

3973

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0349635 8

Cy 5A

ORNL 1706
Progress

5/11/53

4
CA 4

CHEMICAL SEPARATION OF ISOTOPES SECTION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1953

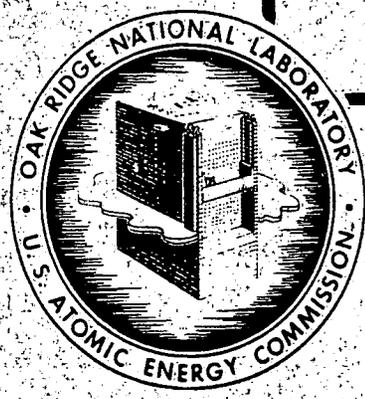
LABORATORY RECORDS
1954

**CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION**

LIBRARY LOAN COPY

DO NOT TRANSFER TO ANOTHER PERSON

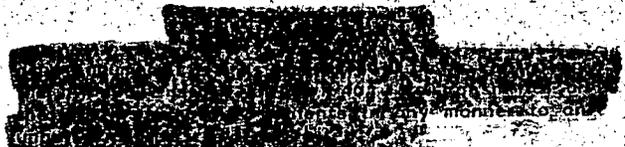
If you wish someone else to see this document,
send in name with document and the library will
arrange a loan.



OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION



POST OFFICE BOX P
OAK RIDGE, TENNESSEE





ORNL 1706

DECLASSIFIED

This document consists of 22 pages.

Copy 5 of 100 copies. Series A.

CLASSIFICATION CHANGED TO:

BY AUTHORITY OF: T-112-1148
BY: P. Manser 2126157

Contract No. W-7405-eng-26

MATERIALS CHEMISTRY DIVISION

G. H. Clewett, Director

CHEMICAL SEPARATION OF ISOTOPES SECTION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1953

J. S. Drury, Supervisor

DATE ISSUED

JUN 2 1954

OAK RIDGE NATIONAL LABORATORY

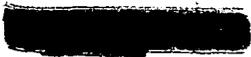
Operated by

CARBIDE AND CARBON CHEMICALS COMPANY

A Division of Union Carbide and Carbon Corporation

Post Office Box P

Oak Ridge, Tennessee



MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES



3 4456 0349635 8

INTERNAL DISTRIBUTION

3. C. E. Center
4. Biology Library
5. Health Physics Library
- 4-5. Central Research Library
6. Director Experimental Engineering Library
- 7-11. Laboratory Records Department
12. Laboratory Records, ORNL R.C.
13. C. E. Larson
14. L. B. Millet (K-25)
15. J. P. Murphy (Y-12)
16. A. M. Weisberg
17. E. H. Taylor
18. E. D. Shiple
19. W. H. Jordan
20. F. C. VonderL...
21. J. A. Swartout
22. S. C. Lind
23. F. L. Culler
24. E. J. Murphy
25. A. H. Snell
26. A. Hollaender
27. M. T. Kelley
28. G. H. Clewett
29. K. Z. Morgan
30. J. H. Frye, Jr.
31. C. P. Keim
32. R. S. Livingston
33. A. S. Householder
34. C. S. Harrill
35. C. E. Winters
36. D. W. Cardwell
37. E. M. King
38. D. D. Cowen
39. J. A. Lane
40. M. J. Skinner
41. P. M. Reyling
42. G. C. Williams
43. J. S. Drury
44. W. R. Grimes
45. K. B. Brown
46. H. M. McLeod
47. K. O. Johnsson
48. G. M. Begun
49. D. A. Lee
50. A. C. Rutenberg
51. R. M. Healy
52. L. Landau

EXTERNAL DISTRIBUTION

- 53-54. Argonne National Laboratory
55. Armed Forces Special Weapons Project, Washington
- 56-57. Atomic Energy Commission, Washington
58. Brookhaven National Laboratory
- 59-61. Carbide and Carbon Chemicals Company (K-25 Plant)
- 62-65. Carbide and Carbon Chemicals Company (Y-12 Plant)
66. Chicago Patent Group
67. Chief of Naval Research
68. duPont Company, Augusta
69. duPont Company, Wilmington
- 70-71. General Electric Company, Ringland
- 72-73. Goodyear Atomic Corporation
74. Hanford Operations Office
75. Iowa State College
- 76-77. Knolls Atomic Power Laboratory
78. Los Alamos Scientific Laboratory
79. Naval Research Laboratory
80. New York Operations Office
81. Patent Branch, Washington
- 82-84. University of California Radiation Laboratory, Berkeley
- 85-99. Technical Information Service, Oak Ridge
100. Division of Research and Medicine, AEC, ORO

CONTENTS

SUMMARY	1
INVESTIGATION OF THE TETRAHYDROFURAN SYSTEM FOR THE CONCENTRATION OF HYDROGEN AND CHLORINE ISOTOPES	2
Description of the System	2
Laboratory Evaluation	2
CHEMICAL SEPARATION OF CHLORINE ISOTOPES	5
Theoretical Considerations	5
Aqueous Chloride-Gaseous Chlorine System	6
NONEXCHANGE OF CHLORINE BETWEEN CHLORATE AND PERCHLORATE IONS	8
EXCHANGE OF WATER WITH HYDRATED LITHIUM IONS	9
Description of Techniques	9
Data and Conclusions	10
BORON ISOTOPE SEPARATION	11
A Liquid-Liquid System	11
Results	12
NITROGEN ISOTOPE SEPARATION	13
Isotopic Separation Equipment	13
Calcium Hydroxide Reflux of the Ammonia-Ammonium Nitrate System	14
Ammonia-Ammonium Carbonate System	17
Summary of Nitrogen Work	18

[REDACTED]

[REDACTED]

5
0



CHEMICAL SEPARATION OF ISOTOPES SECTION
SEMIANNUAL PROGRESS REPORT

SUMMARY

The work on chemical separation of isotopes has been reactivated during this period. A proposed system for the separation of the isotopes of hydrogen and chlorine by means of tetrahydrofuran and hydrogen chloride has been investigated and has been shown to be chemically infeasible. Studies of the chlorine(gas) vs chloride ion(aqueous) system have been initiated. Nitrous acid is presently being used as the refluxing agent in column studies of the isotopic separation factor.

Results are reported on an exchange study in which Cl^{36} is used. No exchange of chlorine was found between chlorate and perchlorate ions in water solution after two years at room temperature. Hydrated lithium ions have been found to exchange all their molecules of solvation in a half-time of less than 0.8 min. Oxygen-18 was used as a stable isotopic tracer in this experiment.

Methods of boron isotope separation have been examined. A liquid-liquid system using boric acid and fluoboric acids distributed between an aqueous phase and an organic phase composed of a mixture of benzene and di(2-ethylhexyl) amine has been investigated, and results on distributions are presented. A gas-liquid type of system is proposed.

Investigations are in progress on modifications of the ammonia(gas) vs ammonium ion(aqueous) system for nitrogen isotope enrichment. An exchange column, stripping column, and associated apparatus have been built. Runs on this system show that calcium hydroxide slurry may be substituted for sodium hydroxide solution as the refluxing agent to convert ammonium ion to ammonia gas at the product (N^{15}) end of the system. This substitution should cut the cost of reflux chemicals considerably. A proposed closed-cycle system which would eliminate or greatly reduce the cost of reflux chemicals is under investigation. This system uses ammonium carbonate in place of ammonium nitrate in the aqueous solution. Initial difficulty has been encountered in plugging of the exchange column by a precipitate. Further runs are planned.

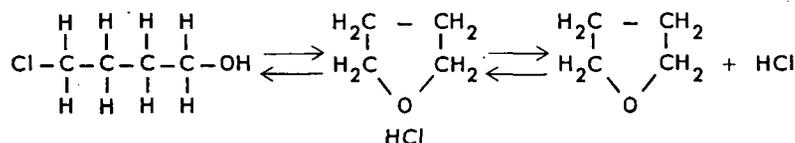
CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

INVESTIGATION OF THE TETRAHYDROFURAN SYSTEM FOR THE CONCENTRATION OF HYDROGEN AND CHLORINE ISOTOPES

D. A. Lee

DESCRIPTION OF THE SYSTEM

The use of tetrahydrofuran has been proposed by H. H. Garretson (consultant) for the simultaneous concentration of isotopes of hydrogen and chlorine. Tetrahydrofuran reacts¹ with hydrogen chloride gas to form 4-chlorobutanol-1. On distillation at pressures greater than 16 mm Hg, 4-chlorobutanol-1 splits off hydrogen chloride and yields tetrahydrofuran.^{2,3} If the reaction



is completely reversible and no other products are formed, the system may be of use for the concentration of hydrogen or chlorine isotopes.

The system would consist essentially of 4-chlorobutanol-1 passing countercurrent to gaseous hydrogen chloride. Exchange would be expected to take place between the chlorine atoms of these two compounds and between the hydrogen of the hydrogen chloride and the hydrogen attached to the oxygen in 4-chlorobutanol-1. It is hoped that appreciable isotopic enrichment would result in one or both cases. Figure 1 shows a flow diagram of the proposed process.

Reflux at the top of the column would be achieved by absorbing hydrogen chloride in tetrahydrofuran and returning the 4-chlorobutanol-1 down the column. At the bottom of the column, reflux would consist of heating the 4-chlorobutanol-1 to form tetrahydrofuran and driving off the hydrogen chloride which would return up the column. The tetrahydrofuran would recycle to the absorber section at the top of the column.

In order for such a system to function certain chemical criteria must be met. The tetrahydrofuran

must be almost completely recovered and must carry none of the "bottoms" hydrogen chloride to the top of the column. The bottom reflux (heating of 4-chlorobutanol-1 to produce hydrogen chloride) should not result in side products which will remove hydrogen or chlorine from the system.

There are possibilities of other products in the reaction of tetrahydrofuran with hydrogen chloride

gas. Heating of 4-chlorobutanol-1 with hydrogen chloride in the liquid phase at 110°C under pressure yields 4,4-dichlorodibutyl ether. The cleavage of tetrahydrofuran to form corresponding dihalides can be carried out with hydrogen iodide, bromide, and chloride or with thionyl chloride.

LABORATORY EVALUATION

To determine the chemical feasibility of the system mentioned, the following experiment was performed. Tetrahydrofuran was purified by fractional distillation over calcium carbide. This tetrahydrofuran was saturated with dry hydrogen chloride gas at room temperature. One hundred fifty milliliters of the hydrogen chloride saturated solution was placed in the still pot of a fractional distillation still equipped with a 30-in.-long concentric-tube column. Heat was slowly applied. Any hydrogen chloride that was evolved was trapped in two aqueous sodium hydroxide traps in series at the head of the column. Hydrogen chloride was evolved until the pot temperature reached 80°C; then the gas evolution subsided. Heat input was increased and the pot temperature rose to 106°C, at which point hydrogen chloride evolution was observed again. No liquid reflux was yet attained at the head of the column. The heating was stopped and the still pot and sodium hydroxide traps were sampled. When heat was applied again the pot

¹D. Starr and R. Hixon, *Organic Synthesis, Collective Volume II*, 1st ed., ed. by A. H. Blatt, p 571, Wiley, 1943.

²W. R. Kirner and G. H. Richter, *J. Am. Chem. Soc.* 51, 2505 (1929).

³G. M. Bennett and F. Heathcoat, *J. Chem. Soc.* 1929, p 268.

UNCLASSIFIED
ORNL-LR-DWG 665

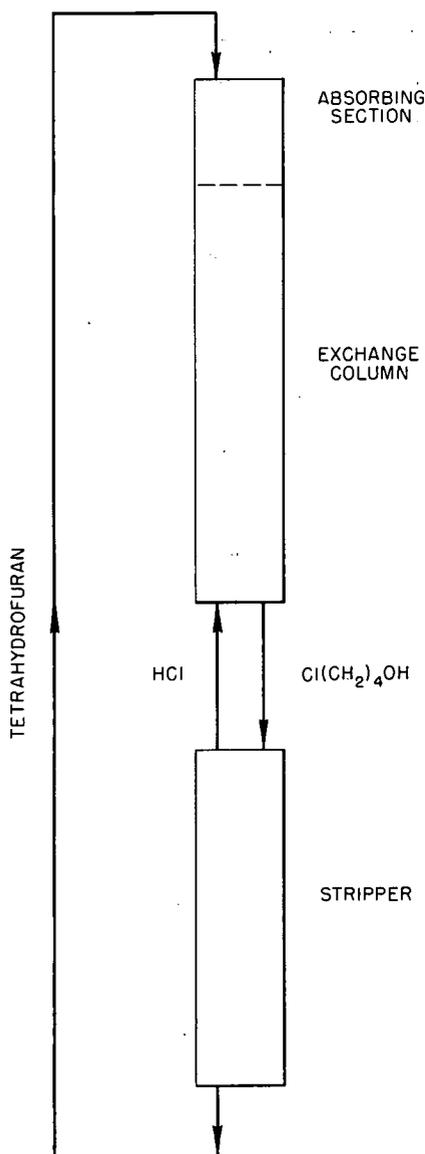


Fig. 1. Proposed Tetrahydrofuran System.

temperature reached 112°C, and tetrahydrofuran refluxed at the head of the column at 62.5°C. The column was left at total reflux until minimum reflux temperature was attained and then distillate was collected at a reflux ratio of approximately 100 to 1.

Distillate was collected continuously for two days. When the volume of liquid in the still pot became low, the distillation was stopped. The head temperature at this time was 64°C and the still-pot temperature was 128°C. The solution in the still pot was slightly yellow and had separated into two liquid phases. There were 6 ml of the heavier phase and 40 ml of the lighter phase. Analytical data on the various fractions are shown in Table 1. From these data a rough chlorine material balance may be made:

Distillate	23.1%
Residues	47.9%
Traps	4.1%
Unaccounted	24.9%

Part or all of the chlorine not accounted for may have been in the lower layer of the pot residue or in the distillates, as the chlorine in these samples was determined after alkaline hydrolysis. Such a treatment would remove the chlorine from 4-chlorobutanol-1 but probably would not effect more stable chlorine-containing compounds. This is illustrated by the analysis of the upper layer of the still pot which showed 0.48 meq/ml of chlorine on alkaline hydrolysis, but after peroxide bomb treatment the value obtained was 11.5 meq/ml.

It was concluded that the starting material was largely 4-chlorobutanol-1 in equilibrium with tetrahydrofuran hydrochloride with some excess tetrahydrofuran. The distillate was largely tetrahydrofuran with dissolved hydrogen chloride producing some 4-chlorobutanol-1. Considerable side reaction takes place in the still pot which forms other products and which would remove material from the cycle. Under the conditions of the experiment, very little hydrogen chloride (4.1%) was actually separated from the system and removed by the sodium hydroxide traps.

The data show that considerable decomposition or side product formation occurs when 4-chlorobutanol-1 is heated to produce tetrahydrofuran and hydrogen chloride. Difficulty was also encountered in separating hydrogen chloride from tetrahydrofuran. The stripping operation appears to be quite difficult. For these two reasons, it was concluded that further work on this system is not justified.

CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

TABLE 1. ANALYTICAL RESULTS FOR THE TETRAHYDROFURAN-HYDROGEN CHLORIDE SYSTEM

SAMPLE	meq/ml			REFRACTIVE INDEX	DENSITY
	H ⁺	Cl ⁻	Cl After NaOH Digestion		
Starting material: tetrahydrofuran saturated with hydrogen chloride	0.72	0.82	7.0		
Still pot before head reflux	0.36	0.38	7.1	1.4422	
Lower layer of still-pot residue (6 ml)			7.14	1.3905	
Upper layer of still-pot residue (40 ml)			0.480 (11.5)*	1.4522	1.093 (30°C)
First distillate sample, 25 ml	1.12	1.10	1.84	1.4285	
Second distillate sample, 25 ml	1.53	1.49	2.75	1.4372	
Third distillate sample, 25 ml	2.48	2.53	4.56	1.4476	
Fourth distillate sample, 3 ml	2.91	2.94	4.7		
First NaOH trap (before head reflux)		0.02			
Second NaOH trap (before head reflux)		0.01			
First NaOH trap (end of distillation)		0.09			
Second NaOH trap (end of distillation)		0.10			
4-Chlorobutanol-1**				1.4551	1.125 (25°C)
Tetrahydrofuran**				1.4073	0.888 $\left(\frac{20^\circ}{4^\circ} C\right)$

*Cl after peroxide bomb.

**Literature values.

CHEMICAL SEPARATION OF CHLORINE ISOTOPES

A. C. Rutenberg

THEORETICAL CONSIDERATIONS

The lower valence states of chlorine are being investigated as possible candidates for use in a chemical process to separate chlorine isotopes. Calculated separation factors between various chlorine-containing species are shown in Table 2.

The numbers are the equilibrium separation factors calculated by Urey¹ for exchange between the gaseous species shown. The separation factor is defined as the quotient of the atom ratios of $\text{Cl}^{37}/\text{Cl}^{35}$ in the two species at equilibrium. As set up, Cl^{37} would concentrate in the species at the left of the table.

Exchange between the higher and lower valence states of chlorine gives impressive calculated values. However, the rates of exchange are exceedingly slow. Exchange between the upper valence states of chlorine with the exception of chlorine dioxide vs chlorite ion (which only re-

quires transfer of an electron) is also quite slow.² Rapid exchange occurs among chloride ion, hypochlorite ion, and molecular chlorine in aqueous solution.

The following types of systems utilizing these valence states merit study, although the separation factors are expected to be small (<1.01):

1. chloride ion in aqueous solution vs gaseous chlorine,
2. chloride ion in aqueous solution vs molecular chlorine in an organic solvent,
3. chloride ion in aqueous solution vs complexed minus-one chlorine in an organic solvent,
4. chloride ion in aqueous solution vs a gaseous minus-one chlorine compound,
5. hypochlorite ion in aqueous solution vs gaseous chlorine,
6. minus-one chlorine in an organic solvent vs gaseous chlorine.

¹H. C. Urey, *J. Chem. Soc.* 1947, p 574.

²H. Dodgen and H. Taube, *J. Am. Chem. Soc.* 71, 2501 (1949).

TABLE 2. SEPARATION FACTORS FOR CHLORINE EXCHANGE AT 25°C

	$\frac{\text{Cl}^{37}\text{O}_4^-}{\text{Cl}^{35}\text{O}_4^-}$	$\frac{\text{Cl}^{37}\text{O}_3^-}{\text{Cl}^{35}\text{O}_3^-}$	$\frac{\text{Cl}^{37}\text{O}_2}{\text{Cl}^{35}\text{O}_2}$	$\left(\frac{\text{Cl}_2^{37}}{\text{Cl}_2^{35}}\right)^{1/2}$	$\frac{\text{HCl}^{37}}{\text{HCl}^{35}}$
$\frac{\text{Cl}^{37}\text{O}_4^-}{\text{Cl}^{35}\text{O}_4^-}$	1.000	1.035	1.052	1.077	1.080
$\frac{\text{Cl}^{37}\text{O}_3^-}{\text{Cl}^{35}\text{O}_3^-}$		1.000	1.016	1.040	1.043
$\frac{\text{Cl}^{37}\text{O}_2}{\text{Cl}^{35}\text{O}_2}$			1.000	1.024	1.027
$\left(\frac{\text{Cl}_2^{37}}{\text{Cl}_2^{35}}\right)^{1/2}$				1.000	1.003

CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

The first system listed appears to offer less experimental difficulties than do the others, and it is being investigated first. Some preliminary experiments in which chlorine gas was passed counter-current to an aqueous solution of hydrolyzed chlorine (chloride and hypochlorite ions) did not appear to yield any isotopic separation. A probable explanation is that even though one ion tends to enrich Cl^{35} the other ion enriches Cl^{37} , and so the net effect is very small. More careful experiments are necessary to establish the degree of separation in this case.

AQUEOUS CHLORIDE-GASEOUS CHLORINE SYSTEM

In the aqueous chloride-gaseous chlorine system, now under investigation, chlorine gas is being used as the continuous reservoir and is passed counter-current to an acidified, aqueous, chloride-ion solution. The chlorine is reduced in the top section of the column and the chloride-ion solution passes down the column. A small amount of chlorine dissolves in the aqueous-chloride solution and goes down the column, slightly reducing the efficiency of the process. It is hoped that the reduction of chlorine at the top of the column can be made to be quantitative.

The equipment used for the experimental work is shown in Fig. 2. A 15-mm-ID water-jacketed column with a 9-ft exchange section was assembled. The column was originally packed with $\frac{1}{8}$ -in. glass helices and had a 15-in.-long reflux section with a sampling port at the lower end. The sampling port consisted of a capillary stopcock connected to a 12/2 ball joint. The sampling bulbs were equipped with vacuum-type hollow-bulb capillary stopcocks. Capillary tubing and compact design reduced the holdup of the sampling system to a minimum. Sampling was accomplished by plugging an evacuated sample tube into the sample port and momentarily opening the two stopcocks. A similar sampling arrangement was used at the chlorine feed point.

An attempt was made to operate the column with the liquid phase continuous, a "stick" with sintered glass sides being used to disperse the gas. The initial dispersion was quite good, but the fine gas bubbles rapidly coalesced and large bubbles rose through the packed column. The system was quite sensitive to variations in gas pressure, and the liquid phase would back up into the gas-feed system. The column was subsequently tried by using

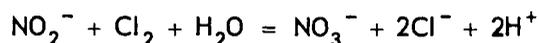
air as the continuous phase and by trickling water containing a dye down the packing. A small amount of channeling was noted. It was decided to operate the column with the gas phase continuous.

The column was then tested by running aqueous sodium chloride solution countercurrent to chlorine gas. Reflux was accomplished by introducing slightly acidified sodium bromide at the top of the column. Bromine was liberated and came down the column primarily as droplets of liquid. The top of the reflux section was almost colorless but it could not be determined how far down the column the reflux was occurring. Liquid bromine accumulated in the overflow head device at the bottom of the column, and bromine attacked the Tygon tubing of the waste-stream lines.

On the basis of these preliminary experiments, it seemed desirable to make some changes in the system. The reflux section was doubled in length and equipped with two sampling ports. The entire column (including the reflux section) was packed with $\frac{1}{16}$ -in. glass helices. A substitute reflux agent for bromide ion was sought.

The chlorine-reducing agent must react rapidly and completely with chlorine. It is desirable that the reagent and all reaction products be quite water soluble. The reaction should be accompanied by a color change, or a change in some chemical property such as pH, so that an indicator can be added to give the desired color change. It would be possible to locate the reflux by change in temperature or concentration of some ion other than H^+ , but no provisions for doing so are incorporated into the present column.

Sodium nitrite seemed to have most of the desired properties for the reducing agent in this system. It was presumed that the primary reaction would be the one indicated below in which 1 mole of nitrite ion is consumed for each mole of chlorine reduced.



Initial experiments revealed that as many as 2.5 moles of nitrite ion per mole of chlorine were necessary to reduce the chlorine. The stoichiometry seemed to vary and made control of the reflux level difficult. On the assumption that much of the nitrite decomposition occurred in the highly acid medium resulting from the reaction, some experiments were performed with base added to the nitrite solution. This change appeared to improve the reproducibility

and the efficiency of the nitrite reduction. A deficiency of base was used so that the chloride ion solution going down the column would be acidic

and the chlorine hydrolysis would be at a minimum. Optimum operating conditions have not been worked out as yet.

UNCLASSIFIED
ORNL-LR-DWG 666

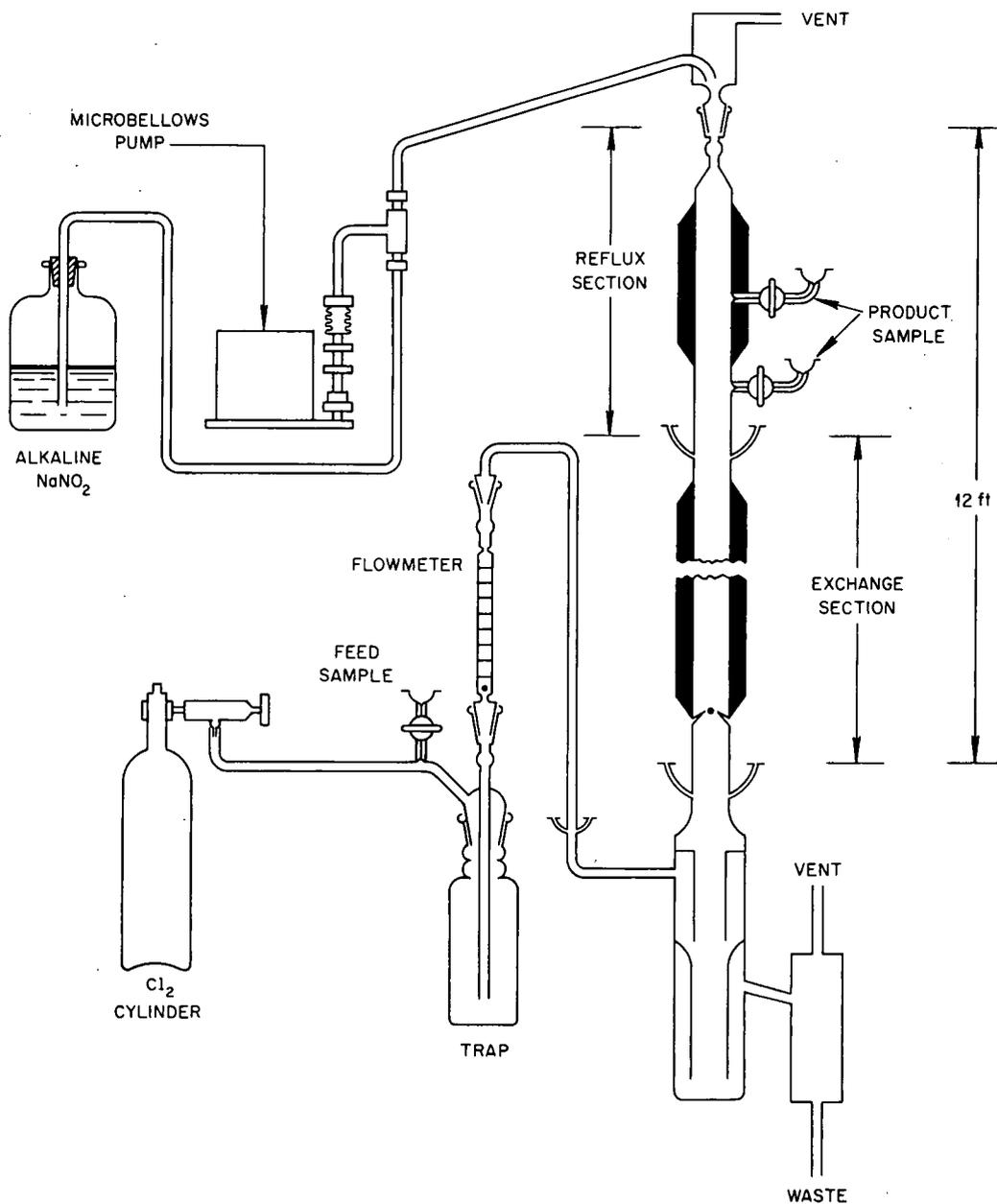


Fig. 2. Equipment Used in Investigation of Aqueous Chloride-Gaseous Chlorine System.

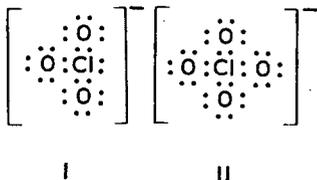
CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

NONEXCHANGE OF CHLORINE BETWEEN CHLORATE AND PERCHLORATE IONS

D. A. Lee

Two years ago an experiment was started to investigate the possibility of exchange between chlorate and perchlorate ions in aqueous solution, and the effect of catalysts on this exchange. This was undertaken because of the attractive isotopic separation factor calculated by Urey¹ (1.035 at 25°C) for this exchange. Because of other work the experiments have just recently been completed and are reported here.

Dodgen and Taube^{2,3} have studied the mechanism of interaction of chlorine oxidation states, but they made no attempt to exchange chlorine between chlorate and perchlorate. The structures of perchlorate and chlorate ions are known to have Cl-O bonds which are shorter than the sum of the single-bond covalent radii for the atoms.^{4,5,6} Pauling⁷ attributes this bond shortening to double-bond character. This picture provides a possible mechanism for an effective exchange of chlorine atoms between chlorate (I) and perchlorate (II) ions by transfer of an oxygen atom:



Pitzer⁸ states that bond shortening in these ions is not necessarily due to pi-bonding. This statement is also supported by the molecular orbital

treatment of the structure of the perchlorate ion by Wolfsberg and Helmholtz.⁹ Since oxygen in perchlorate and chlorate does not exchange with oxygen in water,¹⁰ no intermediate involving water can be postulated. Therefore a very slow oxygen transfer would be expected.

An electrolytic method described by Walton¹¹ was used to prepare $\text{KCl}^{36}\text{O}_3$. The $\text{KCl}^{36}\text{O}_3$ was purified by double recrystallization from water.

A water solution of 0.056 N $\text{KCl}^{36}\text{O}_3$ and 0.056 N NaClO_4 was equilibrated. The chlorate ion was reduced to chloride ion with sulfurous acid ($\text{Na}_2\text{S}_2\text{O}_5$ and H_2SO_4). The excess sulfite ion was oxidized to sulfate ion with hydrogen peroxide, and the excess hydrogen peroxide was decomposed by heat in the presence of platinum. The chloride was collected as silver chloride on a microfilter crucible.

The filtrate containing perchlorate ion was reduced to chloride ion by the addition of a sulfuric acid solution of titanium oxysulfate and by the passage of this solution through a Jones reductor. The reduced solution was allowed to reflux for 30 min to ensure complete reduction. The titanous solution was then oxidized with hydrogen peroxide, and the hydrochloric acid was distilled into a silver nitrate solution and the silver chloride collected as above.

The results of the experiments are given in Table 3.

These experiments show that there is no exchange of chlorine between chlorate and perchlorate ions in water solution at room temperature in two years. Also, there is no exchange in 0.1 N H_2SO_4 and 0.1 N NaOH in 19½ hr. Increasing the temperature to 99°C did not increase the exchange rate in 1 hr.

¹H. C. Urey, *J. Chem. Soc.* 1947, p 574.

²H. Dodgen and H. Taube, *J. Am. Chem. Soc.* 71, 2501 (1949).

³*Ibid.*, p 330.

⁴R. G. Dickinson and E. A. Goodhue, *J. Am. Chem. Soc.* 43, 2045 (1921).

⁵W. H. Zachariasen, *Z. Krist.* 71, 517 (1929).

⁶W. H. Zachariasen, *J. Am. Chem. Soc.* 53, 2123 (1931).

⁷L. Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, N. Y., 1939, p 227.

⁸K. S. Pitzer, *J. Am. Chem. Soc.* 70, 2140 (1948).

⁹M. Wolfsberg and L. Helmholtz, *J. Chem. Phys.* 20, 837 (1952).

¹⁰E. R. S. Winter, M. Carlton, and H. V. A. Briscoe, *J. Chem. Soc.* 1940, p 131.

¹¹H. J. Walton, *Inorganic Preparations*, Prentice-Hall, New York, 1948, p 169.

TABLE 3. CHLORATE AND PERCHLORATE ACTIVITIES
AFTER EQUILIBRATION AT ROOM TEMPERATURE

THE 0.056 N KCl ³⁶ O ₃ -0.056 N NaClO ₄ SYSTEM	EQUILIBRATION TIME	ACTIVITY (counts/min/μg of AgCl)	
		ClO ₃ ⁻	ClO ₄ ⁻
In water	2 min	33.3	0.06
	19 hr, 45 min	36.2	0.06
	2 yr	66.4*	1.04
	1 hr**	47.0	0.00
In 0.1 N H ₂ SO ₄	19 hr, 34 min	38.2	0.07
In 0.1 N NaOH	19 hr, 25 min	35.9	0.02
In water with platinum black	2 yr	66.1*	-0.03
In water with V ₂ O ₅	2 yr	65.0*	0.79

*Higher activities are due to a different geometry in the counting apparatus.

**99°C.

EXCHANGE OF WATER WITH HYDRATED LITHIUM IONS

A. C. Rutenberg

In the field of isotope separation by chemical means it is of interest to know the species undergoing exchange. The number and type of bonds which surround the exchanging atoms in the two states involved determine the magnitude of the isotopic separation factor. In a system containing the element of interest as a solvated ion, the number of molecules of solvent which do not exchange or exchange slowly may indicate the actual coordination number of the ion in solution. Because of these facts, an attempt was made to measure the rate of water exchange between hydrated lithium ion in aqueous solution and the bulk of the aqueous solvent. The stable isotopic tracer employed for this purpose was O¹⁸.

DESCRIPTION OF TECHNIQUES

The method used was similar to that employed by Hunt and Taube¹ to study the water exchange of a number of cations in aqueous solution.

Ten milliliters of a 9.36 M solution of lithium chloride in normal water was placed in a vessel from which small samples could be rapidly distilled at room temperature under reduced pressure. To this solution was added 5 ml of water about eightfold enriched in O¹⁸. The solutions were stirred magnetically and after a short period of mixing, most of the excess air was pumped off. If all the excess air is removed, the subsequent distillation will be violent but if too much air remains, the distillation will be slow. The exchange vessel was immersed in water to prevent excessive cooling during the low-pressure distillation. A sample of water from the exchange vessel was distilled into a cold trap from which it was transferred to a sample tube, and a measured small amount of purified carbon dioxide was introduced from a calibrated gas-delivery system. The

¹J. P. Hunt and H. Taube, *J. Chem. Phys.* 19, 602 (1951).

CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

initial sample was taken as soon as possible and the final sample a day later. Carbon dioxide was also added to a sample of normal and eightfold-enriched water. The samples were allowed to equilibrate for ten days at 25°C. The sample tubes were then frozen in a dry-ice bath and the dry carbon dioxide was transferred to a breakseal tube at liquid-nitrogen temperature. The isotopic ratio (46/44) of the samples was determined by the Mass Assay Laboratory.

DATA AND CONCLUSIONS

The data from the experiments are summarized in Table 4.

The value of the equilibrium constant (K) used in the calculations² was 2.078 at 25°C where

$$K = \frac{[C^{12}O^{16}O^{18}][H_2O^{16}]}{[C^{12}O_2^{16}][H_2O^{18}]}$$

The mole fraction (N) of O^{18} in the water is calculated from the equation

²*Ibid.*, p 604.

$$N = \left[\frac{R}{K + R} \right] + \left[\frac{R}{Q(1 + R)} \right] - \frac{R_0}{Q}$$

where R is the ratio of $CO^{16}O^{18}$ to CO_2^{16} and Q is the molar ratio of water to carbon dioxide in the equilibration. The isotopic composition of the water for complete random mixing was calculated from the isotopic analysis of the normal and enriched water and the concentration and density of the initial lithium chloride solution. The random mixing value ($N = 0.00740$) differs by about 0.5% from the observed values for the distillate, and the fractionation is of the order of magnitude observed for distillations of this type.

Since the initial and final water samples were of the same isotopic composition and were in good agreement with the value for complete exchange, exchange was complete at the time of the first sampling. An estimated upper limit on the half-time of this exchange, based upon the time of mixing and sensitivity of this method, is 0.8 min. From these results it can be concluded that hydrated lithium ions exchange all their molecules of solvation with solvent molecules more rapidly than can be detected by this technique.

TABLE 4. EXCHANGE OF WATER WITH HYDRATED LITHIUM IONS

	MOLES OF H ₂ O PER MOLE OF CO ₂ , Q	CO ₂ ISOTOPIC ANALYSIS (46/44),* R	MOLE FRACTION O ¹⁸ IN H ₂ O, N
CO ₂ Sample Equilibrated with:			
Normal H ₂ O	749	0.00418 ± 0.00006	0.00201**
H ₂ O eightfold enriched	374	0.03383 ± 0.00016	0.01610
H ₂ O distilled 3.5 min after mixing	179	0.01529 ± 0.00003	0.00736
H ₂ O distilled 51.0 min after mixing	206	0.01530 ± 0.00004	0.00736
H ₂ O distilled 25.5 hr after mixing	168	0.01526 ± 0.00007	0.00736

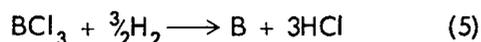
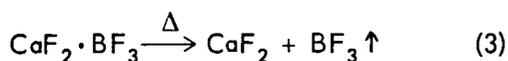
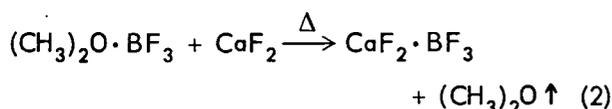
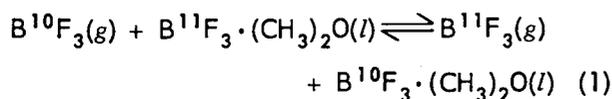
*95% confidence interval.

** R_0 .

BORON ISOTOPE SEPARATION

R. M. Healy

The present method for the separation of boron isotopes (B^{10} and B^{11}) consists of the equilibrium distillation of the dimethyl ether-boron trifluoride complex $(CH_3)_2O \cdot BF_3$. This method was developed during the Manhattan Project and has been described in detail.¹ The complete process to produce crystalline B^{10} can be summarized by the following equations:



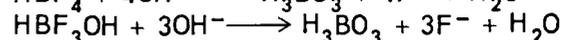
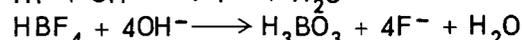
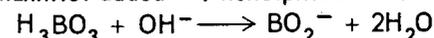
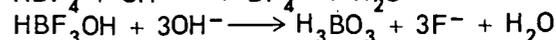
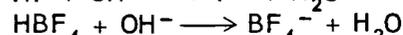
For the study of reactions 1 and 2, two vacuum racks, one for the preparation of the dimethyl ether-boron trifluoride and similar complexes and the other for studying the thermal decomposition of the complexes, have been built. These racks are similar to those used in the original investigation.¹ Some of the compounds of interest have been prepared or ordered. No data have yet been accumulated on these systems. Instead, attention has been turned to the liquid-liquid type of system.

A LIQUID-LIQUID SYSTEM

An effort has been made to find a countercurrent liquid-liquid process because these systems offer the advantage of high throughput. In such a system the element to be enriched isotopically must be distributed between two immiscible phases with, preferably, quite dissimilar bonding of the element in the two phases. One such possible system is that containing boric and fluoboric acids. Extraction experiments were carried out by contacting aqueous solutions containing boric and fluoboric

acids with a benzene solution of di(2-ethylhexyl) amine. The boric acid solutions were made by mixing weighed amounts of boric acid into plastic beakers, dissolving, adding a weighed amount of 48% hydrofluoric acid solution, and diluting to the desired volume. Knowledge of the complexity of these solutions has recently been expanded by Wamser.^{2,3} Besides fluoboric and boric acids, these solutions contain mono-, di-, and trihydroxyfluoboric acids. The last-named acid has not been isolated; its presence is inferred. The indicated concentration of the monohydroxy acid includes the other hydroxyfluoboric acids. The method used here has followed Wamser's except that the fluoborate ion is determined by hydrolyzing the solution completely instead of by using nitron to precipitate it.

If two aliquots are taken and if two titrations of each are made, then the four values obtained allow three unknowns to be determined and also provide a check on the internal consistency. They do not allow the calculation of a fourth unknown because they are not all independent. The acids whose concentrations can be calculated are fluoboric acid, the sum of the hydroxyfluoboric acids, and boric or hydrofluoric acid. Only boric or hydrofluoric acid is present in significant amount in a given solution. The reactions which take place during the titrations and the conditions under which the titrations are made are summarized in the following equations:

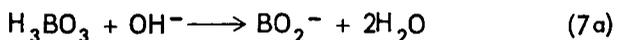


¹G. M. Murphy (ed.), *Separation of the Boron Isotopes*, NNES III-5, McGraw-Hill, New York, 1952.

²C. A. Wamser, *J. Am. Chem. Soc.* 70, 1209 (1948).

³C. A. Wamser, *J. Am. Chem. Soc.* 73, 409 (1951).

CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT



Consistent results were obtained by the foregoing method on several solutions. However, considerable difficulty has been experienced in reducing the analyses to routine procedure.

RESULTS

A series of extraction experiments was performed; in each experiment 25 ml of an aqueous solution of the mixed boric acids was contacted with the same volume of 0.8 M di(2-ethylhexyl) amine in benzene.

Representative data from these experiments are presented in Table 5.

It is possible to conclude from these data that the organic phase extracts very little of the boric acid from the aqueous phase. Approximately one-half of the fluoboric acids are extracted into the organic phase, while roughly one-sixth of the fluoboric acids remain in the aqueous phase. The remaining one-third of the fluoboric acids are converted into boric acid and hydrofluoric acid, the latter extracting into the organic phase.

TABLE 5. DISTRIBUTION OF BORIC AND FLUOBORIC ACIDS BETWEEN ORGANIC* AND AQUEOUS PHASES

EXPERIMENT NUMBER	CONDITION	ORGANIC PHASE** (mole/liter)			AQUEOUS PHASE** (mole/liter)			
		H ₃ BO ₃	HF + HBF ₄ + HBF ₃ OH	Total B	H ₃ BO ₃	HF ₃ OH	HF ₄	Total B
1	Before contacting	0.0			0.786			0.786
	After contacting	0.02		0.02	0.77			0.77
2	Before contacting	0	0	0	0.632	0.093	0.119	0.844
	After contacting		0.17	0.124	0.679	0.02	0.02	0.719
3	Before contacting	0	0	0	0.625	0.097	0.114	0.836
	After 2 min of contacting		0.164	0.102	0.666	0.01	0.05	0.726
	After 16 hr of contacting		0.167	0.094	0.685	0.0	0.04	0.725
4	Before contacting	0	0	0	0.57	0.37	0.67	1.61
	After contacting		0.105***	0.109***	0.742	0.148	0.057	0.947

*0.8 M di(2-ethylhexyl) amine in benzene.

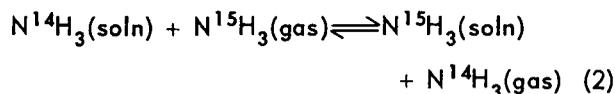
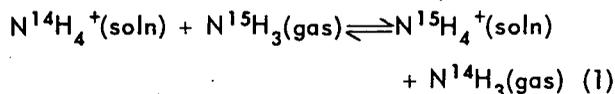
**25 ml.

***60 ml of organic phase. These data are not in good agreement with the results by difference from the aqueous phase. The data from the aqueous phase are believed to be more nearly correct in this case.

NITROGEN ISOTOPE SEPARATION

A. A. Palko

The only extensively studied chemical-exchange system for nitrogen isotope enrichment is that using countercurrent chemical exchange between gaseous ammonia as one phase and ammonium ion in solution as the other phase. This system was first proposed and demonstrated in 1937 by Urey and his co-workers¹ who passed ammonia gas vs 60% ammonium nitrate in aqueous solution. Later, Kirshenbaum² determined the equilibrium constants for the two competitive exchange reactions occurring in the system and found that the separation factors at 25°C were 1.034 and 1.005, respectively, for reactions 1 and 2.



These separation factors agree very well with values obtained by other investigators^{1,3-10} whose results vary from 1.006 for the ammonia-ammonium hydroxide exchange to 1.023 for the ammonia-ammonium ion exchange. The observed separation factor would be expected to fall between 1.005 and 1.034, since reactions 1 and 2 both take place in any system where ammonia gas exchanges with ammonium ion in solution.

¹H. C. Urey, M. Fox, J. R. Huffman, and H. G. Thode, *J. Am. Chem. Soc.* 59, 1407 (1937).

²I. Kirshenbaum, J. S. Smith, T. Crowell, J. Graff, and R. McKee, *J. Chem. Phys.* 15, 440 (1947).

³H. C. Urey, J. R. Huffman, H. G. Thode, and M. Fox, *J. Chem. Phys.* 5, 856 (1937).

⁴H. G. Thode and H. C. Urey, *J. Chem. Phys.* 7, 34 (1939).

⁵K. Clusius, E. W. Becker, and H. Lauckner, *Chem. Zentr. II* 1942, p 1089.

⁶K. Clusius and E. W. Becker, *Z. physik Chem.* 193, 64 (1943).

⁷E. W. Becker and H. Baumgartel, *Z. Naturforsch.* 1, 514 (1946).

⁸E. W. Becker and H. Baumgartel, *Angew. Chem.* A59, 88 (1947).

⁹A. Sugimoto, R. Nakane, R. Shibata, T. Watanabe, S. Motonaga, and S. Isomura, *Repts. Sci. Research Inst. (Japan)* 26, 1 (1950).

¹⁰A. Sugimoto, R. Nakane, and T. Watanabe, *Bull. Chem. Soc. Japan* 24, 153 (1951).

The ammonia-ammonium nitrate system, as usually run, uses 60 wt % aqueous ammonium nitrate solution which is passed countercurrent to ammonia gas. In laboratory work an infinite reservoir of ammonium nitrate is used as a feed. Reflux at the top, however, may be accomplished by absorbing the ammonia in nitric acid and then returning the ammonium nitrate solution to the head of the column. Reflux at the bottom of the column is accomplished by adding sodium hydroxide to the nitrate solution and then boiling to remove the ammonia gas from the solution. The large amounts of nitric acid and sodium hydroxide required for this process are one of the major costs of the N¹⁵ produced. The interest in this Division has been in studying more economic variations of this system and possible ways of reducing reflux costs.

ISOTOPIC SEPARATION EQUIPMENT

An apparatus has been built to test variations of the ammonia-ammonium ion system. It should be possible to use this equipment on any gas-liquid or liquid-liquid countercurrent chemical-exchange system. Figure 3 shows a schematic drawing of the setup and Fig. 4 is a photograph of the lower section of the apparatus.

The 2.1-cm-ID exchange column is made of glass, is 22 ft high, and has a 20-ft section packed with 1/8-in. glass helices. The column is jacketed for temperature control. Provisions are made for feeding or withdrawing either phase at the top and the bottom. This column is shown at the right in the photograph. The reflux column is made of 2-in.-ID glass, is 15 ft high, and has a 14-ft section packed with 1/2-in. ceramic saddles. It is wrapped with five 6-ft sections of heating tape, each individually controlled so that any desired temperature gradient may be maintained throughout the column. At the top of the column is a water-cooled condenser. Slurry entering the stripping column first passes through a 1-liter preheater. At the bottom is a 2-liter boiler for refluxing the stripping solution. Both the boiler and the preheater are heated by controlled Glas-col heating mantles and contain a magnetic stirrer. Feed or withdrawal may be made from either phase at both top and bottom. In addition, a feed point is located

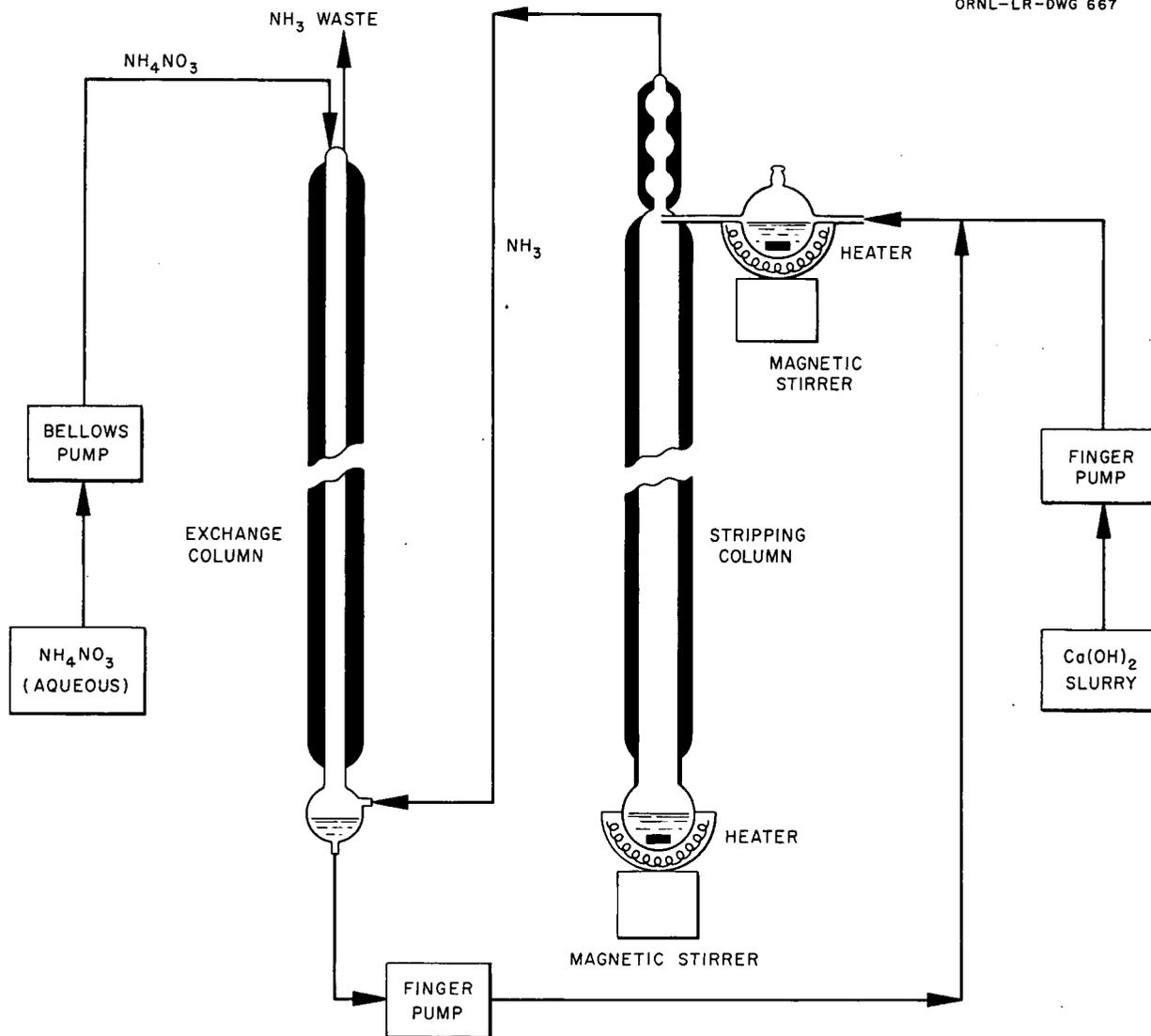


Fig. 3. Exchange Column and Stripper for the $\text{NH}_3(\text{gas})$ vs $\text{NH}_4^+(\text{soln})$ System.

4 ft from the top of the stripping column. Two Sigmamotor pumps controlled by variable-speed drives are used to pump reflux feed, and a bellows pump with a capacity from 0 to 6 liters/hr is used to pump exchange-column feed. Tygon tubing is used throughout the apparatus for liquid and gas transfer.

CALCIUM HYDROXIDE REFLUX OF THE AMMONIA-AMMONIUM NITRATE SYSTEM

The use of calcium hydroxide in place of sodium hydroxide as the refluxing agent to convert am-

monium ion to ammonia has been suggested in this laboratory. If this is possible, the chemical cost for this part of the process will be cut sixfold. The use of calcium hydroxide as a refluxing agent involves the substitution of a lime slurry for the sodium hydroxide solution used in previous systems. In order to find whether this reflux could be run efficiently in the regular stripping apparatus, several runs were made with the equipment described. A 60 wt % solution of ammonium nitrate (0.9 M) was used as exchange feed for all runs. The effluent from the exchange column was fed

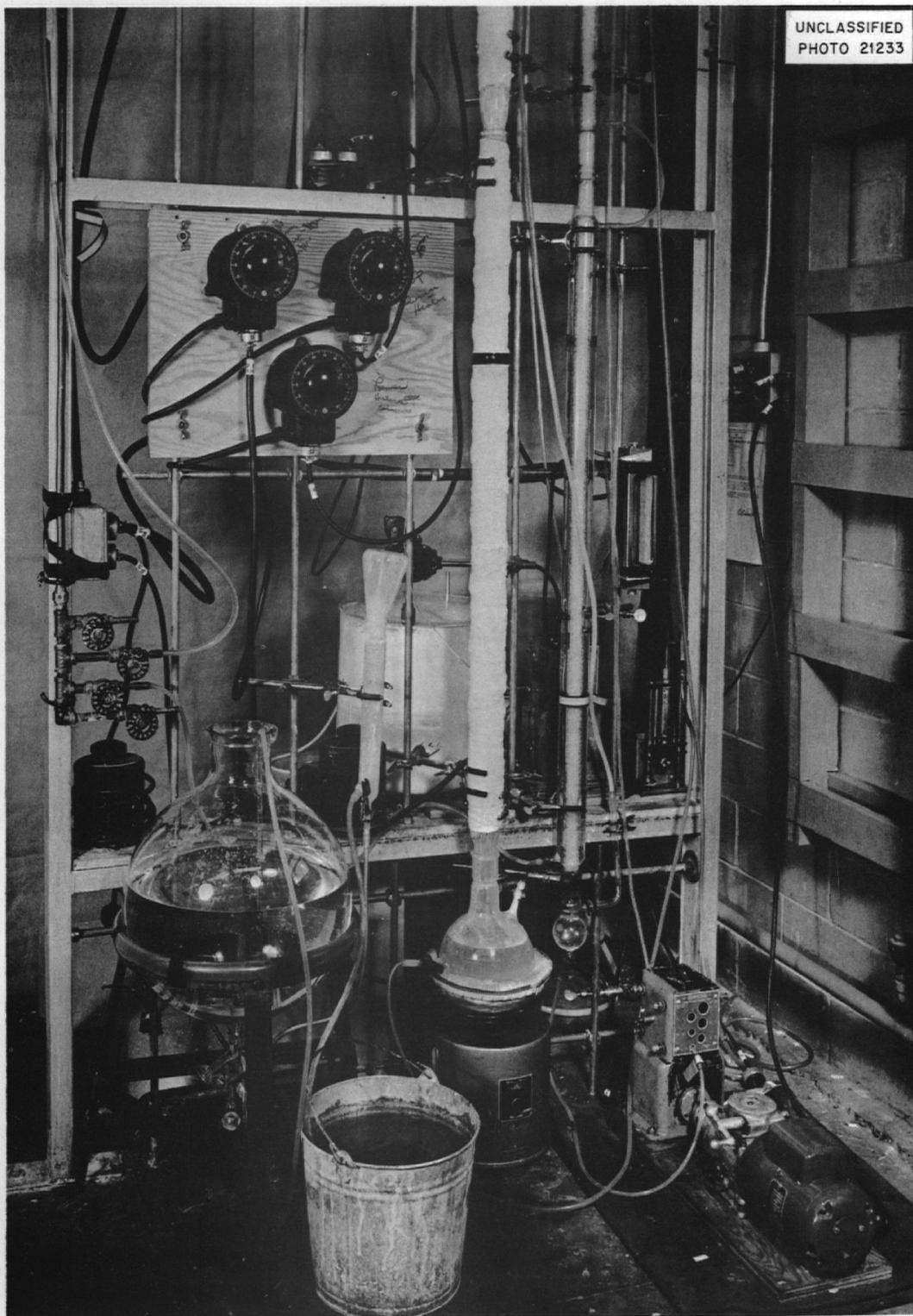


Fig. 4. Laboratory Equipment for $\text{NH}_3(\text{gas})$ vs $\text{NH}_4^+(\text{soln})$ Exchange.

CHEMICAL SEPARATION OF ISOTOPES PROGRESS REPORT

TABLE 6. AMMONIUM NITRATE-AMMONIA EXCHANGE RUNS AT 16°C AND 740 mm Hg

RUN NUMBER	EXCHANGE FEED (cc/hr)	MOLARITY OF Ca(OH) ₂ IN STRIPPER	SLURRY FEED (liters/hr)	LENGTH OF RUN (hr)	TOTAL NH ₄ ⁺ IN STRIPPER EFFLUENT (moles/liter)	STRIPPER BOILER TEMPERATURE (°C)
1	600	2	3	3½	0.004	99
2	550	2	3	4		99
3	450	1.7	4	7½	<0.001	99

into the preheater at the top of the stripper concurrent with the calcium hydroxide slurry. Table 6 is a summary of the three runs.

Run No. 1 was made to calibrate flow rates and to determine the time required for the system to reach chemical equilibrium. Approximately 3 hr was required. Run No. 2 was a repetition of the first run; after 4 hr a leak developed in one of the feed lines, and the run had to be terminated. It was found that a less concentrated slurry could be pumped more easily; consequently, calcium hydroxide concentration and flow rates were changed on run No. 3. Run No. 3 proceeded very smoothly for approximately 7½ hr. Samples were taken from the bottom of both columns after 4.5, 6.0, and 7.5 hr. The stripper column samples were analyzed for total ammonia and found to contain less than 0.001 mole/liter. The ammonium nitrate solution samples from the bottom of the exchange column were converted to nitrogen gas by means of the method described by Rittenberg¹¹ (oxidation with sodium hypobromite) and submitted to the Y-12 Mass Assay Laboratory.

The analyses of the effluent from the stripper show that the lime reflux was working quite well; the results of the isotopic analyses are shown in Table 7.

The values from Table 7 are plotted in Fig. 5. At the end of 7.5 hr a total separation of 1.19 had been obtained, and equilibrium had not yet been reached. A rough extrapolation to equilibrium yields a total separation of 1.26. If the effective separation factor is assumed to be 1.012, a stage length of less than 12 in. may be calculated. Better stage lengths could undoubtedly be obtained by optimizing flow conditions. The ratio of

¹¹D. Rittenberg, *Preparation on Measurement of Isotopic Tracers*, Edwards Bros., Ann Arbor, Michigan, 1948, pp 34-39.

TABLE 7. ISOTOPIC ANALYSES - RUN NO. 3

TIME (hr)	ATOM RATIO N ¹⁵ /N ¹⁴
0	0.00364
	0.00356
	0.00351
4.5	0.00412
	0.00406
6.0	0.00423
	0.00417
7.5	0.00427
	0.00426

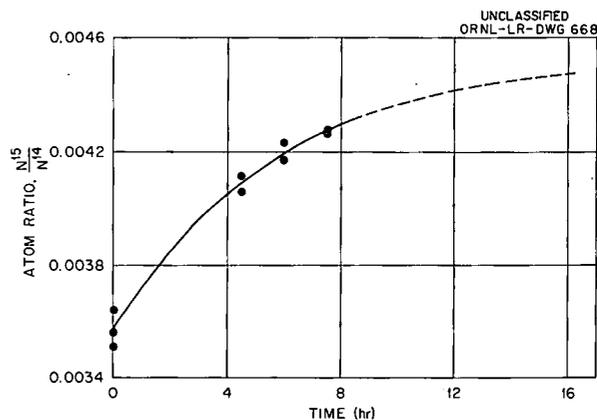


Fig. 5. Enrichment of N¹⁵ - Run No. 3.

dissolved ammonia in the aqueous phase to total ammonia plus ammonium ion in that phase was found by analysis to be 0.78. Since operation was at atmospheric pressure and 16°C, this ratio was high and resulted in an effective separation factor of 1.011 (calculated).

AMMONIA-AMMONIUM CARBONATE SYSTEM

It has been suggested¹² that ammonium carbonate might be used in place of ammonium nitrate in the ammonia-ammonium ion exchange system. Use of ammonium carbonate would enable a closed-cycle reflux which would greatly lower the cost of the process. The system as proposed is illustrated in Fig. 6. Ammonium carbonate would flow down the column in equilibrium with ammonia gas flowing up the column. At the bottom of the column, lime would be added in a heated stripper and ammonia would be driven back up the column. Calcium carbonate would be formed, would be filtered out, and would be calcined to produce calcium oxide and carbon dioxide. Calcium oxide and water would be recycled as calcium hydroxide slurry and the carbon dioxide reacted at the top of the column with ammonia and water for the other reflux.

The ammonia-ammonium carbonate system is not quite so simple as it might appear. Ammonium carbonate solution is a complex mixture of ammonium bicarbonate, ammonium carbonate, and ammonium carbamate. If an appreciable amount of the nitrogen in the solution is tied up in the ammonium carbamate and if exchange between ammonia and the carbamate is slow, N¹⁴ will be carried from the top to the bottom of the exchange column and the isotopic gradient will be destroyed.

In order to study this system several runs were made on the apparatus described. In all three runs the feed was a saturated solution of commercial ammonium carbonate (an equimolar mixture of ammonium bicarbonate and ammonium carbamate).

Sodium hydroxide was used as the refluxing agent in the first two runs and calcium hydroxide was used in the third. The operating conditions are shown in Table 8.

In early stages of operation it was found necessary to feed ammonia-saturated carbonate effluent from the exchange column into the stripping column at a point below the top of the stripper. On heating above 58°C ammonium carbonates decompose into ammonia, water, and carbon dioxide. Since the stripping column was operated at a temperature

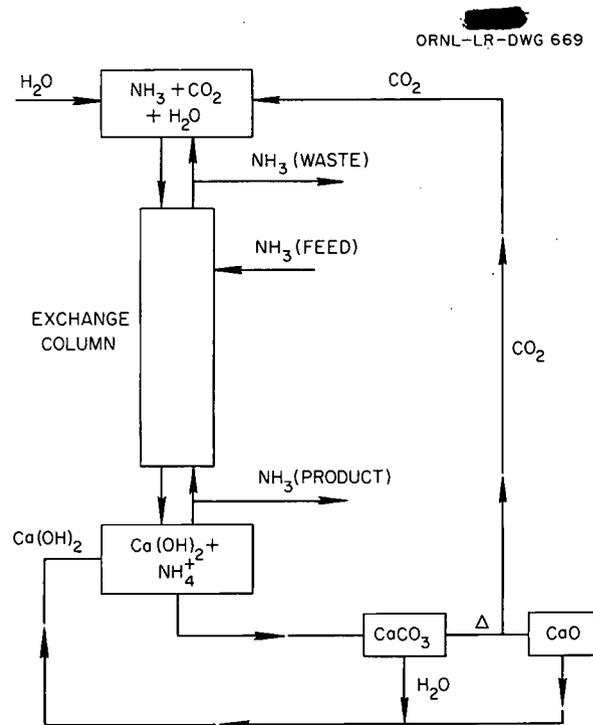


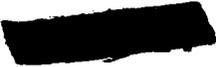
Fig. 6. Proposed Ammonia-Carbonate Closed-Cycle System.

¹²H. C. Urey, Report of the Committee on Isotope Separation, WASH-100 (Dec. 12, 1951), p 19.

TABLE 8. AMMONIA-AMMONIUM CARBONATE EXCHANGE RUNS AT 16°C AND 740 mm Hg

RUN NUMBER	EXCHANGE FEED OF 5.3 N (NH ₄) ₂ CO ₃ (ml/hr)	NaOH STRIPPER FEED		LENGTH OF RUN (hr)	TOTAL NH ₄ ⁺ IN STRIPPER EFFLUENT (moles/liter)	STRIPPER BOILER TEMPERATURE (°C)
		(liters/hr)	(M)			
1	600	4	2	3	0.001	99
2	600	4	2	3½	0.001	99
3	600	3	2*	3	0.0019	99

*Ca(OH)₂.



considerably higher than 58°C, a section of column above the carbonate feed point was kept saturated with hydroxide solution in order to ensure complete removal of carbon dioxide. Otherwise, the carbon dioxide, ammonia, and water vapor passing up the column would have recombined in the cold portion of the condenser into ammonium carbonate and soon would have plugged the apparatus.

The apparatus performed very smoothly throughout this series of runs. The first run was made to test the sodium hydroxide reflux and to determine the amount of sodium hydroxide needed for complete stripping of the ammonia from the exchange effluent. The run was terminated after 2½ hr. The second run was intended to furnish a sample for isotopic analysis, but after 3½ hr of operation a precipitate began to form at the bottom of the exchange column. During the next 20 min the lower 6 ft of the column became plugged and run No. 2 had to be terminated. Run No. 3 also had to be terminated after 3 hr because of precipitate formation.

The analyses of the effluents from the stripping column showed very low total nitrogen content, which indicated very good stripping action in the reflux section. The exchange-column effluent was found to contain 11.3 moles/liter total nitrogen and

2.5 moles/liter carbonate plus bicarbonate. This composition indicated a solution deficient in carbonate and highly saturated in ammonia. Analysis of the precipitate from the exchange column gave 15.0 mmoles/g total nitrogen and 7.5 mmoles/g total carbonate, which indicated either the normal ammonium carbonate or ammonium carbamate.

SUMMARY OF NITROGEN WORK

It has been demonstrated that calcium hydroxide slurry may be substituted for sodium hydroxide solution as a refluxing agent for the ammonia-ammonium ion system for nitrogen isotope separation. Ammonium ion was satisfactorily converted to ammonia in a stripping column in a run where isotopic fractionation was also demonstrated. A considerably cheaper process for N¹⁵ production should result.

Investigation of the substitution of ammonium carbonate for ammonium nitrate has given a precipitate under the operating conditions used (16°C with a feed of commercial ammonium carbonate). Whether or not this is due to a nonequilibrium condition has not been established. Further studies are in progress.