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MOLAR VOLUMES OF DEUTERIUM AND OF A DEUTERIUM-TRITIUM MIXTURE BETWEEN 19.5 AND 24.5° K

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LAMS 1206

Los Alamos	1-20

Standard Distribution

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Hanford Operations Office	28
Knolls Atomic Power Laboratory	29-30
Patent Branch, Washington	31
Technical Information Service, Oak Ridge	32-36
University of California Radiation Laboratory	37-40
Chicago Patent Group	41
du Pont Company	42-45
New Operations Office	46

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ABSTRACT

The molar volumes of deuterium and of a 1:1 atom ratio mixture of deuterium and tritium have been measured in the temperature range of 19.5 to 24.5° K. The equation

$$V_M \text{ (cm}^3\text{/mole)} = 20.188 + 0.03587T + 0.006565T^2$$

represents the combined data of this research and of earlier measurements in the range 18.7 to 20.5° K by Clusius and Bartholemé.

The data for the tritium-deuterium mixture may be represented by:

$$V_M \text{ (cm}^3\text{/mole)} = 18.155 + 0.1294T + 0.004203T^2$$

INTRODUCTION

The only previous determination of the molar volume of deuterium is that by Clusius and Bartholomé[1] who made eight measurements between 18.8 and 20.5° K. This report presents the results of molar volume measurements in the range 19.5 to 24.5° K for pure deuterium and for a 50:50 atom percent mixture of deuterium and tritium.

[1] K. Clusius and E. Bartholomé, Z. Physik. Chem. B30, 237, (1935).

APPARATUS AND PROCEDURE

The apparatus used consisted essentially of (1) a calibrated gas pipette and constant volume manometer to measure the amount of gas added to the condensing system, (2) a mercury "pusher" to compress the gas into the condensing system, (3) a small volume line leading to the pycnometer and including a Wallace and Tiernan differential pressure gauge for measuring the system pressure, and (4) the pycnometer proper.

The pycnometer was connected to the filling line by a small glass capillary tube on which a fine mark was etched to define the liquid volume. The pycnometer volume to this mark was 0.06417 cm^3 and the capillary volume in the vicinity of the mark was 0.000360 cm^3/mm.

A double compartmented dewar vessel containing liquid nitrogen and liquid hydrogen served as a cryostat for the apparatus. It was attached by means of a sliding seal so that the liquid hydrogen bath level could be maintained at a constant level with respect to the fiduciary mark on the pycnometer. Various temperatures were attained by varying the bath pressure up to 30 lbs gauge pressure by an auxiliary pressure regulating device. Temperatures were measured by a strain-free platinum resistance thermometer which had been calibrated at the Bureau of Standards. Occasional temperature checks were made by comparing the resistance thermometer temperature with that obtained from the vapor pressure of the liquid hydrogen bath.

Molar volume measurements were made by adding known amounts of gas (measured in the gas pipette) to the condensing system until liquid was condensed in the pycnometer up to the vicinity of the calibration mark. The system was allowed to equilibrate for about 30 minutes and then the meniscus level with respect to the mark was noted by means of a cathetometer, the resistance thermometer current and potential were measured on a White double potentiometer, and the bath and system pressures were observed. After this, the bath temperature was changed and a new set of similar readings was made.

The pycnometer volume was determined in the same manner except that pure hydrogen was used as a calibrating liquid, the data of Scott and Brickwedde[2] being used to establish the volume. The

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[2]R. B. Scott and F. G. Brickwedde, J. Research NBS 19, 237, (1937).

"noxious volume" of the gas in the connecting lines was determined by independent measurements as a function of the bath temperature in order to compensate for the uncertain part of the volume just above the bath level which was in a severe temperature gradient region.

The deuterium used contained 0.4 atom percent of protium as the only impurity determinable by the mass spectrograph. The tritium was originally 99.7% pure, but, once the 50:50 mixture was made up, a gradual increase in He^3 due to disintegration and an increase in protium content due to exchange with stopcock grease was evident. These impurities interfered with condensation of the T-D mixture when attempts were made to make measurements in the temperature region above 24.5° K.

RESULTS

A. Deuterium:

The molar volumes of deuterium in the temperature range 19.5 to 24.2° K are shown in Table I. The five experimental values of this

research were combined with the eight measurements of Clusius and Bartholemé by the Least Squares method to obtain the following equation:

$$V_M \text{ (cm}^3\text{/mole)} = 20.188 + 0.03587T + 0.006565T^2$$

The maximum deviation of the experimental points from this equation is 0.025 cm^3/mole (or 0.1%) and the standard deviation is 0.01 cm^3/mole (or 0.04%).

B. Deuterium-Tritium Mixture:

A mixture containing 49.7 mole percent tritium and 50.3 mole percent deuterium was used in these measurements. Since T_2 and D_2 equilibrate rapidly even at room temperatures, the mixture was actually a three component one containing approximately 50% TD as shown by mass spectrometric analysis.

The ten experimental points are shown in Table II and can be represented by the equation:

V_M (cm^3/mole) = $18.555 + 0.1294T + 0.004203T^2$ with a maximum deviation of 0.08 cm^3/mole (or 0.35%) and a standard deviation of 0.05 cm^3/mole (or 0.2%).

Table I

Molar Volume of Deuterium

T °K	V_M (cm^3/mole)	Dev. (calc.-obs.)
24.205	24.905	- 0.003
23.41	24.620	+ .006
22.375	24.281	- .004
21.14	23.889	- .009
19.51	23.411	+ .025

Table II

Molar Volume of a 50:50 Atom Percent Tritium-Deuterium Mixture

T °K	V_M (cm^3/mole)	Dev. (calc.-obs.)
24.06	24.11	- 0.01
23.28	23.79	+ 0.06
22.64	23.68	- 0.04
22.56	23.695	- 0.08
22.46	23.53	+ 0.05
21.75	23.39	- 0.03
21.12	23.09	+ 0.07
20.73	23.05	- 0.01
19.56	22.66	+ 0.04
19.55	22.74	- 0.05