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14

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THE PREPARATION OF A PRIMARY STANDARD OF TRITIUM WATER

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ABSTRACT

A primary standard of tritium water has been prepared by the reaction of tritium with copper oxide. The tritium water was diluted with ordinary water to give a tritium concentration of 19.55 ± 0.10 curies/liter on March 10, 1954.

1. Introduction

Although the Los Alamos Scientific Laboratory and other AEC installations require the determination of the tritium content of water samples, including urine samples, only inaccurately known primary standards exist for these determinations. The tritium water sample described in this report was prepared to fill the need for a primary standard in these determinations.

The reaction employed to prepare this sample was one commonly used in quantitative analytical procedures.[1] $T_2 + CuO \rightarrow T_2O + Cu$. A measured amount of T_2 was oxidized to T_2O and then diluted to a known volume with ordinary H_2O.

2. Experimental

2.1 Materials

The T_2 was obtained from Group CMR-4 (LASL). A sample of the gas was analyzed on a mass spectrometer with the following results: T_2, 97.6%; D_2, 0.49%; H_2, 1.58%; He, 0.31%. The CuO was wire-form, A. R. grade, made by Mallinckrodt Chemical Works. The H_2 was Linde Air Co. tank H_2. Distilled water was used in all dilutions.

2.2 Apparatus

The apparatus is shown in Fig. 1. A Toepler pump circulated T_2 over CuO (B, Fig. 1) heated by a resistance furnace. A U-tube trap, C, cooled with liquid N_2 was used to remove the T_2O from the gas stream. Material was introduced or removed from the system at A. The tube, D, held gas samples to be analyzed on a mass spectrometer.

2.3 Procedure

The T_2 in a bulb was connected to the line at A. After evacuation of the system, the T_2 was transferred by means of the Toepler pump to the burette and sample tube through the cold trap, C, cooled with liquid N_2. The line was evacuated and the CuO outgassed at 450°C. The gas in the burette, after being measured, was circulated over the CuO kept at 400°C and then through the liquid N_2 trap at C. This was continued until the pressure was down to 1 mm or less. Hydrogen was then admitted to a pressure of 150 mm and the procedure repeated. Two such flushes with H_2 were used during this stage of the preparation.

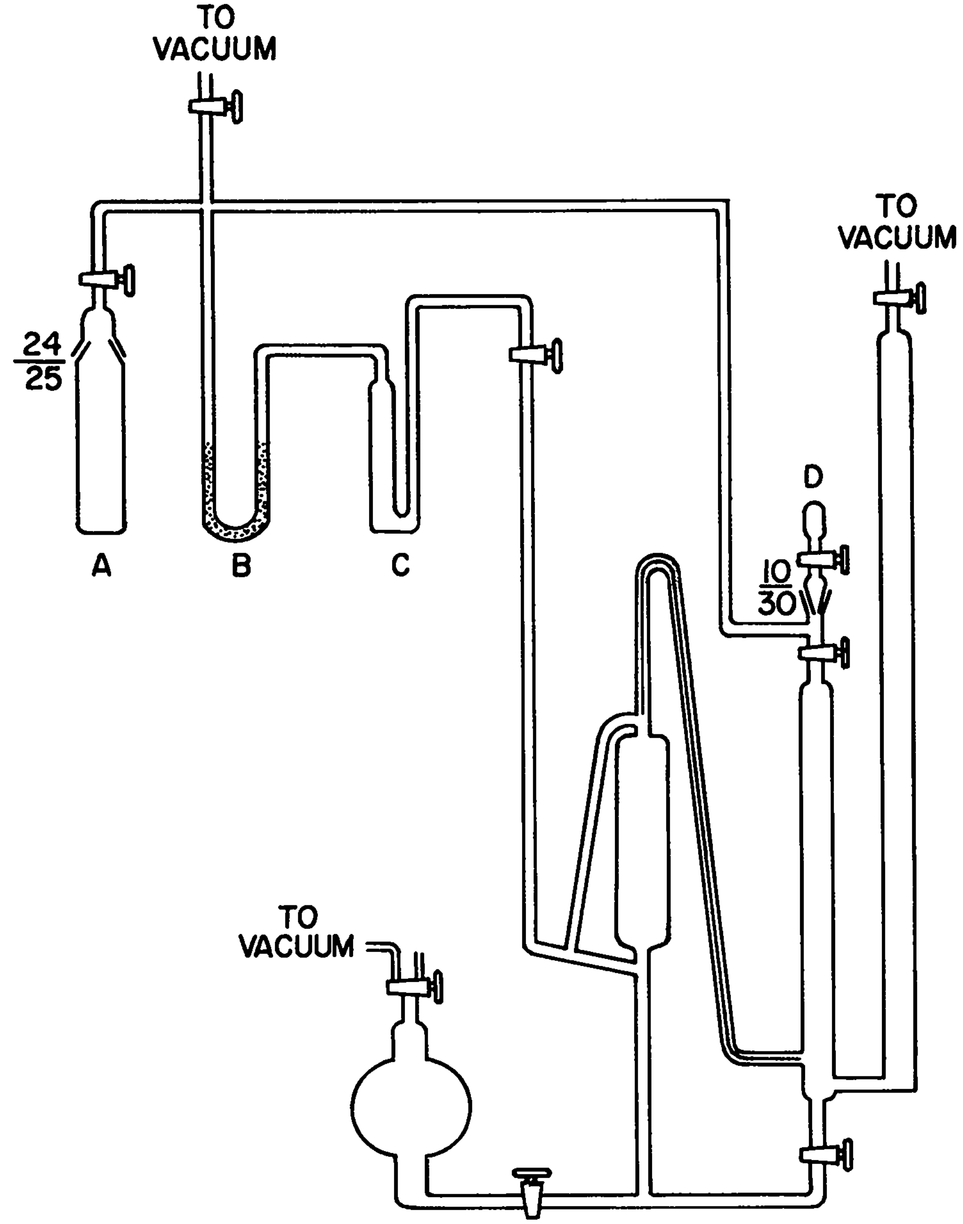

FIG. I

The small amount of residual gas was pumped into the burette, the CuO was cooled to room temperature, and the T_2O-H_2O was distilled into the liquid N_2 cooled storage tube, A, and kept frozen there. The flushing of the reaction system with H_2 to form H_2O was then repeated twice, using the same experimental conditions as employed during the combustion of the T_2. This H_2O was added to that in the storage tube. A fifth H_2 flushing following all the above procedures was carried out. The combined H_2O samples were thus frozen in a thin film at the bottom of the storage tube. This cold tube was taken off the line and approximately 50 cc of distilled H_2O was poured in through the 24/25 standard taper joint to melt the ice. This solution was transferred rapidly to a 1 liter volumetric flask partially filled with water. The repeated rinsings of the storage tube were also added to the contents of the volumetric flask before diluting to volume.

3. Experimental Results

3.1 Calculations

The 97.6 mole % pure T_2 exerted a pressure of 32.095 cm at 25.7°C in a volume of 19.96 cc so that there was 7.519 cc of pure T_2 at STP. Assuming a half-life of 12.26 years,[2] tritium gas has a specific activity of 2.60 curies/cc. Consequently, the solution had an activity of 19.55 curies/liter.

3.2 Possible Errors

The volume of the burette used and the room temperature were each known to ±0.1%. The pressure was read to ±0.016%. Since both the burette and manometer had been made from the same piece of 10 mm I. D. tubing, no manometer correction was applied. In the mass spectrometer analysis there were several different species of the same mass present. In order to resolve this, the equilibrium constants among the various hydrogen species had to be employed.[3] This assumes, of course, equilibrium conditions to be present in the sample. An error of 10% in this determination of the 2.4% impurities in the tritium was combined with the other errors and rounded off to ±0.5%.

The indeterminate errors include possible adsorption of T_2 in the Cu-CuO mixture, evaporation of the concentrated T_2O-H_2O upon dilution, and exchange of T_2 with the stopcock grease.

4. Summary

A sample of tritium-containing water was prepared as a preliminary standard for tritium counting. It contained 19.55 ± 0.10 curies/liter on March 10, 1954.

References

1. A. Farkas and H. W. Melville, Experimental Methods in Gas Reactions, p. 177, Macmillan and Co., London, (1939).
2. W. M. Jones, unpublished manuscript.
3. W. M. Jones, J Chem Phys, 17, 1062 (1949).