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

The Direct Determination of the Critical Temperature and Critical Pressure of Normal Deuterium. Vapor Pressures between the Boiling and Critical Points[1]

BY ABRAHAM SOLOMON FRIEDMAN, DAVID WHITE AND HERRICK L. JOHNSTON

Critical constants for pure normal deuterium have been obtained by a slight extrapolation from direct measurements on normal deuterium of 99.7 atomic-per cent purity. The corrected values are 38.35°K. and 16.432 atmospheres, respectively. Vapor pressures of 99.7% deuterium have been measured between 29°K. and the triple point. The vapor pressure of deuterium from the triple point to the critical point can be represented by the equation, $\log p_{(\text{atmospheres})} = 3.57979 - 74.2894/T - 0.029345T + 0.00047507T^2$. Critical constants of normal deuterium exceed those of normal hydrogen by 5.11° and 3.625 atmospheres, respectively.

Introduction

There have been no previous reported measurements of the critical constants of deuterium and accurate determinations of the vapor pressure[2] have been limited to temperatures below the boiling point. We have determined the critical temperature and critical pressure of normal deuterium with the apparatus, previously described, with which we made direct determinations of the critical constants of hydrogen. We have measured the vapor pressure of normal deuterium between the boiling and critical points in the same apparatus, which required about one cubic centimeter of liquid.

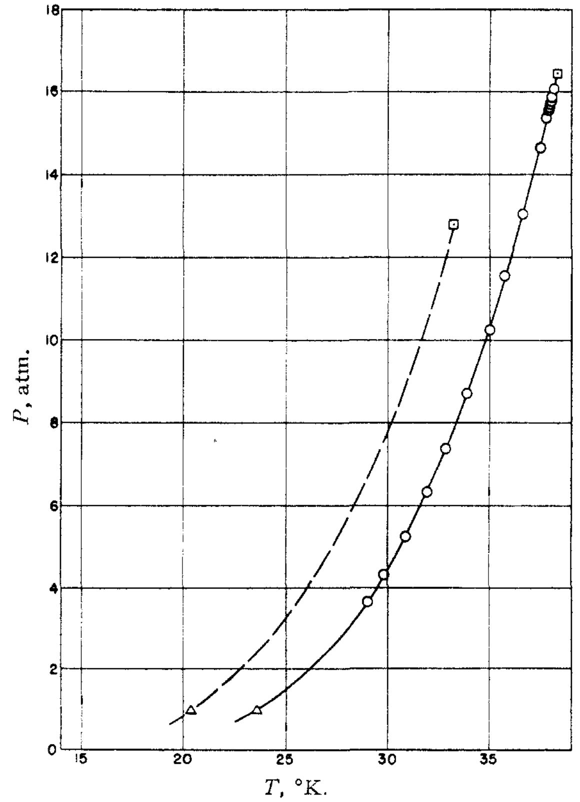

Fig. 1.—Comparison of the vapor pressure of deuterium with that of hydrogen for temperatures above boiling: – – – –, hydrogen curve; ——, deuterium curve; □, critical points; △, boiling points; ○, vapor pressure points for deuterium.

The deuterium that we employed was obtained from the Stuart Oxygen Company and represented by them to be of 99.7 atomic-per cent D, the balance being protium combined with deuterium in the form HD.

Because of the very long half-life for the conversion of para to ortho deuterium, in the liquid phase,[3] and the rapidity with which we were able to carry out our measurements, self conversion of para to ortho deuterium in the course of our experiments can be regarded as negligible.

Experimental Procedures

(1) **Vapor Pressure Measurements.**—The apparatus was first cooled to 29°K., with the aid of liquid hydrogen, and held at that approximate temperature until both temperature and pressure were constant for 10 minutes, to within limits of sensitivity, which amounted to ±0.002° in temperature and to less than 1 part in 30,000 in the pressure. The temperature and the pressure were then accurately read. The cell that contained the liquid deuterium was then heated to the next higher temperature and the equilibration and temperature and pressure determinations repeated. This procedure was followed, with decreasing temperature intervals, until the critical point was reached.

Temperatures were measured by means of a standard thermocouple which had been calibrated against a helium thermometer. The thermocouple calibration is believed accurate, in an absolute sense, to within 0.02°. Pressures were measured on a dead weight gage, of the type developed by F. G. Keyes.[4] The gage was calibrated by using the vapor pressure of pure carbon dioxide at the ice point as standard, and pressures were measured to 1 part in 10,000 within the range covered by these experiments.

Details of procedure were similar, in general, to those we employed for hydrogen, with a different apparatus.[5]

(2) **Critical Constants.**—The method employed in determining the critical constants by direct observation of the disappearance of the meniscus was the same as described in an earlier paper[6] except for the fact that we approached the critical point from only the low temperature side. This appeared justified since in our previous measurements with hydrogen we observed no significant differences in the approach from the low side (disappearance of meniscus) and the high side (reappearance of meniscus). To conserve our limited amount of deuterium we ran through the critical point only once.

It is of interest to note that no opalescence appeared at the critical point as the meniscus disappeared.

Experimental Results and Discussion

(1) **Vapor Pressure.**—The results of the vapor pressure measurements (uncorrected for the small concentration of HD) are shown in Table I. Table I also compares the experimental data

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

(2) F. G. Brickwedde, R. B. Scott and H. S. Taylor, *Natl. Bur. Standards J. Res.*, **15**, 463 (1935); *J. Chem. Phys.*, **3**, 653 (1935).

(3) Unpublished work from this Laboratory.

(4) F. G. Keyes, *Ind. Eng. Chem.*, **23**, 1375 (1931).

(5) D. White, A. S. Friedman and H. L. Johnston, THIS JOURNAL, **72**, 3927 (1950).

(6) D. White, A. S. Friedman and H. L. Johnston, *ibid.*, **72**, 3565 (1950).

TABLE I

THE VAPOR PRESSURE OF NORMAL DEUTERIUM

Run no.	Temp., °K.	Press. obsd., atm.	Equation (1) Press., atm.	ΔP obsd. − calcd.	ΔT obsd. − calcd.
Triple point[a]	18.72	0.1691	0.1692	−0.0001	0.00
[a]	21.00	.4239	.4320	− .0081	.04
[a]	22.00	.6033	.6128	− .0095	.04
[a]	23.00	.8371	.8398	− .0027	.01
Boiling point[a]	23.57	1.0000	1.0004	− .0004	.00
1	29.00	3.6988	3.6864	.0124	− .02
2	29.85	4.3644	4.3490	.0154	− .02
3	30.90	5.2747	5.2777	− .0030	.00
4	31.95	6.3265	6.3386	− .0121	.01
5	32.89	7.3895	7.4100	− .0205	.02
6	33.91	8.7122	8.7136	− .0014	.00
7	35.00	10.2530	10.283	− .030	.02
8	35.79	11.526	11.544	− .018	.01
9	36.65	13.062	13.045	.017	− .01
10	37.49	14.636	14.648	− .012	.00
11	37.81	15.357	15.297	.060	− .02
12	37.93	15.575	15.546	.029	− .01
13	37.97	15.639	15.630	.009	.00
14	37.99	15.701	15.672	.029	− .01
15	38.02	15.754	15.735	.019	.00
16	38.06	15.829	15.819	.010	.00
17	38.19	16.071	16.097	− .026	.01
18 Critical point	38.34	16.4215	16.420	.001	.00

[a] *Cf.* ref. 7.

with the results of our four-constant equation obtained by the method of least squares.

Equation 1

$$\log p_{(\text{atmospheres})} = 3.57979 - 74.2894/T - 0.0293457T + 0.00047507T^2 \quad (1)$$

represents the data to within 0.02°K., which is the absolute uncertainty in the temperature scale. This equation fits values computed from the Bureau of Standards vapor pressure equation[7] fairly well down to the triple point.

The isotopic effect on hydrogen vapor pressures above the boiling point is illustrated in Fig. 1 which compares our curve for hydrogen[5] with that for deuterium. Critical and boiling points are shown on the same diagram.

(2) **Critical Constants.**—The critical temperature and critical pressure were found to be 38.34°K. and 16.421 atmospheres, respectively. Correction for the 0.3 atomic per cent. of H would raise the critical temperature of pure deuterium to 38.35°K. if it be assumed that the critical constants change linearly with this composition, and would raise the critical pressure to 16.432 atmospheres.

It is interesting to note that the critical temperature of pure normal deuterium exceeds that of normal hydrogen by 5.11° and that its critical pressure exceeds that of hydrogen by 3.635 atmospheres.

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(7) H. W. Woolley, R. B. Scott and F. G. Brickwedde, *Natl. Bur. Standards J. Res.*, **41**, 379 (1948).

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[CONTRIBUTION FROM AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Determination of Diffusion Coefficients by Measurements of Surface Tension

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A new experimental method for the determination of diffusion coefficients has been developed. The process of diffusion of a surface active solute through a liquid in a calibrated capillary is followed by measurements of surface tension. The diffusion coefficient may be calculated by either an application of Fick's second law or an application of a heat conduction equation of Ingersoll and Zobel. The value of the diffusion coefficient for normal butyl alcohol in water as determined by this method is of the same order of magnitude as the values recorded in the literature.

The possibility of using the results of capillarimetric measurements of surface tension in the calculation of diffusion coefficients of surface-active solutes was suggested by Bigelow and Washburn.[2] The ordinary type of capillarimeter is not applicable to the making of pertinent measurements since the length of the liquid column through which diffusion occurs changes as the surface tension changes. This feature would lead to calculations of great complexity.

In other methods for the determination of surface tension as the drop weight methods, maximum bubble pressure method and others, the length of the diffusion column is variable or reduced to so small a value that calculations based on these measurements are generally invalidated by barriers to diffusion that may occur in the surface phase.[3]

For these reasons the manometric capillarimeter suggested by Ferguson[4] and used more recently by De Witt, Makens and Helz[5] seems almost uniquely qualified for the determination of diffusion coefficients. With this instrument, modified by calibration of the capillary throughout its length, it is possible to establish a constant column through which diffusion to the surface occurs. Measurements of surface tension afford a record of the varying concentration at a hypothetical plane very near the meniscus. This hypothetical plane is located at the point nearest the surface at which concentration is still unaffected by the "surface excess" that accumulates at the surface of solutions of surface-active substances. The capillary protrudes into the container so the assumption may be made that the concentration at one end of the column is constant. Therefore, the instrument is readily used in studies of diffusion in solution.

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[1] E. I. de Pont de Nemours and Co. Fellow, 1948–1949; Standard Oil Company Fellow, 1949–1950.

(2) Bigelow and Washburn, *J. Phys. Chem.*, **32**, 321 (1928).

(3) Ward and Tordai, *J. Chem. Phys.*, **14**, 453 (1946).

(4) Ferguson and Dowson, *Trans. Faraday Soc.*, **17**, 384 (1921).

(5) De Witt, Makens and Helz, THIS JOURNAL, **57**, 796 (1936).