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The Vapor Pressure of Deuterium Water from 20 to 230°

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Comparative measurements of the vapor pressures of ordinary water and deuterium water were undertaken in this extended range because similar comparative measurements were contemplated on the vapor pressures of saturated solutions and on the dissociation pressures of salt hydrates containing these two varieties of water.

The Material Used.—The deuterium water was prepared in this Laboratory in the manner previously reported.[1] After electrolysis the residue, which contained NaOD, was distilled three times as follows: first, after passing carbon dioxide in excess; second, after adding barium oxide to precipitate carbonate; and third, without addition of any reagent. This yielded a product of d^{25}_{25} 1.1079 as compared with 1.1074 as reported by others.[2] Each of the two experimental runs, A and B, utilized a different sample of deuterium water. The degree of dilution of these by ordinary water was estimated from melting point determinations performed upon the water after sealing it within the completed apparatus, yielding, for sample A, 3.76 ± 0.02° and, for sample B, 3.73 ± 0.03°, as measured by a Beckmann thermometer calibrated against a platinum resistance thermometer whose readings were good to 0.01°. Linear interpolation between 3.802 and 0.00°, taken as melting points[3] of deuterium and com-

mon water, respectively, indicated concentrations of D_2O of 98.9 and 98.1% for samples A and B, respectively. The observed values of vapor pressure difference were accordingly corrected by multiplying them by the ratios of 100 to these percentages.

Pressure.—Differential tensimeters of Pyrex glass were used, with mercury as manometric liquid. For temperatures up to 100°, where small differences of pressure were of greater importance, the manometer bore (apparatus A) was 12 mm., and readings were made with a cathetometer. For the higher temperatures, the manometer bore (apparatus B) was 8 mm., and readings were made against a millimeter scale without use of a telescope. Permanent gases were eliminated from the water in A by distilling the water to a portion of the apparatus cooled by solid carbon dioxide while the vacuum pump was in operation; and in B by the customary technique of boiling out. Permanent gas was likewise expelled from glass and from mercury by the customary techniques of heating, boiling and evacuation. After sealing off, when both sides of apparatus A were cooled by solid carbon dioxide, the pressure difference found was 0.02 mm. This was attributed to permanent gas, and the appropriate correction applied to the differential pressure readings. Essential absence of permanent gas from apparatus B was shown by the agreement of the differential pressure values near 100° with those yielded by apparatus A, both before and after heating to 228°. This also showed that the results were not affected to more than ±0.1% by the solution of substances from the glass which might lower the vapor pressure more on one side than on the other. Mercury pressures were reduced to 0° by use of the densities of mercury found in "International Critical Tables."[4] For the purposes of comparative study, we used the values of the vapor pressure of H_2O up to 100°

(1) H. S. Taylor, H. Eyring and A. A. Frost, *J. Chem. Phys.*, **1**, 823 (1933).

(2) Tronstad, Nordhagen and Brun, *Nature*, **136**, 515 (1935).

(3) V. K. La Mer and W. N. Baker, THIS JOURNAL, **56**, 2641 (1934).

(4) "International Critical Tables," Vol. II, p. 457.

as given in "International Critical Tables"[5] and above 100° as given by Smith, Keyes and Gerry.[6]

Temperature.—Up to 50° a water thermostat of 320 liters capacity was used, held constant to ±0.03°. Temperatures were measured to ±0.02° by use of a Reichsanstalt certificated thermometer after redetermination of the zero point. Near 100°, four measurements were made in apparatus A immersed in a thermostat of 11 liters water content. Temperatures were read on a Beckmann thermometer whose scale was known to 0.02° by measurement of the boiling point of water at different barometric pressures. Above 100°, the tensimeter B was immersed in an oil-bath of 4 liters capacity. Temperatures were measured to ±0.1° by means of completely immersed Anschütz thermometers whose readings were converted to the scale of the Bureau of Standards by comparison with certificated Allihn thermometers, whose zero points were determined after preheating. To secure uniformity of temperature, violent stirring was especially necessary at the higher temperatures. Identical pressure values were obtained upon doubling the speed of the stirrer, and also upon reversing its direction. Inspection of Table II will show that error in pressure measurement was throughout several fold more important than that due to the uncertainty of absolute temperature reported above.

Results.—The experimental results are tabulated in the first three columns of Table I. In order to obtain a smooth curve for purposes of interpolation, we were reluctantly obliged to employ a five-constant equation

$$\log \frac{p_{D_2O}}{p_{H_2O}} = -16.998671 + \frac{268.8426}{T} + 7.4971604 \log T - 9.761107 \times 10^{-3} \times T + 4.4288 \times 10^{-6} \times T^2 \quad (1)$$

Simpler equations gave values falling outside our estimated experimental error. Column 4, Table I, gives the differences of pressure at the temperatures of experiment as derived from this equation and column 5 shows the closeness of fit.

TABLE I

VALUES OF p_{D_2O}-p_{H_2O} DETERMINED EXPERIMENTALLY

Observation number	T, °C.	$p_{D_2O} -$ p_{H_2O}obsd., mm.	$p_{D_2O} -$ p_{H_2O}calcd., mm.	Δpobsd. $-$ Δpcalcd. mm.
A1	25.0	− 3.13	− 3.18	+0.05
A2	30.0	− 3.97	− 4.01	+ .04
A3	50.0	− 9.14	− 9.14	.00
A4	100.0	−37.7	−37.7	.0
B1	122.7	−55.5	−56.4	+ .9
B2	143.2	−73.4	−72.7	− .7
B3	166.7	−87.0	−84.9	−2.1
B4	181.9	−83.9	−84.5	+0.6
B5	204.2	−61.0	−61.3	+ .3
B6	228.7	+22.4	+22.0	+ .4

The values tabulated in Table II for each 10° interval are derived from this equation, with ex-

(5) "International Critical Tables," Vol. III, p. 210.

(6) L. B. Smith, F. G. Keyes and H. T. Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 137 (1934).

trapolated values in italics. For purposes of interpolation, log p_{D_2O} and $1/T_A$ should be used as variables. Column 5 of this table shows the values of Lewis and Macdonald.[7] These authors give the normal boiling point of deuterium water as 101.42° while our equation yields 101.40 ± 0.016°. We find the temperature at which the vapor pressure of these two varieties of water is identical as 224.3°, which may be within 0.5° of the truth. Urey and Teal[8] estimated this temperature as about 160° using the data of Lewis and Macdonald;[7] while Riesenfeld and Chang's[9] estimate was about 200°.

TABLE II

VAPOR PRESSURES OF D₂O CALCULATED FROM EQUATION 1 AND COMPARED WITH THE RESULTS OF LEWIS AND MAC-DONALD

T, °C.	$p_{D_2O} - p_{H_2O}$ (M. & M.), mm.	p_{D_2O} (M. & M.), mm.	Estimated limit of exptl. error, mm.	$p_{D_2O} - p_{H_2O}$ (L. & M.), mm.
10	− 1.46	7.75	±0.1	
20	− 2.48	15.06	± .1	− 2.3
30	− 4.01	27.81	± .1	− 3.9
40	− 6.19	49.13	± .1	− 6.1
50	− 9.14	83.37	± .1	− 9.1
60	−12.97	136.41	± .2	−13.1
70	−17.8	215.9	± .3	−18.0
80	−23.5	331.6	± .3	−23.9
90	−30.2	495.6	± .4	−30.7
100	−37.7	722.3	± .4	−38.4
110	−45.7	1028.9	± .7	−47.0
120	−54.1	1435.1	±1.0	
130	−62.5	1963.8	±1.0	
140	−70.4	2640.4	±1.5	
150	−77.3	3493.4	±2	
160	−82.6	4553.9	±2	
170	−85.6	5856.1	±2	
180	−85.1	7436.9	±2	
190	−80.1	9336.3	±2	
200	−68.9	11596.3	±2	
210	−49.1	14262.5	±2	
220	−17.9	17384.6	±2	
230	+28.8	21014.6	±2	
240	+96.2	25207.3	±5	

Latent Heat of Vaporization.—From the simplified approximate form of the Clapeyron-Clausius equation and equation (1) we can calculate the difference between the latent heats of vaporization of D₂O and H₂O as follows

$$L_{D_2O} - L_{H_2O} = 2.303 \times RT^2 \frac{d \log (p_{D_2O}/p_{H_2O})}{dT} = -1230 + 14.90 \times T - 0.04466 \times T^2 + 4.052 \times 10^{-5} \times T^3 \quad (2)$$

(7) G. N. Lewis and R. T. Macdonald, THIS JOURNAL, **55**, 3057 (1933).

(8) H. C. Urey and G. K. Teal, *Rev. Mod. Phys.*, **7**, 34 (1935).

(9) E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B28**, 408 (1935).

Values for $L_{D_2O} - L_{H_2O}$ calculated from this equation are given in Table III. The estimated limits of error given in Table III are derived from the estimated limits of error of the vapor pressure results. Since the necessary simplifying assumptions depart further from the facts with rising

TABLE III

VALUES FOR THE DIFFERENCE OF THE LATENT HEATS OF VAPORIZATION OF HEAVY AND LIGHT WATER, $L_{D_2O} - L_{H_2O}$, CALCULATED FROM EQUATION 2

T, °C.	$L_{D_2O} - L_{H_2O}$. g. cal. per mole	Estimated limit of exptl. error. g. cal. per mole
40	30_0	± 20
60	27_5	± 10
80	24_6	± 10
100	21_6	± 10
120	18_6	± 15
140	15_9	± 16
160	137	± 10
180	12_1	± 10
200	113	± 5
220	115	± 4

temperature, the degree of trust we can place upon these latent heat differences is measured by the degree of similarity of behavior of the two forms of water.

The value for this difference reported by Lewis and Macdonald[7] was based on assumed rectilinearity of the log p_2/p_1 against $1/T$ graph between 20 and 90°, and their value agrees with ours for a temperature near 70°.

Summary

The vapor pressures of deuterium water have been compared with those of ordinary water in the range 20 to 230°. The vapor pressures are identical at about 224°.

The differences of the latent heats of vaporization are evaluated approximately from the changes of vapor pressure over the same temperature range.

Sonic Activation in Chemical Systems: Oxidations at Audible Frequencies

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During the past few years there have appeared numerous reports of oxidations, as well as other types of chemical reactions, induced or accelerated by intense ultrasonic vibrations.[2-4]

Schmitt, Johnson and Olson[3] observed the liberation of iodine from potassium iodide solution. They further reported that "upon the addition of radiated potassium bromide or chloride solution to starch–iodide reagent, a blue color developed which indicated either the oxidation of the bromide and chloride ions or that some other substance is produced in the presence of these salts which oxidizes the iodide ion instantaneously. Radiated distilled water produced the effect to a less marked degree." Hydrogen peroxide was found in small amount, insufficient to account for the observed rate of oxidation of halogen or of sulfide. Ozone production, if any, was in amounts too small to be detectable and consequently could not be considered as the oxidizing

(1) Fellow of the Josiah Macy, Jr., Foundation. Now at the Montefiore Hospital, New York City.
(2) Richards and Loomis, THIS JOURNAL, 49, 3086–3100 (1927).
(3) Schmitt, Johnson and Olson, ibid., 51, 370 (1929).
(4) Szu-Chik Liu and Hsien Wu, ibid., 56, 1005 (1934).

agent. It was further found that dissolved oxygen gas was essential to the oxidations and it was suggested that the gas was activated in association with ultrasonic cavitation. Direct absorption of energy by the molecules in solution was believed to be inconsistent with results that were obtained under pressures sufficient to inhibit visible cavitation.

Liu and Wu[4] confirmed the findings of Schmitt, Johnson and Olson, in the case of potassium iodide oxidation by ultrasonic radiation, with respect to the essential presence of dissolved oxygen gas and to the insufficient production of hydrogen peroxide or ozone to account for the observed effects. Liu and Wu presented experimental evidence in favor of the view that activation of oxygen gas is associated with cavitation. It is questionable, however, whether the conditions of radiation in a gel, whereby cavitation is suppressed and no oxidation is observed, are otherwise sufficiently comparable to justify without further evidence their conclusion concerning the influence of cavitation.