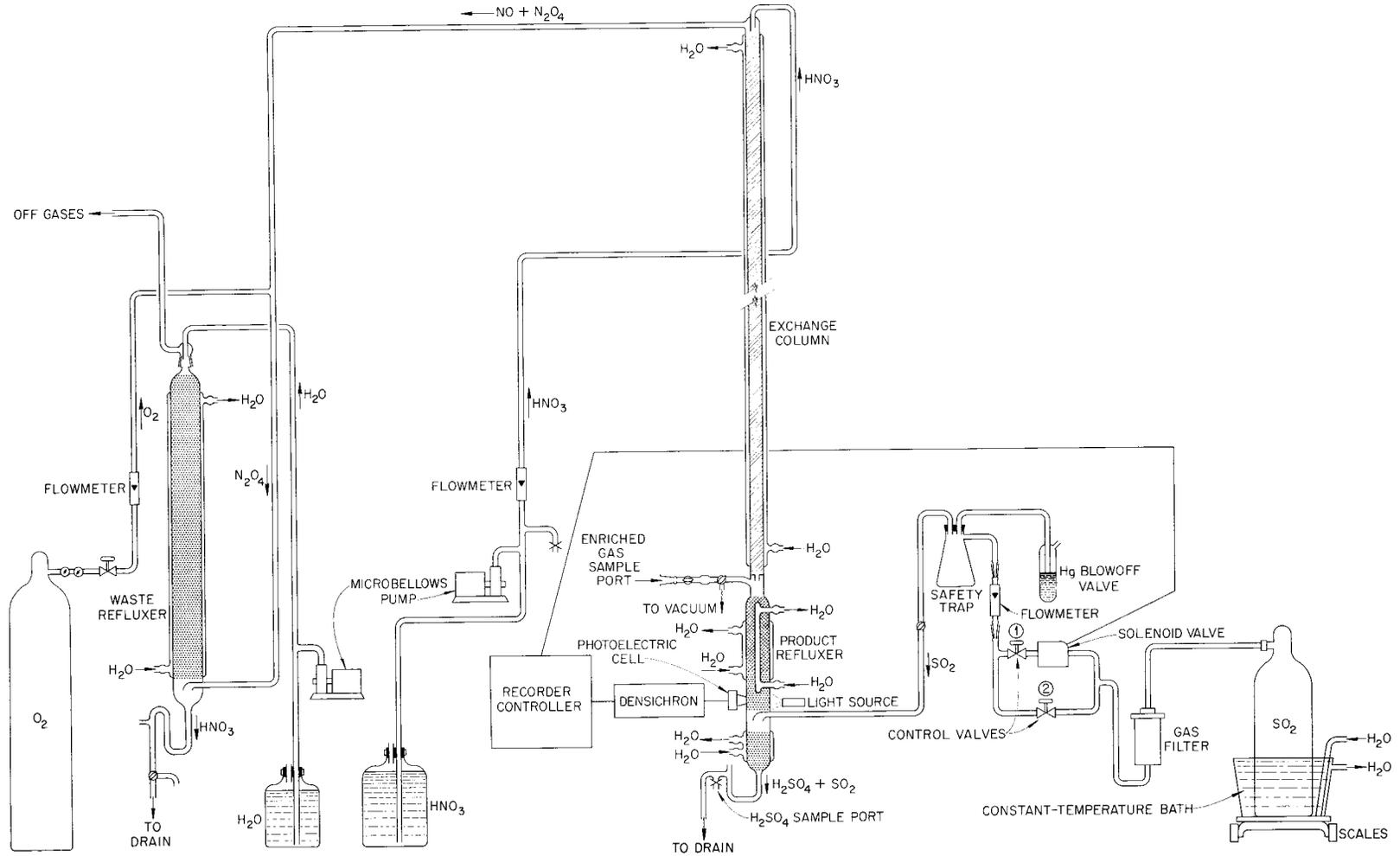
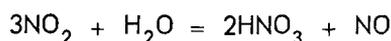


Fig. 21. Apparatus for Studying the Nitrox System.

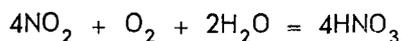
CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

both refluxers were constructed of glass. The delivery lines were, for the most part, $\frac{1}{4}$ -in.-OD stainless steel tubing. Glass-to-stainless-steel connections were made with heavy-walled Teflon tubing.

The procedure was to deliver approximately 7 M HNO_3 , by means of a microbellows pump, from an "infinite reservoir" to the top of the exchange column. As the acid passed down the column it exchanged with a countercurrent stream of NO containing a small fraction of NO_2 and N_2O_4 . In the product refluxer the HNO_3 , enriched in the N^{15} isotope, reacted with SO_2 without cooling.¹³ The reaction produces NO, NO_2 , N_2O_4 , N_2O_3 , and H_2SO_4 saturated with SO_2 . The latter mixture flowed from the bottom of the refluxer while the oxides of nitrogen passed up the refluxer and into the exchange column. By the time these gases had proceeded a few inches into the exchange column, chemical equilibrium had been established with the 7 M HNO_3 . Therefore, mainly NO, with a low concentration of NO_2 , contacted the downward flowing HNO_3 . After leaving the exchange section, the NO reacted with O_2 to produce NO_2 , which then rose countercurrent to water in the waste-end refluxer. The reaction which takes place between the water and this particular nitrogen oxide is:



The reaction was, therefore, carried out in the presence of excess O_2 in order to convert all the NO_2 to HNO_3 :



In the course of normal plant operation, where the economies of the system are of major importance, a high percentage of this HNO_3 would be returned to the system as feed material.

An automatic control of the flow of the reducing gas was utilized to minimize the shifts in the isotopic gradient caused by the movement of the reaction zone in the product refluxer. It was based upon the fact that there is a sharp color difference at the reaction zone - red-brown NO_2

above the reaction interface and clear solution below. The intensity of the light transmitted horizontally by the refluxer depends upon whether the clear solution or the red-brown solution intercepts the light beam. A light source was placed on one side of the refluxer, directly opposite a photoelectric cell whose electrical output was rectified and amplified by a Densichron unit. The output of this unit was fed to a recorder which controlled a normally closed solenoid valve (see Fig. 21). During column operation, a constant flow of SO_2 to the product refluxer was maintained through control valve 2. This flow was slightly less than the stoichiometric flow of SO_2 required to hold the reaction zone at a constant level; hence, the red-brown color moved downward in the refluxer and finally intercepted the light path. The solenoid valve then opened, increasing the flow of SO_2 . This sensitive device functioned well and resulted in smooth column operation.

During operation of the column for the first experiment, 7.1 M HNO_3 was pumped from an "infinite reservoir" at the rate of 210 ml/hr. Distilled water was supplied to the waste-end refluxer at a flow rate of 240 ml/hr. Enriched gas was sampled periodically at the head of the product refluxer. Approximately 5 ml of gas at 0.5 atm pressure constituted a sample, and it was captured in an evacuated break-seal tube containing a small quantity of iron powder. The samples were heated overnight at 350°C to reduce the oxides of nitrogen to molecular nitrogen. A mass analysis was then made of these samples. Samples were also taken for chemical analysis of the H_2SO_4 effluent from the product refluxer and of the HNO_3 produced by the waste refluxer. The results of this experiment are plotted in Fig. 22. The normal abundance of N^{15} was used as the zero time (t_0) value in the calculation of total separation. Total separation is defined in the following manner:

$$\text{Total separation} = S = \frac{(\text{N}^{14}/\text{N}^{15})_t}{(\text{N}^{14}/\text{N}^{15})_{t_0}}$$

The system was still far from equilibrium at the end of 7 hr.

The waste-end refluxer was found to be producing 4.2 M HNO_3 , which represents a 70% recovery of the oxides of nitrogen from the top of the exchange column. It is believed that the

¹³For best product refluxer operating conditions, see L. B. Yeatts, Jr., *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955*, ORNL-2005, p 15.

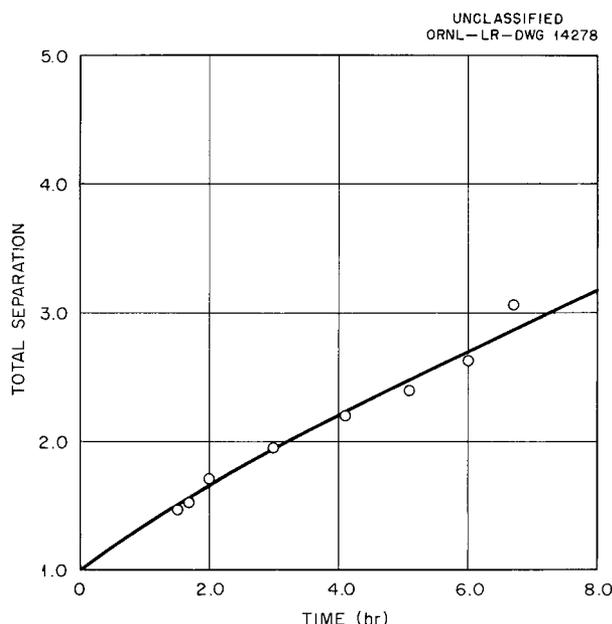


Fig. 22. Time-Total Separation Curve for Experiment I (Nitric Oxide vs Nitric Acid).

percentage recovery can be increased appreciably by increasing the flow of O_2 to this refluxer. The product-end refluxer produced 9.1 M H_2SO_4 containing 0.22 M SO_2 , which would be recovered in a large operation. The average total nitrogen losses detected in the H_2SO_4 effluent was 10 ppm, on a gram-atom basis, representing about 5% of the permissible N^{15} withdrawal at the 95% level.

In an attempt to reduce the time required for the exchange column to attain equilibrium, the flow rate of 7.1 M HNO_3 was increased to 390 ml/hr, which was close to flooding. The relative flow of oxygen to the waste refluxer was also increased in an attempt to recover a higher percentage of the oxides of nitrogen as HNO_3 . The remainder of the experimental procedure was the same as described for the previous run. The temperature of the cooling water varied from 23 to 31°C during the course of operation.

The relationship between time and total separation is plotted in Fig. 23. Isotopic equilibrium was not attained after approximately 60 hr of continuous operation.

As shown by the automatic recorder-controller unit, during the first night the flow of SO_2 fell below that required to maintain the reaction interface in the product refluxer at a constant level.

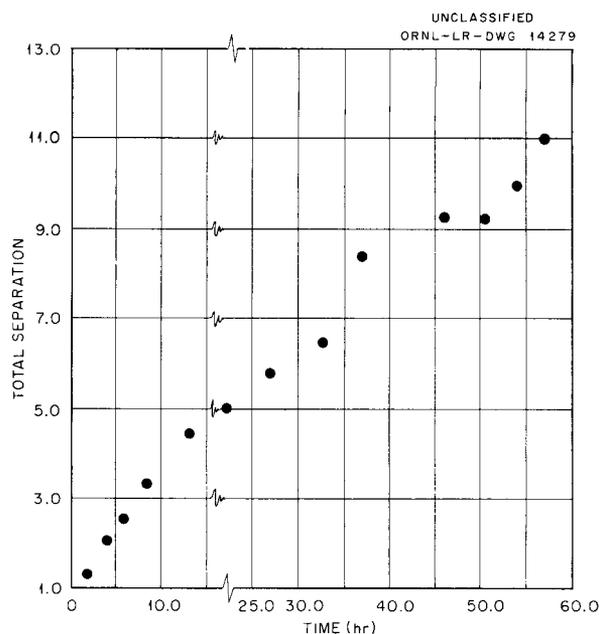


Fig. 23. Time-Total Separation Curve for Experiment II (Nitric Oxide vs Nitric Acid).

The reaction zone had moved downward, and the following morning the H_2SO_4 effluent was discovered to be slightly contaminated with NO_2 . This situation had existed for approximately 5 hr; hence a correction for this period of time has been made along the time axis in Fig. 23. The N^{15} losses during this interval must have been relatively low, because the isotopic gas sample taken immediately after this situation was corrected showed a further enrichment over the previous sample.

Approximately 87% recovery of the nitrogen oxides was realized in the waste refluxer by the increased relative flow of oxygen to this section, which produced 6.2 M HNO_3 . Again, 9.1 M H_2SO_4 came from the product refluxer, and the dissolved SO_2 was 0.29 M. The average value for total nitrogen found in the H_2SO_4 effluent during operation was somewhat less than 5 ppm, on a gram-atom basis.

In preparation for a third column experiment, the holdup in the product refluxer was reduced by approximately one-half in order to reduce the isotopic equilibrium time for the exchange column. This was accomplished by reducing the diameter of the refluxer and the amount of packing. It was packed, as shown in Fig. 21, with $\frac{3}{32}$ -in. glass

helices to a height of 6½ in. above the SO₂ inlet. Extending 8½ in. above this was a coarse stainless steel Demister material, which had an insignificant holdup and aided in the dissipation of heat to the cooling surface. With this reduction in packing material, chemical equilibrium between the oxides of nitrogen and the HNO₃ was no longer achieved in the refluxer, but at the base of the exchange section. This should not seriously decrease the effectiveness of this portion of the exchange column with regard to isotope enrichment.

The tank containing SO₂ to be used in this operation was placed in a constant-temperature bath regulated at 32°C in an effort to overcome fluctuations in the flow which were observed in the past two experiments. An attempt to begin column operation at this time was thwarted because of vigorous pulsation of the SO₂ flow again. Upon disassembling the line between the tank and the control valves on the line, liquid was found to be present. The installation of heating tape between these two points on the line eliminated this difficulty and it has not arisen again.

On this occasion the system was operated continuously for approximately 9 days with 6.97 M HNO₃. For the first 7 days the HNO₃ flow was 360 ml/hr; for the last 2 days, 164 ml/hr. The temperature of the cooling water leaving the exchange column jacket varied from 21 to 24°C. The experimental method has been described previously.

A partial tabulation of the results from this run can be found in Table 15 and a complete plot of the N¹⁵ content as a function of time is presented in Fig. 24.

Most of the isotopic samples taken in the morning after a night of operation without sampling appeared to be low in N¹⁵ and the data fit the curve (Fig. 24) poorly. Many of these samples were heated for only 10–20 min at 450°C, instead of several hours at 350°C, and reduction might have been incomplete; however, some of the initial morning samples reduced at 350°C were also low indicating that other sources of error were contributing to the low values. In Fig. 21, it can be seen that there is a small stagnant gas volume between the top of the product refluxer and the first stopcock leading to the enriched gas sample port. During the early stages of column operation, this section was flushed before taking an isotopic sample; however,

TABLE 15. ISOTOPIC ANALYSES FOR EXPERIMENT III

HNO ₃ Feed Flow (ml/hr)	Time (hr)	N ¹⁴ /N ¹⁵ Ratio	N ¹⁵ (atom %)	Total Separation
360	0	277	0.36	1.0
	8.3	58.8	1.67	4.71
	18.0	34.6	2.81	8.01
	32.7	21.1	4.53	13.1
	44.6	16.2	5.80	17.1
	67.1	12.3	7.52	22.5
	96.9	10.2	8.91	27.1
	127.3	9.93	9.15	27.9
	165.7	8.72	10.3	31.8
	164	170.1	6.96	12.6
194.0		5.22	16.1	53.1
212.8		5.49	15.4	50.4
217.8		5.32	15.8	52.1

after several days of operation this practice was discontinued because of the danger of withdrawing too much product. The time at which flushing of this gas volume was ceased corresponds with the time at which the lowest results began to appear. The explanation for this was the dilution by the stagnant gas of the more highly enriched gas in the product refluxer. The longer the period of time between sampling, the greater the dilution; hence, the initial morning samples yielded the poorest results. Again, it is believed that this is not the complete explanation, particularly for the data at the lower flow rate where results were so inconsistent. Two samples taken in rapid succession after a night of operation showed little difference in N¹⁵ abundance, although if the above explanation was completely valid, the N¹⁵ content of the second sample should have risen sharply.

From Fig. 24, it has been estimated that the isotopic equilibrium time is approximately 200 hr for this system when 6.97 M HNO₃ is used at a flow of 360 ml/hr. From the relationship:

$$\alpha_{\min}^n = \frac{(N^{14}/N^{15})_{t_0}}{(N^{14}/N^{15})_t} = \text{total separation} ,$$

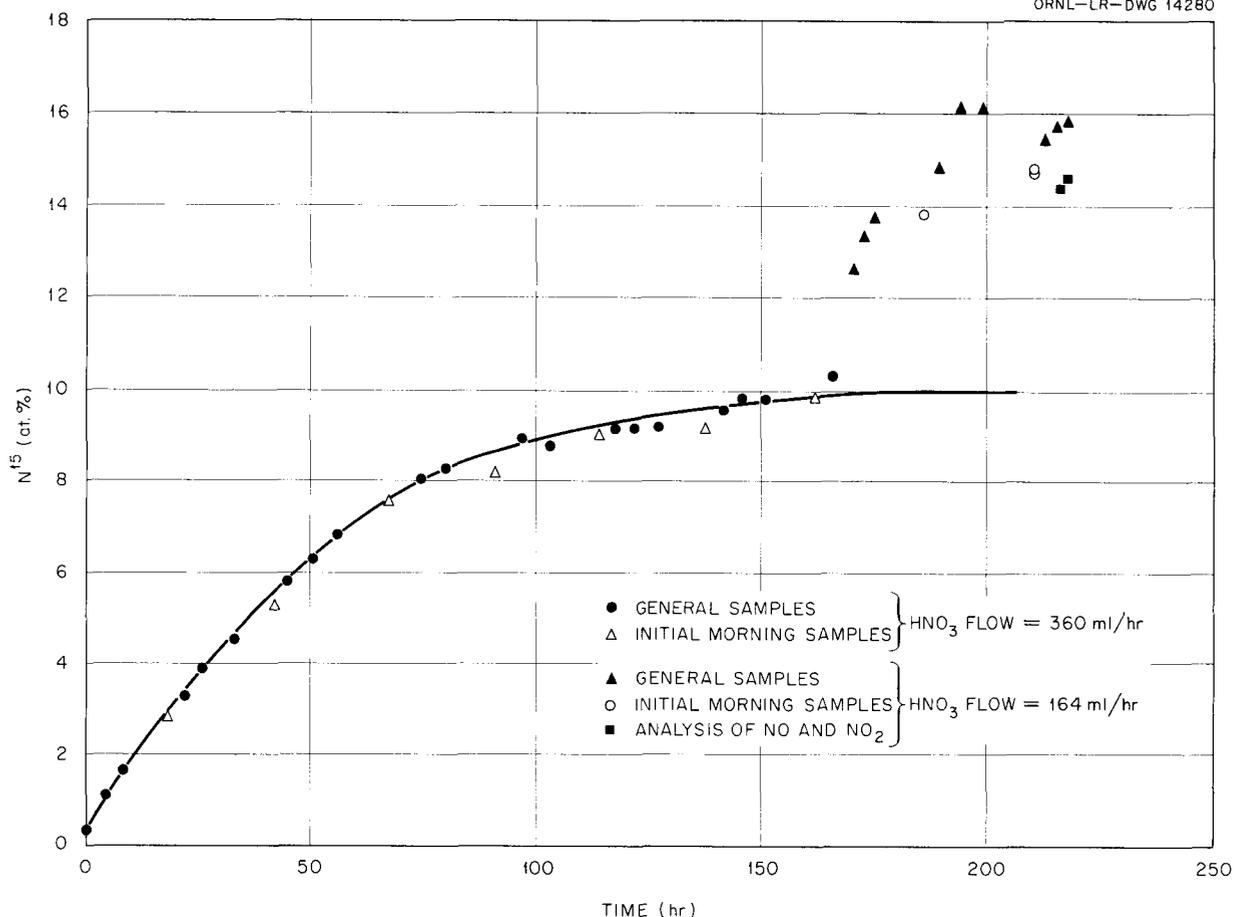
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Fig. 24. Time vs Per Cent N^{15} Plot of Data from Experiment III (Nitric Oxide vs Nitric Acid).

and letting $\alpha = 1.05$, the minimum number of stages in the exchange column (n_{min}) have been calculated. At a flow rate of 360 ml/hr of HNO_3 , there were 71 stages yielding a stage height of 1.2 in.; at 164 ml/hr, the total separation was larger, and 81 stages with a 1.0-in. stage height were indicated. The product refluxer effluent averaged 9.0 M H_2SO_4 and 0.31 M SO_2 . An average of 8 ppm, on a gram-atom basis, was found to be the total nitrogen loss in this effluent.

A concluding experiment was performed in an attempt to establish the effect, if any, of the presence of N_2 in the SO_2 upon the rate of enrichment of N^{15} in the Nitrox system. Heretofore, it has not been established experimentally whether N_2 will undergo isotopic exchange under the conditions found in the Nitrox system. Some consideration is being given to the possibility of refluxing the product end, on a commercial scale,

with a mixture of 20% SO_2 and 80% N_2 ; therefore, this fact should be established.

The flow rate of 7 M HNO_3 during this operation was 175 ml/hr. A mixture of 28% SO_2 and 72% N_2 , as determined by flowmeters, was contacted with the HNO_3 in the product refluxer. The danger of flooding in the exchange column did not permit the raising of the N_2 flow to 80% of the total gas flow. The cooling water temperature varied from 18.5 to 20°C. The mass assay determinations listed in Table 16 and plotted in Fig. 25 were made only of the NO and NO_2 in the gas phase.

The results in Table 16 show that there was slightly enriched gas present in the refluxer at the time isotopic sampling was begun.

Curve IV in Fig. 25 was drawn from the data of this experiment. The other three curves are a result of the three runs previously described. From curves I, II, and III, it can be concluded that the

holdup of the product refluxer, rather than the HNO_3 flow rate, largely determined the rate of approach to isotopic equilibrium. The difference in this rate shown by curves I and IV could be attributed to: (1) the difference in acid flow rate, (2) the increased stage height caused by the N_2

TABLE 16. ISOTOPIC ANALYSES FOR EXPERIMENT IV

Time (hr)	$\text{N}^{14}/\text{N}^{15}$ Ratio	N^{15} (at. %)	Total Separation
0.0	248	0.40	1.12
1.0	185	0.54	1.50
2.0	166	0.60	1.66
3.0	152	0.65	1.82
3.8	145	0.69	1.91
6.0	129	0.77	2.14
9.3	116	0.85	2.38

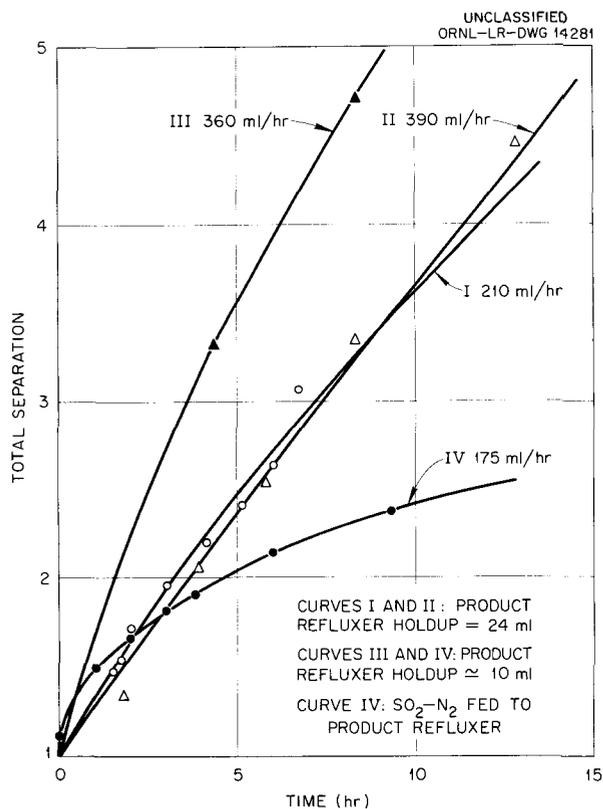


Fig. 25. Total Separation as a Function of Time for Four Nitrox Experiments.

diluted gas, and (3) isotopic exchange with the N_2 . Unfortunately, there are too many variables present to state unequivocally there is no exchange with N_2 . However, it is not unreasonable to expect that the slow rate of approach to equilibrium can be explained by the reduced acid flow rate and the smaller number of stages.

Product-End Reflux

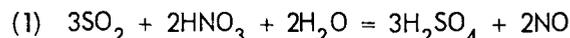
L. B. Yeatts, Jr.

The cost of producing enriched N^{15} by the Nitrox system is strongly dependent upon the sale of the H_2SO_4 produced by the product reflux reaction. In previous experiments, in which 7 M HNO_3 was used, 60% H_2SO_4 was obtained from the product refluxer. Since H_2SO_4 of this concentration is less valuable than higher grades, a series of experiments were performed to determine the relationship between the concentration of H_2SO_4 produced by the Nitrox product-end refluxer and the concentration of HNO_3 fed to the system.

Since the separation factor for the Nitrox system decreases with an increase in HNO_3 concentration,¹⁴ the relationship between the separation factor and the concentration of H_2SO_4 produced by the refluxer can be maximized from such data.

The product refluxer was operated for 3 to 5 hr at each HNO_3 concentration. Three H_2SO_4 samples were taken for each experiment at intervals after the first hour of operation. The experimental results are presented in Table 17 and plotted in Fig. 26.

From this data it is apparent that the highest concentration of H_2SO_4 which can be produced by this reflux is approximately 11 M, or 68%, which is below the concentration desired. The leveling off in H_2SO_4 concentration as the HNO_3 concentration becomes greater than 9 M is caused by two factors. The first of these is the fact that the concentration of NO_2 in equilibrium with the more concentrated HNO_3 is quite high and continues to rise rapidly.¹⁵ From the equations for the net reactions which occur in the product refluxer:



the H_2SO_4 concentration might be expected to pass

¹⁴L. L. Brown, *Chemical Separation of Isotopes Section Semiann. Prog. Rep.* June 30, 1955, ORNL-2005, p 19.

TABLE 17. HNO₃-H₂SO₄ EFFLUENT DATA FOR PRODUCT-END REFLUX

Average HNO ₃ Concentration in Feed (moles/liter)	Average Concentration in Effluent	
	H ₂ SO ₄ (moles/liter)	SO ₂ (moles/liter)
15.4	11.0	0.26
13.9	10.9	0.31
11.9	10.9	0.35
9.4	10.7	0.37
7.0	9.0	0.31
4.7	6.5	0.41
2.8	4.1	

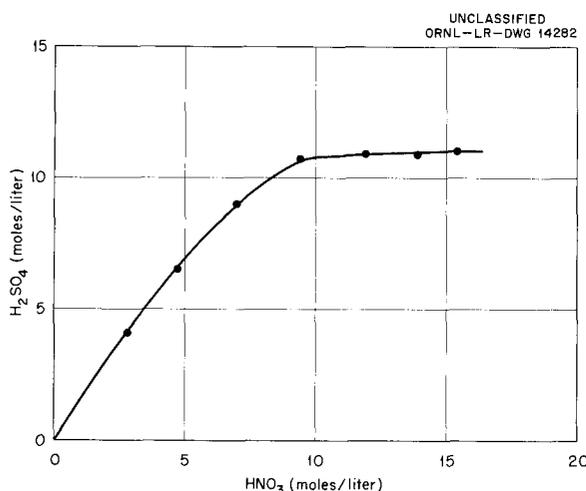


Fig. 26. HNO₃-H₂SO₄ Relationship in Nitrox System.

through a maximum value, and then begin to decrease when the partial pressure ratio of NO₂/NO in equilibrium with HNO₃ becomes greater than unity, at approximately 12 M HNO₃. The second factor is that the H₂SO₄ produced from the higher concentrations of HNO₃ occupies an appreciably smaller volume than the HNO₃ solution from which it was made. From the data of Abel, Schmid, and Stein-Wein¹⁵ and Lange's *Handbook of Chemistry*,

¹⁵H. E. Abel, H. Schmid, and M. Stein-Wein, *Z. Electrochem.* **36**, 692 (1930). For a graph containing this data, see L. L. Brown, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955*, ORNL-2005, Fig. 15, p 19.

using Eqs. 1 and 2, it can be shown that the volume change and the change in the NO₂/NO ratio are compensatory at the higher concentration.

FRACTIONATION OF NITROGEN ISOTOPES BETWEEN METAL-AMMONIA COMPLEXES AND AQUEOUS AMMONIUM HYDROXIDE

A. C. Rutenberg

The study of the fractionation of nitrogen isotopes by various metal-ammonia complexes has continued. The experimental procedure was described in a previous report,¹⁶ and will only be summarized very briefly here. The metal-ammonia complex was adsorbed on Dowex 50 resin, and equilibrated with an aqueous solution of NH₄OH. The phases were separated and samples of NH₃ from both phases were oxidized to N₂, which was isotopically analyzed. The isotope N¹⁵ was found to concentrate in the complexed ammonia on the resin. The measured separations are presented in Table 18.

The observed separations do not appear to be closely related to the stability constants for these metal-ammonia complexes in aqueous solution. Zinc in particular appears to be out of line. An experiment was tried with Co(NH₃)₆⁺⁺ being used, but essentially no fractionation was found after 8 days of agitation. The experiment was put aside for possible sampling at some future date to determine how rapidly equilibrium was being attained. The separation measured between NH₄⁺

¹⁶A. C. Rutenberg, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955*, ORNL-2005, p 26.

TABLE 18. FRACTIONATION OF NITROGEN ISOTOPES BY METAL-AMMONIA COMPLEXES AT 25°C

Metal	NH ₃ /Metal	NH ₄ OH (moles/liter)	$\frac{15/14 M(NH_3)_x^{n+}}{15/14 NH_4OH}$
Ni	3.5	0.07	1.009*
Cu	3.8	0.13	1.012*
Zn	3.8	0.16	1.015*
Cd	3.3	0.18	1.007
Ag	2.1	0.26	1.009

*Average values normalized to 25°C.

on Dowex 50 and NH_4OH (1.027) was greater than that observed for any of the metal-ammonia complexes tried thus far.

FRACTIONATION OF NITROGEN ISOTOPES BY USING AN ION EXCHANGE COLUMN

A. C. Rutenberg

Some experiments based on the system developed at the Ames Laboratory for enriching the isotopes of nitrogen were described in a previous report.¹⁷ The system consists in moving a band of NH_4^+ down a column of Dowex 50 (in the H^+ form) with a solution of NaOH . Isotopic enrichment is accomplished by the exchange between aqueous NH_4OH and NH_4^+ on the resin. In a recent article, Spedding, Powell, and Svec¹⁸ described a continuously operating column and gave data on the variation of stage height with the rate of band travel. They found a larger increase in stage height upon increasing the concentration than for a corresponding change in flow rate.

A number of experiments were performed in this

laboratory to determine the extent to which the separations achieved were affected by thermostating the column. Cooling the column should increase the fractionation factor and reduce the mixing due to the heat evolved at the front interface; on the other hand, greater stage heights would be expected at the lower temperature. The results of these experiments and of some earlier unthermostatted experiments are presented in Table 19. The resin bed of the unjacketed column was 4 in. longer than that of the jacketed column. The difference in band length should not alter the separation appreciably, since the system was far from isotopic equilibrium.

The data show a marked decrease in isotopic fractionation when the rate of band travel was increased. Cooling the column decreased the separation achieved, except for the front (N^{14}) edge in the case of rapid rates of band travel. A single constant-temperature experiment was performed with the column heated to 43°C , and an improvement was noted over the 20°C runs. It appears that some cooling is desirable only if the band is to be moved very rapidly. For a given concentration and flow rate of eluting solution there is an optimum column temperature to achieve maximum isotopic separation.

¹⁷*Ibid.*, p 24.

¹⁸F. H. Spedding, J. E. Powell, and H. J. Svec, *J. Am. Chem. Soc.* **77**, 6125 (1955).

TABLE 19. VARIATION OF SEPARATION WITH RATE OF BAND TRAVEL

Experiment ^a	Band Length (in.)	Average Rate of Band Travel (in./hr)	NaOH Concentration (moles/liter)	Average Liquid Flow Rate (ml/hr)	Isotopic Analysis ^b	
					Front Edge	Rear Edge
A-1	12.7	4	0.250	500	0.25 (8) ^c	2.88 (12)
A-2	9.7	10	0.495	670	0.38 (4)	2.96 (3)
A-3	9.0	32	2.40	560	0.75 (4)	1.61 (2)
B-1	10.5	48	2.40	680	0.62 (4)	1.33 (13)
B-2	9.2	44	2.40	620	0.60 (7)	1.38 (7)
B-3	9.7	9	0.495	500	Lost	2.01 (10)
B-4	9.8	7.5	0.490	450	0.42 (4)	2.17 (3)
C-1	9.8	14	0.490	780	0.36 (4)	2.50 (4)

^aA series unthermostatted experiment, 84 in. resin bed

B series experiment at 20°C , 80-in. resin bed

C series experiment at 43°C , 80-in. resin bed

^b
$$\frac{(\text{N}^{15}/\text{N}^{14})_{\text{sample}}}{(\text{N}^{15}/\text{N}^{14})_{\text{normal std}}}$$

^cNumbers in parentheses indicate sample size in milliequivalents.

ENRICHMENT OF OXYGEN ISOTOPES

A new program has been initiated by the Isotope Separation Section to study chemical methods for enriching the isotopes of oxygen. Of special interest is O^{17} (normal abundance 0.04%), since this isotope can be analyzed by the nuclear magnetic resonance (NMR) method with little disturbance to the system under study. Although O^{18} (normal abundance 0.20%) is a useful tracer, it can be used only in systems in which it is permissible to sample the oxygen-containing material for subsequent mass analysis. The radioactive isotopes of oxygen are of too short a half life to be useful in tracer studies. As a tracer, O^{17} would be particularly valuable for use in the study of systems of biological interest, as, for example, in elucidating some aspects of the mechanism of photosynthesis.

The older methods for oxygen enrichment are reviewed by Dole¹ and include distillation, thermal diffusion, electrolysis, and chemical exchange. Table 20 lists some previously reported systems with their separation factors. Low concentrations of O^{17} are available as a by-product of deuterium enrichment in water. The chemical exchange of oxygen between CO_2 and H_2O has been studied by Boyd and White² in a 70-ft exchange column. Except for its inconvenient slow rate of exchange, this latter system with a separation factor of 1.04

¹M. Dole, *Chem. Rev.* **51**, 263 (1952).

²W. T. Boyd and R. R. White, *Ind. Eng. Chem.* **44**, 2202 (1952).

TABLE 20. OXYGEN ISOTOPE SEPARATION FACTORS OF SOME PREVIOUSLY REPORTED SYSTEMS

System	Temperature (°C)	Separation Factor	Remarks	Reference
$2H_2O^{18} + O_2^{16} = 2H_2O^{16} + O_2^{18}$	0	1.017	H_2O gas, calculated	<i>a</i>
$2H_2O^{18} + O_2^{16} = 2H_2O^{16} + O_2^{18}$	0	1.006	H_2O liquid, calculated	<i>a</i>
$2H_2O^{18} + CO_2^{16} = 2H_2O^{16} + CO_2^{18}$	0	1.047	H_2O liquid, slow to exchange	<i>a</i>
H_2O distillation	{ 10 100 }	{ 1.011 1.003 }	Vapor pressure ratio H_2O^{16}/H_2O^{18}	<i>b</i>
CH_3OH distillation	(65)	1.003	Vapor pressure ratio $CH_3O^{16}H/CH_3O^{18}H$	<i>c</i>
O_2 distillation	-183	1.0065	Vapor pressure ratio O_2^{16}/O_2^{18}	<i>d</i>
CO distillation	-192	1.008	Vapor pressure ratio $C^{12}O^{16}/C^{12}O^{18}$	<i>e</i>
H_2O electrolysis		1.03	Typical value	<i>f</i>

^aH. C. Urey, *J. Chem. Soc.* **1947**, 562.

^bM. H. Wahl and H. C. Urey, *J. Chem. Phys.* **3**, 411 (1935).

^cP. Baertschi, W. Kuhn, and H. Kuhn, *Nature* **171**, 1018 (1953).

^dH. G. Thode and S. R. Smith, *The Separation of the Oxygen Isotopes by the Distillation of Technical Liquid Oxygen*, MC-45, March, 1944.

^eT. F. Johns, H. Kronberger, and H. London, "Enrichment of Heavy Isotopes of Carbon and Oxygen by Fractional Distillation of Carbon Monoxide," p 141-147 in *Report of a Conference Organized by the Mass Spectrometry Panel of the Institute of Petroleum Held in Manchester, England, April 20-21, 1950*, Institute of Petroleum, 1952.

^fL. Tronstad and J. Brun, *Trans. Faraday Soc.* **34**, 766 (1938).

would have promise for large-scale production. While O^{17} was the isotope of principal interest, the factor for O^{16}/O^{18} separation was more easily determined in the mass spectrometer and is reported in the following experiments. Based on the rule of the geometric mean, it was assumed that the enrichment factor ($\alpha - 1$) for O^{16}/O^{17} would be almost exactly one-half the value measured for O^{16}/O^{18} .

CUPROUS CHLORIDE COMPLEXES
WITH CO AND O_2

L. L. Brown

Cuprous chloride solutions are used in gas analysis for quantitative absorption of carbon monoxide. The solute combines with the CO in an undetermined manner when in solution but has been isolated as a solid³ with the composition $Cu_2Cl_2 \cdot 2CO \cdot 4H_2O$. The CO absorbed by the solution can be recovered by boiling. In all likelihood, CO does not exchange oxygen with water at a fast rate so that only the CO need be refluxed. A countercurrent gas-liquid system is visualized which might separate either carbon or oxygen isotopes or both.

Urey and co-workers⁴ have reported the separation of carbon isotopes by the method just described. In an 8-meter column, 1 cm in diameter, they obtained a total separation of 1.69 for C^{13} ; however, neither the single-stage factor for carbon nor any oxygen data were reported. The lack of oxygen data pertinent to our interests was sufficient reason to repeat the experiment on a single-stage basis and, simultaneously, to get additional carbon data.

Twenty grams of Cu_2Cl_2 was dissolved in 300 ml of 4 M HCl in the presence of clean copper turnings. The CO was prepared from freshly boiled formic acid and H_2SO_4 in vacuum apparatus. Since CO and N_2 both give peaks at mass No. 28, helium purges were used to make the apparatus air-free. The contactor used was the same as previously described for Nitrox studies.⁵ Ninety milliliters of liquid was introduced into the contactor, which was thermostatted at 27.8°C. After

the helium was pumped off, CO was added by means of a Toepler pump to a total pressure of 70 cm. The gas phase occupied a volume of 550 ml and had a pressure of 68 cm at equilibrium. The CO was circulated at the rate of 500 ml/min through the liquid for 80 min and then sampled directly in evacuated break-seal tubes. A portion of the liquid was transferred to a vacuum line and frozen while the gas train was being evacuated. Subsequent boiling freed the complexed CO which was collected in break-seal tubes. The samples were submitted for C^{12}/C^{13} and O^{16}/O^{18} ratios.

It is readily seen from the data of Table 21 that isotopic fractionation of both carbon and oxygen occurred in the system. The light isotope of each element was concentrated in the gas phase. The separation factor, defined as the ratio of the light to the heavy isotope in gas phase divided by that ratio for the liquid phase, was 1.019 ± 0.004 for carbon and 1.041 ± 0.003 for oxygen at the 95% confidence level. By using the above separation factor for carbon, a reasonable stage height of 11 in. was calculated for Urey's column. This system should give a separation factor of $\sim 1.02 [1 + (0.04/2)]$ for O^{16}/O^{17} .

Since the cuprous chloride reagent used for the analysis of CO also absorbs O_2 , it was hoped that reversibility of O_2 absorption might exist. The same experiment performed with CO was repeated, but with a tank of O_2 being substituted for the CO.

The following observations were made in the 30 min of gas circulation. First, the solution became quite dark in color because of the complexing of O_2 . Small isolated drops of the solution

TABLE 21. ISOTOPIC ANALYSIS OF CO FROM CUPROUS CHLORIDE-CO EXPERIMENT

C^{12}/C^{13}		O^{16}/O^{18}	
Gas	Liquid	Gas	Liquid
94.03	92.66	494	474
94.26	92.59	503	487
94.21	92.53	498	494
94.16	92.02	501	464
93.88	92.15	496	470
	92.34		483
Av 94.11	92.38	498.4	479.7

³W. A. Jones, *Am. Chem. J.*, **22**, 287 (1899).

⁴I. Roberts, H. G. Thode, and H. C. Urey, *J. Chem. Phys.*, **7**, 137 (1939).

⁵L. L. Brown, *Chemical Separation of Isotopes Section Semiann. Prog. Rep.* June 30, 1955, ORNL-2005, p 20.

on the reactor walls turned lime green, indicating that CuCl_4^{--} was formed by oxidation of Cu^+ . The bulk of the solution retained the dark color. The pressure fell from 70 to 35 cm, indicating a consumption of O_2 .

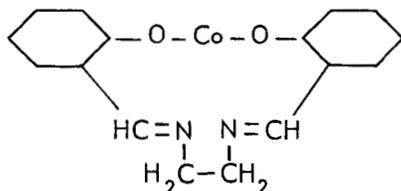
Despite the obviously unsuitable conditions for an isotope separation system, samples of the feed gas and gas phase were taken. It was impossible to remove any O_2 from the liquid by boiling under vacuum. Analysis of the two sets of samples proved them to be identical within the error limits of the analysis.

COBALT DI(SALICYLAL)ETHYLENEDIIMINE OXYGEN COMPLEX

L. L. Brown

Investigations of O_2 carriers of various nature show that O_2 is sometimes recoverable from the carrier in nearly quantitative amounts. Some solids have been used to concentrate O_2 by alternate absorption-desorption cycles for naval applications. Martell and Calvin⁶ review concisely the properties of a number of O_2 -carrying chelates. There is no mention of isotopic oxygen data for chelates, but the likelihood of some separation between gaseous and complexed O_2 seemed worthy of investigation.

In general, O_2 is complexed by these chelates at atmospheric pressure and room temperature and is removed by heat and/or low pressure. The literature had some reference to chelates in solution,⁷ but the preponderance of work has been on solids. The chelates of cobalt(II) combine with oxygen in the molar ratio of 2 chelates per molecule of O_2 . The simplest chelate is cobalt di(salicylal)ethylenediimine (CoSaEn), and was chosen for determination of the separation factor between O^{16} and O^{18} . The structural formula for $\text{CoC}_{16}\text{H}_{14}\text{N}_2\text{O}_2$ is



⁶A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, chap. VIII., Prentice-Hall, New York, 1952.

⁷O. L. Harle and M. Calvin, *J. Am. Chem. Soc.* **68**, 2612 (1946).

This compound was prepared according to the directions given by Bailes and Calvin.⁸ The compound has no affinity for N_2 (nor CO), so the active crystals were handled in a dry box with a N_2 atmosphere. Approximately 3 g of the solid was placed in a cylindrical pyrex tube 30 cm long with a stopcock used to admit and remove O_2 . The total volume of the tube was 120 ml. A total of 160 ml of O_2 at 26°C and 75 mm pressure was added. The chelate complexed approximately 40 ml of O_2 under these conditions. The solid changed color from brown to black, and heat was evolved upon absorption of O_2 . The tube was set aside at room temperature (26°C) with occasional shaking to disturb the solid phase. After 40 hr the gas phase was sampled by expansion into break-seal tubes. The remainder of the gas was pumped out and discarded. The tube was then heated with a hot air blast until the solid color had changed from black to light tan. The released O_2 was put into break-seal tubes. Upon cooling, the solid reabsorbed some of the remaining O_2 in the tube but did not darken in color to the extent that it did upon the first exposure. The oxygen samples were submitted for determination of the $\text{O}^{16}/\text{O}^{18}$ ratio along with samples of the feed oxygen. Six tubes from each group were taken.

The isotopic assays of the tank oxygen used for feed, of the gas phase, and of the solid phase are shown in Table 22. It is seen that there was

⁸R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.* **69**, 1886 (1947).

TABLE 22. ISOTOPIC ANALYSIS OF O_2
FROM CoSaEn- O_2 EXPERIMENT

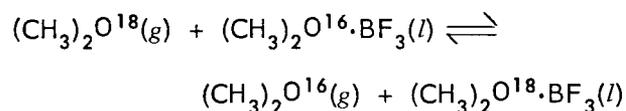
Gas	Isotopic Ratio ($\text{O}^{16}/\text{O}^{18}$)	
	Solid	Feed O_2
479.6	486.7	481.1
480.0	485.9	483.2
479.8	486.5	482.2
480.1	485.2	482.7
479.3	485.7	482.4
		482.6
Av 479.7	486.0	482.4

a separation of isotopes, since the separate phases assay differently than the feed from which they were made. The separation factor was 1.013 ± 0.002 (95% C.I.) with the O^{18} isotope concentrating in the gas phase, which is the same direction found for the O_2-H_2O exchange.

OXYGEN SEPARATION FACTOR IN THE BF_3 -METHYL ETHER SYSTEM

R. M. Healy

Previous work⁹ in this laboratory has indicated the probability of an $O^{16}-O^{18}$ separation factor larger than 1.016 for the reaction:



A single-stage experiment was carried out by equilibrating approximately equimolar amounts of gaseous methyl ether and liquid methyl ether- BF_3 complex. Tank methyl ether was redistilled over sodium before using, and BF_3 was freed from noncondensable gases.

The gas phase was sampled, after the complex was quickly frozen, by leading it through concentrated sodium hydroxide solution on to sodium metal. The ether was distilled from the metal at about $-5^\circ C$. The middle portion was taken for mass analysis. To sample the liquid phase a few milliliters was poured onto an excess of CaF_2 . The mixture was warmed to $100^\circ C$ to drive off

⁹G. M. Begun, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1955*, ORNL-2005, p 31.

the methyl ether, which was led through traps in a manner similar to the methyl ether from the gas phase.

Mass analysis on eight replicates from each phase yielded a separation factor:

$$\alpha = 1.017 \pm 0.005 \text{ (95\% C.I.) ,}$$

with O^{18} concentrating in the liquid complex.

It seems probable that this system could be refluxed by the scheme shown in Fig. 27. The organic complexing agent, R, would be a high-boiling, fairly strong Lewis base such as dimethyl-aniline.

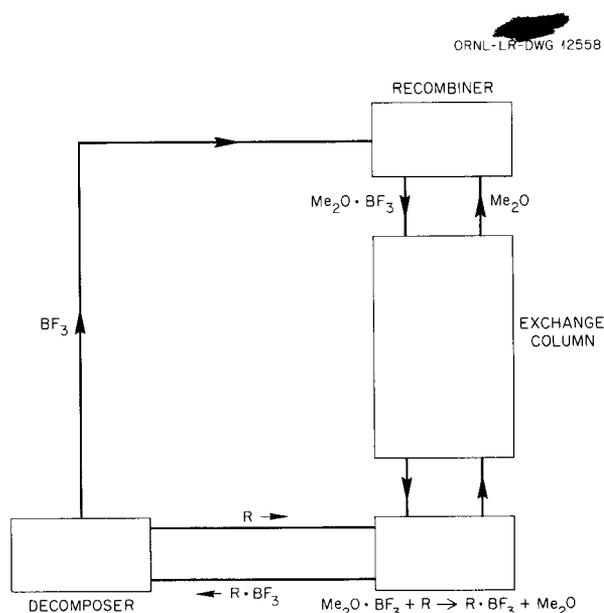


Fig. 27. A Method for Separating Oxygen Isotopes.