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CHEMICAL SEPARATION OF ISOTOPES SECTION

SEMIANNUAL PROGRESS REPORT

FOR PERIOD ENDING DECEMBER 31, 1954

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G. H. Clewett, Director

CHEMICAL SEPARATION OF ISOTOPES SECTION

SEMIANNUAL PROGRESS REPORT

For Period Ending December 31, 1954

J. S. Drury, Supervisor

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CHEMICAL SEPARATION OF ISOTOPES SECTION SEMIANNUAL PROGRESS REPORT

SUMMARY

New systems involving the exchange of boron between boron trifluoride and boron trifluoride addition compounds have been explored. These systems have large separation factors and potentially simple reflux mechanisms. A precise determination of the separation factor for the anisole–boron trifluoride system gave the value

$$\alpha_{(95\%\ C.I.)} = 1.0291 \pm 0.0009 \ .$$

Boron exchange was found to occur between BF_3 and BCl_3.

Several homogeneous catalysts have been found which activate the hydrogen-water exchange, but none are adaptable to the production of deuterium because of the slow exchange rate. Platinum or platinum oxide may be usable as a heterogeneous catalyst with proper support or dispersion techniques. The high-pressure solubility of hydrogen in several amalgams was investigated in connection with a unique countercurrent exchange system.

A proposed system involving isotopic exchange between lithium dipivaloylmethane in diethyl ether and lithium hydroxide in aqueous solution was shown to give little or no isotopic separation.

Column studies of the carbonate system exchange reaction were concluded with a 40°C run. Slightly higher enrichment of N^{15} was obtained than at 30°C. The temperature dependence of α_{eff} in this system was measured between 15 and 45°C. The factor increases with temperature, showing a tendency toward a maximum near 45°C. Isotopic exchange was found to occur between ammonia gas and aqueous carbamate ion. The exchange appears to be complete in less than 3 min. A qualitative examination was made of the carbonate system waste reflux reaction in laboratory equipment. No insurmountable difficulties are anticipated in connection with this reaction. The critical product-reflux reaction is being studied in pilot-scale equipment. Preliminary data are encouraging. Additional nitrogen exchange reactions have been studied to provide a broader basis for selecting a system for large-scale production of enriched nitrogen isotopes.

A proposed system for enriching potassium isotopes was found to have a single-stage separation factor of

$$\alpha_{(95\%\ C.I.)} = 1.006 \pm 0.002 \ .$$

The single-stage fractionation factor between uranyl ion on Dowex 50 resin and an aqueous solution of uranyl ion in the presence of Versene was found to be approximately 1.00006. Very little enrichment resulted from passing a band of uranyl ion down an ion exchange column.

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SEPARATION OF BORON ISOTOPES

R. M. Healy A. A. Palko

Because of the nature of the physical and chemical properties of boron, it is believed that an isotope separation system for boron might be developed that would be better than the system now being used.[1] One promising reaction,[2] the exchange between BF_3 and anisole·BF_3, has been examined in a preliminary fashion. Cursory studies of other reactions have now been made. When these screening studies are complete, the most encouraging system will be selected for study in greater detail.

BUTYL SULFIDE–BORON TRIFLUORIDE SYSTEM

In all chemical exchange processes for enriching isotopes, it is very important to have a simple, efficient method of refluxing the product stream. This requirement may be satisfied in systems where boron trifluoride addition compounds are used if the addition compound can be dissociated quantitatively by heat. Since this property had been claimed for the butyl sulfide–boron trifluoride complex,[3] it was of interest to measure α for the reaction

$$(C_4H_9)_2S{\cdot}B^{11}F_3(l) + B^{10}F_3(g) \rightleftharpoons (C_4H_9)_2S{\cdot}B^{10}F_3(l) + B^{11}F_3(g)$$

A five-stage batch determination of the separation factor was made in the apparatus previously used to study the BF_3–anisole·BF_3 system.[2] The procedure followed was to react a weighed amount of butyl sulfide with sufficient BF_3 to produce the complex plus an equimolar amount of BF_3. The amounts of material were calculated so that the pressure within the reaction bulb was 1 atm. The two phases were equilibrated at room temperature by rotating the reaction bulb, usually overnight. Separation of phases was accomplished by freezing the complex in a dry ice–acetone bath and condensing the BF_3 with liquid nitrogen in another part of the vacuum system. Samples from both phases were obtained for isotopic analysis. Boron trifluoride from the gas phase, enriched in B^{11}, was used as starting material for the next pass. This process was continued until five equilibrations were made. Isotopic analyses of the samples are shown in Table 1. When these data are plotted as shown in Fig. 1, the slope of the lines is related to α. Treatment of these data by the method of least squares[4] yields the value

$$\alpha_{(95\%\ C.I.)} = 1.033 \pm 0.005 .$$

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

[2] R. M. Healy, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1954*, ORNL-1815, p 3.

[3] W. N. Axe (to Phillips Petroleum Co.), U.S. Pat. 2,378,968 (June 26, 1945).

[4] G. M. Begun, J. S. Drury, and A. A. Palko, *Lithium Isotope Separation Factors of Some Two-Phase Equilibrium Systems*, ORNL CF-53-8-221 (Aug. 14, 1953).

TABLE 1. ISOTOPIC ANALYSES FROM FIVE-STAGE BATCH EXPERIMENT (BF_3–BUTYL SULFIDE·BF_3 SYSTEM)

Pass Number	Atom Ratio B^{11}/B^{10}	
	Gas Phase	Liquid Phase
0*	4.011	
1	4.116	4.059
2	4.186	4.101
3	4.221	(Sample lost)
4	4.294	4.208
5	4.389	4.317

*Normal BF_3.

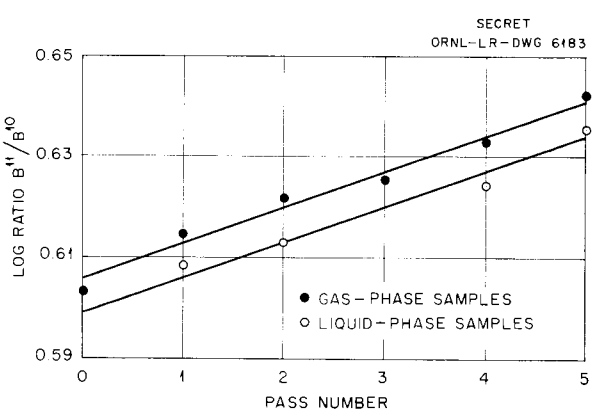

Fig. 1. Isotopic Analyses from Five-Stage Batch Experiment (BF_3–Butyl Sulfide·BF_3 System).

Further study of this system will be deferred until screening tests have been completed on other boron systems.

PHENOL–BORON TRIFLUORIDE SYSTEM

Phenol reacts with boron trifluoride to form an addition compound which is commercially available and inexpensive. It is reported that BF_3 can be regenerated quantitatively from this complex by heat alone.[5] Because of these attractive properties, an experiment was performed to estimate α for the reaction

$$C_6H_5OH{\cdot}B^{11}F_3(l) + B^{10}F_3(g) \rightleftharpoons C_6H_5OH{\cdot}B^{10}F_3(l) + B^{11}F_3(g)$$

A measurably large isotopic fractionation was expected, so a single-stage equilibration was made, rather than a multistage batch run. The experimental procedure was similar to that described for the butyl sulfide–boron trifluoride system. From the isotopic analyses of the resulting samples (Table 2), it was calculated that

$$\alpha_{(95\%\ C.I.)} = 1.027 \pm 0.014 \ .$$

Further consideration may be given to this system if screening-test results warrant it.

[5]Private communication, P. E. Chalet, August 12, 1954, Product Development, General Chemical Division, Allied Chemical and Dye Corp., New York.

[6]H. C. Urey, *J. Chem. Soc.* **1947**, p 570.

TABLE 2. ISOTOPIC ANALYSES OF SAMPLES FROM SINGLE-STAGE RUN (PHENOL–BF_3 SYSTEM)

Atom Ratio B^{11}/B^{10}	
Liquid Phase	Gas Phase
3.996	4.131
4.025	4.134
4.045	4.142
4.054	4.156

BORON TRIFLUORIDE–BORON TRICHLORIDE EXCHANGE

Based on spectral data, a theoretical α value of 1.09 has been calculated[6] for the exchange reaction

$$B^{10}F_3(g) + B^{11}Cl_3(g) \rightleftharpoons B^{11}F_3(g) + B^{10}Cl_3(g)$$

at room temperature. In order to determine if exchange of boron between these species actually occurs at room temperature, the following experiment was performed in the equipment shown in Fig. 2.

Technical grade BCl_3 was purified by shaking the condensed liquid overnight with sodium amalgam. It was then condensed and expanded in the same manner that was used to remove noncondensable gases from BF_3. Approximately 12.4 cm of normal BCl_3 was condensed, with the use of liquid nitrogen, in the 2-liter reaction flask, followed by the condensation of 0.5 cm of enriched BF_3 (95% B^{10}).

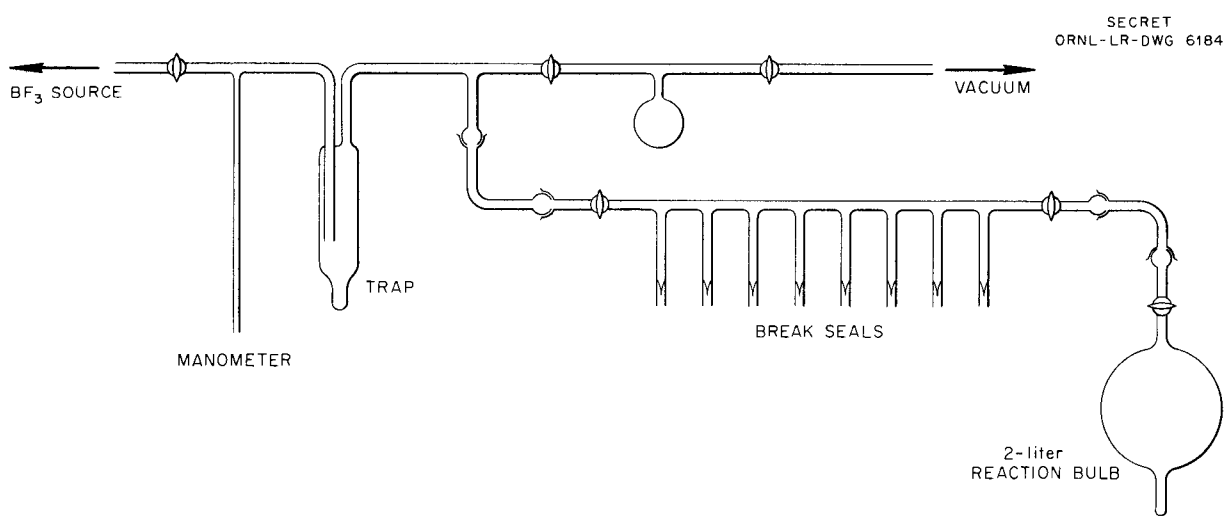

Fig. 2. Apparatus for Studying the Exchange of Boron Between BF_3 and BCl_3.

After the introduction of both gases, the flask was gently warmed. For timing purposes, the exchange reaction was considered to begin when one half the liquid BCl_3 had vaporized. At specified intervals the BF_3 in the system was sampled in the following way. The reaction was quenched in liquid nitrogen. After the gases had solidified, the liquid nitrogen was replaced with an ethanol slurry. When the pressure in the system rose to a few millimeters, the stopcocks on the break-seal manifold were closed, and one of the break-seals was removed. The remaining gas was recondensed in the reaction bulb, and the cycle was repeated for each subsequent sample.

The isotopic composition of the samples taken (Table 3) indicates that exchange was complete by the time the reaction was first quenched. If the exchange is first-order with respect to BF_3 and BCl_3, the half time for the reaction should be low enough to warrant its further consideration. A determination of α for the reaction will be made next.

TABLE 3. ISOTOPIC ANALYSES FROM BF_3-BCl_3 EXCHANGE EXPERIMENT

Elapsed Time (min)	B^{10} in $BF_3(g)$ (%)
0	89.6
60	23.5
120	23.3
240	24.7

ANISOLE–BORON TRIFLUORIDE SYSTEM

Preliminary measurements were given in a previous report[7] for the isotopic separation factor, α, for the reaction

$$B^{10}F_3 + C_6H_5OCH_3 \cdot B^{11}F_3 \rightleftharpoons B^{11}F_3 + C_6H_5OCH_3 \cdot B^{10}F_3$$

Further measurements have been made to obtain a precise determination of this factor.

The procedure used in measuring α was as follows: A known amount of purified and distilled anisole (80 to 100 g) was placed into a jacketed reaction flask (see Fig. 3) containing a glass-encased stirring magnet. The flask was attached to the vacuum line, the anisole was frozen, and the apparatus was evacuated by means of the vacuum pump; the reaction flask was then isolated from the rest of the system. Boron trifluoride was admitted to the system from the BF_3 tank. The temperature and pressure of the gas were measured, and, from a knowledge of the total volume of the system, the exact number of moles of BF_3 present were calculated. Enough BF_3 was admitted to the system so that approximately 150 cc (STP) of gas was present in excess of the amount required to prepare the 1:1 $C_6H_5OCH_3 \cdot BF_3$ complex. The BF_3 was now purified by freezing it with liquid nitrogen and evacuating the system to remove air or any noncondensibles. Stopcock A was closed, and the gas was allowed to vaporize. Eight initial samples of gas were taken by sealing off the break-seal tubes.

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

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

Two runs were made under the conditions indicated in Table 4. The isotopic analyses of the 12 pairs of samples resulting from each run are given in Table 5. From these data, the maximum likelihood estimate of the separation factor is

$$\alpha_{(95\%\ C.I.)} = 1.0291 \pm 0.0009 \ .$$

[7] R. M. Healy, *Chemical Separation of Isotopes Section Semiann. Prog. Rep. June 30, 1954*, ORNL-1815, p 3.

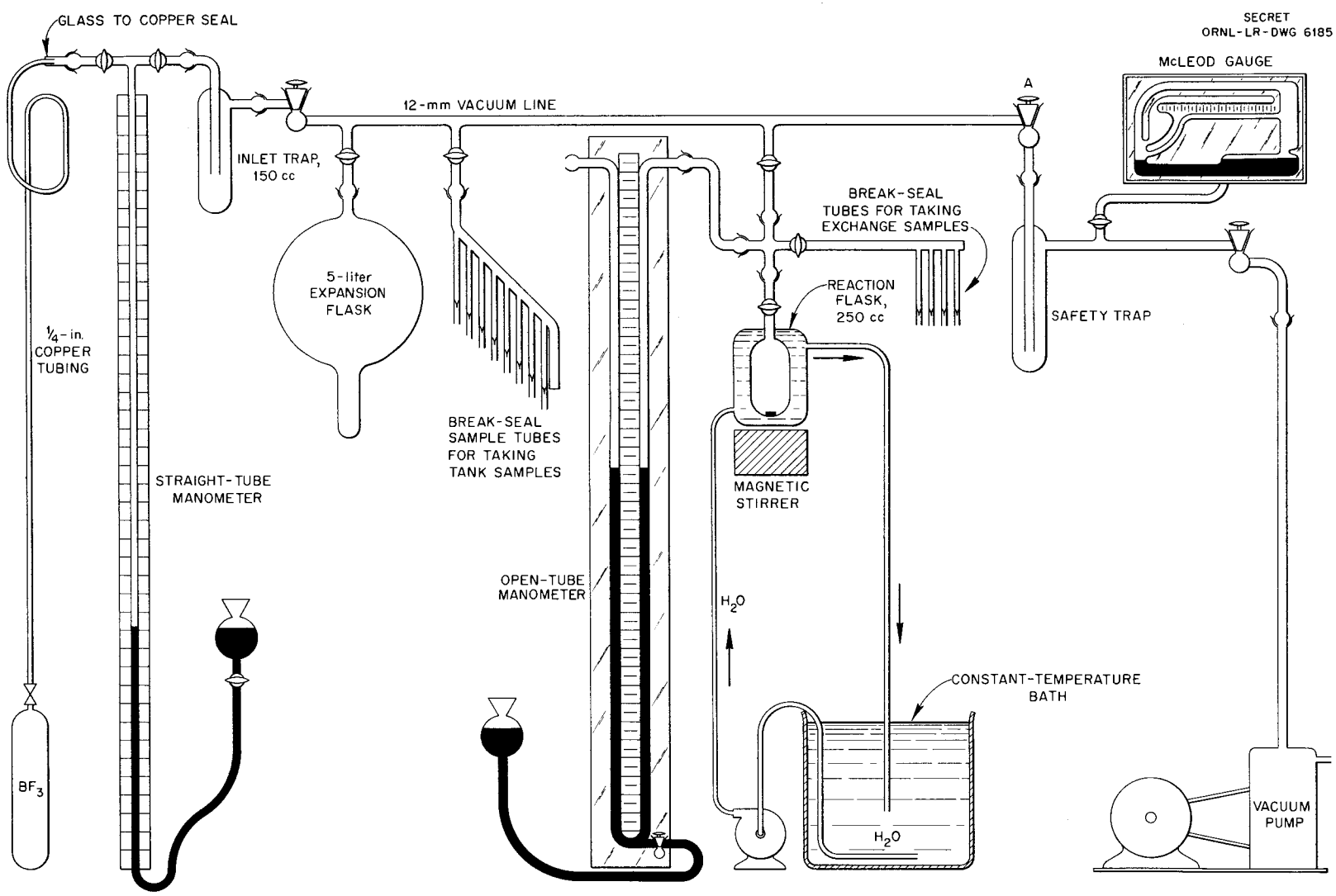

Fig. 3. Apparatus for Studying the System $BF_3(g)$–Anisole·BF_3 Complex(l).

TABLE 4. EXPERIMENTAL CONDITIONS FOR α DETERMINATIONS (ANISOLE-BF_3 SYSTEM)

	Run No. 1	Run No. 2
Anisole, moles	0.9720	0.8310
Total BF_3, moles	0.9790	0.8385
$\frac{BF_3\ (complex)}{BF_3\ (gas)}$, mole ratio	138.9	110.8
Equilibration temperature, °C	19.7	19.7
Total agitation time, hr		
First set of four samples	3	2
Second set of four samples	5	4
Third set of four samples	7	7

TABLE 5. ISOTOPIC ANALYSES OF SAMPLES FROM ANISOLE–BORON TRIFLUORIDE SYSTEM

Atom Ratio B^{10}/B^{11} in Arbitrary Units	
$BF_3(g)$ Before Equilibration	$BF_3(g)$ After Equilibration
Run No. 1	
6690	6528
6680	6485
6680	6482
6673	6477
6668	6480
6664	6463
6688	6484
6688	6503
6693	6504
6666	6497
6719	6477
	6490

$\alpha_{(95\%\ C.I.)} = 1.0297 \pm 0.0016^*$

TABLE 5 (continued)

Atom Ratio B^{10}/B^{11} in Arbitrary Units	
$BF_3(g)$ Before Equilibration	$BF_3(g)$ After Equilibration
Run No. 2	
6731	6538
6724	6537
6719	6530
6720	6533
6724	6542
6724	6536
6721	6531
6721	6551
6733	6545
6731	6543
6725	6540
6723	6539

$\alpha_{(95\%\ C.I.)} = 1.0284 \pm 0.0006^*$

$$^*\alpha = \frac{(B^{10}F_3/B^{11}F_3)_{gas}\ \text{before equilibration}}{(B^{10}F_3/B^{11}F_3)_{gas}\ \text{after equilibration}}.$$

DEUTERIUM ENRICHMENT

D. A. Lee L. Landau

CATALYSIS OF THE HYDROGEN-WATER EXCHANGE REACTION

The investigation of numerous compounds as possible catalysts for the molecular hydrogen–liquid water exchange reaction has been continued. As stated previously,[1] the cost of deuterium may be substantially reduced by using this reaction catalyzed by a catalyst transported in the water phase.

The equipment and procedure used in these studies were described in an earlier report.[1] The number of contactors was increased to three to permit a greater number of investigations. The use of deuterium in the water phase and of hydrogen in the gaseous phase has been reversed to facilitate mass assay. Since the aim of this work is to find a catalyst that will promote the exchange in a few seconds, rather than to make a kinetic study of any one catalyst, only a minimum number of isotopic samples were taken during each run. Most of the compounds tested were homogeneous with the liquid phase.

Metal ions with multiple valence states whose oxidation-reduction potentials are near the potential of hydrogen may act, either in an acid or basic solution, as a catalyst for the hydrogen-water exchange. A vanadium complex made from sodium catechol disulfonate, V_2O_5, and D_2O was reduced with sodium amalgam. The solution was equilibrated with hydrogen for 375 min, and no catalytic activity was noted.

A "molybdenum blue" solution was prepared[2] and tested. After introducing the solution into the contactor, the molybdenum precipitated. The slurry of precipitate was equilibrated with hydrogen for 400 min and the final HD/H_2 analysis was 0.00106, as compared with 0.00026 for the starting material. This represented very little exchange. Another "molybdenum blue" solution which did not precipitate gave no measureable exchange in 380 min.

The compound $K_4Co(CN)_6$ appeared to have a catalytic effect on the exchange. The assay (HD/H_2) rose from 0.00073 to 0.01235 in 360 min. Another experiment was made in which a more concentrated solution was used. The assays again showed what appeared to be a rapid exchange rate; however, the exchange soon stopped. The assumed exchange was actually the reaction of $K_4Co(CN)_6$ with D_2O to form $K_3Co(CN)_6$ and D_2. The oxidation-reduction potential for

$$Co(CN)_6^{4-} = Co(CN)_6^{---} + e^-$$

is 0.83, the potential for

$$H_2 + 2OH^- = 2H_2O + 2e^-$$

is 0.828, and the potential for

$$CN^- + Ni(CN)_3^{--} = Ni(CN)_4^{--} + e^-$$

is 0.82. Since the hydrogen potential is between the nickel and cobalt potentials, there appeared to be a possibility that a mixture of nickel and cobalt cyanides would act as a catalyst. The initial percentage of hydrogen in the deuterium was 0.6; after 360 min it was 2.0, which indicated slow exchange.

Other cyanides which were tested for catalysis were those of vanadium, cobalt(III), copper(II), silver and copper(II), silver, and copper(I). The only compound that showed any measurable activity was cuprous cyanide; there was 3.4% hydrogen in the deuterium after 360 min.

Another oxidation-reduction reaction that was considered as a possibility in the catalysis of the hydrogen-water exchange reaction was

$$H_3AsO_4 + 2HI \rightleftharpoons I_2 + H_2O + H_3AsO_3$$

The degree of acidity determines the direction toward which the reaction proceeds. Two experiments were made: one in which no iodine was produced and one in which iodine was produced. In neither case was a catalytic effect noted.

Chromates, vanadates, molybdates, tungstates, and certain reduced products of these compounds are known to be heterogeneous hydrogenation catalysts.[3] Therefore, several solutions of these compounds were examined for catalytic activity.

Experiments were made in which tungstates in various combinations were used. Cupric tartrate in

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

[2] I. Koppel, *Abegg's Handbuch der anorganishen Chemie*, Vol. 4, 1st section, 2nd half, p 621–630, Leipzig, 1921.

[3] S. Berkman *et al.*, *Inorganic and Organic Catalysis*, pp 274, 277–280, Reinhold, New York, 1940.

excess sodium tungstate solution produced no catalytic activity. The same was true of a mixture of cupric and manganous tartrates in sodium tungstate solution. Cupric tungstate was found to be soluble in concentrated KOH solutions; it did not act as a catalyst for the exchange.

Similar experiments were made in which vanadates were used. Cobalt tartrate, as well as a mixture of cupric and manganous tartrates, and ferrous tartrate in sodium metavanadate solutions were noncatalytic. Neither cupric metavanadate in KOH nor a platinum vanadate saturated with KOH were catalysts for the reaction. Palladium metavanadate saturated with KOH solution caused the percentage of hydrogen in the deuterium to rise from 0.58 to 3.07 in 260 min. However, catalysis was probably due to a black precipitate of palladium oxide which developed almost immediately. Palladium oxide is known[1] to be a catalyst for the hydrogen-water exchange.

Cupric molybdate in water solution was not catalytic; however, cupric molybdate in a saturated KOH solution produced a slight exchange. In 335 min the deuterium contained 1.84% hydrogen.

Since it has been demonstrated[4] that hydrogen and water are equilibrated, with no shaking, at room temperature over platinum oxide in 3 hr, experiments for measuring the exchange were made in the apparatus here at a stirring rate of 1200 rpm. Twenty five milligrams of PtO_2 in 25 ml of water at 73°C catalyzed the exchange. After 1 min of equilibration the analysis (D_2/HD) was 0.989; after 7 min this ratio was 0.465. The physical appearance of the platinum oxide changed during the experiment. The volume of the catalyst decreased, and the color changed from dark brown to black. The black form of the catalyst was used again in another experiment, and the results were similar. After 1 min of equilibration the ratio D_2/HD was 1.10, and after 345 minutes it was 0.133. An estimate of the half time of this exchange reaction is 8 min.

Materials which were found to have no catalytic activity were cobalt thiocyanate, a slurry of Dowex 1 resin, silver sulfide in sodium cyanide solution, sodium sulfide, silver and zinc sulfides in sodium cyanide solution, sodium polysulfide, selenium dissolved in sodium sulfide solution, concentrated sulfuric acid, cupric formate, cobaltous formate, and nickelous formate.

In summary, several homogeneous catalysts have been found which activate the hydrogen-water exchange, but none are adaptable for the production of deuterium because of the slow exchange rate. Platinum or platinum oxide may be usable as a heterogeneous catalyst with proper support or dispersion techniques.

SOLUBILITY OF HYDROGEN IN SOME AMALGAMS

Lithium amalgam under high pressure with hydrogen has been observed to froth when the pressure was removed.[5] Although it was realized that the frothing might have been the result of other factors, this observation motivated a series of measurements of the solubility of hydrogen at high pressure in several amalgams. If hydrogen were sufficiently soluble, an exchange system for enriching deuterium might be possible in which one reflux would be accomplished by dissolving hydrogen in an amalgam under pressure, and the other reflux would be effected by release of the pressure.

The hydrogen waste stream could be re-used for feed after equilibration with high-pressure steam, since deuterium readily exchanges between hydrogen and water vapor without benefit of catalyst[6] at temperatures above 500°C. Furthermore, since little isotopic fractionation would occur at these elevated temperatures, the replenished hydrogen would contain almost as much deuterium as normal hydrogen. A schematic representation of this system, assuming deuterium enrichment in the amalgam phase, is shown in Fig. 4.

Since liquids are easier to handle than solids, only fluid amalgams were considered for testing. These were further screened on the basis of hydrogen solubility or hydride formation. The following amalgams were chosen: lithium, magnesium, and lead. In each case, the amalgam was placed in a bomb at room temperature, and hydrogen was forced in at about 2000 psi while the amalgam was being agitated. Some of the amalgam was then forced out of the bomb into an evacuated flask

[4] R. B. Fischer, R. A. Potter, and R. J. Voskuyl, *Analysis of Heavy Water by Equilibration*, CC-2994 (May 15, 1945).

[5] Personal communication, F. B. Waldrop, June 1954.

[6] H. S. Taylor, "Catalysis in the Exchange Reaction $H_2 + HDO \rightleftharpoons HD + H_2O$," *Laboratory Studies for Separation Processes* (Secret), NNES III-4D, Chap. 3, p 59, Technical Information Service, Oak Ridge, Tenn., 1951.

attached to a manometer. Evolution of hydrogen from the amalgam should result in a readily detectable increase in pressure in the flask. However, this did not occur with any of the amalgams mentioned. Thus, there was no reversible, high-pressure solubility of hydrogen in these cases and very probably no solubility at all. Attempts were made to dissolve lithium hydride and lithium aluminum hydride in mercury at room temperature, but they were unsuccessful.

Because of the lack of favorable results, further experiments were discontinued.

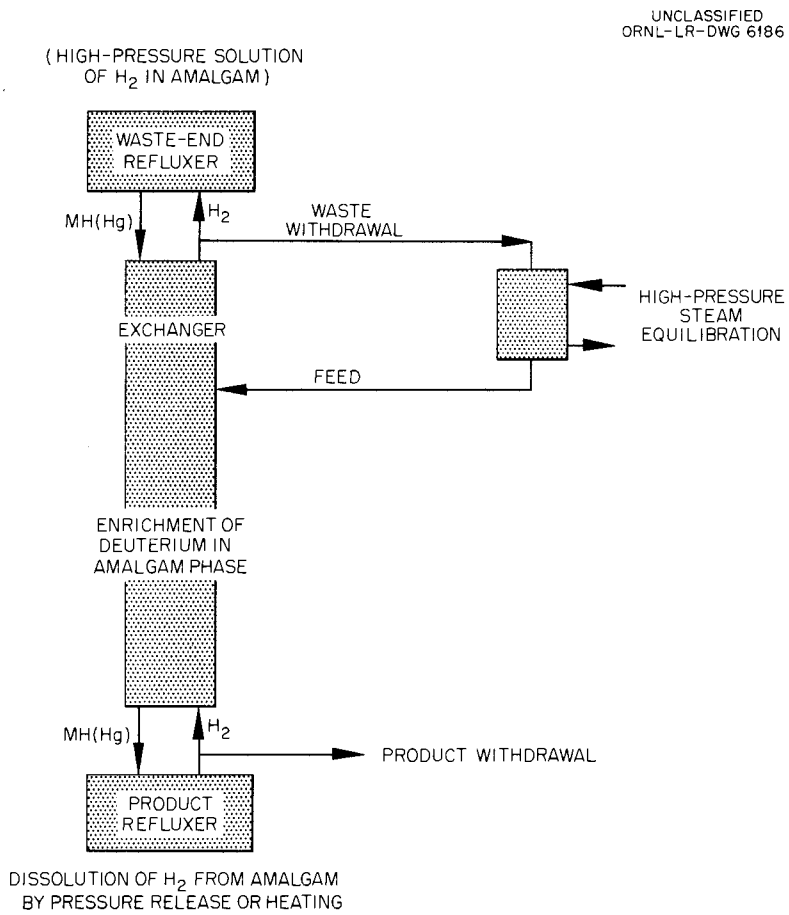

Fig. 4. Generalized Exchange System for Metal Hydride Amalgam and Hydrogen.

DETERMINATION OF THE ISOTOPIC SEPARATION FACTOR IN THE LITHIUM HYDROXIDE–LITHIUM DIPIVALOYLMETHANE SYSTEM

G. M. Begun

It has been reported[1] that dipivaloylmethane is a chelating agent which binds lithium ions selectively and that the lithium chelate can be quantitatively extracted from aqueous alkaline solution into diethyl ether. This suggested the possibility of a two-phase system for lithium isotope separation that would employ aqueous lithium hydroxide vs lithium dipivaloylmethane dissolved in diethyl ether.

The following experiment was performed to determine the amount of isotopic separation in the system. Dipivaloylmethane,[2] 0.86 g, was dissolved in 50 ml of diethyl ether and was contacted with 23.3 ml of 0.4 *N* lithium hydroxide solution. The two-phase system was vigorously agitated for 4 hr at room temperature. The phases were then separated, and lithium sulfate samples from each phase were prepared for mass assay. The analytical results are given in Table 6.

TABLE 6. ISOTOPIC ANALYSES OF THE LITHIUM DIPIVALOYLMETHANE SYSTEM

Atom Ratio Li^6/Li^7	
Diethyl Ether Phase	Aqueous Phase
0.0784	0.0782
0.0785	0.0775
0.0783	0.0781
0.0782	0.0778
0.0780	0.0775
0.0776	0.0783
0.0778	0.0778
0.0784	0.0781

These isotopic analyses yield the value

$$\alpha_{(95\%\ C.I.)} = 1.003 \pm 0.005 \ .$$

The results of the experiment may be interpretated in either of two ways. Either exchange is slow between the lithium dipivaloylmethane in the ether phase and the lithium ion in the aqueous phase, or the separation factor is close to 1.000. A tagged exchange experiment would differentiate between the two cases. In either case, the system would not be practicable as a means of enriching lithium isotopes.

[1] G. A. Guter and G. S. Hammond, *Abstracts of Papers – 126th Meeting, American Chemical Society*, American Chemical Society News Service, Washington, D. C., Sept. 1954, p 26B.

[2] Synthesized by G. A. Ropp of the Organic Chemistry Group.

CONCENTRATION OF N^{15}

L. L. Brown
E. F. Joseph
A. A. Palko
L. B. Yeatts

COLUMN STUDIES OF THE CARBONATE SYSTEM

A comprehensive summary of the closed-cycle ammonium carbonate system (Fig. 5) may be found in earlier reports.[1,2] An additional column exchange experiment (run 9) has been made with the use of the apparatus and methods described previously in order to observe the effect of temperature on the effective separation factor. The operating temperature was increased to 40°C while flow rates and concentrations of the opposing streams remained essentially the same as those used previously. Operating conditions for run No. 9 are shown in Table 7. Figure 6 shows the total separation achieved as a function of time. Extrapolation of this curve to equilibrium gives a total separation of 1.45. Run 8 made previously[2] at 30°C gave a total separation of 1.41. These results indicate that there is little advantage in going to the higher temperature.

To substantiate this conclusion and to provide additional data for optimizing the operating temperature of this system, a study of the temperature dependence of the effective separation factor was made. These studies are reported in the next section.

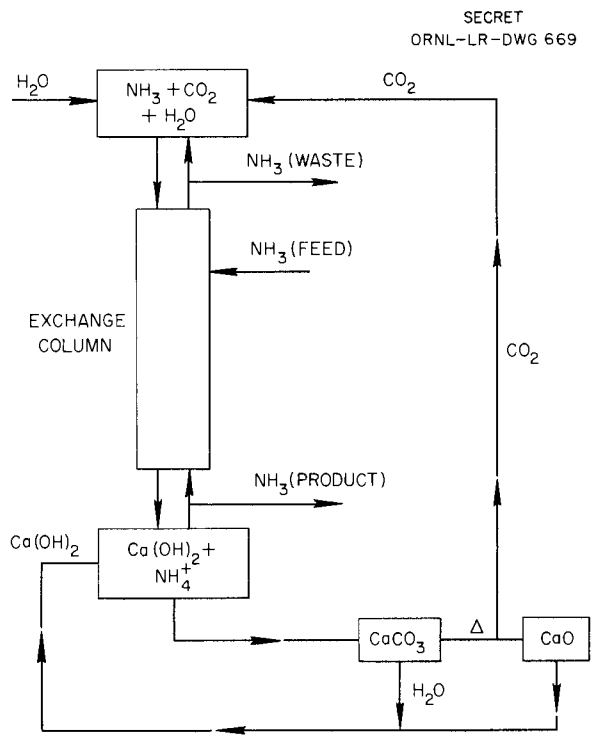

Fig. 5. Closed-Cycle Ammonium Carbonate System.

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

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

TABLE 7. OPERATING DATA FOR RUN 9

$NH_3(g)-(NH_4)_2CO_3(aq)$

Temperature, °C	40
Atmospheric pressure, mm Hg	742
Length of run, hr	14
Carbonate feed flow rate, cc/hr	300
Carbonate feed concentration, total moles/liter	18.65*
	7.3**
NaOH reflux feed rate, cc/hr	3000
NaOH reflux concentration, moles/liter	2
Loss of NH_3 in reflux column, %	0.0066 (interstage flow)

*Total nitrogen as NH_3.

**Total carbon dioxide as CO_3^{--}.

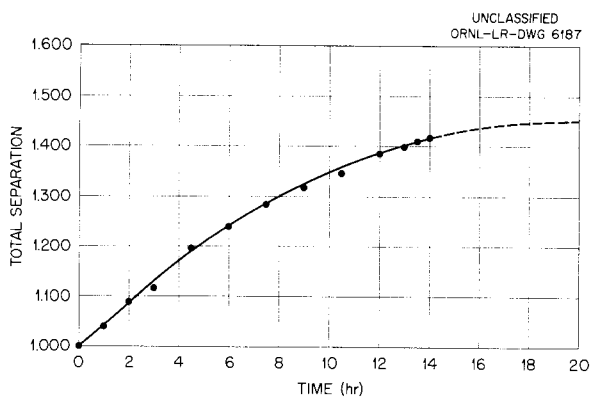

Fig. 6. Total Separation at 40°C as a Function of Time [NH_3-$(NH_4)_2CO_3$ System].

TEMPERATURE DEPENDENCE OF THE SEPARATION FACTOR IN THE CARBONATE SYSTEM

In a simple isotope reaction, the separation factor decreases with increasing temperature. However, in the carbonate system, several temperature-dependent equilibria contribute to the separation factor, and it is not possible to predict accurately the best operating temperature for the exchange reaction. To determine the optimum operating temperature, a series of single-stage batch experiments were performed in which the separation factor was measured as a function of temperature.

These runs were made in a 1-liter round-bottom reaction flask fitted with a stirrer and with outlets for sampling the liquid and gaseous phases. The reaction flask was submerged almost entirely beneath the surface of a constant-temperature bath. Care was taken to protect the sample outlets from the bath water.

The liquid phase used in these experiments was prepared by saturating water with both ammonium carbonate and ammonia. This saturated solution was held at constant temperature for a minimum of five days before use to ensure chemical equilibrium between all possible molecular species. The gas phase used in these runs was anhydrous tank ammonia. Both gas and liquid phases were of normal N^{15} content.

When a run was made, ammonia was blown through the flask for several minutes to replace all the air. About 60 ml of ammonium carbonate solution was added, and the stirrer was inserted to seal the system. Stirring was started and continued for 2 to 2½ hr. After this time the flask was removed from the bath and the phases were separated quickly. The portion of the liquid phase reserved for isotopic analysis was neutralized with HCl. The remainder of the liquid sample was kept for chemical analysis. The gas phase was collected by aspirating air through the flask and then passing the exhaust gas into 1 *N* HCl. Runs were made at four temperatures ranging from 15 to 44°C. Runs of higher temperature were not made because of the thermal instability of the carbonate solution. Samples intended for chemical analysis were analyzed immediately to avoid changes in the composition of the solution on standing. Results of these analyses are given in Table 8.

Total NH_3, total CO_2, and $COONH_2^-$ concentrations were determined directly. The NH_4^+ concentration was calculated from the anionic concentration of the solution, assuming complete ionization. The dissolved NH_3 was calculated by deducting the NH_4^+ and $COONH_2^-$ concentrations from the total amount of NH_3 in the solution. Carbonate and bicarbonate ions represented only a small portion of the total CO_2 content of the solution; the ratio of their concentrations was calculated from the bicarbonate ionization constant.

The isotopic samples were stored as aqueous NH_4Cl solutions until all runs were completed. All samples were then converted to N_2 and were submitted in a group to facilitate analysis under comparable instrument conditions. Values of α resulting from these measurements are given in Table 9 and in Fig. 7. From this figure it may be seen that the effective separation factor increases with increasing temperature, reaching a maximum in the neighborhood of 45°C. However, the rate of change of α between room temperature and 45°C is so small that any temperature in this range would serve reasonably well. Thus, considerations other than the magnitude of the separation factor should determine the choice of operating temperature for the exchange reaction in this range.

EXCHANGE BETWEEN AMMONIA AND CARBAMATE ION

Chemical analysis of the liquid phase used in the carbonate system shows a high concentration

TABLE 8. CHEMICAL COMPOSITION OF LIQUID PHASES FROM SINGLE-STAGE BATCH RUNS (CARBONATE SYSTEM)

Temperature of runs, °C	15.6	25.8	35.9	44.3
Total NH_3, *M*	19.35	20.05	20.1	18.10
Total CO_2, *M*	3.94	6.20	7.50	8.03
$COONH_2^-$, *M*	3.71	5.82	6.68	6.81
NH_4^+, *M**	4.12	6.51	8.02	8.64
NH_3 dissolved, *M**	11.52	7.72	5.40	2.65
pH	10.8	10.9	10.5	
Barometric pressure, mm Hg	747	742	738	751

*Calculated values.

TABLE 9. SINGLE-STAGE BATCH DETERMINATIONS OF α* IN THE CARBONATE SYSTEM

	$\frac{(N^{15}/N^{14})_{liquid}}{(N^{15}/N^{14})_{gas}}$			
	At 15.6°C	At 25.8°C	At 35.9°C	At 44.3°C
	1.0124	1.0180	1.0213	1.0179
	1.0160	1.0184	1.0222	1.0238
	1.0158	1.0185	1.0227	1.0232
	1.0159	1.0185	1.0191	1.0223
		1.0212		
$\alpha_{(95\% \text{ C.I.})}$*	1.015 ± 0.003	1.019 ± 0.002	1.021 ± 0.003	1.022 ± 0.004

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

of ammonium carbamate. Approximately one third the total nitrogen present is in the form of carbamate ion. Mellor[3] indicates that the formation of carbamate from carbonate takes some days to reach equilibrium. This suggests the possibility that nitrogen contained in the carbamate ion might not exchange rapidly with other nitrogen species in the system. If the nitrogen contained in the carbamate ion did not exchange with other nitrogen species, or if it exchanged very slowly, serious limitations might be imposed upon the degree of isotopic enrichment obtainable in the carbonate system. This condition arises from the fact that in the product refluxer ammonia is formed from the carbamate ion as well as from all the other nitrogen species in solution. If the carbamate nitrogen did not exchange in the exchange column, it would not be enriched in N^{15} and would dilute the product with large quantities of N^{14}. The experiments to be described were performed to determine the rate of exchange of the carbamate-ion nitrogen with ammonia gas.

[3] J. W. Mellor, *Inorganic and Theoretical Chemistry*, Vol. II, p 792, Longmans, Green, London, 1922.

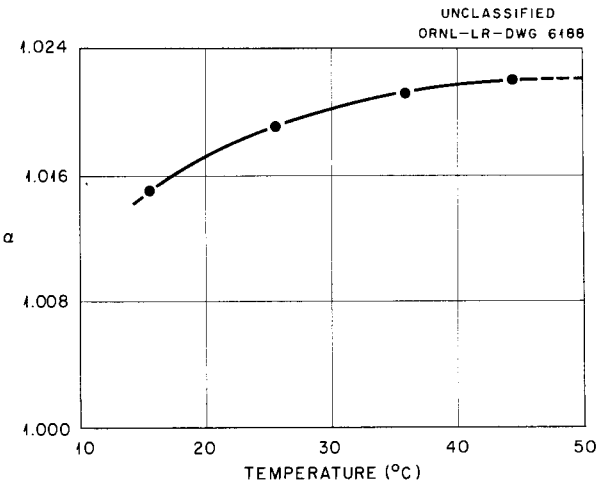

Fig. 7. Temperature Dependence of α for the Carbonate System.

The reaction vessel was a 1-liter round-bottom flask equipped with a capillary stopcock for gas sampling, a self-sealing rubber diaphragm for admitting the liquid phase from a hypodermic needle, and a 10-cm-long nipple which served as a cold trap during the introduction of the ammonia gas.

At the beginning of the experiment the liter flask was evacuated and weighed. Ammonia gas enriched in N^{15} was added, and the flask was reweighed to determine the amount of gas added. Aqueous ammonium carbonate solution, aged three weeks or longer to ensure chemical equilibrium, was injected through the rubber diaphragm by means of a hypodermic syringe. The weight of solution added was found by weighing the syringe before and after addition of the liquid. The flask was shaken vigorously by hand, and samples of the gas phase were taken in evacuated bulbs at specified intervals. The temperature of the system was 31°C.

Since impurities in the ammonia would lead to erroneous results, an attempt was made to prepare ammonia that was anhydrous and free from other gases. The following procedure was used: Solid ammonium nitrate containing 32% N^{15} was placed in a flask with an excess of freshly ignited, solid calcium oxide. The flask was evacuated, then the mixture of solids was gently warmed with a gas flame while being constantly stirred magnetically to avoid overheating. The ammonia which evolved was passed through a CaO drying tube several times, with alternate condensation and distillation from liquid-nitrogen traps. The product was finally condensed in the reaction flask and weighed.

Tables 10 and 11 give the conditions and the results of the two runs which were made. In the first run, isotopic equilibrium was obtained in less than 3 min. However, the N^{15} inventory for the system differed considerably from the calculated value. Since no experimental explanation for this discrepancy was apparent, a second run was made in which special attention was given to the purifying of the labeled ammonia used in the reaction. In addition to the other precautions, the flask was pumped down to constant weight,

TABLE 10. CHEMICAL DATA FOR CALCULATING ISOTOPIC EQUILIBRIUM VALUES IN AMMONIA-CARBAMATE ION EXCHANGE

	Run 1	Run 2
Gas phase NH_3, g	0.283	0.232
Liquid phase		
Solution, ml	4.54	4.21
Total NH_3, *M*	20.70	19.40
Total CO_2, *M*	6.30	6.15
$COONH_2^-$, *M*	5.82	5.79

TABLE 11. ISOTOPIC ANALYSES OF GAS PHASE FROM AMMONIA-CARBAMATE ION EXCHANGE

Sample Exchange Time (min)	N^{15} (%) Run 1	N^{15} (%) Run 2
Assay		
0	32.60	3.17
3	3.04	0.694
20	3.12	0.695
45	3.07	0.673
Calculated		
Complete exchange	5.13	0.770
Carbamate nonexchange	6.63	0.908

with the ammonia frozen. Also, ammonia containing less N^{15} was used, since some difficulties were encountered in obtaining reproducible assays on highly enriched N^{15} samples. The results of this second experiment were similar to the first: isotopic equilibrium was attained in less than 3 min, but the equilibrium composition was lower in N^{15} than that calculated.

These experiments show that carbamate nitrogen exchanges with gaseous ammonia. The results suggest that the exchange is complete in less than 3 min. If exchange occurs this rapidly, the presence of carbamate ion is not expected to impose limitations upon the degree of isotopic enrichment obtainable in the carbonate system.

CARBONATE SYSTEM – WASTE REFLUX STUDIES

In order to maintain a high effective separation factor and high throughput in the proposed closed-cycle carbonate system (see Fig. 5), it is necessary that a concentrated ammonium carbonate solution be used. Solutions 18 *M* in total ammonia and 6 *M* in combined carbon dioxide have proven to be practical in exchange experiments conducted in columns.

In practice, this concentrated aqueous phase must be formed in the waste-end refluxer from nearly stoichiometric amounts of ammonia, water, and carbon dioxide. Although it is well known that these materials react to form aqueous ammonium carbonate solutions, no data were available for the reaction under the conditions required in the waste-end refluxer. In order to examine the reaction and to qualitatively define the nature of the problems which might be associated with it, a small jacketed column 12 mm ID and 70 cm long was set up in the laboratory to simulate the refluxer. The column was equipped with stopcock inlets, near the bottom, through which ammonia and carbon dioxide could be introduced. Fritted glass disks were placed in the gas inlet tubes to finely disperse the gas through the liquid contained in the column.

Because of certain engineering simplifications, it first seemed desirable to treat the reaction as a stepwise process occurring in the following way:

(1) $NH_3 + H_2O \longrightarrow NH_4OH$

(2) $NH_4OH + CO_2 \longrightarrow NH_4HCO_3$

(3) $NH_4HCO_3 + NH_3 \longrightarrow NH_4COONH_2 + H_2O$

However, upon filling the column with 6 *M* NH_4OH and bubbling in the required amount of CO_2, the less soluble ammonium bicarbonate precipitated from solution. To avoid the formation of the undesirable solid phase, it was found necessary to add ammonia simultaneously with carbon dioxide at approximately equal molar rates. When this was done, no further difficulties were encountered with solids formation in the column.

Three runs were made at 30°C to determine what solution concentration could be obtained in this equipment. By using the amounts of reactants indicated in Table 12, solutions containing about 15 *M* total ammonia were prepared. In the most favorable cases, as much as 90% of the ammonia and 100% of the carbon dioxide were absorbed.

Since even greater over-all yields may be expected from equipment designed for efficient gas-liquid contact and since solids formation is not troublesome, it appears to be worthwhile to study the reaction in larger, more efficient apparatus. Subsequent studies of the reaction are planned in pilot-scale equipment.

CARBONATE SYSTEM – PRODUCT REFLUX STUDIES

Reflux of the product stream in the proposed carbonate system is accomplished by distilling ammonia gas from the aqueous phase of the system after calcium hydroxide has been added to it. This

TABLE 12. MATERIAL BALANCE OF WASTE-END REFLUX AT 30°C

Experiment No.	Amount Added (moles)				Amount Found (moles)		Concentration Found (*M*)	
	$NH_3(g)$	$NH_3(aq)$	Total NH_3	CO_2	NH_3	CO_2	NH_3	CO_2
1	1.20	0.59	1.79	0.61	1.33	0.56	15.5	6.5
2	1.18	0.59	1.77	0.59	1.59	0.54	15.7	5.4
3	0.68	0.30	0.98	0.30	0.83	0.30	15.1	5.5

reaction must be very efficient; it is desirable that the aqueous effluent stream from the refluxer contain only about 1 ppm ammonia.

Attempts to study this critical reaction in conventional laboratory equipment were unsuccessful because of the deposition of solids on the walls and packing of the reflux column. For this reason, special equipment was designed to study the problem, in order to determine (1) whether the ammonia content of the effluent calcium carbonate stream could be reduced to the desired level and (2) whether the lime slurry reflux column could be made to operate for extended periods of time without objectionable solid deposits.

The equipment (Fig. 8) consists of a 2-in.-ID glass column 19.4 ft high, having a 16.7-ft section packed with ½-in. unglazed porcelain Intalox saddles. Sample ports and thermocouple connections are located at regular intervals along the column and in all streams entering the column. Heat for the column is supplied by a 6-gal steam-jacketed stainless steel reboiler tank, which is baffled and equipped for agitation. The water-cooled condenser and gas scrubber is of 6-in.-ID glass pipe and is 24 in. long. It contains 34 ft of ⅜-in. stainless steel tubing as the cooling coil. Stainless steel Yorkmesh Demister material packed into the condenser acts as a scrubber for the condensed moisture in the gas. The ammonia absorption tank and the feed makeup tank have a 20-gal capacity; each is jacketed, baffled, and provided with agitation. Addition of ammonium carbonate solution to the reflux column is controlled by a Lapp Pulsafeeder pump which has a capacity of 2.9 gph. Two 70-gal agitated tanks with steam-heating coils are used in making up the calcium hydroxide slurry. The slurry is fed at a controlled rate by a Sigma-motor finger pump.

With the use of concentrated ammonium hydroxide as feed solution, an exploratory run was made for checking the operation of the column with ammonia gas present and for determining the extent that ammonia can be stripped from ammonium hydroxide by distillation. After 3 hr of operation, samples were taken at various points along the column. The ammonia content of these samples is shown in Table 13. From these data, it is apparent that ammonia can be removed from water very effectively by distillation. The unexpectedly high result for the reboiler sample is probably due to nonequilibrium operation of the column prior to sampling.

TABLE 13. DATA ON THE STRIPPING OF NH_3 FROM NH_4OH

Sample Point Location[a] (in.)	NH_3 Concentration (ppm)	Standard Error (%)
Feed	221,000[b]	2
32.25	391.4[c]	10
94.75	0.7[c]	10
127.0	0.14[c]	25
Reboiler	3.78[b]	20

[a]Distance below feed point.
[b]Sample from liquid.
[c]Sample from vapor phase.

The feed solution for the next runs was prepared by absorbing the required amount of CO_2 in a solution of concentrated ammonium hydroxide. After the addition of the CO_2 was completed, the resulting solution was maintained at 30°C and saturated with ammonia gas. The solution was 17.6 *M* in total nitrogen and 5.11 *M* in total carbon dioxide.

Runs 2 and 3 were made for determining the nature and extent of the plugging in the column. Run 2 was terminated after 4 hr, primarily because of plugging of the column with impurities found in the lime. These impurities were removed by passing the calcium hydroxide slurry through a 140-mesh screen before the next run was started. Despite this precaution, run 3 had to be terminated after only 6 hr of operation because the column flooded. Examination of the column packing after this run showed a heavy coating of precipitated calcium carbonate on each piece immediately above and below the feed point of the column. Samples of smooth Teflon and nylon, which had been placed in the column near the feed point, were similarly coated with heavy layers of calcium carbonate which could not be removed readily with water.

This evidence suggested that the plugging of the column was caused by the calcium carbonate which formed on the surface of the packing, rather than by preformed particles lodging and accumulating in the crevices of the packing. To test this diagnosis, a precontact loop (Fig. 9) was added to the column system; ammonium carbonate and calcium

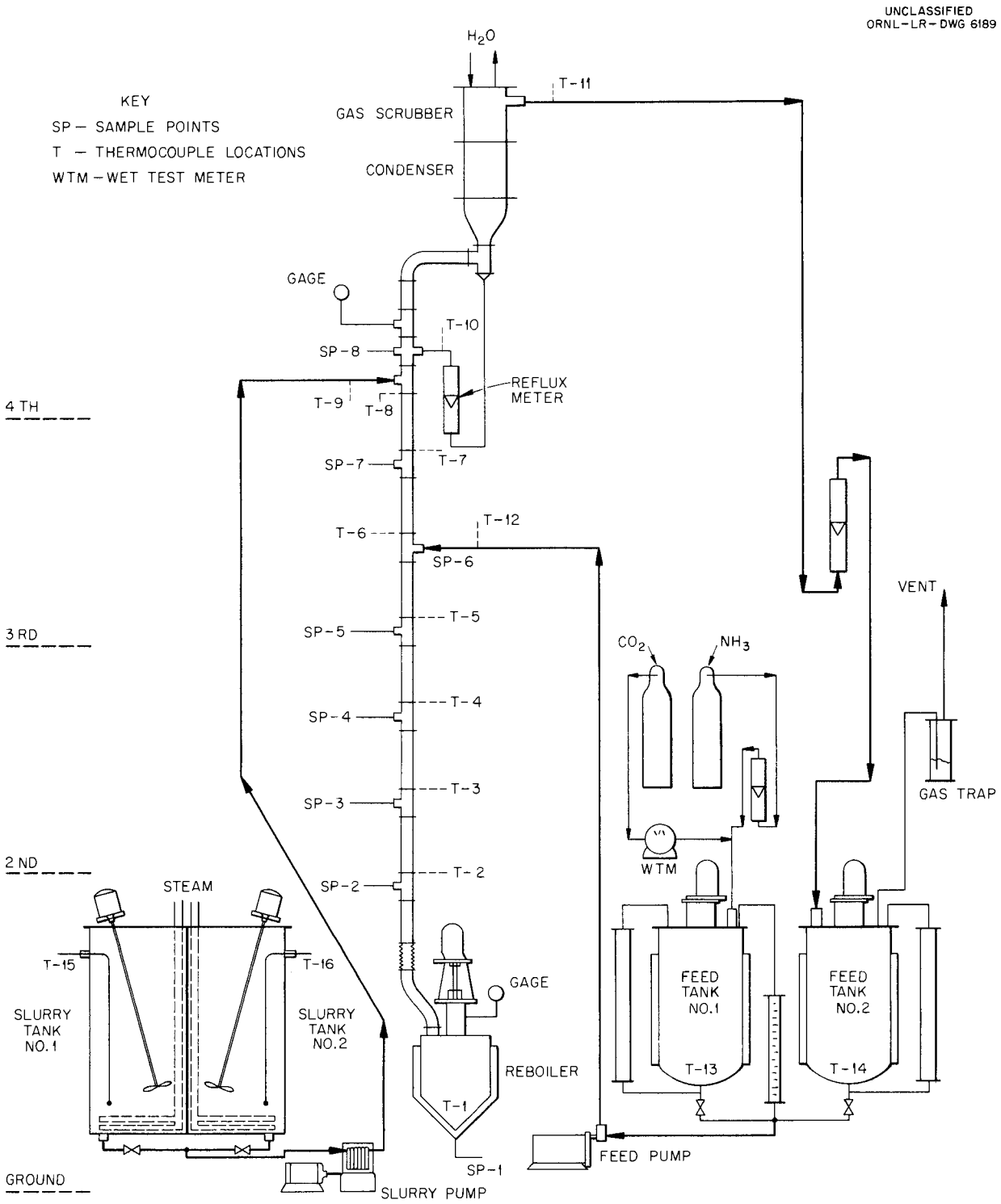

Fig. 8. Test Equipment for Product Reflux (Carbonate System).

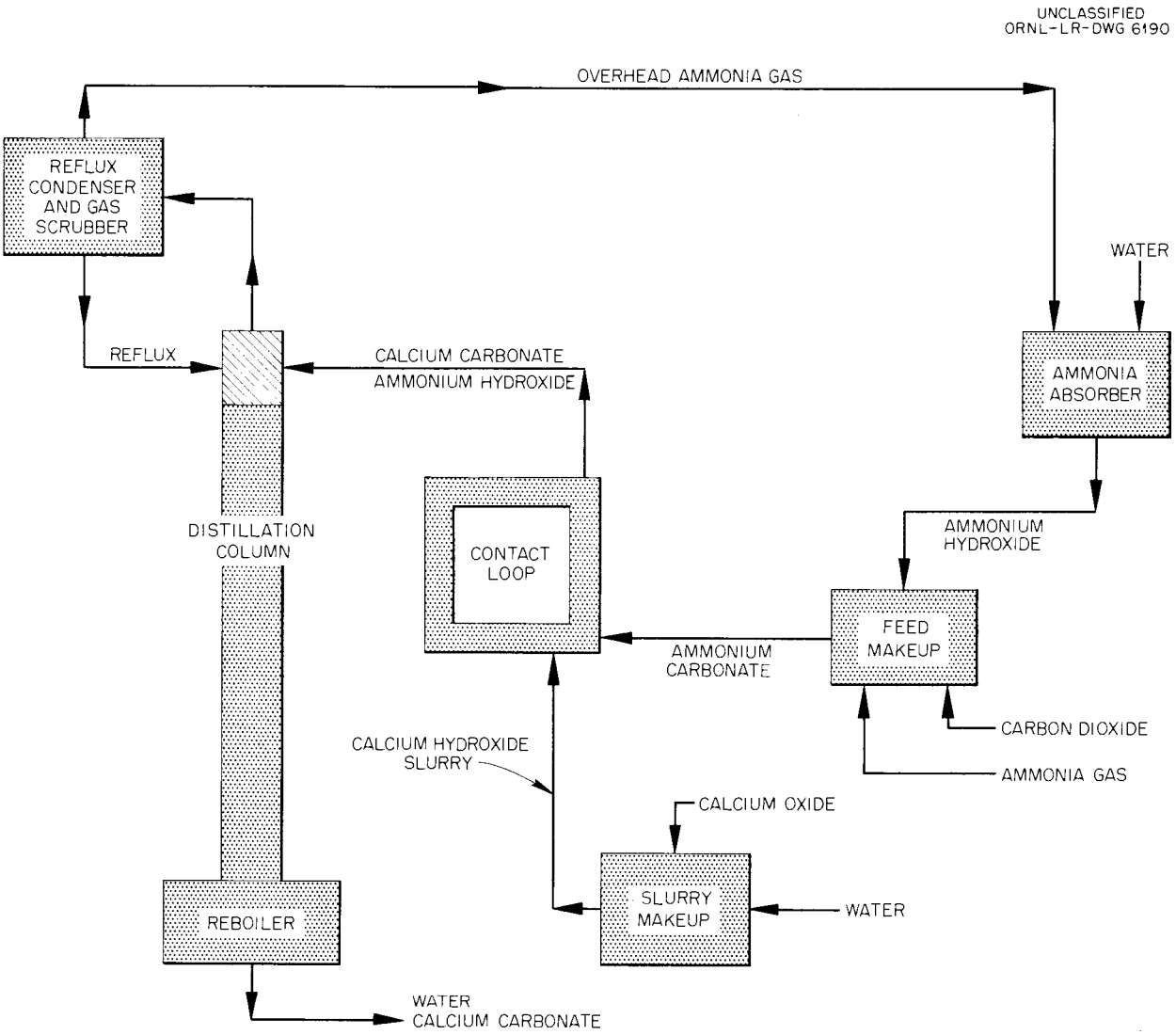

Fig. 9. Flow Diagram of Modified Test Equipment.

hydroxide solutions are reacted in this loop prior to being introduced into the packed column.

Preliminary operation of the loop was very successful. When preformed calcium carbonate was introduced into the reflux column, it did not adhere to the packing or walls of the column. Furthermore, it was easily washed down the column with water. The reaction of ammonium carbonate with calcium hydroxide in the loop was so complete that no free carbon dioxide reached the reflux column. As a consequence, it was possible to move the feed point to the top of the reflux column, thus increasing the number of plates available for removing ammonia from the aqueous effluent stream.

Preliminary testing of the modified equipment has been completed. Quantitative runs will be made next to measure the efficiency of the system in removing ammonia under these new conditions.

EXCHANGE BETWEEN AMMONIA AND CUPRIC AMMONIA ION

Isotopic separation factors have been measured for only a few nitrogen exchange reactions. Factors have been calculated for a few other reactions, but these values are subject to errors of unknown magnitude because of the uncertainties in the model assumed as the basis of the calculation. To provide a broader basis for evaluating nitrogen

enrichment processes, a variety of nitrogen exchange reactions are being studied.

One such system involved the following reactions:

$$(1)\quad Cu(N^{14}H_3)_4^{++}(aq) + N^{15}H_3(g) \rightleftharpoons Cu(N^{15}H_3)_4^{++}(aq) + N^{14}H_3(g)$$

and

$$(2)\quad N^{14}H_3(aq) + N^{15}H_3(g) \rightleftharpoons N^{15}H_3(aq) + N^{14}H_3(g)$$

To determine whether rapid nitrogen exchange occurred in this system, 16 ml of a saturated aqueous solution of cupric ammonia nitrate (~0.54 *M*) was contacted vigorously for approximately 15 sec with nearly 6 mmoles of gaseous ammonia enriched in the N^{15} isotope. A few grams of pulverized sodium nitrate was then added to the system, the mixture shaken, and the precipitated cupric ammonia nitrate filtered rapidly by means of suction. Ammonia samples were produced by treating the precipitated complex salt with aqueous sodium hydroxide and by applying heat. The evolved ammonia was swept into dilute hydrochloric acid, and the ammonium chloride product was reacted with sodium hypobromite to provide nitrogen samples for mass assay. As a result of these analyses (Table 14), nitrogen exchange was found to be complete; the exchange half time was calculated to be 3 sec or less.

After it was established that rapid exchange occurred between the complex and the gas, an experiment was performed to measure the resulting isotopic fractionation between these species. The procedure consisted in isotopically equilibrating approximately 10 ml of saturated cupric ammonia nitrate solution with ammonia gas, at the equilibrium vapor pressure of the solution, in a 1-liter vessel and at a temperature of 33°C. The small volume of solution was drained from the vessel before sampling of either phase. A portion of this solution was analyzed for both its cupric ion and total ammonia concentration. From these data, the concentration of dissolved but uncomplexed ammonia could readily be derived, assuming a coordination number of 4 for cupric ion toward ammonia. Mass assays were made of vapor phase and aqueous phase samples, in the form of nitrogen, to determine the ratio of the N^{15} isotope to the N^{14} isotope in each phase. The data resulting from this experiment are presented in the first line of Table 15.

The effective separation factor for the system was found to be the same, within the limits of experimental error, as the value, $\alpha = 1.005$, found by Kirshenbaum and co-workers[4] for reaction 2 given above. This unusably low separation factor was obviously due, in part, to the large amount of uncomplexed ammonia dissolved in the aqueous phase. In order to improve the ratio,

$$Cu(NH_3)_4^{++}(aq)/NH_3(aq)\ ,$$

and thus to improve the effective separation factor for the system, a second experiment was performed in which cupric ammonia chloride was used as the source of the complex ion. As can be seen from Table 15, this change resulted in a fourfold improvement in the ratio,

$$Cu(NH_3)_4^{++}(aq)/NH_3(aq)\ ,$$

and led to a larger effective separation factor.

Since the separation factor for reaction 1 represents the maximum effective factor possible in the system, it was of interest to determine this quantity.

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

TABLE 14. NITROGEN EXCHANGE BETWEEN $Cu(NH_3)_4(NO_3)_2(aq)$ AND $N^{15}H_3(g)$

Experiment No.	N^{15} Assay of Initial NH_3 (%)	Mole Ratio of $NH_{3\,complex}/NH_3(g)$	Phase Sample	N^{15} Content After Equilibration (%)	
				Calculated	Observed
1	31.7	3.4	Gas	7.2	6.4
2*a*	30.8	5.9	Aqueous	4.5	5.0
2*b*	32.7*			4.7**	

*Reanalysis of starting material.

**Calculated N^{15} content based on second analysis of starting material.

TABLE 15. EQUILIBRIUM DATA AT 33°C FOR THE SYSTEM $NH_3(g)$ vs $NH_3(aq) + Cu(NH_3)_4^{++}(aq)$

Complex Salt	$Cu(NH_3)_4^{++}$ Concentration (M)	Complexed NH_3 Concentration (M)	Dissolved NH_3 Concentration (M)	α_{eff}* at 95% C.I.
$Cu(NH_3)_4(NO_3)_2$	0.89	3.6	12.6	1.004 ±0.005
$Cu(NH_3)_4Cl_2$	2.1	8.4	9.6	1.0084 ±0.0018

$$^{*}\alpha_{eff} = \frac{(N^{15}/N^{14})_{aqueous}}{(N^{15}/N^{14})_{gas}} .$$

The determination may be made by use of the equation derived by Kirshenbaum and co-workers if it is assumed that cupric ammonia chloride does not appreciably affect the isotopic equilibrium between gaseous ammonia and aqueous ammonia:

$$\alpha_{eff} = M(K_2 - K_1) + K_1 ,$$

where

M = ratio of dissolved NH_3 to total NH_3,

K_2 = separation factor for $NH_3(g)$ vs $NH_3(aq)$ = 1.005,

K_1 = separation factor for $NH_3(g)$ vs $Cu(NH_3)_4^{++}(aq)$.

By use of this formula, the factor for the exchange between $NH_3(g)$ and $Cu(NH_3)_4^{++}(aq)$ was calculated to be 1.012. Since this value is based on the assumption of no solubility of ammonia gas in the aqueous phase, it probably cannot be achieved in practice. Even disregarding this aspect, the factor for this system is still smaller than that of the carbonate system.

THE ISOTOPE SEPARATION FACTOR FOR THE SYSTEM POTASSIUM AMALGAM–AQUEOUS POTASSIUM HYDROXIDE

H. H. Garretson

Kilogram quantities of enriched potassium isotopes have been requested for fast-neutron cross-section measurements. The isotopic exchange reaction

$$K^{41}(Hg) + K^{39}OH = K^{39}(Hg) + K^{41}OH$$

has been studied to determine whether it could be used for the economical production of large quantities of enriched potassium isotopes. Preliminary considerations of the chemistry of the reaction seemed to be encouraging. Relatively high potassium concentrations could be achieved in both phases. This would tend to reduce the size and cost of the cascade needed to concentrate the isotopes. Decomposition of the amalgam phase would not seem to be a problem, since the amalgam is known to be stable toward aqueous KOH solutions. Simple methods of refluxing the exchange reaction appeared to be possible. Thus, electrolysis of the KOH solution would yield K(Hg) at one end of the exchange section, while at the other end the catalytic decomposition of the K(Hg) would form a KOH solution. In view of the favorable chemistry of the exchange reaction, a multistage batch run was made for measuring the isotopic separation factor.

A cylindrical electrolysis vessel fitted with a glass stopcock drain and having a capacity of 1 liter was used. The vessel was provided with a motor-driven glass stirrer for agitation of the mercury phase, and a platinum electrode was inserted in the aqueous phase. A volume of 200 ml of aqueous phase and 500 ml of amalgam phase

was maintained in each equilibration.

At the beginning of the run, 200 ml of 9.644 *M* KOH solution and 500 ml of mercury were placed in the flask. Amalgam was formed by electrolysis until the concentration of the KOH was reduced one half. The amalgam and KOH phases were then stirred for 5 hr to ensure isotopic equilibrium. The aqueous phase was removed from the reaction flask and stored for subsequent use. Both phases were sampled. Water was then added to the amalgam phase in the reaction vessel and half the potassium in the amalgam phase was electrolyzed into the water. These phases were equilibrated, separated, and sampled as before. Fresh water was added, and the cycle was repeated until five successive equilibrations were made, following the amalgam phase (see Fig. 10). The reaction vessel was then emptied, and the aqueous phase from the first pass, together with 500 ml of mercury, was placed in the reaction vessel. Half the potassium of the aqueous phase was then electrolyzed into the mercury to form amalgam. These phases were equilibrated as before, and the process was continued until five passes were made on the aqueous phase. The conditions for each pass are shown in Table 16. The concentration of potassium in each phase was determined by taking weighed samples and titrating them with standard hydrochloric acid solution. In order to compute the percentage of potassium in each phase, it was necessary to calculate the weight of water produced during the formation of the amalgam and the amount of water decomposed when the amalgam was leached. Isotopic analyses of samples from each phase were obtained from the fifth pass when the aqueous phase was followed and from the fifth pass when the amalgam phase was followed. The results are shown in Table 17.

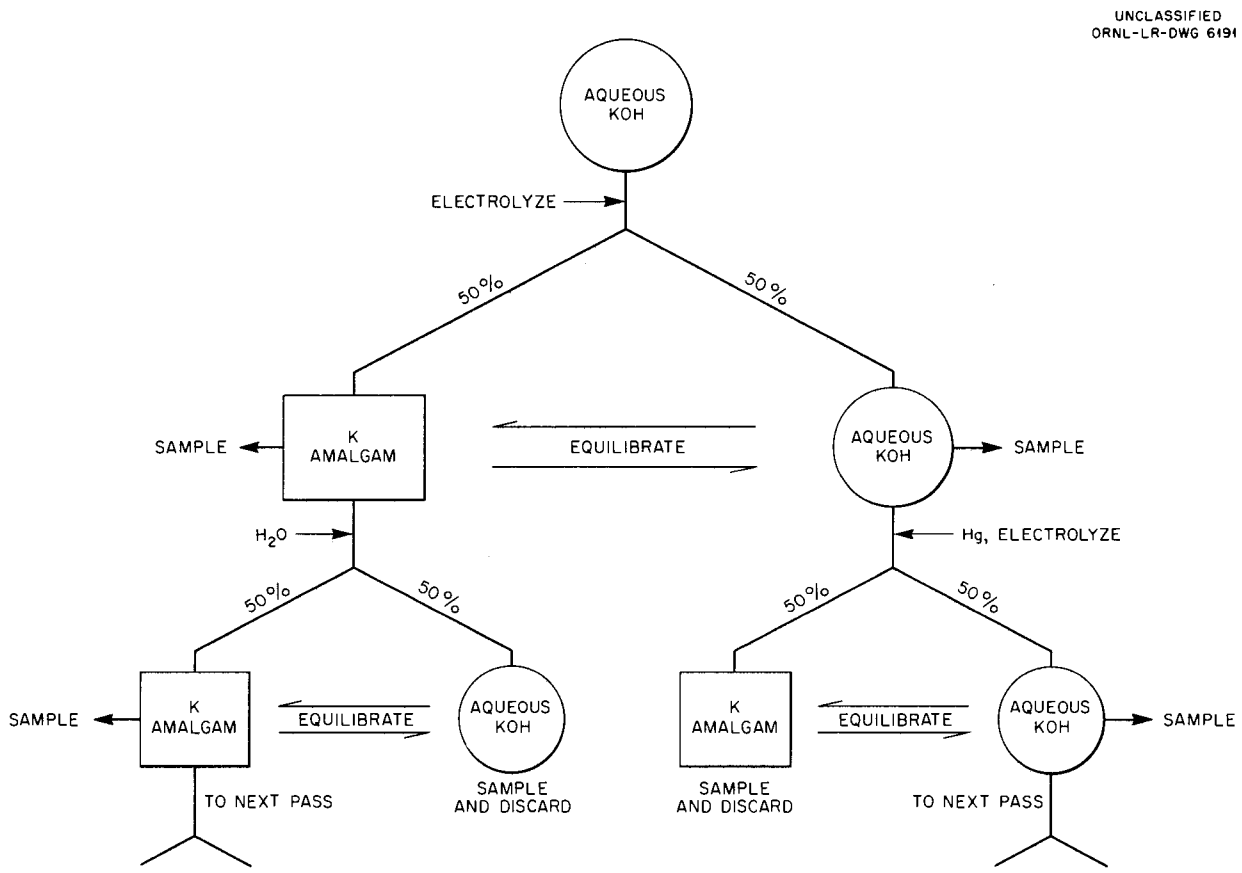

Fig. 10. Flow Diagram of Procedure Used in K(Hg)-KOH Multistage Batch Experiment.

From the data obtained, an estimate of the separation factor is

$$\alpha_{(95\%\ C.I.)} = 1.006 \pm 0.002 \ .$$

The value of α is too low for this system to be useful in the economical production of kilogram quantities of the less abundant isotopes of potassium. However, further enrichment of the abundant K^{39} may be feasible, depending upon the desired level of enrichment.

TABLE 16. CONDITIONS FOR THE MULTISTAGE BATCH RUN [K(Hg)-KOH SYSTEM]

Pass No.	KOH(*aq*) (*m*)	$K(Hg)_x$ (*M*)	K in Aqueous Phase (%)	Equilibration Time (min)	Temperature (°C)
			Amalgam Phase Equilibration		
0	9.644				
1	4.468	1.723	48	300	31
2	2.016	0.881	45	370	33
3	1.147	0.409	50	270	35
4	0.470	0.206	47	240	34
5	0.247	0.0956	50	270	35
			Aqueous Phase Equilibration		
1	4.468	1.723	48	300	31
2	1.886	0.732	52	130	34
3	0.992	0.338	53	240	
4	0.534	0.140	60	300	29
5	0.256	0.0832	56	210	

TABLE 17. ISOTOPIC ANALYSES OF FIFTH-PASS SAMPLES FROM MULTISTAGE BATCH RUN [K(Hg)-KOH SYSTEM]

Atom Ratio K^{39}/K^{41} for Amalgam Phase	Atom Ratio K^{39}/K^{41} for Aqueous Phase	Atom Ratio K^{39}/K^{41} for Amalgam Phase	Atom Ratio K^{39}/K^{41} for Aqueous Phase
Amalgam Phase Equilibration		Aqueous Phase Equilibration	
13.65	13.80	13.92	14.06
13.33	13.82	13.74	14.20
13.95		14.19	
13.65		14.01	

FRACTIONATION OF URANIUM ISOTOPES BY ION EXCHANGE

A. C. Rutenberg

Significant fractionation of uranium isotopes was reported[1] recently in an experiment in which a 1-ft band of uranyl ion adsorbed on Dowex 50 resin was eluted with magnesium ammonium versenate through a 2-ft bed of Dowex 50 in the copper form. At the request of the AEC, this Laboratory agreed to estimate the single-stage fractionation factor for this process.

A multistage batch run was performed so that a measurably large difference might exist in the isotopic ratios of the final samples. The species in solution in the multistage batch run were somewhat different from those in the original column experiment. In most of the passes the uranium concentration in the aqueous phase was higher than in the column experiment. There was some variation in the concentration and pH of the solution from one pass to the next. The batch experiments always contained at least one additional cation, both on the resin and in solution. An additional cation on the resin might not affect the system, but the cation in solution would compete with the uranyl ion for the complexing agent. These different conditions were imposed because of the necessity of doing the experiment batchwise and in laboratory-size equipment in a reasonable length of time.

The starting material for the multistage batch run was prepared by converting the hydrogen form of Dowex 50-X8 resin to the uranyl form by contacting it several times with uranyl nitrate solution. After this resin was thoroughly washed, enough magnesium ammonium versenate, $Mg(NH_4)_2V$, was added to elute half the uranium from the resin. The two phases were then vigorously agitated for at least 90 min to ensure attainment of isotopic equilibrium. After the phases were separated and sampled, the resin phase was stored for later processing. The aqueous phase was treated with enough of the copper form of the resin, CuR_2, to convert about half the uranyl ion to the uranyl form, UO_2R_2. Equilibrium-constant data were lacking for the various ions in solution and in contact with different forms of the resin, so the exact amounts of reagents needed could not be calculated accurately. The UO_2R_2 resulting from this treatment was equilibrated with the uranium remaining in the aqueous phase. The resin was discarded, and the uranium was chemically separated from the other components of the aqueous phase. This uranium was placed on some fresh resin, and the whole process was repeated two additional times, as described above. After the third recovery, little uranium was left, and only the $Mg(NH_4)_2V$ elution was performed. The resulting aqueous solution, after equilibration, was the source of uranium for the aqueous phase isotopic analysis. A flow diagram of this procedure is shown in Fig. 11.

Starting with the resin phase from the first equilibration, three resin-phase passes were made. The mixed magnesium uranium resin was reacted with $Mg(NH_4)_2V$ and equilibrated. The aqueous phase was discarded. The resin was isolated, and the procedure was repeated twice.

The solutions in equilibrium with the resin varied in UO_2^{++} concentration from 0.01 to 0.1 *M*, and the pH varied from 3 to 5. A few difficulties were encountered. Precipitation occurred during the first equilibration, therefore only the approximate distribution of uranium is known for this pass. Fortunately, it was not necessary to know the distribution of uranium or the amount of precipitate in this pass, since both phases were being followed. The isotopic ratios of the uranium on the resin and the uranium in solution differ by α, regardless of concentration or any fractionation of uranium by the precipitate. After the uranium had been recovered from the second pass of the aqueous leg, only 64% of it was put on the resin as the starting material for pass 3. In this case only, an undesired fractionation was obtained, since the aqueous phase was being investigated at the time. If it is assumed that the fractionation in this case was the same as in the main isotopic exchange reaction, the amount of separation "lost" can be estimated.

The distribution of uranium between resin and aqueous phases was determined from analytical data and is shown in Table 18. Isotopic enrichment corresponding to approximately five single stages of separation was achieved in the multistage batch run.

[1] F. H. Spedding *et al.*, *The Separation of Isotopes by Ion-Exchange. Progress Report on the Separation of Isotopes on Ion-Exchange Columns*, ISC-475, p 13 (April 7, 1954).

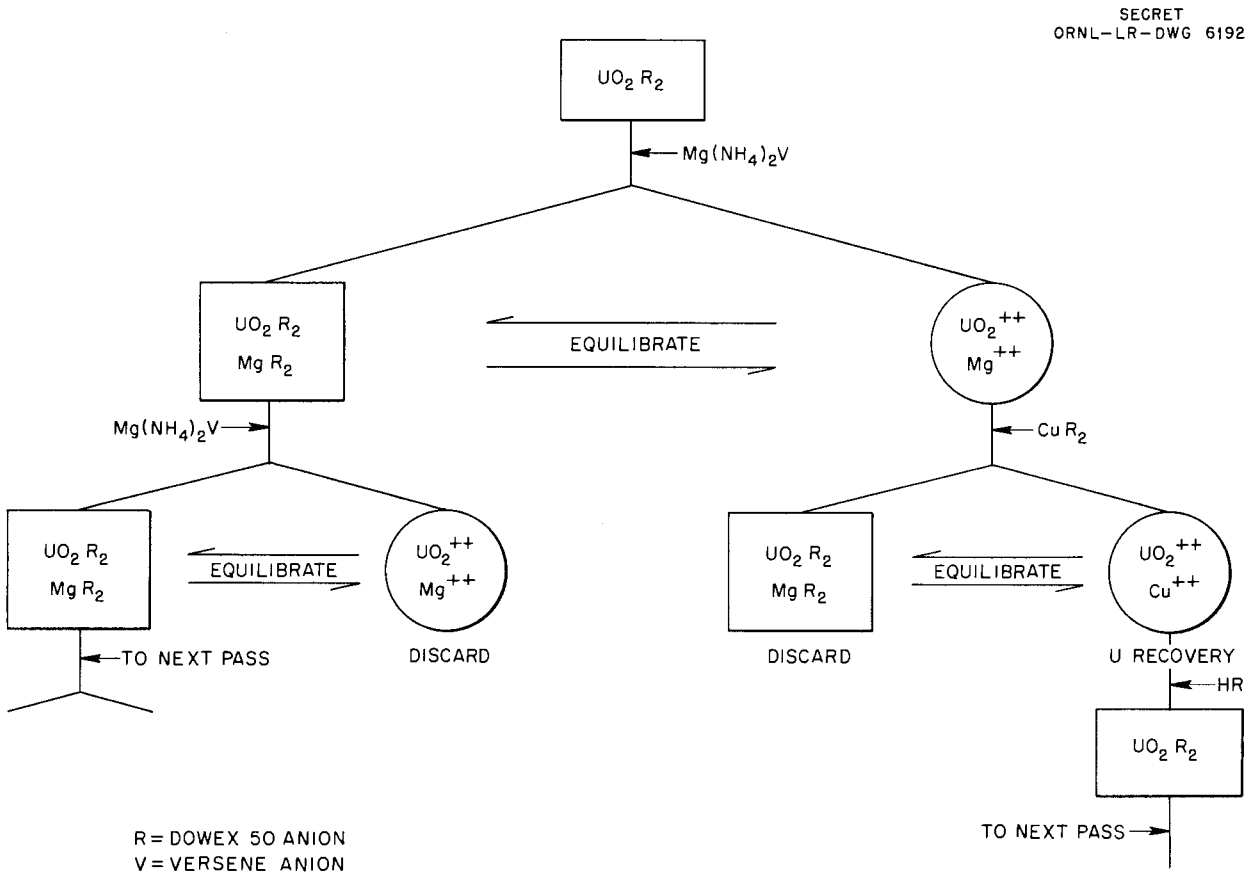

Fig. 11. Flow Diagram of Procedure Used in Uranium Multistage Batch Experiment.

TABLE 18. DISTRIBUTION OF URANIUM BETWEEN RESIN AND SOLUTION

Phase	Pass No.	Fraction of Uranium in Liquid
Resin	1	*
	2	0.71
	3	0.55
	4	0.43
Aqueous	1	*
	2	0.45
	3	0.53
	4	0.76
	5	0.53
	6	0.46
	7	0.45

*Data not obtained, see text for explanation.

At the completion of the experiment, uranium from the final resin phase, uranium in the final aqueous phase, and a standard uranium sample were carefully analyzed by special mass spectrometer techniques to provide an estimate of the total separation achieved in the experiment. Results of these analyses are shown in Table 19.

A total separation of 1.00029 ± 0.00027 (95% C.I.) was observed in the experiment. This value represents about five stages of separation, thus the single-stage separation factor may be shown to be approximately 1.00006.

Since the conditions of the original experiment could not be exactly reproduced in a batch experiment, it was decided to duplicate the original column experiment, using a longer column.

The column used had a 1-in. ID and was packed with 75 in. of Dowex 50W-X8 (50 to 100 mesh) resin:

TABLE 19. ISOTOPIC ANALYSES OF SAMPLES FROM URANIUM MULTISTAGE BATCH RUN

	Atom Ratio U^{235}/U^{238}		
	"Normal" Standard	Aqueous Phase	Resin Phase
	0.72544	0.72481*	0.72481*
	0.72554	0.72554	0.72523
	0.72564	0.72564	0.72544
	0.72564	0.72564	0.72544
	0.72564	0.72564	0.72554
	0.72576	0.72576	0.72554
	0.72585	0.72576	0.72554
	0.72595	0.72585	0.72564
	0.72595	0.72595	0.72564
	0.72605	0.72605	0.72595
Mean	0.725746	0.725759	0.725551
Variance of mean ($\times 10^{10}$)	396.0	274.9	378.9
Standard deviation of mean	0.000199	0.000166	0.000195
95% C.I. of mean	±0.00014	±0.00013	±0.00015

Total separation** (95% C.I.) = 1.00029 ± 0.00027

*Excluded at the 99% confidence level.

$$**\text{Total separation} = \frac{(U^{235}O_2^{++}/U^{238}O_2^{++})_{\text{aq versenate soln}}}{(U^{235}O_2^{++}/U^{238}O_2^{++})_{\text{resin}}} .$$

11 in. of the uranyl form of the resin on top of 64 in. of the copper form. The liquid level was maintained constant at 1 ft above the top of the resin bed. The eluting agent was a 0.005 *M* solution of magnesium ammonium versenate of pH 6.5. The column was operated at room temperature, and about 180 hr was required for the uranyl band to pass completely through the column. The flow rate of the eluting solution was 650 ± 100 ml/hr during most of the experiment. On two occasions 8 in. of resin was carefully removed from the top of the column to increase the flow rate. This was done late in the experiment, at which time the uranium band was nearing the bottom of the column and was not disturbed. The resin removed from the top was found to be free of uranium.

The front edge of the band was tilted almost from the start of the experiment; this same contour was maintained throughout the experiment. The rear edge was difficult to see and was observed with the aid of an ultraviolet lamp. It appeared to be tilted less than the front edge.

The ends of the band were sampled in increments, and a number of samples were combined to give sufficient material for mass assay. Twelve samples each, from the starting uranium resin, from the front edge, and from the rear edge of the band, were prepared. They were divided into three sets of six pairs of samples. The ratio of the U^{235}/U^{238} ratios was measured for each pair by the Y-12 Mass Spectrometer Laboratory. The uranium in the samples from the front edge represented about 1.5% of the total uranium content of the band, and the samples from the rear edge comprised 2.0% of the total uranium. A total separation,[2]

$$S_{(95\%\ \text{C.I.})} = 1.0008 \pm 0.0009 ,$$

was calculated from these analyses. A tabulation of the analytical data is shown in Table 20.

The very small amount of enrichment observed in these experiments fails to substantiate the initial claims made for this system.

[2]Determined as $\dfrac{(U^{235}/U^{238})_{\text{front edge of band}}}{(U^{235}/U^{238})_{\text{rear edge of band}}}$.

[redacted]

TABLE 20. ISOTOPIC ENRICHMENT OBTAINED IN URANIUM COLUMN EXPERIMENT

	Isotopic Enrichment			
	Front* / Rear	Front / Feed	Rear / Feed	Front/Feed ** / Rear/Feed
	1.0006	1.0002	1.0001	
	1.0008	1.0009	1.0000	
	1.0012	0.9996	No assay	
	0.9992	0.9999	0.9991	
	1.0006	1.0000	0.9987	
	1.0010	1.0000	0.9977	
Mean	1.00057	1.00010	0.99912	1.00098
Variance of mean ($\times 10^8$)	8.378	3.200	19.64	22.92
Standard deviation of mean	0.00029	0.00018	0.00044	0.00048
95% C.I. of mean	±0.00074	±0.00046	±0.00123	±0.00133
Pooled estimate of ratio, front/rear: 1.0008 ± 0.0009 (95% C.I.)				

*For convenience, let "front" and "rear" represent the atom ratio, U^{235}/U^{238}, in the leading and trailing edges of the uranium band, and let "feed" represent the atom ratio, U^{235}/U^{238}, in the starting material.

**Calculated from data in second and third columns of table.

[redacted]