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The Preparation of
Oxygen-17 Enriched Water
from Enriched Nitric Oxide Gas

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by

Daniel Pavone
Mohammed Alei, Jr.

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THE PREPARATION OF OXYGEN-17 ENRICHED WATER
FROM ENRICHED NITRIC OXIDE GAS

by

Daniel Pavone and Mohammed Alei, Jr.

ABSTRACT

A process and equipment designed to produce water enriched in oxygen-17 and oxygen-18 isotopes from correspondingly enriched nitric oxide gas is described. Approximately 1450 ml of high purity enriched water containing 1 to 3% oxygen-17 and 10 to 20% oxygen-18 have been produced for use primarily in nuclear magnetic resonance experimentation. Substantial quantities of nitrogen enriched in nitrogen-15 have been recovered as a by-product.

1. Introduction

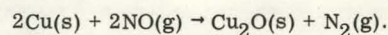
The availability of water enriched in oxygen-17 provides a unique material for the study of the physical chemistry of aqueous solutions using the techniques of nuclear magnetic resonance.

The process adopted for the enrichment of the oxygen-17 isotope, by Group CMF-4 of this Laboratory, is the low temperature distillation of nitric oxide (1). The distillation process yields a product, nitric oxide gas, which is enriched in oxygen-18 and nitrogen-15 in addition to oxygen-17. This isotopically enriched product must be chemically processed to produce water containing the oxygen isotopes and to recover nitrogen enriched in nitrogen-15 as a by-product. Because of the high value of the enriched oxygen, the conversion process must be efficient in recovery, and, in addition, should produce water of high purity for experimental use.

2. Conversion Process

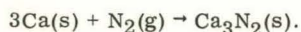
A two-stage batch process is used to convert the enriched nitric oxide into two products, water and calcium nitride.

The initial stage of the process effectively separates the nitrogen from the oxygen by reacting the nitric oxide in a helium stream with metallic copper to form solid copper oxide and nitrogen gas according to the following reaction.



$$\begin{aligned}\Delta H_R^\circ &= H_f^\circ(\text{Cu}_2\text{O}) - 2H_f^\circ(\text{NO}) \\ &= (-39.84) - 2(21.6) \\ &= -83.04 \text{ Kcal.}\end{aligned}$$

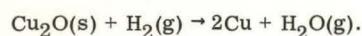
The gaseous nitrogen is carried in the stream of helium through a bed of calcium metal maintained at 650°C. Calcium nitride is formed according to the reaction



$$\begin{aligned}\Delta H_{\text{R}}^{\circ} &= H_{\text{f}}^{\circ}(\text{Ca}_3\text{N}_2) \\ &= -103.2 \text{ Kcal.}\end{aligned}$$

The solid calcium nitride is periodically recovered and stored conveniently in tightly sealed bottles.

Following the passage of a quantity of nitric oxide through the apparatus, the temperature of the copper furnace is decreased to about 500°C and hydrogen gas in a stream of helium is passed through the oxidized copper. The hydrogen reduces the copper oxide to metallic copper and forms water vapor according to the reaction



$$\begin{aligned}\Delta H_{\text{R}}^{\circ} &= H_{\text{f}}^{\circ}(\text{H}_2\text{O}) - H_{\text{f}}^{\circ}(\text{Cu}_2\text{O}) \\ &= -57.8 - (-39.8) = -18.0 \text{ Kcal.}\end{aligned}$$

The water vapor is carried by the helium stream through a trap maintained at near 0°C with an ice water coolant. Most of the water vapor is condensed to liquid water and is collected in a receiver vessel. The remainder of the water vapor is frozen in a liquid-nitrogen cooled trap downstream and is recovered by distillation into the receiver vessel after the reduction of the copper oxide is completed.

If deuterium oxide enriched in oxygen-17 is desired, deuterium gas is substituted for the hydrogen during the reduction step.

3. Apparatus

Figure 1 is a schematic diagram of the apparatus. The principal sections of the apparatus are a gas supply, purification, and metering section, a copper reaction chamber, condensation traps, and a calcium reaction chamber. Each section of the apparatus may be evacuated independently through connections to a conventional high vacuum system.

3.1 Gas Supply, Purification, and Metering Section. The enriched nitric oxide is received in a 300-ml stainless steel storage vessel constructed of a Hoke No. HD-300 gas sampling cylinder to which is welded a Pressure Products, Inc. high pressure valve. The valve has a non-rotating stem and was selected to give a reliable

leak-free closure. A monel metal Matheson pressure reducing valve serves to admit the nitric oxide, at reduced pressure, to the system through a Hoke orifice-type metering valve. Hydrogen and helium are supplied in standard 220 ft³ laboratory cylinders through pressure reducing valves and Hoke metering valves.

Hydrogen is purified by passing the gas through a Pyrex glass tower, 36-mm o. d. x 25-cm long, filled with reduced copper on silica gel heated to 400°C followed by a column of magnesium perchlorate contained in a Pyrex glass tower 35-mm o. d. x 30-cm long. The helium is purified by a column of copper metal prepared by reduction of wire-form copper oxide in a column 34-mm o. d. x 25-cm long followed by a similar column of magnesium perchlorate for adsorption of water.

All of the gases are metered through two similarly constructed flowmeter assemblies. One assembly is used for either hydrogen or nitric oxide depending upon the stage of the process, and the other is used to meter the helium flow. The Pyrex glass flowmeters are of the differential-pressure, capillary type. They use F. W. Dwyer Co. Magnehelic gages to measure the differential pressure across the capillary. The size of the capillary was determined by trial and error during calibration to give flow rates of 0 to 15 STP l/hr for hydrogen and helium and 0 to 8 STP l/hr for nitric oxide.

3.2 Copper Reaction Chamber. The copper reaction chamber is constructed of quartz glass, 54-mm o. d. x 40-cm long, with a 22-mm o. d. concentric central tube to approximately double the path length through the hot zone of the furnace. It contains approximately 160 grams of copper prepared by hydrogen reduction of wire-form copper oxide mixed with a nearly equal volume of 6-20 mesh aluminum oxide granules. The aluminum oxide is used to prevent plugging of the chamber by sintering of the copper metal.

3.3 Condensation Traps. The primary condensation trap consists of an outer envelope, 60-mm o. d. x 30-cm long, to the lower end of which is attached a drip-tip extending through a 19/22 standard-taper female ground-joint. The ice water coolant is contained in a re-entrant concentric tube, 46-mm o. d. x 30-cm long, closed at the bottom.

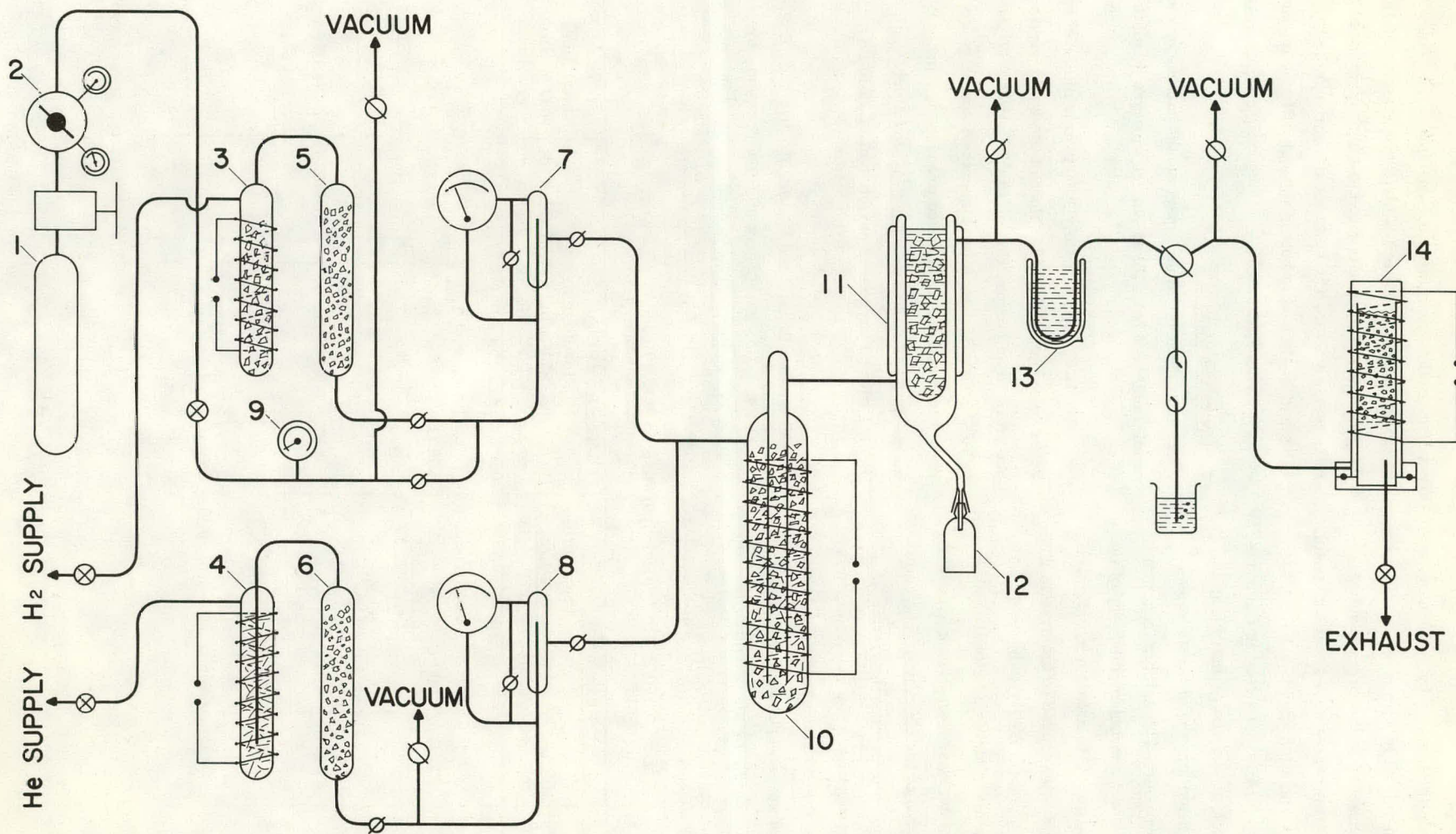


Fig. 1. Conversion apparatus.

- | | |
|--------------------------------------|----------------------------------|
| (1) Nitric oxide storage vessel | (9) Vacuum gauge |
| (2) Matheson pressure reducing valve | (10) Copper reaction chamber |
| (3) Reduced copper on silical gel | (11) Primary condensation trap |
| (4) Reduced copper | (12) Receiver vessel |
| (5 & 6) Magnesium perchlorate | (13) Secondary condensation trap |
| (7 & 8) Flowmeter assemblies | (14) Calcium reaction chamber |

The cold portion of the trap is insulated by a vacuum jacket. A commercial 30-ml bottle with a 19/22 standard-taper male ground-joint attached to the corresponding joint at the bottom of the trap serves as a receiver vessel. Following the primary condensation trap is a U-trap of 14-mm o. d. glass tubing which is immersed in liquid nitrogen. Water vapor which passes the primary trap is frozen here and later distilled into the receiver vessel.

3.4 Calcium Reaction Chamber. The calcium reaction chamber is designed to permit convenient recovery of the calcium nitride and recharging with calcium metal. The furnace and outer envelope are secured to the system and remain fixed. A stainless steel tube 2 1/2-in. o. d. x 12-in. long with a welded stainless steel end closure, silver-soldered to a brass flange containing an O-ring groove serves as the outer envelope of the chamber. The end of the steel tube is water cooled to protect the O-ring seal and brass flange from overheating. The calcium metal, approximately 200 grams of 8-20 mesh granules, is supported on a stainless steel screen spot-welded to a 1/4-in.-thick stainless steel plate containing six 3/8-in.-diameter holes mounted midway in a stainless steel tube fitting

concentrically within the outer envelope. The inner tube is silver-soldered to a brass plate that mates with the flange of the outer envelope and to which is attached a Hoke toggle valve. The helium exits through the toggle valve and is allowed to bubble through silicone oil and exhaust to the atmosphere.

4. Operating Results

Data demonstrating experimental parameters and results obtained from three typical runs are tabulated in Table I.

To date, approximately 1450 grams of enriched water have been produced. Most of the water produced had an isotopic composition of 1 to 3% oxygen-17 and 10 to 20% oxygen-18. Smaller amounts of specially enriched material have also been processed, some containing as much as 20 to 30% oxygen-17 and a substantial amount with an oxygen-18 enrichment of 95 to 98%.

REFERENCE

- (1) McInteer, B. B., and Potter, R. M., Ind. Eng. Chem., Process Design and Development, Vol. 4, No. 1, p. 35, (1965).

TABLE I. Typical Operating Data and Results

| Description of NO | | Reaction of NO | | | | Reduction of Cu ₂ O | | | H ₂ O Yield, grams | Theoretical H ₂ O Yield, grams |
|--|----------------|----------------|----------|--------------------|-----|--------------------------------|--------------------|-----|-------------------------------|---|
| Isotopic Comp. | Quantity, STPL | Cu Temp. | Ca Temp. | Flow Rates STPL/hr | | Cu ₂ O Temp. | Flow Rates STPL/hr | | | |
| | | | | NO | He | | H ₂ | He | | |
| ¹⁷ O = 1.996% ¹⁸ O = 29.25% ¹⁵ N = 33.50% | 13.2 | 730°C | 690°C | 4 | 3 | 600°C | 7 | 3 | 10.88 | 10.96 |
| ¹⁷ O = 3.48% ¹⁸ O = 78.31% ¹⁵ N = 80.39% | 16.7 | 710°C | 620°C | 5 | 2.5 | 545°C | 3 | 2.5 | 14.50 | 14.63 |
| ¹⁷ O = 22.15% ¹⁸ O = 46.84% ¹⁵ N = 16.96% | 3.05 | 700°C | 620°C | 4 | 2.5 | 540°C | 4 | 2.5 | 2.63 | 2.61 |