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CHEMICAL SEPARATION OF ISOTOPES SECTION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING JUNE 30, 1955

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G. H. Clewett, Director

CHEMICAL SEPARATION OF ISOTOPES SECTION

SEMIANNUAL PROGRESS REPORT

For Period Ending June 30, 1955

J. S. Drury, Supervisor

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CONTENTS

SUMMARY 1

SEPARATION OF BORON ISOTOPES 2

The ANCO System for Boron Isotope Enrichment 2

Determination of the Isotopic Separation Factor 2

Rate of Isotopic Exchange 2

Regeneration of BF_3 from Complex 3

Vapor Pressure of Anisole·BF_3 Complex 6

Semi-Pilot-Plant Studies 7

Boron Trifluoride–Boron Trichloride Exchange 10

CATALYSIS OF THE HYDROGEN-WATER EXCHANGE REACTION 13

CONCENTRATION OF N^{15} 15

Nitrox Product-End Reflux 15

Single-Stage Separation Factors for Nitrox System 18

Gas-Liquid Contactor 19

Carbonate-System Pilot-Plant Studies 21

Nitric Oxide–Ferronitroso Ion System for Concentration of N^{15} 23

Fractionation of Nitrogen Isotopes on Ion-Exchange Resins 24

Fractionation of Nitrogen Isotopes Between Metal-Ammonia Complexes and Aqueous Ammonium Hydroxide 25

Nitrogen and Oxygen Isotope Effects in the Distillation of N_2O_4 27

OXYGEN ENRICHMENT IN SAMPLES FROM THE BORON ISOTOPE PLANT 31

ISOTOPE SEPARATION FACTOR FOR THE SYSTEM KI(DIMETHYL CELLOSOLVE) vs NaK 32

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CHEMICAL SEPARATION OF ISOTOPES SECTION SEMIANNUAL PROGRESS REPORT

SUMMARY

The countercurrent gas-liquid system $BF_3(g)$–anisole·$BF_3(l)$ for the concentration of boron isotopes has been studied. The single-stage separation factor varies from 1.039 at 0°C to 1.029 at 30°C. Rate of exchange is rapid, and, with efficient contacting equipment, complete exchange may be obtained in less than 15 sec. A total separation of 1.525 has been realized in laboratory equipment. The critical-product reflux reaction is quite efficient. Only about 55 moles of BF_3 remain in each million moles of effluent solvent under laboratory conditions. The vapor pressure of BF_3 over the complex rises sharply as the temperature is increased. At 0°C the pressure is 150 mm Hg, and at 40°C the pressure has risen to 1800 mm Hg. From vapor-pressure measurements, an approximate upper limit of $\Delta H = -12$ kcal per mole of complex was calculated for the reaction

$$BF_3(g) + \text{Anisole}(l) \rightleftharpoons \text{Anisole} \cdot BF_3(l)$$

Qualitative tests indicate good resistance of anisole to decomposition by BF_3 under plant conditions.

The uncatalyzed exchange of boron between BF_3 and BCl_3 was found to be too slow to be exploited in a countercurrent system.

The single-stage, equilibrium separation factor for the Nitrox system is a function of acid concentration. At 26°C the factor ranges from 1.064 with 1 *M* acid to 1.020 with 15 *M* acid.

A contactor is described for studies on gas-liquid equilibria.

A product-end refluxer for the Nitrox system, $NO(g)$ vs $HNO_3(aq)$, was designed and operated and was found to be satisfactory for use in this exchange system.

The nitrogen-isotope separation factor for the system $NO(g)$ vs $FeNO^{++}(aq)$ was found to be 1.009 at 16.5°C. The N^{15} concentrated in the liquid phase.

The fractionation of nitrogen isotopes between aqueous ammonium hydroxide and metal-ammonia complexes adsorbed on Dowex 50 resin is being studied. The separation factors for complexes of Ni, Cu, and Zn have been measured; further experiments are in progress.

A number of experiments have been performed to evaluate the Ames ammonium resin–ammonium hydroxide moving-band ion-exchange system for enriching the isotopes of nitrogen. A separation factor of 1.027 (24°C) was measured, and the total separation was shown to decrease upon increasing the rate of band travel.

A number of platinum metals have been investigated as possible heterogeneous catalysts for the low-temperature hydrogen-water exchange. Rhodium was found to be an active exchange catalyst.

The compounds studied as possible homogeneous catalysts were noncatalytic.

The equilibrium distillation of N_2O_4 has been found to enrich N^{15} in the liquid phase and O^{18} in the gaseous species. Estimated single-stage separation factors are approximately 1.004 for both N^{15} and O^{18} concentration.

It has been found that the $B^{10}F_3$·dimethyl ether complex produced by the multistage distillation of BF_3·dimethyl ether complex is more than threefold enriched in O^{18}. The effective single-stage separation factor for oxygen separation by this system is estimated to be greater than 1.01.

The equilibrium constant for the reaction

$$NaK^{41} + K^{39}I(DMC) = NaK^{39} + K^{41}I(DMC)$$

was found to be approximately 1.015 at 23°C.

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SEPARATION OF BORON ISOTOPES

THE ANCO SYSTEM FOR BORON ISOTOPE ENRICHMENT

R. M. Healy A. A. Palko

The ANCO (anisole-complex) system utilizes the exchange reaction between $BF_3(g)$ and anisole·$BF_3(l)$ to enrich the isotopes of boron. Boron-11 is concentrated in the gas phase, and B^{10} is concentrated in the complex. Reflux is accomplished at the B^{10} end of the system by dissociating the complex with heat, and at the B^{11} end by absorbing the BF_3 in anisole. The ANCO system appears to offer several advantages over the BF_3·dimethyl ether system currently in use: (1) The separation factor is higher, (2) the system is operated at atmospheric pressure (this simplifies operation and permits a greater throughput from equipment of a given size), and (3) the product can be readily withdrawn as BF_3.

Determination of the Isotopic Separation Factor

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

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

The apparatus and the experimental techniques for determining the separation factor as o function of temperature were presented, along with some preliminary results, in the previous report.[1] The results obtained to date are summarized in Table 1, and a plot of the separation factor vs temperature is presented in Fig. 1.

The single-stage separation factor was found to vary from 1.039 at 0°C to 1.029 at 30°C. As with the BF_3·dimethyl ether system, the B^{11} was found to concentrate in the gaseous phase. The gas phase of the ANCO system, in contrast with the BF_3·dimethyl ether system, contains very little undissociated complex, and this contributes to the increased separation factor. The effective enrichment factor (separation factor − 1) for the ANCO system is approximately twice that of the BF_3·dimethyl ether system.

[1]R. M. Healy and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. Dec. 31, 1954*, ORNL-1874, p 2, esp. p 4.

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

Temperature (°C)	Separation Factor*
30	1.0288
28	1.0307
26	1.0295
25	1.0346
22	1.0345
20	1.0297**
20	1.0284**
20	1.0280
15	1.0344
0	1.0364
0	1.0410

$$*\frac{B^{10}/B^{11}\ (\text{anisole}\cdot BF_3\ \text{complex})}{B^{10}/B^{11}\ (BF_3\ \text{gas})}.$$

**Average of three analyses.

Rate of Isotopic Exchange

In order for a system, such as the ANCO system, to be effective it is necessary that isotopic exchange be rapid between the gas and liquid countercurrent phases. The apparatus used to determine the rate of exchange between BF_3 gas and the anisole·BF_3 1:1 complex is shown in Fig. 2. This apparatus consisted of a 300-cc round-bottom flask to which a 28/15 ball joint and a three-way stopcock were attached. The flask was used as a gas-liquid contactor. The 28/15 ball joint was used to attach a thin-wall break tube that contained a known amount of anisole·BF_3 complex. The three-way stopcock was used to attach a set of sampling tubes and also provided a means of evacuating the entire apparatus. Experiments with contacting times of the order of 4 sec were possible.

The procedure for making a determination was as follows: After the apparatus had been cleaned and dried and a weighed amount of anisole·BF_3 complex introduced into the thin-wall break tube, it was assembled, attached to a vacuum manifold, and evacuated. The break-seal gas-sampling tubes were then isolated from the rest of the apparatus, and a known pressure of BF_3 gas was admitted to the 300-cc flask. The flask was closed, and the

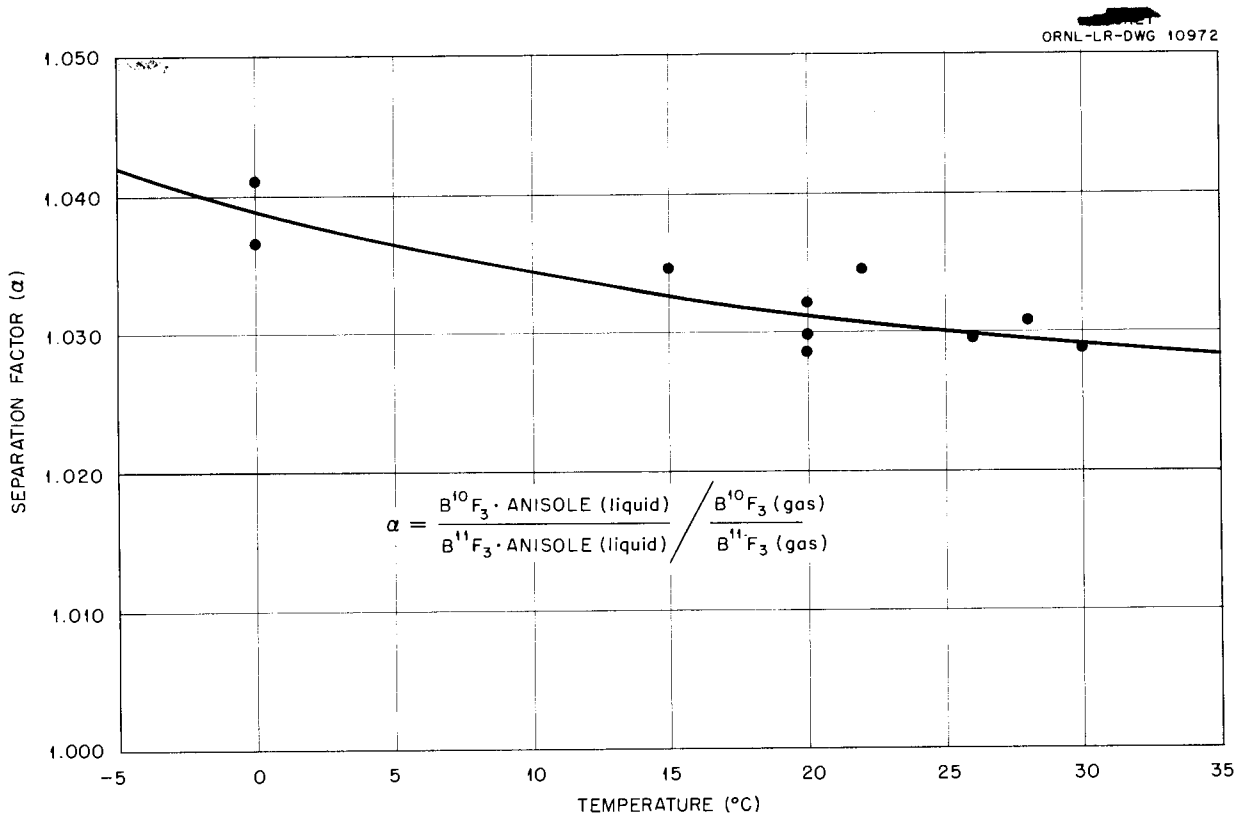

Fig. 1. Temperature Dependence of Separation Factor for the ANCO System.

apparatus was removed from the vacuum line. The 28/15 ball joint was then tilted until the thin-walled break tube was fractured, allowing the liquid complex to drop into the flask containing the BF_3 gas. The entire apparatus was then vigorously shaken by hand for the desired interval of time, after which the three-way stopcock was momentarily opened, allowing gas to enter the evacuated break-seal gas-sampling tubes. The tubes were sealed off, and the ratio of B^{10}/B^{11} was determined by mass spectrometer analyses.

From a knowledge of the total volume of the apparatus, the amounts of gas and liquid present, and the initial concentration of B^{10} in both phases, the concentration of B^{10} resulting from complete exchange could be calculated. From mass analyses of the gas phase before and after contacting, the degree of exchange during the interval of contact could be determined.

Three separate runs were made, as shown in Table 2. The first run was made with normal BF_3 gas and normal anisole·BF_3 complex in order to check the operation of the equipment. The last two runs were made with 40% $B^{10}F_3$ gas and normal anisole·BF_3 complex. The results show that isotopic exchange is rapid and that the reaction is suitable for countercurrent operation in conventional contacting equipment. The time measurement shown in the table is the total elapsed time for the experiment. Approximately 3 sec was necessary for manipulating stopcocks, etc. Hence, contact time for the 7-sec experiment was of the order of 4 sec.

Regeneration of BF_3 from Complex

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

In order to determine whether BF_3 could be quantitatively removed from the anisole·BF_3 complex, laboratory experiments were performed in which the complex was heated and the BF_3 allowed to escape.

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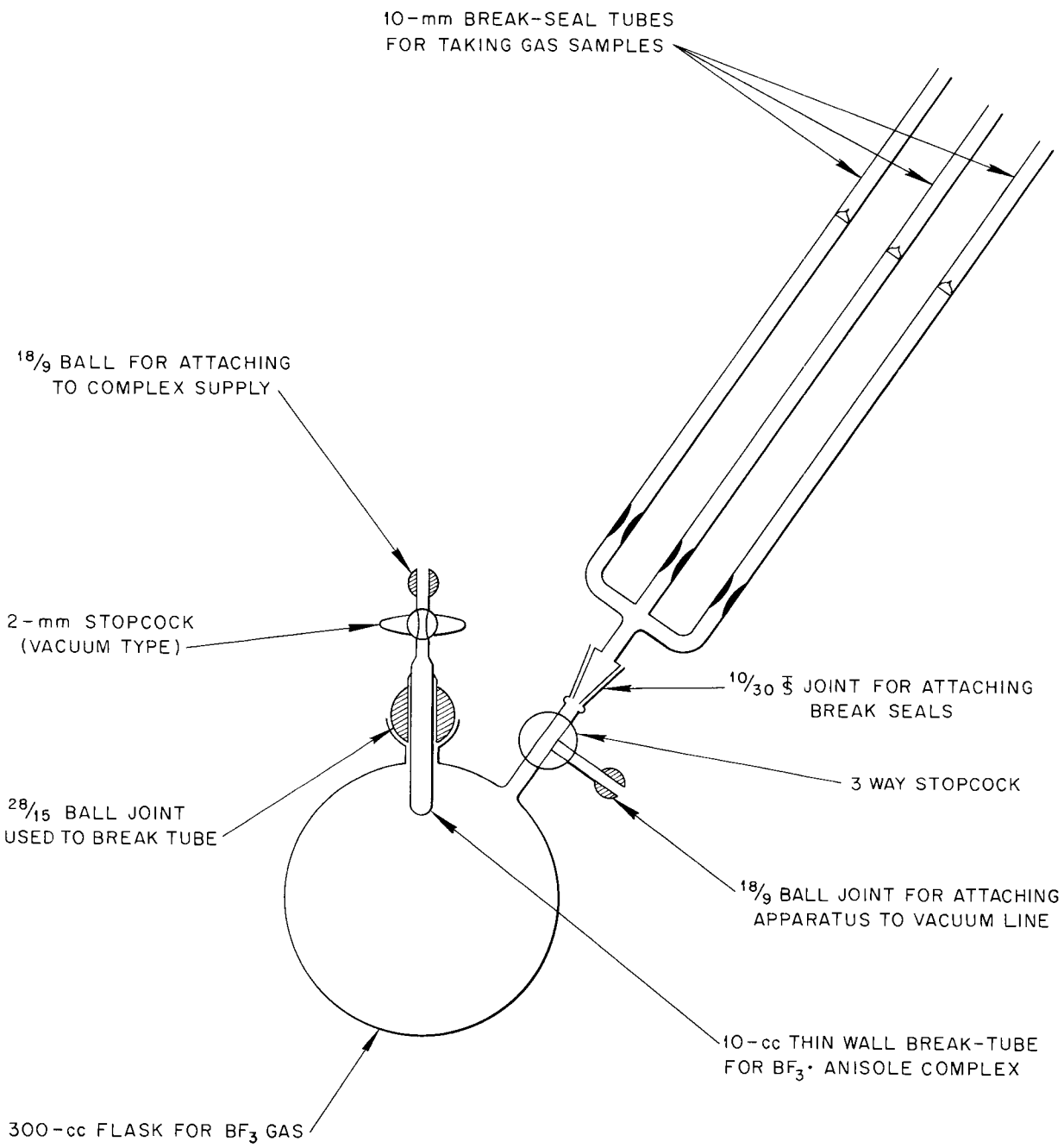

Fig. 2. Apparatus Used to Study Exchange Rate for the System $BF_3(g) \rightleftharpoons$ Anisole·$BF_3(l)$.

TABLE 2. RATE OF EXCHANGE FOR $B^{10}F_3(g) + C_6H_5OCH_3 \cdot B^{11}F_3(l) \rightleftharpoons B^{11}F_3(g) + C_6H_5OCH_3 \cdot B^{10}F_3(l)$

Complex* (g)	BF_3 (cc STP)	Time	Measured B^{10} (%) Before	Measured B^{10} (%) After	Equilibrium B^{10} Calculated (%)	Exchange (%)
9.04	170.6	2 min	(1.034)**			100
10.523	224.5	15 sec	40.71	23.05	23.2	100
10.207	164.0	7 sec	40.82	23.96	21.45	90

*Complex analyzed 35.2% BF_3, equal to 0.87 mole of BF_3 per mole of anisole.

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

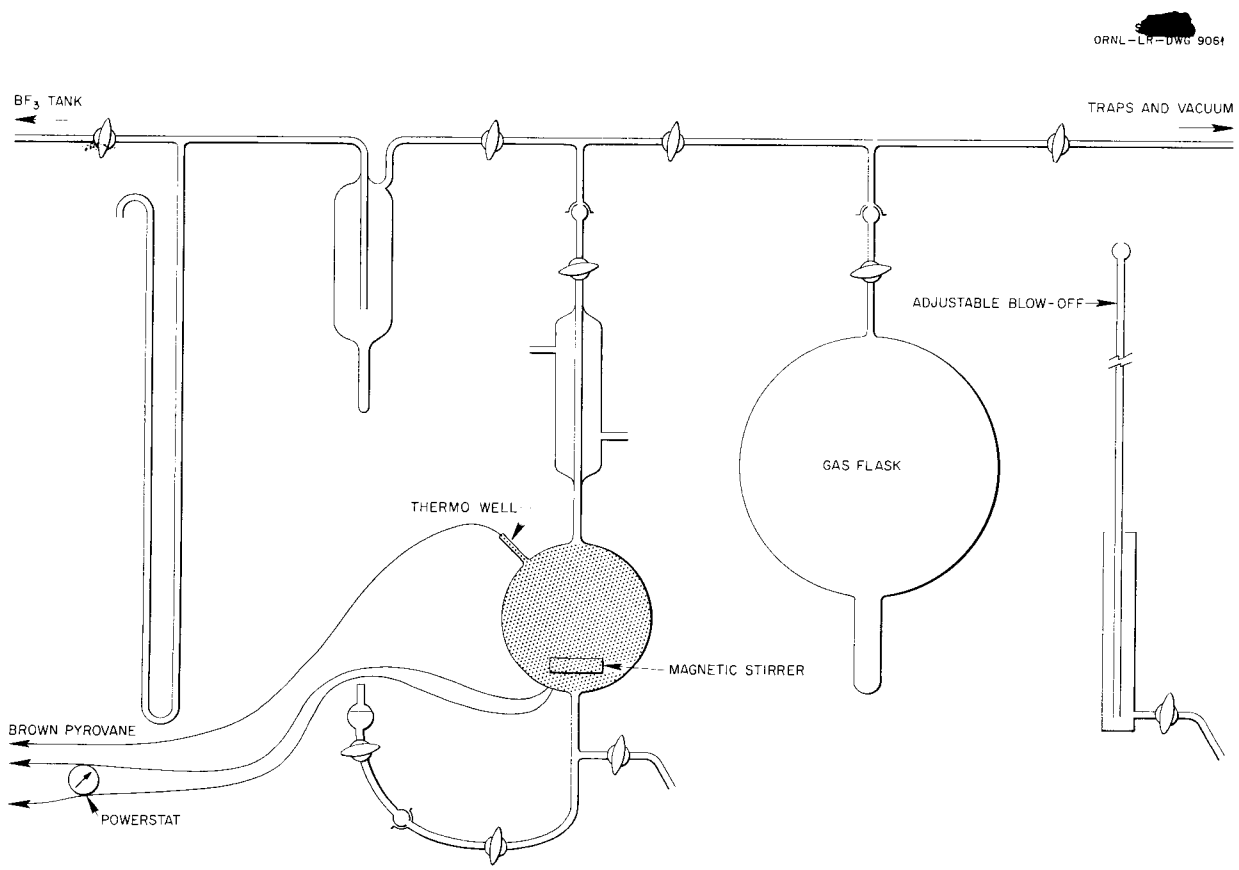

Fig. 3. Apparatus for Studying Reflux Reaction in the ANCO System.

The reflux was studied in the apparatus shown in Fig. 3. Anisole was introduced into the reaction vessel, air was removed, and complex was formed by the addition of BF_3. The blowoff manometer, which determined the pressure at which BF_3 escaped from the system, was connected. The reaction vessel was heated, and its temperature rose until the mixture in the vessel reached its "boiling point" under the pressure chosen. Anisole did not pass the water condenser. When the

BF_3 ceased to escape, the liquid in the reaction vessel was sampled. The results are given in Table 3.

TABLE 3. DECOMPOSITION OF ANISOLE·BF_3 COMPLEX

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

The amount of BF_3 left in the anisole was reduced to about 55 ppm on a mole basis and was found to be essentially independent of the BF_3 pressure over the complex in the range studied. This was apparently due to the increased boiling temperature of the liquid under an increased head of BF_3. If, in plant operation, the BF_3 content of the recirculating anisole can be reduced to this order of magnitude, operation of the reflux should be satisfactory, since this would constitute a very small per cent of the total product drawoff.

Vapor Pressure of Anisole·BF_3 Complex

In conjunction with the measurements of the isotopic separation factor and the study of the decomposition of the anisole·BF_3 complex, preliminary measurements of the vapor pressure of the complex (~1 mole of BF_3 to 1 mole of anisole) were made.

The vapor-pressure measurements were made in the apparatus used to measure the isotopic separation factor.[2] After an α determination was completed, the complex in the reaction flask was frozen with a dry-ice–acetone mixture, and any excess BF_3 was pumped off. Since the complex freezes at approximately −12°C and BF_3 gas freezes at about −101°C, the use of dry-ice–acetone mixtures allowed excess BF_3 to be removed from the complex. There was no indication that BF_3 gas was soluble in the liquid complex.

After the excess gas was removed, the stopcocks on the apparatus were adjusted in such a manner that only the manometer was connected to the jacketed reaction flask. Water at a constant temperature was then circulated through the jacket, melting the complex and equilibrating the system at that specific temperature. After several readings were made to ensure that equilibrium was attained, the temperature was changed and the process was repeated. Readings were taken from several separate batches of complex from 0 to 39°C. Since the volume of the thermostatted part of the apparatus was large compared with the volume of the external system and since pressure measurements were made at temperatures not too far removed from room temperature, no corrections were applied to these readings. Figure 4 shows the results of these measurements.

Vapor-pressure measurements of the anisole·BF_3 complex containing much smaller amounts of BF_3

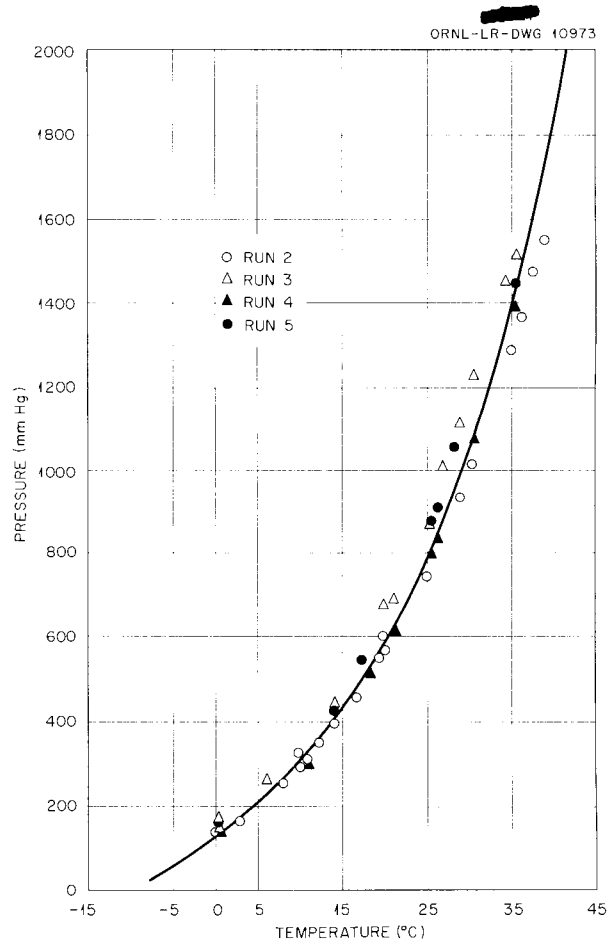

Fig. 4. Vapor Pressure of Anisole·BF_3 Complex.

[2] R. M. Healy and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. Dec. 31, 1954*, ORNL-1874, p 5, Fig. 3.

were made in the apparatus used to study the reflux reaction (Fig. 3). The results of these measurements are shown in Fig. 5. Both series of results are shown in Fig. 6. By using the integrated Clausius-Clapeyron equation with these data, an approximate value of $\Delta H = -12$ kcal/mole was estimated for the heat of formation of the complex in the reaction

$$BF_3(g) + \text{Anisole}(l) \rightleftharpoons \text{Anisole}\cdot BF_3(l)$$

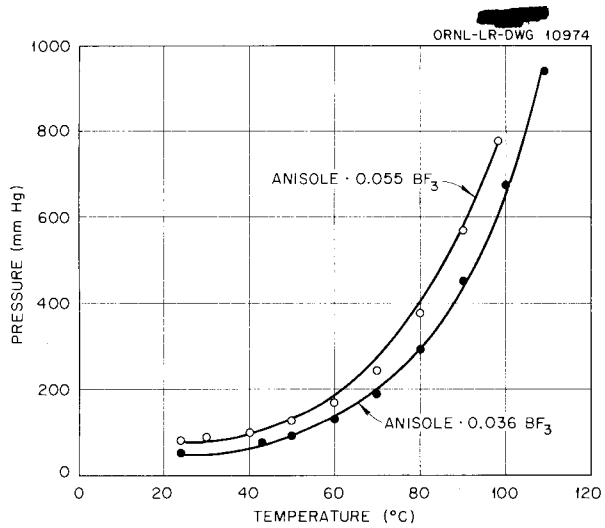

Fig. 5. Vapor Pressure of BF_3 over Anisole·BF_3 vs Temperature.

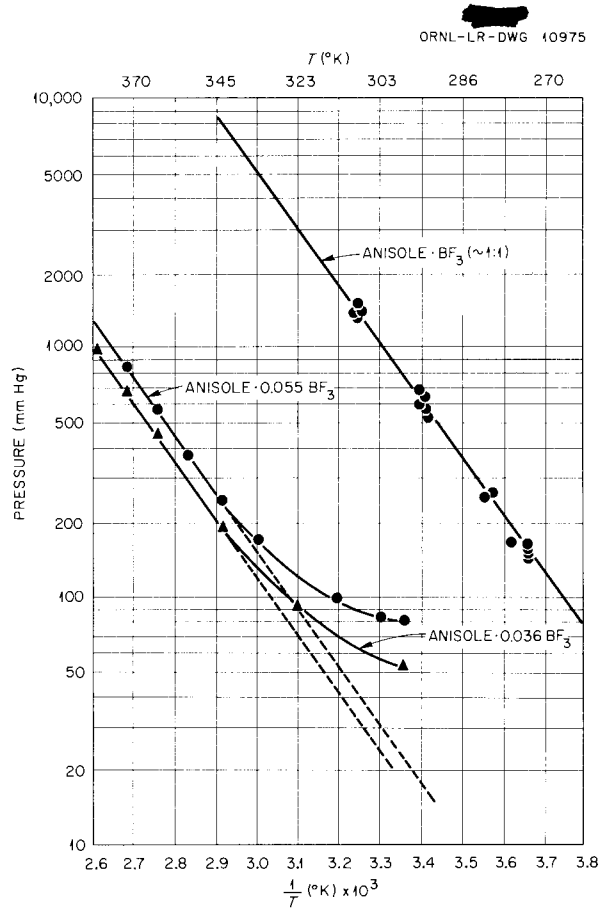

Fig. 6. Vapor Pressure over Anisole·BF_3 Complex.

Semi-Pilot-Plant Studies

In order to demonstrate the actual feasibility of the ANCO system, a small-scale laboratory apparatus was built in which tests could be made of the complete cycle as visualized for an isotope separation plant. This apparatus is shown schematically in Fig. 7. It consisted of an exchange column, a recombiner column, a decomposer, and accessory equipment. The exchange column was a 1-in.-OD pyrex, 30-plate bubble-cap column, 36 in. high, with a silvered vacuum jacket. The recombiner was a 22-in. section of 2-in. jacketed pyrex tubing packed with ⅛-in. pyrex helices. It had a thermocouple well down the center and was attached directly to the top of the exchange column. The decomposer was a separate piece of apparatus consisting of a 1-liter, mantle-heated, boiler pot to which was attached a 2-ft section of 1½-in. pyrex tubing packed with ⅛-in. glass beads. To the top of this tube was attached a Friedricks condenser.

All pressure and sampling lines were ⅛-in.-OD copper tubing; water lines were ⅜-in. Tygon tubing. Copper-to-glass connections were made by means of Kovar or Housekeeper seals. Microbellows stainless steel pumps transferred anisole and liquid complex, while a small centrifugal pump circulated refrigerated water. All valves used were either ¼-in. stainless steel Crane replaceable copper bellows valves with D-29 seats or ¼-in. Kerotest stainless steel diaphragm valves. The two heat exchangers were made from ¼-in. copper tubing coiled inside a 2-liter stainless steel jacket through which 8°C water was circulated. A standard office-type Westinghouse water cooler was used to refrigerate cooling water. The manometer was 7 ft high and was capable of registering

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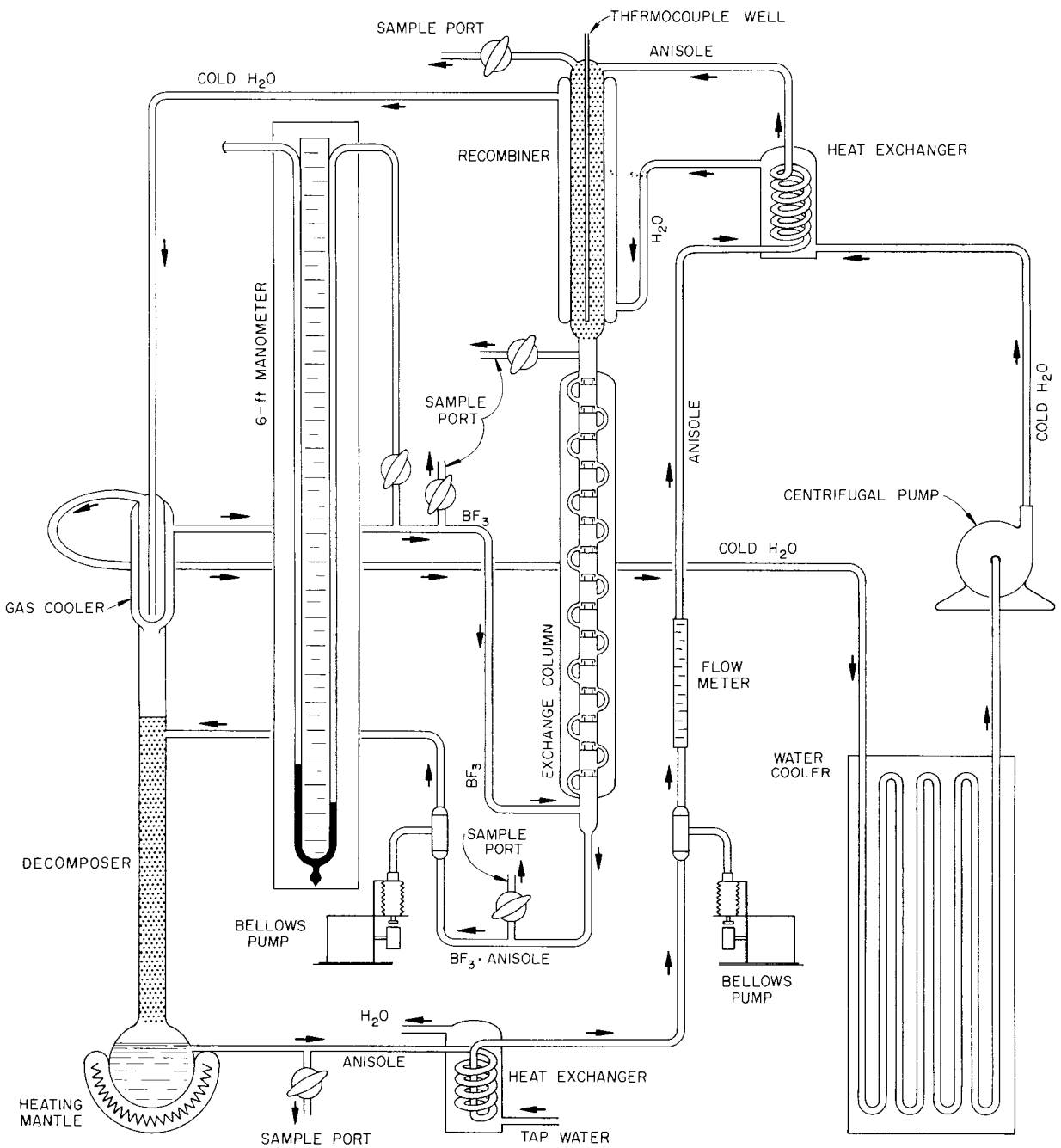

Fig. 7. Semi-Pilot-Plant Apparatus Used to Study the System $BF_3(g) \rightleftharpoons$ Anisole·$BF_3(l)$.

2000 mm Hg absolute pressure. Temperatures at various points throughout the system were recorded with a Brown electronic recorder.

Several preliminary runs were made with this apparatus to determine operating procedures and flow rates. The apparatus was cleaned, dried, and evacuated, and enough clean, dry, distilled anisole was admitted to the decomposer pot to fill the pot plus the two feed-pump bellows, the transfer lines, and the chambers of the bubble-cap exchange column. This required about 700 ml of anisole. The inlet valve was then closed, and the feed and cooling-water pumps were started. Heat was applied to the decomposer pot until the anisole began to boil; the temperature at this time was about 42°C. Purified BF_3 gas was then admitted slowly to the bottom of the exchange column through the gas-sampling port. As the gas was added, the pressure began to rise, causing the boiling temperature of the anisole in the decomposer pot to increase. Addition of gas was continued until the pressure on the system was at 1 atm. By this time the boiling temperature in the decomposer had risen to 154°C; approximately 1 mole of BF_3 gas was added to attain these conditions. Introduction of BF_3 was then stopped, and the system was allowed to come to chemical and isotopic equilibrium before samples were taken.

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

TABLE 4. OPERATING TEMPERATURES AND FLOWS FOR RUNS 3 TO 6 IN THE COUNTERCURRENT $BF_3(g)$ vs ANISOLE·$BF_3(l)$ EXCHANGE

Anisole flow, ml/hr	300
BF_3 flow, liters of gas per hour	62.2
Free volume of apparatus, liters	1
Pot temperature, °C	155
Peak recombiner temperature, °C	52
Cooling water, °C	8
Operating pressure, mm Hg	800
Effluent from recombiner, °C	12
Effluent from exchange column, °C	33
Gas into exchange column, °C	24

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

In general, it was found that operation was simple and was easier to control than anticipated. Total isotopic fractionation showed a bubble-cap efficiency of approximately 50%. Pressure increase was extremely slow after the initial equilibrium was established. The slow buildup of boron decomposition products in the decomposer took place at a decreasing rate as time of operation increased.

The boron content of the stripped anisole was analyzed to be about 0.2 mole per 100 moles of anisole, which was considerably higher than in the static tests. It is believed (1) that this will be considerably less after anhydrous conditions are established or (2) that cleanup of a small fraction of the total anisole flow will substantially reduce this value. The stability and operating characteristics of the system were very satisfactory, and no difficulties are foreseen in larger-scale operation.

TABLE 5. COUNTERCURRENT EXCHANGE RUNS, $BF_3(g)$ vs ANISOLE·$BF_3(l)$

Run No.	Peak Pot Temperature (°C)	Peak Pressure (mm Hg)	Length of Run (hr)	Average Assay (B^{10}/B^{11})		Total[a] Separation	Residual Moles of Boron per 100 Moles of Anisole
				Top	Bottom		
3	152	865	6	0.286	*b*		0.147
4	155	950	5	0.2836	0.1997	1.42	0.163
5	162	1150	6	0.2837	0.1970	1.44	0.220
6	146	680[c]	6	0.317	0.2080	1.525	

[a] $\frac{(B^{10}/B^{11})_{top}}{(B^{10}/B^{11})_{bottom}}$.

[b] Gas sample lost.

[c] Flow rate of anisole during this run was cut to 175 ml/hr, which resulted in a larger total separation.

BORON TRIFLUORIDE–BORON TRICHLORIDE EXCHANGE

R. M. Healy

Previous work[3] in this laboratory has established the exchange of boron between BF_3 and BCl_3. The reaction has now been studied in the expansion chamber of a mass spectrometer.[4] This method obviated the difficult problem of rapid separation of the gases and enabled a better evaluation of the rate of the reaction to be made.

Boron trifluoride enriched to 96% B^{10} and normal BCl_3 were obtained in the usual manner.[3] The gases were then admitted into the expansion chamber. Their pressures were read on a mercury manometer by means of a cathetometer. The $B^{10}F_2^+$ and $B^{11}F_2^+$ peak heights, which changed with time, were recorded on a Brown recorder.

The sum of the two peak heights, $B^{10}F_2^+$ and $B^{11}F_2^+$, decreased substantially during the runs. This was attributed to the disappearance of BF_3 as a result of the formation of the intermediate compounds[5] BF_2Cl and BCl_2F. The reaction was also found to be largely heterogeneous. For these reasons, the exchange reaction deviates from the first-order rate law usually observed for simple exchange reactions.[6]

A typical run is plotted in Fig. 8. It is immediately apparent that, at the start, $B^{10}F_3$ disappeared more rapidly than $B^{11}F_3$ appeared, due to the depletion of BF_3. From the linear portions of the upper curves, a half life of 3 to 4 min can be estimated for the exchange reaction.

Figure 9 illustrates the results of increasing the pressures by factors of 30 and 40. From Fig. 9, a half life of 5 to 7 min is estimated. At the start of the reaction, the intermediate products BF_2Cl and BCl_2F were being formed so rapidly at the expense of BF_3 that, instead of increasing, the $B^{11}F_2^+$ peak decreased.

A different type of graph is shown in Fig. 10. The $B^{11}F_2^+$ peak height is shown as a function of time. At the indicated intervals, additional BCl_3 was let into the expansion chamber. The lower curve shows the slow rate of exchange taking place when the only BCl_3 in the vessel was that remaining on the walls after the container had been evacuated down to 10^{-8} cm Hg. It is clear that, over the range measured, the pressure of BCl_3 has little effect on the rate of introduction of B^{11} into BF_3.

It is known[7] that these gases adsorb strongly on

[3] R. M. Healy and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. Dec. 31, 1954*, ORNL-1874, p 2, esp. p 3.

[4] These experiments were carried out in collaboration with C. E. Melton, Stable Isotopes Research and Production Division.

[5] R. E. Nightingale and B. Crawford, Jr., *J. Chem. Phys.* **22**, 1468 (1954).

[6] A. C. Wahl and N. A. Bonner (eds.), *Radioactivity Applied to Chemistry*, p 7, Wiley, New York, 1951.

[7] C. E. Melton, L. O. Gilpatrick, and Russell Baldock, *Stable Isotope Research and Production Semiann. Prog. Rep. May 20, 1955*, ORNL-1908, p 23.

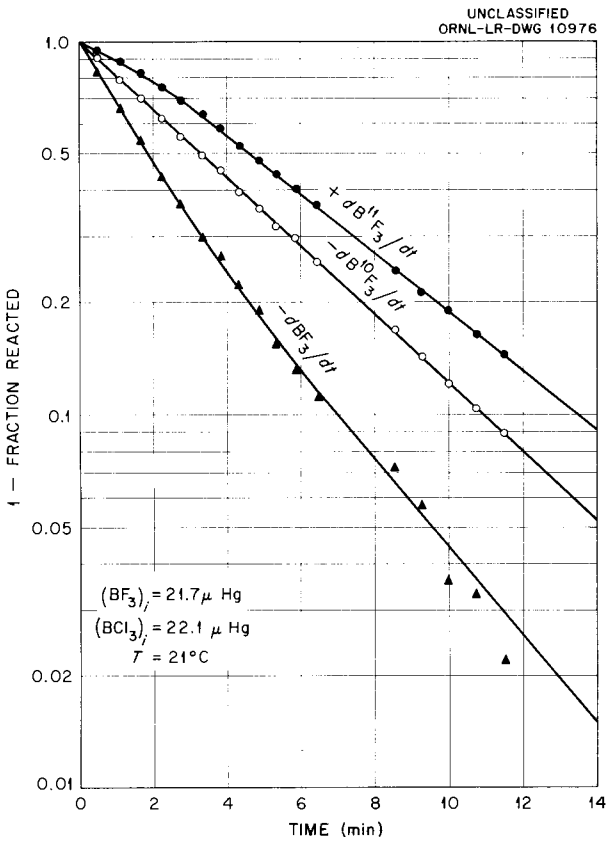

Fig. 8. Reaction and Isotopic Exchange Between BF_3 at 21.7 μ Hg and BCl_3 at 22.1 μ Hg Pressure.

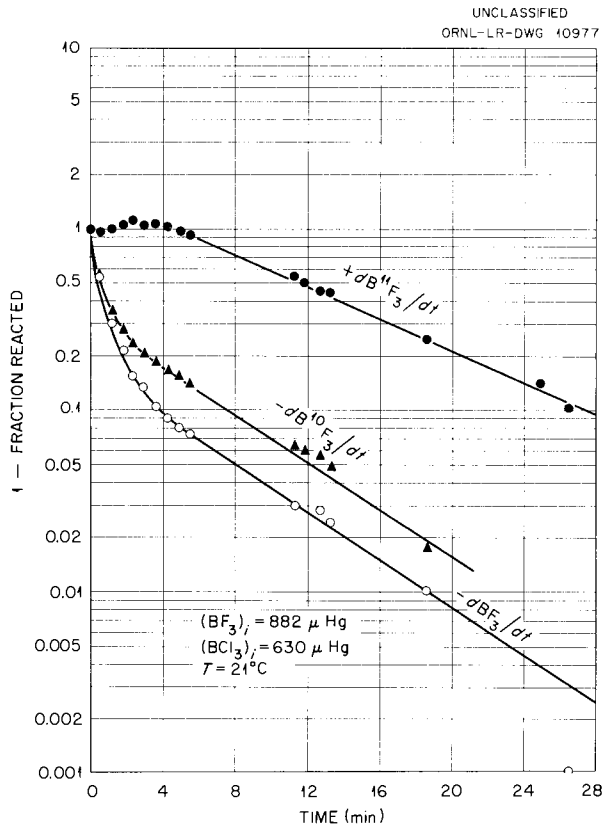

Fig. 9. Reaction and Isotopic Exchange Between BF_3 at 882 μ Hg and BCl_3 at 630 μ Hg Pressure.

a glass surface, BCl_3 preferentially to BF_3. It is also known that exchange of boron takes place between the adsorbed gas and the gas in the vapor phase, as illustrated in the lower curve of Fig. 10. These facts, plus the fact that the rate of approach to isotopic equilibrium is lower at higher pressure, lead to the conclusion that the reaction is largely heterogeneous. The formation of intermediate compounds is markedly accelerated by increasing pressure; this reaction (apparently the first step in the isotopic exchange reaction) may be largely homogeneous.

The exchange reaction is too slow to be of interest in a countercurrent system. However, a surface catalyst might increase the rate of the reaction sufficiently to make it of interest.

It should be pointed out that, since boron does exchange between BF_3 and BCl_3, either compound could be used as a reservoir to supply the other with boron of the desired isotopic ratio. That is, if one is in plentiful supply, but the other works in a system, the depleted isotopic ratio in the waste stream could be brought back to near normal by contacting the waste BF_3 (or BCl_3) with a large amount of normal BCl_3 (or BF_3).

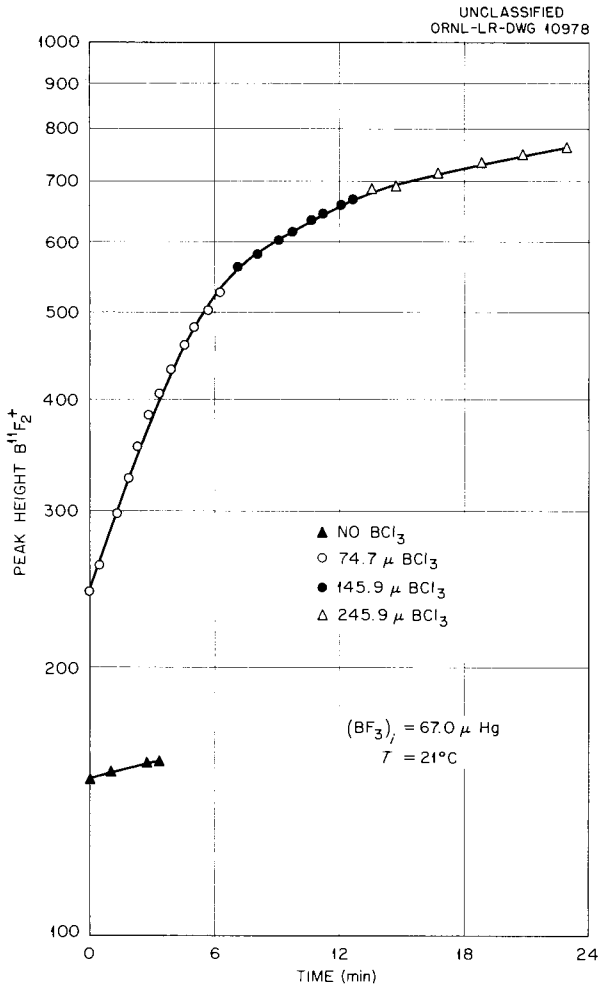

Fig. 10. Rate of Appearance of $B^{11}F_3$ in Enriched BF_3 in Various Concentrations of Normal BCl_3.

CATALYSIS OF THE HYDROGEN-WATER EXCHANGE REACTION[1,2]

D. A. Lee

In recent investigations of methods of catalyzing the molecular hydrogen-water exchange, heterogeneous catalysts have been emphasized. Since rhodium is known to be a very active catalyst in the hydrogenation of certain organic compounds, a study of this metal and the other members of the platinum group has been initiated.

First, catalysts of rhodium and ruthenium metal on a 100-mesh alumina support were tested for catalytic activity. The apparatus and procedure used have been described previously; these catalysts contained 5 wt % metal on alumina. A slurry of 0.1 g of catalyst (ruthenium on alumina) in 20 ml of water was equilibrated with deuterium gas at 73°C. No exchange was found in 350 min. When the slurry was made acid with 5 ml of acetic acid, a very slight exchange was noted.

With the rhodium catalyst in water, a very rapid initial exchange rate was observed which diminished with time. To examine the possibility of water poisoning, a sample of rhodium catalyst in water was allowed to stand for several weeks. After this time, another equilibration was made. The results were very similar to those of the earlier experiment, as shown in Fig. 11. The addition of 5 ml of acetic acid to the rhodium catalyst slurry almost completely stopped the exchange. A slurry of rhodium catalyst in 0.1 *N* KOH produced a slow hydrogen exchange, as shown in Fig. 12.

Heterogeneous-catalyst activity is increased by enlarging the surface area. Extremely fine silica and alumina were obtained from Godfrey L. Cabot, Inc., to be used as catalyst supports. The particle size of these supports is about 0.02 μ, and stable aqueous suspensions, 10% by weight, can be made.

The procedure for preparing these catalyst suspensions was to blend 5 g of silica or alumina with 50 ml of water, add 0.05 g of the precious metal in the form of its chloride, and reduce the chloride to the metal by bubbling hydrogen gas

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

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

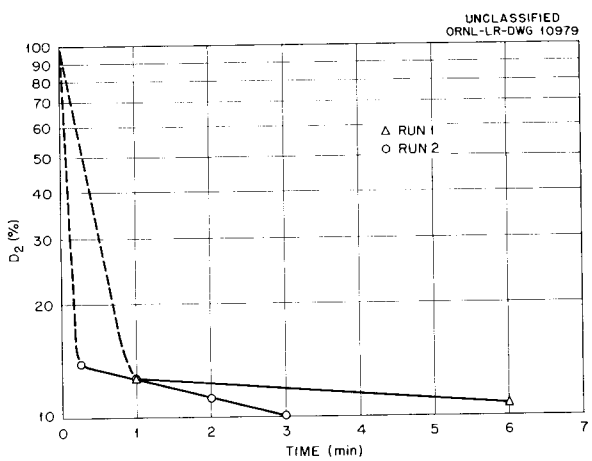

Fig. 11. Rate of D_2 Exchange – Rhodium on 100-mesh Alumina.

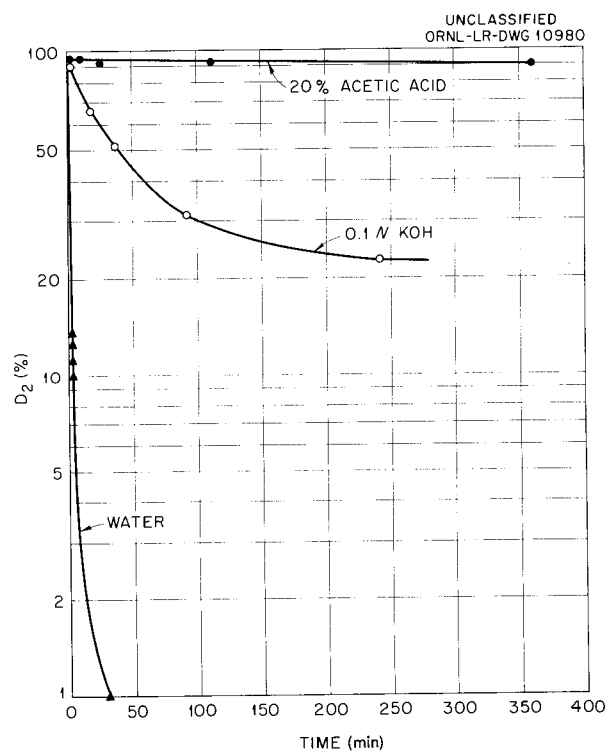

Fig. 12. Effect of Acid and Base on D_2 Exchange – Rhodium on Alumina Catalyst.

through the suspension. Platinum, palladium, and rhodium catalysts were prepared in this manner. The resulting suspensions contained 10 wt % support and 0.1% metal. The metals adhered more readily to the silica support than to the alumina, and acid suspensions were more stable than basic suspensions.

A rhodium suspension on silica containing 0.1% rhodium and 10% silica was equilibrated with deuterium for 295 min. The pH of the suspension was 2.0. By assuming first-order kinetics, the resulting equilibrium constant was 3×10^{-2} min^{-1}, and the half time for the reaction was 23 min. A similar palladium suspension had a pH of 2.7. Its equilibrium constant was 8.6×10^{-3} min^{-1}, and the half time was 81 min. A platinum suspension of pH 2.5 had a k value of 2.2×10^{-3} min^{-1} and a half time of 315 min. The results are plotted in Fig. 13.

Aquadag, a colloidal suspension of graphite in water, was tested for catalytic activity but none was found. No activity was found when a rhodium-on-Aquadag suspension was used. The composition of the Aquadag preparation is unknown; however, it undoubtedly contains something that poisons the rhodium.

A number of experiments were made with homogeneous substances as possible catalysts, but all substances tested were noncatalytic. The aqueous solutions used were cupferron, copper ethylenediamine nitrate, barium diphenylamine sulfonate, formaldehyde, copper ethylacetoacetate + glycol, and nickel ethylacetoacetate + glycol.

Rhodium has been found to be a very active exchange catalyst. Further study will be made to determine its poisons and the proper support

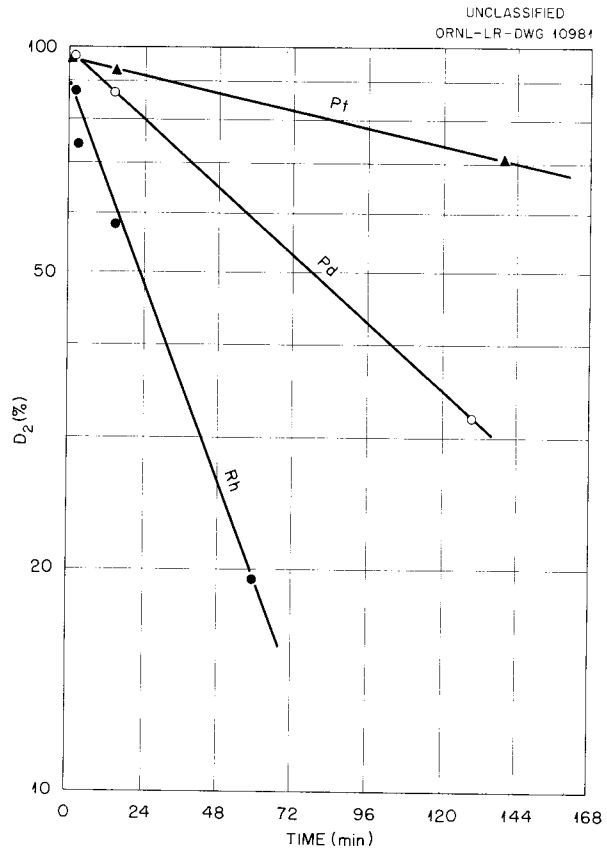

Fig. 13. Rate of D_2 Exchange – Metal, 0.1%, and Silica, 10%, in Aqueous Suspension.

for maximum activity. An attempt will be made to make stable suspensions in the neutral pH range, where rhodium appears to be most active. The other metals of the platinum series will also be studied.

CONCENTRATION OF N^{15}

A new system for enriching N^{15} has been described by Spindel and Taylor[1] of Columbia University. In this system, gaseous oxides of nitrogen pass countercurrent to aqueous nitric acid. Nitrogen-15 concentrates in the liquid phase, as indicated by the following simplified reaction:

$$N^{15}O(g) + HN^{14}O_3(aq) \rightleftharpoons N^{14}O(g) + HN^{15}O_3(aq)$$

At the product end of the system, reflux is accomplished by reducing the nitric acid solution with sulfur dioxide. Nitric oxide containing some nitrogen dioxide and small amounts of other impurities is produced. Sulfuric acid is formed as a by-product. At the waste end of the system, the oxides of nitrogen are reacted with air and water to re-form nitric acid. At room temperature, the separation factor for the system varies from 1.06 down to lower values, depending upon the composition of the gas and liquid phases.

The low cost of chemicals consumed in the waste-end reflux, the recovery of nitric acid, the production of marketable sulfuric acid, and the relatively high α value for the system are factors which make this exchange system seem attractive for the large-scale production of N^{15}. The following research was aimed at further evaluating the practical aspects of the system.

NITROX PRODUCT-END REFLUX

L. B. Yeatts, Jr.

Design and operation of a product-end refluxer were undertaken initially, for it is here that losses of N^{15} are most likely to occur. These losses must be minimized in order to have a producing system. At present, it is considered that losses probably occur by the dissolution of nitric oxide in the sulfuric acid effluent and by the reduction of a small fraction of the nitric acid to nitrous oxide or molecular nitrogen or both. Thermodynamic calculations show that the formation of these last two gases is even more favorable than the formation of nitric oxide and nitrogen dioxide. Nitrogen contained in nitrous oxide and molecular nitrogen gas does not exchange with other nitrogen species under these conditions. If any of the N^{15} in the product refluxer were converted to these two forms, it would pass through the exchange column unaltered and escape from the system in the stream leaving the waste-end refluxer.

Another aspect to be considered for the proper operation of this refluxer is the composition of the gases which leave it and enter the exchange column. The two predominant reactions which take place between the sulfur dioxide and nitric acid are:

$$(1)\quad 3SO_2 + 2HNO_3 + 2H_2O \rightleftharpoons 3H_2SO_4 + 2NO$$

$$(2)\quad SO_2 + 2HNO_3 \rightleftharpoons H_2SO_4 + 2NO_2$$

The composition of the gas mixture leaving the refluxer is a function of the temperature and pressure of the reactants. If the gas mixture entering the exchange column contains too little nitrogen dioxide, the rate of exchange between nitric acid and nitric oxide seems to become so slow that long stage heights result. On the other hand, excess nitrogen dioxide in the gas mixture entering the exchange column lowers the effective separation factor. For these reasons it is important to study the parameters of refluxer operation in terms of the composition of the gas mixture produced.

Spindel and Taylor[1] found, in general, that the concentration of nitrogen dioxide produced by the reflux reactions is greater than that in equilibrium with the nitric acid in the exchange column. They learned further that cooling of the refluxer and water dilution of the nitric acid in the refluxer both tend to reduce the concentration of nitrogen dioxide. On the basis of this information, several refluxers have been designed and operated; for example, see Fig. 14. Each of these has a water-dilution inlet, a nitric acid inlet, and a gas-sampling port at the top of the refluxer; at the bottom is a sulfur dioxide inlet and a sulfuric acid outlet. Columns packed with glass helices were found to produce the contact required between the acid and the sulfur dioxide gas. Three columns of this type were studied. They differed mainly in the placement of the water-cooling devices and in the length of the packed section.

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

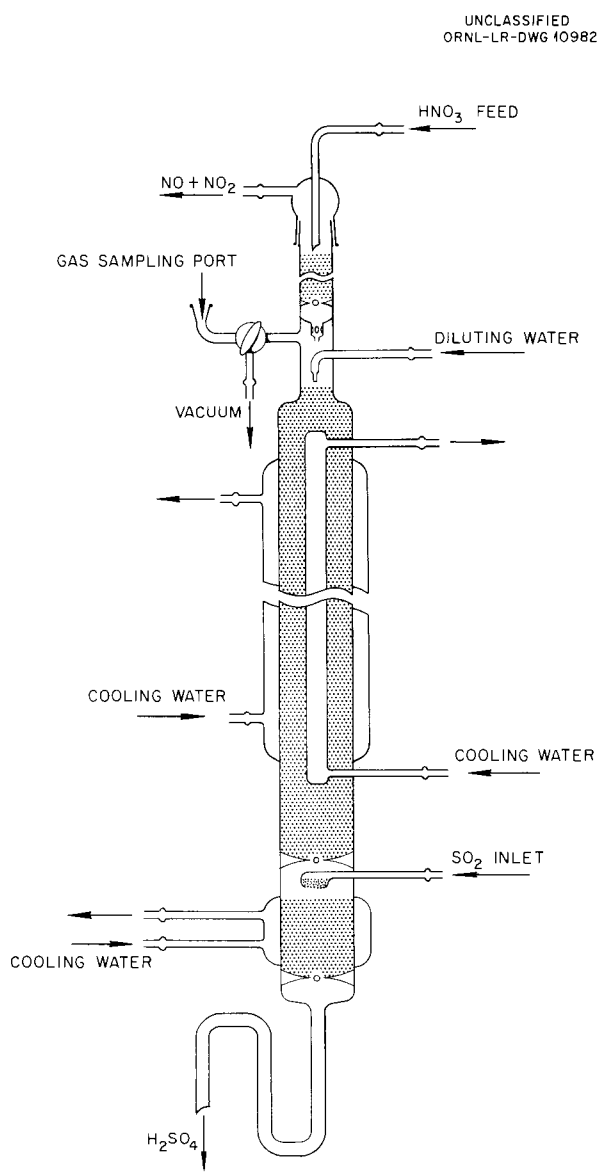

Fig. 14. Product-End Refluxer.

During the operation of a refluxer, tremendous quantities of heat are liberated upon reduction of the nitric acid by sulfur dioxide. The lower portion of this reaction zone is rather sharply defined by the white color of the packing below, contrasted with the intense brown nitrogen tetroxide color where the reaction begins. The reaction zone with the intense brown color was generally about 3 in. long but became considerably longer when the water-cooled area of the refluxer was reduced or eliminated. Above the reaction zone the nitric acid was emerald green in color, presumably due to dissolved nitrogen trioxide. The color intensity decreased as the gases proceeded up the refluxer. The intensity of the brown gas mixture leaving the top of the refluxer varied with the concentration of nitric acid, the area of the cooling surface, and the distance of the reaction zone from the top of the refluxer.

To determine whether molecular nitrogen and nitrous oxide are produced during nitric acid reduction, 200-ml gas samples were taken for chemical analysis while the refluxer was being operated with 6, 7.3, and 10 *M* nitric acid. After absorption of the nitric oxide and nitrogen dioxide from these samples, about 0.5 ml of gas remained. With the macro equipment available it was not possible to identify this residual gas. A method for determining minute quantities of nitrogen and nitrous oxide in the gas mixtures is being developed.

The first refluxer (refluxer A) was 46 cm long, with an inside diameter of 2.5 cm. It had an internal spiral cooling coil and was packed with $\frac{1}{16}$-in. glass helices. Refluxer B had a 30-cm packed section which, through the use of three concentric tubes, had both internal and external cooling surfaces. The packing material was $\frac{3}{32}$-in. glass helices. While cooling water was being circulated, both refluxers were operated for several hours with 10.1 *M* nitric acid delivered at a rate of 80 ml/hr. Following this, refluxer B was continued in operation while water was added at the rate of 37 ml/hr to dilute the nitric acid before reducing it with sulfur dioxide. Samples were taken of the gas mixtures leaving the top of the refluxer and of the sulfuric acid effluent at the bottom. Presented in Table 6 are the data which were obtained from these experiments. Upon comparing the data of the 10.1 *M* HNO_3 experiments, it can be noted that refluxer B yields a gas mixture which is richer in nitric oxide gas than the mixture yielded by refluxer A. This can be attributed only to the difference in the methods of cooling during reflux. In order to study the effect of acid concentrations on reactions 1 and 2, additional runs were made in which water was added to refluxer B during operation. This resulted in a large increase in the ratio $NO(g)/NO_2(g)$.

TABLE 6. EFFECT OF COOLING METHODS AND WATER DILUTION UPON THE PRODUCT-END REFLUX REACTION

	HNO_3 Feed (*M*)	Mole Ratio NO/NO_2	Effluent		
			H_2SO_4 (*M*)	SO_2 (*M*)	Total Nitrogen (ppm*)
Refluxer A	10.1	1.09	10.1	0.46	64
	10.1		9.8	0.57	58
	10.1	0.89	9.6	0.58	67
	10.1		10.0	0.45	
Refluxer B	10.1	1.6	10.6	0.44	32
Refluxer B with water dilution	6.8	5.8	9.7	0.37	136
	6.8	5.4	9.5	0.45	121

*Calculated on the basis of gram atoms of nitrogen.

The total nitrogen losses suffered in each of these experiments, presumably from dissolved nitric oxide, constitute an excessively high fraction of the calculated withdrawal rate of the N^{15} product, that is, about 100 ppm. The sharp increase in the loss of total nitrogen from the system with the use of water dilution of the nitric acid is noteworthy. The concentration of sulfur dioxide found in the sulfuric acid effluent suggests that it must be largely recovered if its loss is not to become a serious economic consideration.

Refluxer B was next operated at constant flow rates of acid and cooling water to determine the effect of nitric acid concentration upon both the mole ratio of NO/NO_2 and the total nitrogen losses. At the same time, the effect of the path length traversed by the nitrogen oxides in the packed section was to be observed. The reaction

$$(3) \qquad 3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$$

will certainly play a major role in determining the concentrations of nitric oxide and nitrogen dioxide which leave the refluxer. If the reaction should reach equilibrium fairly slowly, the path length of the gas becomes an important factor for consideration. The path length is here defined as the distance from the top of the packing to the lower edge of the reaction zone. A tabulation of the experimental results is given in Table 7.

At constant gas path length, the mole ratio NO/NO_2 decreases with an increase in the concentration of nitric acid feed, indicating that reaction 1 proceeds to an increasingly greater extent with more dilute acid. This is also borne out by the relationship between the concentration of sulfuric acid produced and the nitric acid consumed. At constant nitric acid concentration, the NO/NO_2 ratio increases with an increase in the path length of the gases in the refluxer, illustrating the role of reaction 3.

The loss of total nitrogen in the sulfuric acid effluent was found to be least at the highest concentration of nitric acid (10.1 *M*). The concentration of sulfur dioxide in the effluent decreased with a decrease in the sulfur dioxide–sulfuric acid contact time. The results of the above experiments and several additional qualitative ones indicate that the most favorable concentrations of nitric oxide are produced in the refluxer during the use of external and internal cooling surfaces, while permitting good contact to exist between the nitrogen oxides and the downward flowing nitric acid. At the same time, the reflux reaction itself must be allowed to proceed without benefit of cooling. This condition was expected to decrease the losses of total nitrogen, as dissolved nitric oxide, in the sulfuric acid effluent.

With these points in mind, a refluxer with a 44-cm section packed with $\frac{3}{32}$-in. glass helices was designed and operated (Fig. 14). Approximately 7 *M* nitric acid was delivered to the refluxer at a flow rate of 240 ml/hr. Reaction with the sulfur dioxide occurred just below the inside cooling condenser. Under these conditions, the mole ratio NO/NO_2 was nearly the equilibrium

TABLE 7. EFFECT OF NITRIC ACID CONCENTRATION AND GAS PATH LENGTH UPON PRODUCT REFLUXER

Experiment No.	HNO_3 Feed (*M*)	Gas Path Length (cm)	Mole Ratio NO/NO_2	Effluent		
				H_2SO_4 (*M*)	SO_2 (*M*)	Total Nitrogen (ppm*)
1	6.1	8	9.2	8.0	0.68	90
2	8.1	8	3.2	9.5	0.71	121
3	10.1	8	1.9	10.3	0.64	116
4	6.1	20	44.6	8.0	0.57	97
5	8.1	20	5.7	9.6	0.47	96
6	10.1	20	1.8	10.6	0.47	27

*Calculated on the basis of gram atoms of nitrogen.

value for 7 *M* nitric acid, and the total nitrogen losses were reduced to 15 ppm. Approximately 9 *M* sulfuric acid with a sulfur dioxide content of 0.36 mole/liter was produced. Water dilution caused the total nitrogen losses to increase to 128 ppm.

SINGLE-STAGE SEPARATION FACTORS FOR NITROX SYSTEM

L. L. Brown

The gas present in the exchange column of the Nitrox system is primarily a mixture of nitric oxide and nitrogen dioxide. Under equilibrium conditions, the composition of this gas mixture is a function of temperature, pressure, and the concentration of the acid used in the liquid phase. The nitrogen dioxide seems to exert two opposing effects on the operation of the system. Its presence seems to accelerate the rate of exchange between nitric oxide and nitric acid, and from this viewpoint it is desirable. However, the effective separation factor for the system is probably lowered as the amount of nitrogen dioxide in the gas phase increases, since the calculated separation factor for the reaction $NO_2(g)$ vs $HNO_3(aq)$ is considerably smaller than for the reaction $NO(g)$ vs $HNO_3(aq)$. From this point of view, it would seem desirable to operate the exchange column so that the amount of nitrogen dioxide present in the gas phase will be minimized.

To help optimize these opposing effects of NO_2 on the isotopic enrichment obtainable in the system, a series of runs was made in which the isotopic separation was studied as a function of nitric acid concentration.

The starting materials for all determinations in this study were purified NO and nitric acid solutions. As a consequence, it was required that some of the NO be oxidized to NO_2 by HNO_3 to establish chemical equilibrium. Chemical analysis of the gas phase for NO and NO_2 content was made for most of the runs to ensure attainment of equilibrium. In every case the ratio of NO_2/NO was slightly greater than that calculated from the data of Abel, Schmid, and Stein,[2] which indicates that, within experimental error, equilibrium was reached during the 2 hr of equilibration. Figure 15 shows the gas-phase partial pressures plotted from data of Abel, Schmid, and Stein.

Chemical analysis of the liquid phase is more difficult than for the gas. Analyses for NO_3^- and "NO" were made, where "NO" was really a measure of the reducing power of the solution. The separation into individual species such as N_2O_3, NO, NO_2, HNO_2, and HNO_3 was too formidable to be undertaken. Some samples were found to be low in NO content when they were not analyzed until a second or third day, probably because oxidation occurred while they were standing. Figure 15 shows a curve of the "NO" concentration which should be taken as "order of magnitude" for reducing power at this time. The highest points were given greater weight, since

[2]H. E. Abel, H. Schmid, and M. Stein, *Z. Elektrochem.* **36**, 692 (1930).

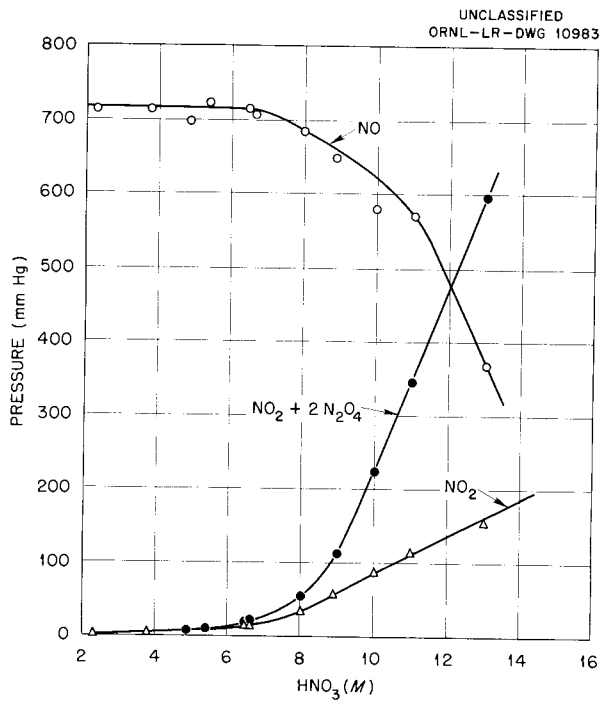

Fig. 15. Gas-Phase Partial Pressures in Nitric Acid Equilibria.

changes occurring before analysis would tend to bring about low values for NO.

Isotopic samples of the gas phase were prepared by sealing some of the gas in tubes containing iron powder. The tubes were heated to 350°C overnight to reduce the oxides to nitrogen. Portions of the liquid phase were neutralized with NaOH and evaporated to $NaNO_3$. From this point on, quantitative recovery of the nitrogen content from the sample was required to preclude additional isotopic fractionation. Three different methods were used:

$$(1)\quad NO_3^- + Hg \xrightarrow[H_2SO_4]{conc} NO(g) \xrightarrow[350°C]{Fe} N_2$$

$$(2)\quad NO_3^- + Fe^{++} \xrightarrow[H_2SO_4]{conc} NO(g) \xrightarrow[350°C]{Fe} N_2$$

$$(3a)\quad NO_3^- + \text{Alloy}^3 \xrightarrow[NaOH]{conc} NH_3(g) \xrightarrow{H^+} NH_4^+$$

$$(3b)\quad NH_4^+ + OBr^- \xrightarrow{OH^-} N_2$$

The third method was found to work most reliably despite its two distinct chemical operations. All three methods are essentially standard methods for nitrate quantitative analysis. The first two occasionally gave some NO_2, which was undesirable, since an isotopically homogeneous sample did not result. Six identical samples of each phase were submitted for isotopic analysis. The assays were obtained as the quotient of the N^{15}/N^{14} ratio for the sample to the ratio for a standard N_2 sample.

The single-stage fractionation factors at 26°C are shown in Table 8 for the equilibrium acid concentrations indicated. Figure 16 shows the same data in graphic form. The 95% C.I. is expressed for the isotopic assays only and not on the experiment as a whole. The pressure was constant for any single concentration, but over the entire range it varied from 695 to 725 mm Hg.

TABLE 8. SINGLE-STAGE FRACTIONATION FACTORS FOR THE NITROX SYSTEM

HNO_3 Concentration (*M*)	α^* (95% C.I.)
1.084	1.064 ± 0.001
3.08	1.057 ± 0.005
5.82	1.060 ± 0.002
6.10	1.062 ± 0.003
7.20	1.053 ± 0.005
9.40	1.053 ± 0.002
10.20	1.040 ± 0.003
13.10	1.018 ± 0.003
14.2	1.027 ± 0.001
15.45	1.020 ± 0.001

$$*\alpha = \frac{(N^{15}/N^{14})_{liquid}}{(N^{15}/N^{14})_{gas}}.$$

Gas-Liquid Contactor

Difficulties are experienced in determining the single-stage separation factor of the Nitrox system in conventional equipment. The reaction must be kept free of air contamination. Oxygen from the air readily oxidizes nitric oxide, upsetting the

[3]Devarda's alloy, 50% Cu, 45% Al, 5% Zn.

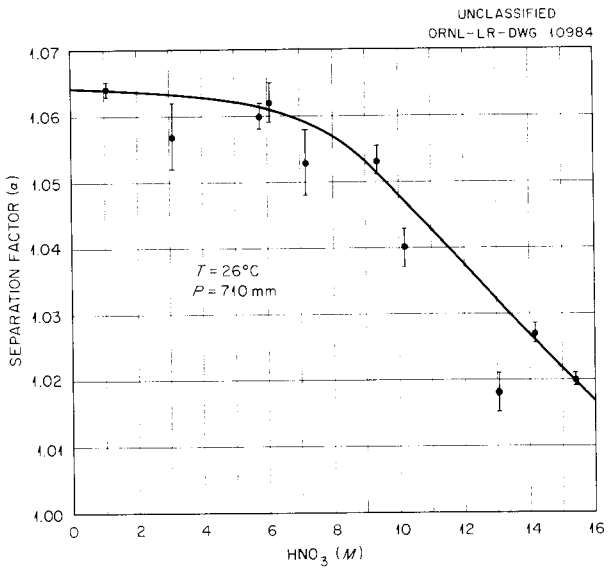

Fig. 16. Nitrox Separation Factor vs Acid Concentration.

chemical equilibrium of the sample. Atmospheric nitrogen introduces errors in the isotopic analysis of the gas phase. The two phases must be separated at equilibrium without changing the composition of either phase.

A new type of contactor is described here which handles these problems satisfactorily and is applicable to other systems. Figure 17 is a scale drawing of the contactor, with the Sigmamotor finger pump schematically indicated. A gas-handling manifold is omitted which has provisions for auxiliaries such as vacuum, helium purge gas, NO purification, and sample tubes for isotopic samples.

The operation of the contactor is described below as it was used in the separation-factor work in the Nitrox system. First, all portions of the system were purged with helium, and 90 to 100 ml of nitric acid was put in the liquid reservoir with stopcock 1 closed. The apparatus was then assembled, with a light coat of silicone stopcock grease on the glass joints. Points A_1 and A_2 were connected by means of a short section of Tygon tubing going through a Sigmamotor finger pump to completely close the loop. By proper use of stopcocks 2 and 3, the whole volume of the loop not occupied by liquid was evacuated, filled with helium, and re-evacuated. Purified NO was then introduced through stopcock 3 until

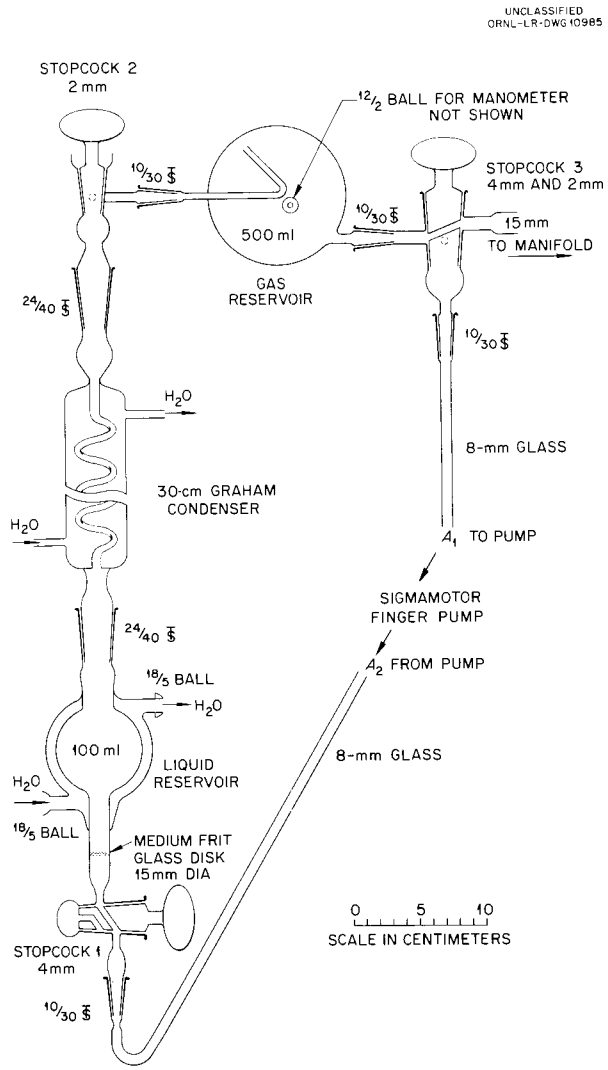

Fig. 17. Gas-Liquid Contact Loop for Single-Stage Isotopic Separation Factors.

the manometer pressure was about 2 cm less than the barometric pressure. Stopcock 3 was turned so as to shut off the manifold and make a path for the gas to flow from the gas reservoir through the pump into the liquid reservoir. The pump was started (set for 450 cc/min) and then stopcock 1 was opened. The pump must be operating before this stopcock is opened or acid will likely flow out of the reservoir. The pressure in the system will begin to fall as some of the NO is used to form NO_2 and N_2O_3, and additional NO can be added through stopcock 3. It is desirable to keep the pressure slightly different from barometric,

so that if a leak develops it can be detected by a pressure change in the system.

The liquid reservoir was temperature-controlled by water from a constant-temperature bath. The Graham-type condenser above the liquid was kept cooler than the reservoir in order to keep water vapor from circulating with the gas phase and thus, in effect, prevent the formation of HNO_3 in the gas. The gas was pumped around the loop for 2 hr at constant pressure. To stop the contacting operation, stopcocks 1 and 3 were turned simultaneously, and then the pump was stopped and stopcock 2 turned. These operations isolated the bulk of the gas from the liquid phase. The liquid phase was left in the liquid reservoir with some gas with which it was already at equilibrium. The gas-phase isotopic samples were taken through stopcock 3 into the manifold and sealed in break-seal tubes. The connection below stopcock 1 was opened to make a sample port for the liquid phase. Helium at atmospheric pressure was run through stopcock 2 to keep a constant pressure over the acid while it was sampled through stopcock 1 for both chemical and isotopic purposes.

The contactor design is adaptable, through modifications, to other gas-liquid systems. The amount of holdup of either phase can be changed by substituting suitable glassware. Use of other stopcocks will allow pressures greater than atmospheric to be employed. Finally, other types of tubing may be found for use in the finger pump. This last point is possibly the most serious shortcoming of the contactor, since the tubing must have both chemical inertness and mechanical strength before it can be used.

CARBONATE-SYSTEM PILOT-PLANT STUDIES

E. F. Joseph

Extensive laboratory studies[4-6] have been made of the ammonium carbonate system for enriching the isotopes of nitrogen; also, preliminary pilot-plant studies of the product-end refluxer of this system have been reported.[6] The primary objectives of the pilot-plant studies were to determine (1) whether the lime-slurry reflux column could be made to operate in a trouble-free manner and (2) whether the ammonia content of the effluent from the product refluxer could be reduced to the desired level.

In the initial experiments, considerable difficulty was experienced because of plugging of the reflux column by $CaCO_3$ precipitated on the packing. A precontact loop in which $(NH_4)_2CO_3$ and $Ca(OH)_2$ reacted prior to introduction into the packed column was incorporated into the system, and preliminary runs were made in which little difficulty was encountered as a result of solids deposition in the exchange column.[6] Three additional runs were made to check the operation and performance of the ammonium carbonate–calcium hydroxide contactor, and the following procedure was used.

Calcium hydroxide slurry and ammonium carbonate solution were metered into the contact loop. The material was circulated within the loop and allowed to reach a temperature of 80°C. Steam was admitted to the packed column, and, when equilibrium was reached, the feed pumps were started, and material flowed from the contact loop to the feed point of the column. The feed passed through a heat exchanger before it reached the column, and the ammonia flashed from the solution as the feed entered the column.

All the runs were of short duration, but it was possible to check the equipment to find the best operating conditions. After the runs were completed, the column was washed with water. No calcium carbonate was found precipitated on the packing or on the walls of the column. The reaction appeared to go to completion in the contact loop, since no carbon dioxide was detectable in the condenser of the column. It was found that slurries of calcium hydroxide of about 1 *M* had better flow characteristics and did not jell in the contact loop or in the column, as was found for the 2 *M* slurries.

After the best conditions for operating the equipment had been determined, attention was turned to the problem of stripping ammonia from the solution in the contact loop. Preliminary runs were made by using concentrated aqueous ammonium hydroxide solution, which was metered into the feed point of the packed column. A heat exchanger in the feed line raised the temperature

[4] A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. Dec. 31, 1953*, ORNL-1706, p 13, esp. p 17.

[5] G. M. Begun and A. A. Palko, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1954*, ORNL-1815, p 20.

[6] L. L. Brown *et al.*, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. Dec. 31, 1954*, ORNL-1874, p 11.

of the solution to its boiling point. As the ammonium hydroxide entered the packed column, it decomposed into ammonia and water. Steam entering the bottom section of the column stripped the remaining traces of ammonia from the water going down the column. The stripped water solution was sampled and the remainder discarded. The overhead vapors from the column were cooled, and the condensed liquid was returned to the column as reflux. The noncondensed vapor (ammonia gas) was absorbed in water and re-used as feed solution.

The results of the experiments are given in Table 9. Figure 18 shows the concentration gradient in the column during a typical (No. 7) run. About 18 stages were necessary to reduce the ammonia content of the effluent stream from the column to approximately 1 ppm.

After this successful performance on ammonium hydroxide solutions, runs 9, 10, and 11 were made to determine the minimum number of stages necessary to reduce the ammonia content of the calcium carbonate slurry to an acceptably low value. The operating procedure used for the runs was similar to that used for the previously described contactor studies in which the calcium hydroxide slurry and the ammonium carbonate solution were metered into the contact loop, heat was applied, and the reaction was allowed to go to completion. The material from the contact loop flowed through a heat exchanger, where the temperature was raised to 80°C, and was then allowed to flash into the packed column, releasing the ammonia. The slurry leaving the column was discharged, after being sampled, to the sewer.

A comparison of the results of the runs is given in Table 10. It was found that in the three runs the ammonia concentration of the total slurry effluent from the column ranged between 10 and 45 ppm. The composition of the bottoms sample from the column for the runs is given in Table 11.

These semi-pilot-scale experiments have demonstrated quite well that the buildup of solids in the packing of the refluxer column can be reduced to a satisfactory level by reacting the ammonium

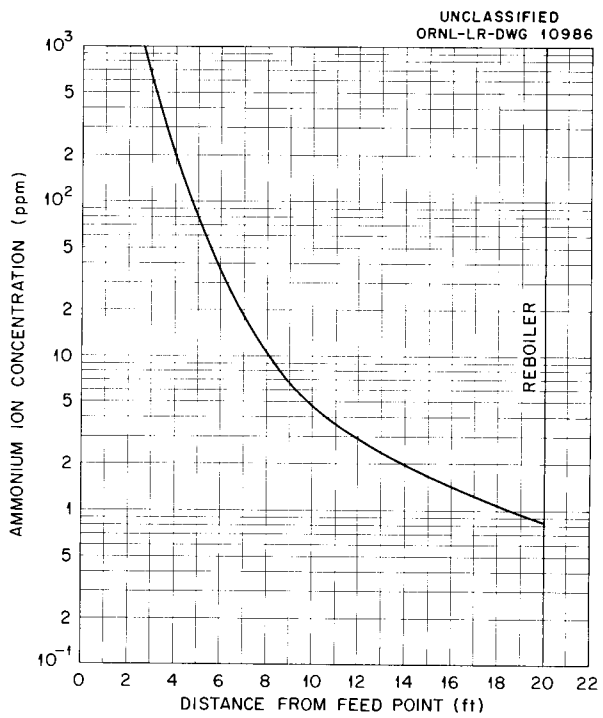

Fig. 18. Ammonium-Ion Distribution in a Packed-Column Distillation of Ammonia from Ammonium Hydroxide.

TABLE 9. SUMMARY AND COMPARISON OF DISTILLATION RUNS

	Run 1	Run 7	Run 8
Column size (inside diameter), in.	2.0	2.0	4.0
Column packing, Intalox saddles, in.	½	½	½
Effective length, stripping section, in.	127.0	199.0	216.0
Ammonium hydroxide feed to column, liters/hr	3.396	4.128	4.176
NH_4OH, *M*	12.0	13.9	13.4
NaOH, *M*	0.0	0.0	0.01
Concentration of ammonia in column effluent, ppm	3.3	0.85	0.08

TABLE 10. SUMMARY AND COMPARISON OF RUNS WITH CALCIUM CARBONATE–CALCIUM HYDROXIDE SLURRY

	Run 9	Run 10	Run 11
Column size (inside diameter), in.	4.0	4.0	4.0
Column packing, Intalox saddles, in.	½	½	½
Effective length, stripping section, in.	216	216	318.0
Concentration of feed			
NH_3, *M*	18.1	18.1	17.5
CO_2, *M*	4.67	5.10	5.4
$Ca(OH)_2$, *M*	0.95	1.15	1.1
NaOH, *M*		0.01	
Concentration of NH_3 in column effluent, ppm	11.6	22.0	42.4
Stages necessary to obtain a loss equal to 1 ppm	15.2	18.8	
Column length necessary to obtain a loss equal to 1 ppm, in.	298	295	
ft	24.8	24.6	

TABLE 11. COLUMN EFFLUENT SAMPLES

Total ammonia, ppm	10–45
Ammonia in supernatant liquid, ppm	2–4
Calcium hydroxide, *M*	0.05–0.07
Calcium carbonate, *M*	0.36–0.60
Metal-ion contaminants	
Cobalt, ppm	1
Copper, ppm	0.21
Chromium, ppm	0.02

carbonate and calcium hydroxide streams prior to introduction into the refluxer. Adequate ammonia removal has been demonstrated, also. Under present operating conditions, the ammonia remaining in the slurry after distillation varies from 10 to 45 ppm. These trace quantities seem to be occluded in the calcium carbonate. The amount of occluded ammonia varies with the pressure or concentration of ammonia in the precontact loop. Metal ions which form insoluble complexes with ammonia are not present in the effluent from the column in sufficient quantities to appreciably increase the losses of ammonia in the effluent slurry.

[7]This complex is formed in the "brown ring" test for nitrate ion.

NITRIC OXIDE–FERRONITROSO ION SYSTEM FOR CONCENTRATION OF N^{15}

L. L. Brown

The possibility of utilizing the ferronitroso ion[7] ($FeNO^{++}$) in a gas-liquid system for enriching the isotopes of nitrogen has been investigated. This ion forms directly when NO gas is passed into a ferrous salt solution. When the solution is boiled the NO is evolved quantitatively.[8] The isotope separation system visualized would have NO passing up a packed exchange column, countercurrent to an aqueous $FeNO^{++}$ solution. At the bottom of the column, reflux would be accomplished by heating the solution and passing the NO evolved up the exchange column. At the top of the column, ferrous solution from the boiler would be recombined with NO.

The stripping of NO from the complex ion has been studied in connection with the recovery of NO in industrial processes.[8] The physical properties of the solutions have also been investigated over several concentrations, temperatures, and pressures.[9,10] From the available data it appeared

[8]S. N. Ganz and L. I. Mamon, *J. Appl. Chem. (U. S. S. R.)* **26**, 927 (1953).

[9]W. Manchot and K. Zechentmayer, *Liebigs Ann. Chem.* **350**, 368 (1906).

[10]W. Manchot, *Z. anorg. u. allgem. Chem.* **140**, 22–36 (1924).

that conditions were sufficiently attractive to warrant the measurement of the isotopic fractionation factor for nitrogen isotopes in a single-stage gas-liquid contactor. The exchange reaction may be written

$$FeN^{14}O^{++}(aq) + N^{15}O(g) \rightleftharpoons FeN^{15}O^{++}(aq) + N^{14}O(g)$$

assuming that the N^{15} concentrates in the liquid phase.

The contactor used in the experiment is described elsewhere in this report (see section entitled "Gas-Liquid Contactor"). It was used in the same manner as that described for the NO-HNO_3 contacting. The liquid phase consisted of 100 ml of 0.91 *M* $FeSO_4$. Purified NO was added until the total pressure in the system above the complex was 715 mm. The aqueous phase was thermostatted at 16.5°C, at which temperature the Fe/NO ratio was expected to be 2 or more at the pressure used. The condenser above the solution was cooled to 2°C to prevent water from circulating with the gas phase. The gas was pumped through the loop contactor for 3 hr, since no equilibrium time had been previously established. The isotopic samples from the gas phase were obtained by expanding the NO directly into evacuated break-seal tubes containing powdered iron. A portion of the liquid phase was frozen with a dry-ice–acetone bath and placed on a vacuum manifold. The solution was boiled, and the evolved NO was collected in a cold trap. This NO was then transferred into break-seals containing iron powder. The two sets of samples were heated overnight at 350°C to reduce the NO to N_2 before submitting them for isotopic analysis. Chemical analysis of the liquid phase showed it to be 0.88 *M* in Fe^{++} and to have an Fe/NO ratio of 2.74.

Table 12 shows the isotopic analyses of six samples taken from each phase. Since the gas and liquid samples are of different assay, exchange did occur and the heavier isotope concentrated in the liquid phase. The separation factor for a single stage is 1.009 ± 0.002 (95% C.I.) at 16.5°C. This small separation factor and the anticipated corrosiveness of ferrous sulfate solutions make this reaction of questionable value as a possible method of enriching N^{15}.

[11] F. H. Spedding *et al.*, *The Separation of Isotopes by Ion Exchange*, ISC-475 (April 7, 1954).

TABLE 12. ISOTOPIC ANALYSES OF SAMPLES FROM NO-$FeNO^{++}$ SYSTEM

	$\frac{(N^{15}/N^{14})_{sample}}{(N^{15}/N^{14})_{tank}}$	
	Liquid	Gas
	0.9770	0.9686
	0.9792	0.9705
	0.9785	0.9695
	0.9793	0.9715
	0.9787	0.9702
	0.9784	0.9665
Av	0.9785	0.9695

FRACTIONATION OF NITROGEN ISOTOPES ON ION-EXCHANGE RESINS

A. C. Rutenberg

A system for utilizing an ion-exchange column for enriching the isotopes of nitrogen has been described by Spedding and his co-workers.[11,12] The system was operated in the following manner. A band of ammonium ion was placed on a column of Dowex 50 that was in the hydrogen form. A solution of NaOH was introduced at the top of the column. At the top of the band, Na^+ was adsorbed on the resin, and NH_4OH appeared in solution. The NH_4OH solution trickled through the bed of ammonium ion adsorbed on the resin, and during this process exchanged occurred. At the bottom of the band the NH_4OH solution reacted with the acid form of the resin, and NH_4^+ was deposited on the resin. Thus, this system affords a method of obtaining chemical reflux at both ends of the band, as well as providing a method of exchanging nitrogen between aqueous NH_4OH and NH_4^+ on the resin. Because of the interest in this laboratory in various processes for enriching the isotopes of nitrogen, a number of experiments were tried in order to have a better basis for comparing this ion-exchange method with other chemical systems.

The single-stage separation factor for this system was measured by adsorbing NH_4^+ on Dowex 50W and shaking it with a solution of NH_4OH at 24°C. The phases were separated, and the resin

[12] F. H. Spedding, J. E. Powell, and H. J. Svec, *J. Am. Chem. Soc.* 77, 1393 (1955).

was washed free of NH_4OH. The ammonia from both phases was oxidized to N_2 for mass spectrometric analysis. Nitrogen-15 enrichment occurred in the resin phase, and a single-stage separation factor of 1.027 was obtained. Kirshenbaum *et al.*[13] determined the separation factors between $NH_4^+(aq)$ vs $NH_3(g)$ and between $NH_4OH(aq)$ vs $NH_3(g)$ to be 1.034 and 1.005, respectively, at 25°C, giving an α value of 1.029 between $NH_4^+(aq)$ and $NH_4OH(aq)$. The separation factor is, therefore, approximately the same whether the NH_4^+ is adsorbed on the resin or is in aqueous solution.

Two conditions limit the rate at which the band of ammonium ion may move down the resin column. First, band movement must be slow enough to permit attainment of equilibrium between the nitrogen on the resin and that in the solution. Secondly, it must be possible to remove adequately the heat evolved by the neutralization reaction at the front interface. Band movement may be increased somewhat by increasing the rate of addition of the eluting solution. However, large increases must be obtained by increasing the concentration of the eluting solution, since the resistance of the column prevents wide variations in the rate of addition of the eluant.

Since the amount of heat evolved at the front interface increases as the concentration of the eluting agent increases, there is a practical limit, also, to the concentration of eluant used. Thermostatically jacketing the column does not entirely solve this problem, since the heat is evolved over a relatively small area.

Table 13 shows the effect of rate of band travel on the separation achieved. The liquid flow rate did not vary significantly in the course of these experiments. The difference in band length should not alter the total separation appreciably, since the band traveled only a relatively short distance and was far from its final equilibrium value. There appears to be a pronounced effect produced by increasing the band travel rate from 10 to 32 in./hr. However, there are insufficient data to apportion this change between the temperature effect and the failure to attain equilibrium. The fact that the separation was changed the most at the front (hot) edge indicates that the temperature effect is quite important and perhaps the major one. It is planned to perform subsequent experiments in a jacketed column.

The distribution of nitrogen isotopes in the ammonium band at the completion of the second experiment (10 in./hr rate of band travel) is shown in Fig. 19. The stage height at the trailing edge of the band was about 0.4 mm.

[13] I. Kirshenbaum *et al.*, *J. Chem. Phys.* **15**, 440 (1947).

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

A. C. Rutenberg

It is of interest to correlate isotopic fractionation factors with the chemical nature of the species involved. Systems involving the isotopes of nitrogen are especially amenable to such a study, since precise isotopic analyses are available. A

TABLE 13. VARIATION OF SEPARATION WITH RATE OF BAND TRAVEL

Band Length (in.)	Average Rate of Band Travel (in./hr)	NaOH (*M*)	Average Liquid Flow Rate (ml/hr)	Isotopic Analysis* (Extrapolated to Band Edge)	
				Front	Rear
12.7	4	0.250	500	0.23	3.1
9.7	10	0.495	670	0.36	3.0
9.0	32	2.40	560	0.74**	1.65**

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

**Estimated; insufficient data for extrapolation.

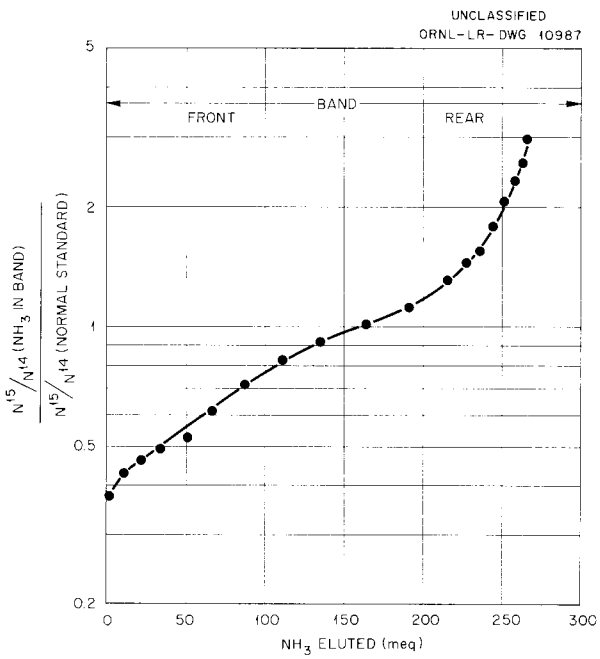

Fig. 19. Isotopic Composition of Ammonium Band.

series of compounds of the type $M(NH_3)_x^{++}$ has been studied. The isotopic composition of the NH_3 complexed with the metal could be compared with either that of the NH_4OH in solution or the NH_3 vapor above the solution in equilibrium with the complex. If the complexed NH_3 is to be compared with NH_3 vapor, the NH_4OH concentration in the solution must be fairly high in order to provide sufficient NH_3 in the vapor for sampling. It is necessary to correct for the dissolved NH_3 that is not complexed by the metal. Another method that might be used is the isolating of the ammonia complex by extraction or precipitation. The method chosen for this set of experiments was to have the complex adsorbed on an ion-exchange resin in equilibrium with a solution of NH_4OH, which gives a two-phase system in which the species can be readily separated.

The experiments were performed in the following manner. The hydrogen form of Dowex 50W-X8 resin was placed in a sintered-glass funnel, and a solution of the metal ion was passed through the resin until the wash liquid no longer came through acidic. The saturated metal resin was then rinsed with distilled water and treated with dilute NH_4OH to obtain the ammonia complex. The resin containing the complex was placed in contact with an aqueous solution, and NH_4OH was added to get the appropriate solution concentration. The resin was then shaken with the solution to attain isotopic equilibrium. The mixture was poured through a sintered-glass disk, and the aqueous phase was collected. The resin was washed with a small amount of water, and suction was applied briefly to remove the excess water. A portion of the moist resin was analyzed for metal and ammonia content. The metal ion and NH_3 were eluted off the remainder of the resin with acid; following this, base was added, and the NH_3 was distilled off. The NH_3 was then oxidized to N_2. The presence of even small quantities of cupric ion in the solution interferes with the quantitative oxidation of NH_3 to N_2, presumably by catalyzing the decomposition of the hypobromite solution used as the oxidizing agent.

Table 14 gives the separations observed in a series of experiments in which a metal-ammonia complex adsorbed on Dowex 50 resin was equilibrated with an aqueous solution of NH_4OH. The confidence intervals refer only to the precision of the isotopic analysis and indicate that the errors in mass assay are smaller than the differences observed among the various species. The measured NH_3/M^{++} ratios are for the washed resin complexes which supplied the ammonia for the isotopic analysis. The NH_3 content of the complexes during the actual equilibration was probably closer to four molecules of ammonia per metal ion.

An experiment was performed in which the copper- and nickel-ammonia complexes on the resin were compared more directly by equilibrating them with the same NH_4OH solution. This solution was allowed to flow back and forth between the two resins on opposite sides of a sintered-glass disk. The difference in fractionation between the complexes (1.0028 ± 0.0009) was essentially the same as that calculated from the individual experiments. The slightly lower values in the combination experiment can be accounted for on the basis of fluctuations in the isotopic analysis. If the differences actually exist, they may result from failure to attain equilibrium in the combination experiments, where the mixing was less efficient. The temperature differences are too small to account for the variation.

No suitable explanation has been advanced for the larger fractionation obtained when zinc was

TABLE 14. FRACTIONATION OF NITROGEN ISOTOPES BY METAL-AMMONIA COMPLEXES

M^{++}	$\frac{NH_3}{M^{++}}$	T (°C)	NH_4OH (M)	$\frac{15/14\ M(NH_3)_xR_2}{15/14\ NH_4OH}$ (95% C.I.)	K_{eq} $M(NH_3)_4^{++} = M^{++} + 4NH_3$
Ni	3.3	25	0.07	1.0095 ± 0.0006	5×10^{-8}
Cu	3.8	24	0.134	1.0122 ± 0.0003	5×10^{-14}
Zn	3.8	21	0.165	1.0157 ± 0.0008	1×10^{-9}
Ni[a]	3.7	28	0.30	1.0086 ± 0.0010	
Cu[a]	3.8			1.0114 ± 0.0009	

[a]Ni and Cu data from same experiment.

used as the cation. Equilibrium-constant data for aqueous solution in the absence of a resin indicate that the copper-ammonia complex is much stronger than the zinc-ammonia complex. The presence of the resin should not change the picture significantly. The complexes $Ag(NH_3)_2^+$ and $Cu(NH_3)_4^{++}$ have been reported[14] to be as stable when adsorbed on a sulfonated polystyrene resin (Permutit Q) as they are in aqueous solution. Data on additional ammonia complexes are required before any valid conclusions or correlations can be made.

NITROGEN AND OXYGEN ISOTOPE EFFECTS IN THE DISTILLATION OF N_2O_4

G. M. Begun

Since N_2O_4 is partially dissociated in the vapor phase, the distillation of N_2O_4 offers the possibility of isotope fractionation as a result of the exchange reaction between $N_2O_4(l)$ and $NO_2(g)$. To examine this effect, N_2O_4 was distilled in a 30-plate bubble-cap column. Nitrogen tetroxide is very reactive with most greases, and it was found necessary to use a specially designed reflux head which permitted removal of a sample of condensed N_2O_4 without contact with grease. This apparatus is shown in Fig. 20. Samples were taken from the head by lifting the glass ball valve with a magnet. Water at 7°C was circulated through the condenser to condense the N_2O_4, which boils at 21.3°C. The distillation head was vented to the atmosphere through a drying tube containing P_2O_5.

The N_2O_4 used was purchased from the Matheson Co., Inc., and was purified by bubbling dry oxygen through it to oxidize any NO to NO_2. It was then distilled through a long drying tube filled with P_2O_5.

In operation of the column, heat was applied to the still pot, and the system was brought to equilibrium with all bubble caps filled. The column was operated at total reflux, and samples were removed at intervals from the top and bottom. Isotopic analysis of these samples was undertaken in two ways. In the first case, samples of N_2O_4 were sealed into glass break-seal tubes with pure iron powder and heated overnight at 350°C to reduce the N_2O_4 to N_2. Isotopic analyses were then run on the N_2 samples, using mass numbers 28 and 29. It was found that copper would not work satisfactorily for this purpose and that the iron must be of high purity to avoid erratic results. Another portion of each sample was kept as N_2O_4, and an attempt was made to analyze directly for nitrogen and oxygen isotopic abundances with the mass spectrometer, using mass numbers 46, 47, and 48. As expected, these analyses proved to be less reliable than the analyses of N_2, and some of them were invalid because of a trace of residual BF_3 in the instrument.

The results of the isotopic analyses are shown in Figs. 21 and 22. All curves have an inflection point between the second and fourth samples. When the second sample was taken, the ball was not seated properly. This resulted in considerable

[14]R. H. Stokes and H. F. Walton, *J. Am. Chem. Soc.* **76**, 3327 (1954).

withdrawal of sample in the interval between the second and third samples. The situation was rectified when the third sample was taken and normal buildup of the isotopic gradient was resumed. It can be seen that the N_2 analyses form smooth curves and that N^{14} concentrates in the gas or NO_2-rich phase. Changes in the still pot were small but measurable as the gradient was built up in the column. The NO_2 analyses were more erratic. The 6- and 25-hr samples were run first on the mass spectrometer, and there was an unexplained shift of the relative values between these samples and the rest of the NO_2 samples, which were run later. For this reason, the data from the 6- and 25-hr samples were rejected. Initial oxygen analyses had to be discarded because of the memory effect of traces of BF_3 left in the mass spectrometer from previous analyses.

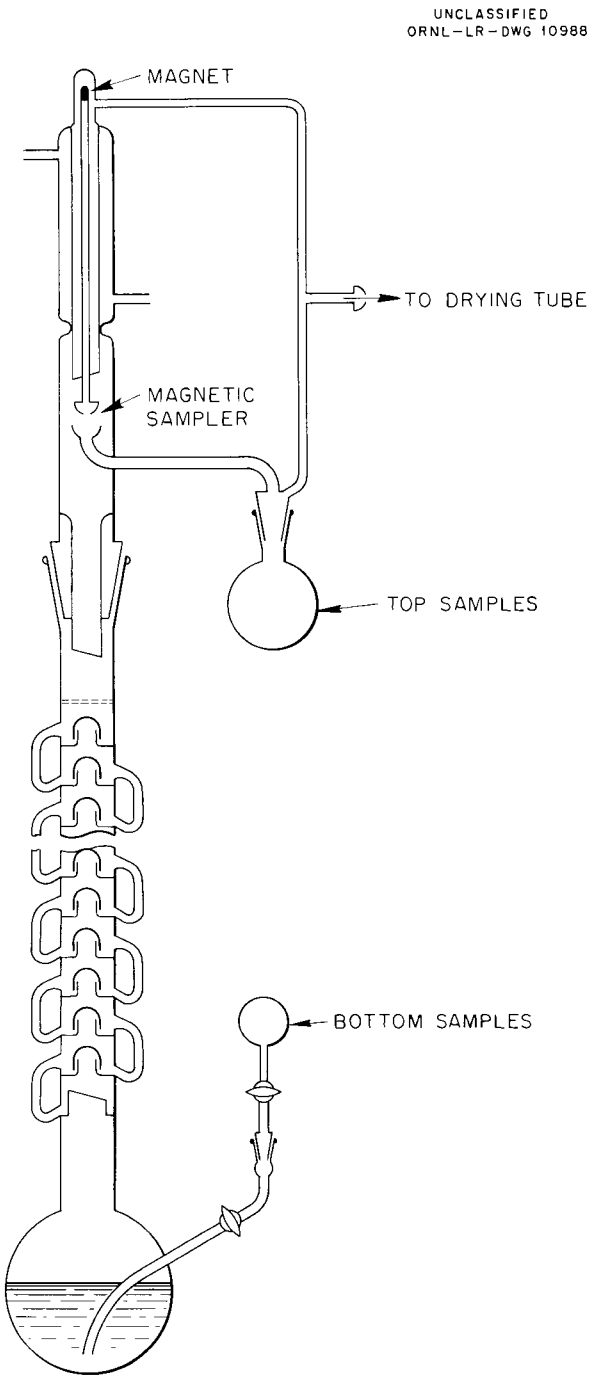

Fig. 20. Apparatus for N_2O_4 Distillation.

The results of the isotopic analyses show that N^{14} concentrates in the gaseous or NO_2-containing phase, as expected. The total separation,[15] estimated from the analyses as N_2, is about 1.070. If a bubble-plate efficiency of 60% is assumed, a single-stage separation factor of 1.0038 is obtained. If, in addition, it is assumed that the separation factor between $N_2O_4(l)$ and $N_2O_4(g)$ is small compared with that between $N_2O_4(l)$ and $NO_2(g)$, the latter separation factor can be calculated to be approximately 1.023, since the $N_2O_4(g)$ is 16.5% dissociated at the boiling temperature.[16] Values taken from the extrapolation of the NO_2 isotopic analyses give approximately the same nitrogen separation factor.

Oxygen-18 was found to concentrate in the gaseous species, with an estimated total separation[17] of 1.08. By using an assumed plate efficiency of 60%, this gives an effective single-stage separation factor of 1.0043. With the same assumptions concerning the separation between $N_2O_4(l)$ and $N_2O_4(g)$ as those used previously, a separation factor of 1.026 can be calculated for O^{18} enrichment between $N_2O_4(l)$ and $NO_2(g)$.

Values for the nitrogen separation factor between the gas and liquid phases were also obtained in two other ways. In one experiment, a single-stage equilibrium was performed in which gas and liquid

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[15] $\dfrac{(N^{14}/N^{15})_{top}}{(N^{14}/N^{15})_{bottom}}$.

[16] D. M. Yost and H. Russel, Jr., *Systematic Inorganic Chemistry*, p 28, Prentice-Hall, New York, 1944.

[17] $\dfrac{(O^{18}/O^{16})_{top}}{(O^{18}/O^{16})_{bottom}}$.

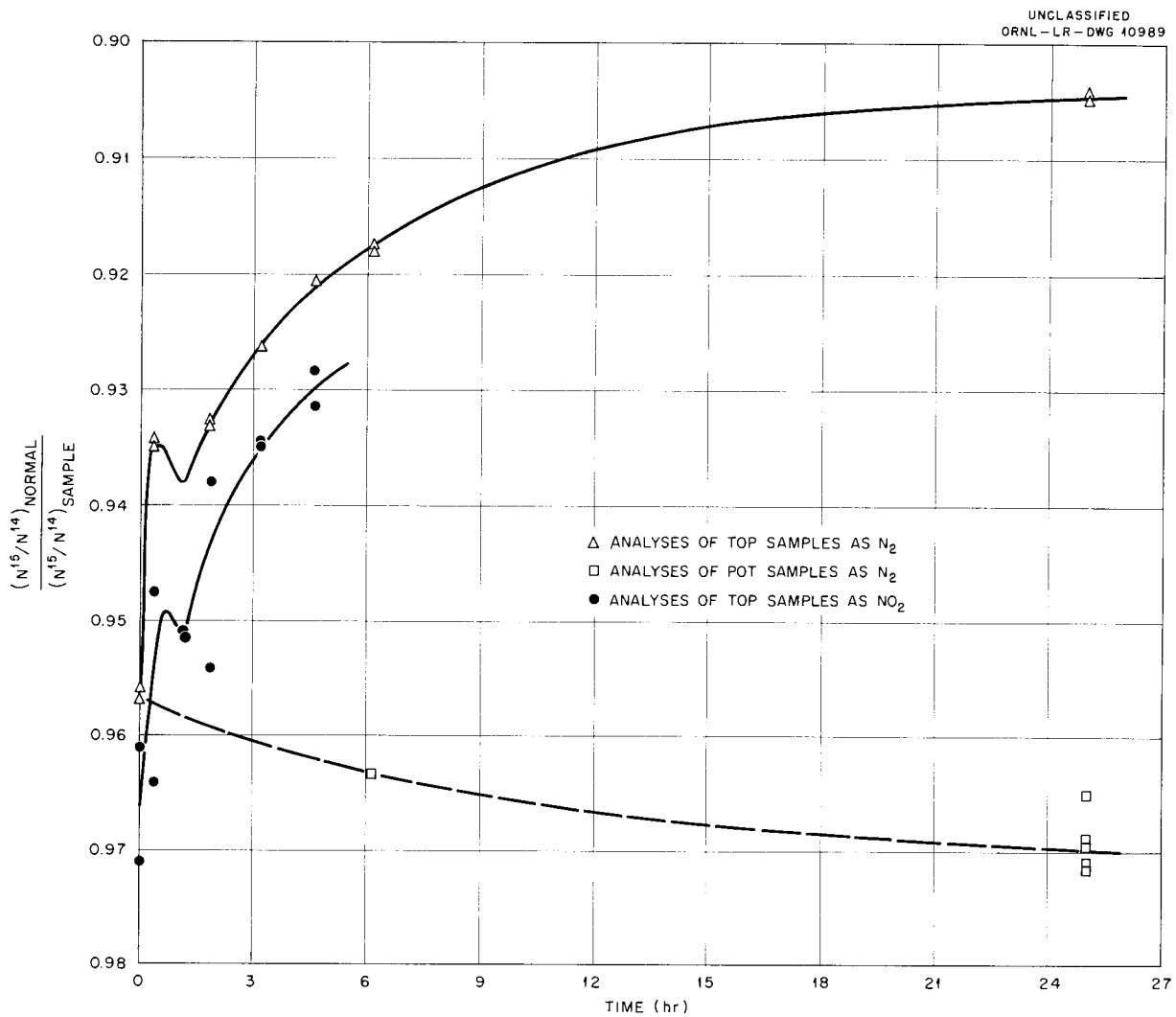


Fig. 21. Nitrogen Isotopic Analyses vs Time for N_2O_4 Distillation.

were equilibrated in a 1-liter bulb at room temperature. The liquid was then drained into another evacuated 1-liter bulb to separate the gas and liquid phases. Samples from the two bulbs were reduced to N_2 in the usual way, and mass analyses were performed in which a direct ratio of the two phases was obtained. This method gave a value for the effective single-stage factor of 1.0031 ± 0.0015 (95% C.I.), with N^{15} concentrating in the liquid phase as before. In another experiment, a Rayleigh distillation of N_2O_4 was carried out in which 168 g of N_2O_4 was distilled from a stirred flask. The final residual gas left in the flask was isotopically analyzed and compared with the original material. A total separation of 1.0177 was obtained, giving a single-stage factor of 1.0042. These values of 1.0031 and 1.0042 are to be compared with the value of 1.0038 obtained by using the assumption of 60% plate efficiency and the column data. It is believed that the single-stage factor is probably low because of wetting of the walls of the vapor flask with liquid, which did not permit a complete vapor-liquid separation, and that the higher two values are more reliable.

An attempt was made to confirm the oxygen factor by analyses from a single-stage equilibration performed as above; the isotopic results

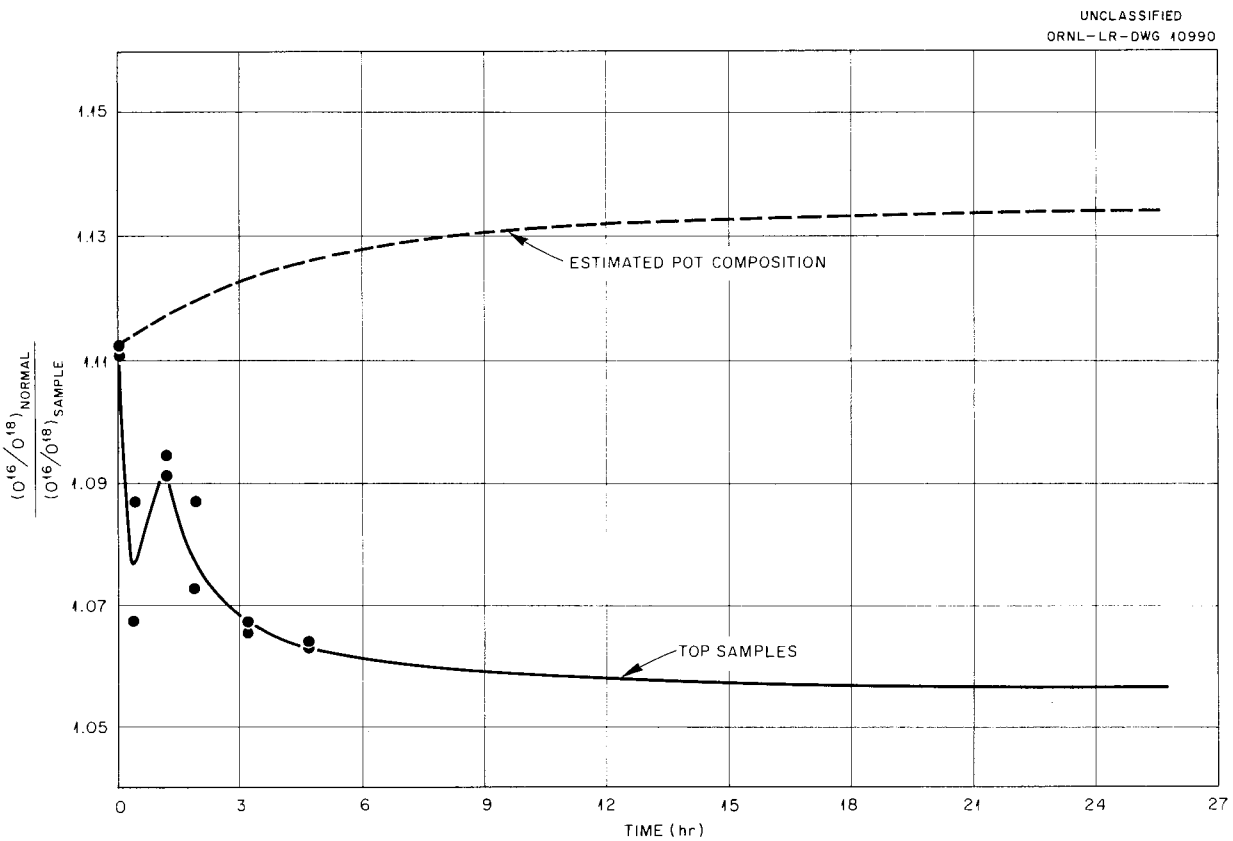
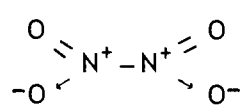


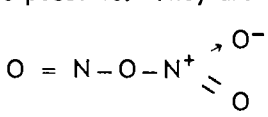
Fig. 22. Oxygen Isotopic Analyses vs Time for N_2O_4 Distillation.

gave an effective single-stage factor of 1.0078, compared with the value of 1.0043. Since not enough samples were run to establish a confidence interval on these results, they serve only to confirm the direction and magnitude of the effect.

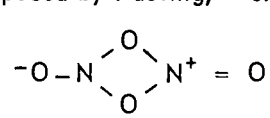
It was expected that the direction and magnitude of the nitrogen isotope effect between N_2O_4 and NO_2 would be about as determined. However, the concentrations of O^{18} in the vapor phase were unexpected. The most generally accepted structure of N_2O_4 involves bonding between the two nitrogens:



Since oxygen is not a central atom here, it was not expected that the heavier atom would have a preference for the N_2O_4 vapor. In the case of exchange between N_2O_4 and NO_2, the oxygen effect would be expected to be small compared with the nitrogen effect if the structure is as postulated. These data indicate that one of the other proposed structures involving oxygen in the bonding may be possible. They are as follows:



which was proposed by Pauling,[18] or



which was proposed by Longuet-Higgens.[19]

[18] L. Pauling, *Nature of the Chemical Bond*, p 251, Cornell University Press, Ithaca, 1940.

[19] H. C. Longuet-Higgens, *Nature* 153, 408 (1944).

OXYGEN ENRICHMENT IN SAMPLES FROM THE BORON ISOTOPE PLANT

G. M. Begun

At the present time, the AEC has in operation a plant employing the distillation of the BF_3·dimethyl ether complex to enrich the isotopes of boron. The complex is partially dissociated (60%) in the vapor phase, and exchange takes place between gaseous BF_3 and the liquid BF_3·dimethyl ether complex, causing B^{11} to concentrate in the vapor phase.[1] Since dimethyl ether is also present in the vapor phase, it seemed likely that oxygen enrichment might also occur in this process because of exchange between the liquid complex and the dimethyl ether vapor. To test this premise, samples were obtained from the AEC plant for analysis.

Three samples of BF_3·dimethyl ether complex were received; they were labeled (1) feed, (2) light polymer from the top of the system, and (3) concentrated polymer from the bottom of the system. These samples were processed for oxygen isotopic analysis in the following manner. A small amount of the liquid complex was mixed with dry CaF_2, and the mixture was heated to 110°C in an oil bath. The $(CH_3)_2O$ evolved was purified of traces of BF_3 by passing it through KOH solution and fractionally distilling it from liquid-nitrogen and dry-ice–acetone traps. The samples produced were analyzed directly in the mass spectrometer, using mass numbers 46 and 48 to determine the O^{16}/O^{18} ratio. The results of these analyses are shown in Table 15, along with the results on tank dimethyl ether samples which were included for comparison.

The average values for O^{16}/O^{18} ratios are 466 for feed material, 839 for waste complex from the B^{11} end of the system, and 144 in the product B^{10} complex. This gives a total separation from the feed point to the waste end of the system of 1.80, with O^{16} concentrating in the waste stream. The total separation between the feed point and the product end of the system is 3.24, with O^{18} concentrating in the product stream. Thus, in the product $B^{10}F_3$·dimethyl ether complex, the O^{18} concentration is more than three times the normal abundance.

It has been estimated that there are approximately 65 stripping stages and 260 enriching stages in the system from which the samples were taken. By using these estimates, single-stage separation factors of 1.0098 and 1.0045 can be calculated from the waste- and product-end analyses, respectively. Of these, the first is probably the better estimate, since the system is not operated in a manner to maximize the oxygen separation values. The stripping part of the plant runs with approximately 3.6% drawoff, which would result in a lowering of the effective single-stage factor determined in this manner. Thus, it is believed that an estimate greater than 1.01 may be placed upon the effective single-stage separation factor for the distillation of BF_3·$(CH_3)_2O$ complex for the separation of O^{16} and O^{18}. The equilibrium constant for the exchange reaction

$$(CH_3)_2O^{18} + BF_3\cdot(CH_3)_2O^{16} \rightleftharpoons (CH_3)_2O^{16} + BF_3\cdot(CH_3)_2O^{18}$$

might then be expected to be greater than 1.016, since the vapor phase is only 60% dissociated in the actual system.

[1] G. M. Murphy (ed.), *Separation of the Boron Isotopes*, NNES III-5, chap. 1, p 25, USAEC Technical Information Service, Oak Ridge, 1952.

TABLE 15. MASS ANALYSES OF $(CH_3)_2O$ SAMPLES

Sample No.	Assay	
	46/47	46/48
Tank	39	475
	39	473
1	39	471
	39	472
	37	454
2	41	835
	40	843
	40	838
3	26	143
	26	144
	26	145

[redacted]

ISOTOPE SEPARATION FACTOR FOR THE SYSTEM KI(DIMETHYL CELLOSOLVE) vs NaK

A. C. Rutenberg

Since the isotopic separation factor for the system potassium amalgam vs aqueous potassium hydroxide was found to be fairly small,[1] it was of interest to determine how large a separation might be achieved between other 0 and +1 valence states of potassium. The best separation might be expected for a system which utilized the molten metal as one phase, in contact with a solution of a potassium salt in a polar solvent which would solvate the potassium ion. Unfortunately, the type of solvent which would interact most strongly with potassium ion would likely be reduced by potassium metal, although some amines may react slowly enough to be used in the experiment. A sodium-potassium alloy (~ 60% K) was chosen so that this experiment could be performed at room temperature. The potassium in NaK is less strongly bonded than the potassium in an amalgam. Some lithium work[2] indicated that a larger separation factor was obtained when a lithium-sodium alloy was substituted for lithium amalgam, in a system consisting of a lithium salt in an organic solvent vs the lithium alloy. A solvent which was fairly stable in contact with NaK was sought for this preliminary experiment. The more stable solvents were found to be relatively poor solvents for potassium salts. The best combination of those tried was KI (0.006 *M*) dissolved in dimethyl Cellosolve (DMC).

The experiment was performed in the following manner. Dimethyl Cellosolve was distilled from a vessel containing NaK and was collected in a flask containing dried KI. The mixture was shaken to saturate the solution, after which the supernatant liquid was transferred to another vessel under an inert atmosphere, and the NaK was introduced with a hypodermic syringe. After this mixture was shaken for 2 hr at 23°C, there appeared to be no reaction of the metal with the solvent. The phases were separated, and the NaK was washed with several portions of dry DMC. The NaK was reacted with isopropanol under an argon atmosphere. Most of the organic matter was driven off by heating, and the remainder was destroyed by successive treatments with nitric and perchloric acids. When the perchloric acid solution was diluted and cooled, most of the potassium perchlorate precipitated. The isotopic analyses were performed on the potassium chloride formed by thermally decomposing the perchlorate. The organic phase was purified in a similar manner, except that no sodium separation was attempted because of the small amount of material. The isotopic analyses of the two phases are given in Table 16.

Considerable difficulty was experienced in analyzing the sample with the mass spectrometer. The analyses were obtained over a three-day period, and each ratio represents a separate loading of the instrument. This experiment did not lend itself readily to a multistage batch operation, and the isotopic analyses were not precise enough to obtain an accurate value from a single-stage experiment. An equilibrium constant of 1.015 was estimated for the following reaction:

$$NaK^{41} + K^{39}I(DMC) = NaK^{39} + K^{41}I(DMC)$$

TABLE 16. POTASSIUM ISOTOPIC ANALYSES (K^{39}/K^{41})

Organic Phase	NaK Phase
14.25	14.00
13.80	14.14
13.73	14.04
13.64	

[1] H. H. Garretson, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. Dec. 31, 1954*, ORNL-1874, p 20.

[2] L. L. Brown, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1954*, ORNL-1815, p 9.

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