

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Condensed Gas Calorimetry. II. Heat Capacity of Ortho-deuterium between 13.1 and 23.6°K., Melting and Boiling Points, Heats of Fusion and Vaporization. Vapor Pressures of Liquid Ortho-deuterium¹

BY EUGENE C. KERR, ELIS B. RIFKIN, HERRICK L. JOHNSTON AND JOHN T. CLARKE

Introduction

The only previous measurements of the calorimetric properties of solid and liquid deuterium are those made by Clusius and Bartholome² who worked with the normal mixture. Their results were in agreement with the anticipated "frozen in" entropy for normal deuterium, predicted by Johnston and Long³ on the basis of a statistical treatment of the deuterium spectrum. Clusius and Bartholome measured the heat of vaporization at 19.65°K. but made no determination at the normal boiling point (23.59°K.). The present work was undertaken with 97.8% ortho-deuterium to obtain a direct measurement at the normal boiling point and to compare the entropy of the nearly pure ortho form with the statistical value for the same mixture.

Preparation of Sample.—Deuterium was prepared by electrolysis of a large quantity of 99.7% D₂O and was stored in a high pressure hydrogen cylinder for nearly two years before use in this research. Unfortunately, no analysis was obtained on the sample of gas removed from the calorimeter, due to accidental loss. However, an analysis was made on a sample of gas withdrawn from the same cylinder two years later. This analysis, made by a pycnometer determination of the density of a sample burned to D₂O, indicated the presence of 99.2% D₂. This result corresponds to 1.6% HD in the gas and compares with 0.6% HD when the cylinder was filled. The relatively large amount of hydrogen contamination must have occurred in some manner during storage, perhaps by slow escape of hydrogen from the steel. We have assumed that the increase in contamination was linear with time over the four-year period of storage and have taken the HD content in the sample used in this investigation as 1.1%. The small uncertainty, which may amount to 0.2 or 0.3% HD, does not significantly contribute to the limits of error of the data included in this paper.

Para-deuterium was converted to the 20.4°K. equilibrium mixture, which corresponds to 97.8% ortho-deuterium,³ by condensation over charcoal. This conversion was carried out at the boiling point of liquid hydrogen in the apparatus

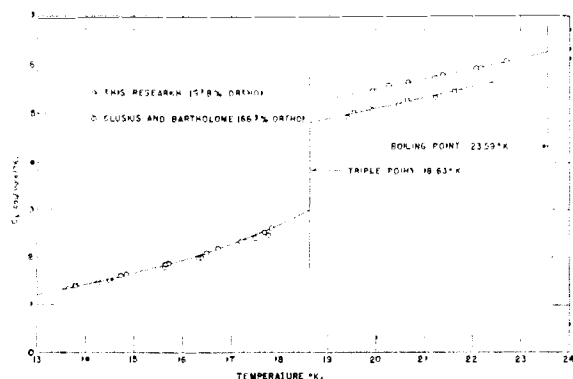


Fig. 1.—Heat capacity of saturated solid and liquid deuterium.

(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) K. Clusius and E. Bartholome, *Z. physik. Chem.*, **30B**, 237 (1935).

(3) H. L. Johnston and E. A. Long, *J. Chem. Phys.*, **2**, 389 (1934).

described in the first paper⁴ of this series. The contact time, however, was increased from 16 to 50 hours in order to compensate for the much slower rate of conversion of deuterium as compared to that of hydrogen.⁵

Apparatus and Temperature Scale.—The apparatus used in these experiments was the same as that used with hydrogen.⁴ A general view of the assembled calorimeter is presented in Fig. 1 wherein the thermostated mercury buret is shown in the rear. It was necessary to extend the temperature scale, since the original calibrations were only carried to 21°K. This extension was accomplished by three major steps. The scale was calibrated against the triple point and vapor pressures of oxygen between 65 and 90°K. and against the triple point and vapor pressures of neon between 23 and 27°K. The standard copper-constantan thermocouple tables were smoothed by graphical and analytical means in such a manner as to fit the hydrogen, neon and oxygen calibration data and, at the same time, to bridge the gap between 27 and 65°K. in a smooth manner.

The neon was taken from a large supply of pure neon, loaned to us through the courtesy of the Research Laboratory of the Linde Air Products Co. The triple point pressure exceeded that reported for neon by Henning and Otto⁶ by 12.8 mm. We credited this difference to the presence of a non-condensable gas, presumably helium. Recognizing that helium would be present almost entirely in the vapor phase, the 12.8-mm. partial pressure of helium in the vapor volume would correspond to 0.05 mole per cent. impurity in the total neon. This conclusion appears reasonable and was confirmed by a mass spectrometer analysis. We corrected all of the vapor pressures by the amount necessary to allow for this quantity of helium which was assumed to be in the gas phase. The calibration obtained in this manner fitted smoothly into a thermocouple table that correctly

TABLE I

HEAT CAPACITIES OF SOLID AND LIQUID ORTHO-DEUTERIUM (97.8% ORTHO MOLECULAR WEIGHT 4.032)

Series I, 4.6595 moles; Series II, 4.6261 moles

| Series | T, °K. | ΔT, °K. | C _p cal./mole/deg. |
|---------------------------|--------|---------|----------------------------------|
| I | 13.66 | 1.074 | 1.344 |
| II | 13.81 | 1.017 | 1.367 |
| I | 14.74 | 0.892 | 1.603 |
| II | 14.85 | .847 | 1.631 |
| I | 15.65 | .774 | 1.831 |
| II | 15.72 | .739 | 1.860 |
| I | 16.50 | .676 | 2.076 |
| II | 16.74 | .943 | 2.175 |
| I | 17.21 | .604 | 2.312 |
| II | 17.71 | .542 | 2.496 |
| I | 17.84 | .535 | 2.590 |
| Melting point at 18.63°K. | | | |
| I | 19.94 | 0.728 | 5.470 |
| II | 20.26 | .955 | 5.577 |
| I | 20.68 | .699 | 5.646 |
| II | 21.22 | .919 | 5.735 |
| I | 21.39 | .677 | 5.781 |
| I | 22.07 | .656 | 5.921 |
| II | 22.17 | .882 | 5.929 |
| I | 22.73 | .636 | 6.062 |

(4) H. L. Johnston, J. T. Clarke, E. B. Rifkin and E. C. Kerr, *THIS JOURNAL*, **72**, 3933 (1950).

(5) Unpublished data from this Laboratory.

(6) Henning and Otto, *Phys. Z.*, **37**, 633 (1936).

represented the hydrogen vapor pressure calibration below 25°K. and the oxygen calibration above 65°K. It was also consistent with an indirect intercomparison between the standard thermocouple of the condensed gas calorimeter and another thermocouple constructed at this Laboratory and calibrated by the National Bureau of Standards.

Experimental Results

Heat Capacities of Solid and Liquid Ortho-deuterium.—Between 13°K. and the boiling point, 23.59°K., eleven points were taken on the heat capacity curve of solid deuterium and eight points in the liquid range. The results are listed in Table I and plotted in Fig. 1. The graph also presents the data of Clusius and Bartholome for normal deuterium.

Since Clusius and Hiller⁷ found no difference between their own results with 94% para-hydrogen, in both the liquid and solid phases, and those of other investigators⁴ who studied the normal mixture, and since our data for solid ortho-deuterium agree well with those of Clusius and Bartholome,² we conclude that there should be no difference between the heat capacities of ortho and normal deuterium in the liquid range. The large difference, shown in Fig. 1, between our results and those of Clusius and Bartholome for liquid deuterium must be the result of an experimental error.⁸

The heat capacities entered in Table I and plotted in Fig. 1 were corrected for the presence of 1.1 mole per cent. HD. In making these corrections, the data of Scott and Brickwedde⁹ and of Brickwedde and Scott¹⁰ for the calorimetric properties of HD were used. Similar corrections were applied to the fusion and vaporization data.

Triple Point Temperature and Pressure.—The triple point temperature was determined by observing the approach of thermal equilibrium on the sensitive resistance thermometer while the calorimeter was maintained at the melting point of the sample for one hour, with the sample half melted. The triple point temperature was found to be $18.63 \pm 0.01^\circ\text{K.}$, which is also the value given by Clusius and Bartholome for normal-deuterium. Lewis and Hanson,¹¹ who worked with very small amounts of deuterium, reported a triple point of 18.66°K. for the normal mixture.

The triple point pressure was found to be 12.75 Int. cm., when corrected for the small amount of HD in the sample.

Heat of Fusion.—Two determinations were made of the heat of fusion, the results of which are given in Table II.

Our mean value of 47.07 ± 0.1 cal./mole for the heat of fusion of 97.8% ortho-deuterium agrees with the value, 47.0 ± 0.4 cal./mole, reported by Clusius and Bartholome² for normal deuterium.

(7) K. Clusius and K. Hiller, *Z. physik. Chem.*, **B4**, 158 (1929).

(8) Our calculations have been carefully rechecked and compared with preliminary data taken in this Laboratory five years ago, with which they are in agreement. Our excellent agreement (*cf. seq.*) with the statistical entropy is further evidence of the reliability of our heat capacity data. Professor Clusius has informed us, by personal communication, that some systematic error may have occurred in their calculations of the heat capacities of the liquid, but that he unfortunately has no opportunity to check this matter since his data books were destroyed during the war.

(9) R. B. Scott and F. G. Brickwedde, *Phys. Rev.*, **48**, 483 (1935).

(10) F. G. Brickwedde and R. B. Scott, *ibid.*, **55**, 672 (1939).

(11) G. N. Lewis and W. T. Hanson, *THIS JOURNAL*, **56**, 1687 (1934).

TABLE II

| HEAT OF FUSION OF 97.8% ORTHO-DEUTERIUM | | | | |
|---|---------------------|-------------------------------|----------------------|------------------------|
| Sample size, mole | Temp. interval, °K. | Total heat input, (cor.) cal. | $\int C_p dT$, cal. | ΔH , cal./mole |
| 4.6261 | 18.12-19.69 | 250.63 | 32.94 | 47.06 |
| 4.6595 | 18.19-19.49 | 246.74 | 27.37 | 47.08 |
| Mean value 47.07 ± 0.1 | | | | |

Heat of Vaporization. Preliminary Measurements by H. L. Johnston, W. E. Wallace, and C. B. Satterthwaite.—In 1945, preliminary measurements of the heat of vaporization of ortho-deuterium were made at this Laboratory with a predecessor of the present condensed gas calorimeter. The preliminary apparatus employed the same block, copper calorimeter, and thermostated gas buret now being used.⁴ It utilized a different cryostat, a smaller filling tube and a different resistance thermometer. The latter was made from an alloy of 75% gold, 12.5% copper and 12.5% silver and had a total resistance at room temperature of 1500 ohms, in contrast to the 300-ohm resistance of 99.85% gold now in use. The earlier thermometer proved somewhat erratic and necessitated the use of less sensitive thermocouple readings to make corrections for heat leak.

The deuterium for the preliminary investigation was the freshly prepared material, containing 99.7 atom per cent. D, that was subsequently stored and used in the current research. The results obtained are listed in Table III, wherein a correction of only 1% has been applied for the 0.6% HD in the sample.

TABLE III

| HEAT OF VAPORIZATION OF 97.8% ORTHO-DEUTERIUM, BOILING POINT 23.59°K., MOLECULAR WEIGHT, 4.032 (Determined by Johnston, Wallace and Satterthwaite) | | | |
|--|------------------------|---------|------------------------|
| Run no. | ΔH , cal./mole | Run no. | ΔH , cal./mole |
| 1 | 291.4 | 7 | 292.3 |
| 2 | 291.2 | 8 | 290.8 |
| 3 | 291.2 | 9 | 293.0 |
| 4 | 294.2 | 10 | Lost |
| 5 | 294.3 | 11 | 290.2 |
| 6 | 293.6 | 12 | 293.3 |
| Mean value 292.3 ± 1.5 | | | |

This Research.—Our recent determinations of the heat of vaporization of 97.8% ortho-deuterium, at its normal boiling point, are listed in Table IV, wherein a correction amounting to only 0.16% was applied for the 1.1 mole per cent. HD

TABLE IV

| HEAT OF VAPORIZATION OF 97.8% ORTHO-DEUTERIUM (THIS RESEARCH) | | |
|---|-------------------------|------------------------|
| Boiling Point 23.59°K., Molecular Weight 4.032 | | |
| Run | Amount evaporated, mole | ΔH , cal./mole |
| 1 | 0.22065 | 293.35 |
| 2 | .22026 | 293.21 |
| 3 | .21372 | 294.01 |
| 4 | .20957 | 294.76 |
| 5 | .21773 | 294.43 |
| 6 | .21576 | 293.84 |
| Mean value 293.93 ± 0.5 | | |

present in the deuterium. The HD vapor pressure data of Brickwedde and Scott¹⁰ were used in making the small correction; other corrections were the same as those applied for hydrogen.⁴

Clusius and Bartholome² obtained 302.3 ± 0.6 cal./mole for the heat of vaporization of normal deuterium at 19.65°K. This value corresponds to 299.0 cal./mole at 23.60°K. which is obtained when our heat capacity data for the liquid are used for the correction. The difference between this corrected value and our mean value of 293.93 ± 0.5 amounts to almost 2%. This discrepancy cannot be ascribed to the difference in the ortho and para composition present in each case since Brickwedde, Scott and Taylor¹² have shown that the variation between the heats of vaporization of normal and 20.4° equilibrium deuterium is only 0.0 ± 0.5 cal./mole.

Vapor Pressure of Liquid Ortho-deuterium.—

Vapor pressures were measured from the triple point (18.63°K.) to 23.72°K. by use of a mercury manometer having a 15-mm. bore. The data are presented in Table V wherein corrections have been applied for capillary depression, for temperature of the mercury and of the standard scale, for the acceleration due to gravity, and for the 1.1% HD content. These data fit the vapor pressure equation

$$\log p \text{ (mm.)} = 4.70099 - (56.7247/T) + 0.02478T \quad (1)$$

to within $\pm 0.013^\circ\text{K.}$, as is shown in the last column of the table. At a pressure of 760 mm., the calculated temperature is 23.590°K.

TABLE V

VAPOR PRESSURE OF LIQUID ORTHO-DEUTERIUM (97.8% ORTHO)

| T , °K. | P , mm. | $P_{\text{calcd.}} - P_{\text{obsd.}}$, mm. | $T_{\text{calcd.}} - T_{\text{obsd.}}$, °K. |
|--------------|--------------|---|---|
| 18.632 | 127.45 | -3.75 | -0.072 |
| 19.503 | 189.70 | -1.02 | + .013 |
| 20.503 | 275.90 | +1.03 | - .010 |
| 21.470 | 389.10 | +0.78 | - .006 |
| 22.372 | 525.47 | -0.91 | + .005 |
| 23.071 | 651.82 | -0.43 | + .003 |
| 23.673 | 779.70 | -0.98 | + .004 |
| 23.717 | 787.67 | +1.05 | - .004 |

The heat of vaporization at the boiling point was calculated from equation 1 as 294.4 cal./mole. The liquid volume used was taken from the data of Scott and Brickwedde,⁹ and the vapor values were obtained from the virial coefficients of deuterium determined earlier at this Laboratory.¹³ The calculated value agrees with our experimental value of 293.93 cal./mole to within 0.2%.

Entropy of 97.8% Ortho-deuterium.—Table VI summarizes the experimentally determined entropy of gaseous ortho-deuterium (97.8% ortho) at its normal boiling point, 23.59°K., and includes a correction to the ideal gaseous state and a correction for the entropy of mixing. The latter correction is based on the assumption that the entropy contributed to the equilibrium mixture formed at

20.4°K., from internal degrees of freedom, remained "frozen in" at the lowest temperature to which our measurements extended. This corresponds to the fourth possibility as applied by Johnston and Long³ to normal deuterium.

TABLE VI

EXPERIMENTAL ENTROPY OF 97.8% ORTHO-DEUTERIUM

| | |
|---|------------------------|
| 1 Solid, 0-13°K., Debye extrapolation ($\theta = 89$) | 0.448 \pm 0.03 |
| 2 Solid, 13-18.63°K. (graphical) | 0.681 \pm 0.01 |
| 3 Fusion, 18.63°K. (47.06/18.63) | 2.526 \pm 0.01 |
| 4 Liquid, 18.63-23.59°K. | 1.338 \pm 0.01 |
| 5 Vaporization, 23.59°K. (293.9/23.59) | 12.459 \pm 0.02 |
| Total calorimetric entropy | 17.452 \pm 0.08 |
| 6 Correction to the ideal gaseous state | 0.195 \pm 0.01 |
| 7 Frozen in entropy of mixing | 3.780 \pm 0.00 |
| | 21.43 \pm 0.09 e. u. |

The correction to the ideal gas state was made by use of the virial relationship

$$S_{\text{ideal}} - S_{\text{real}} (dB/dT)P \quad (2)$$

with the temperature coefficient of B taken from measurements in this Laboratory.¹³

The "frozen in" entropy of mixing was calculated from the equation

$$S_{\text{mixing}} = -R(0.978 \ln 0.1630 + 0.022 \ln 0.00244) \quad (3)$$

which recognizes that the 97.8% of ortho molecules carry a statistical weight of 6 while the 2.2% of para carry a total statistical weight of 9.

The corrected value 21.43 \pm 0.09 e.u., which represents entropy with nuclear spin included, compares with the spectroscopic value 21.35 ± 0.01 e.u. computed for the ideal gas. The excellent agreement between these two values confirms the supposition that solid deuterium behaves like solid hydrogen in "freezing in" the mixing entropy associated with its distribution between ortho and para states.

Acknowledgment.—We wish to acknowledge the assistance of Mr. E. M. Carr who assisted in taking data.

Summary

The heat capacities of solid and liquid ortho-deuterium (97.8%) have been measured and tabulated, for the temperature range 13.66 to 22.73°K. In addition, the pressure and the temperature at the triple point were determined as $18.63 \pm 0.01^\circ\text{K.}$ and 12.75 ± 0.5 Int. cm., respectively. Heats of fusion and of vaporization were found to be 47.07 ± 0.1 and 293.93 ± 0.5 cal./mole, respectively.

Vapor pressures were measured for the liquid range, and fitted accurately by the equation

$$\log P \text{ (mm.)} = 4.70099 - (56.7247/T) + 0.02478T$$

The entropy of the ideal gas at 23.59°K. and 1 atm. pressure totals 21.43 ± 0.09 e.u., with nuclear spin entropy included, which is in good agreement with the value of 21.35 ± 0.01 e.u., calculated from the spectra of deuterium.

(12) Brickwedde, Scott and Taylor, *J. Chem. Phys.*, **3**, 653 (1938).

(13) H. L. Johnston, David White and A. S. Friedman, unpublished data.