

Vapor Pressure of Heavy Water at 283-363 K

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New data for the logarithmic vapor-pressure ratio for water, $\ln R = \ln [P(\text{HOH})/P(\text{DOD})]$, are presented at 57 temperatures and critically compared to extant data. Numerical analysis results in an equation valid from 283 to 363 K with an uncertainty of $\sim 0.3\%$ in $\ln R$; in $R = 44220/T^2 - 124.90/T + 0.0684$. Since $\ln R$ itself varies between 0.2 and 0.06 in that range, and because $P(\text{HOH})$ is known to better than 0.01% over the bulk of the range, it follows that $P(\text{DOD})$ is established to $\sim 0.03\%$, at least above 293 K, and not quite as well below 293 K. The new values that we recommend for $\ln R$ lie significantly above currently accepted values.

Introduction

Continuing interest in the thermodynamic properties of isotopic waters and their solutions, particularly solutions in D_2O (1, 2), makes it useful to have as accurate and precise an understanding of the vapor pressure of this material as is possible. The data available in the literature (3-17) are quoted in Table I. In the temperature range of interest to us, 263-373 K, only four groups (those at Budapest, Knoxville, Los Alamos, and Western Australia) have reported data since World War II. Table II reviews previously reported correlating equations for the vapor pressure of D_2O or the logarithmic ratio, $\ln R$. All but two extend from near the triple point to close to the critical temperature. The equations reflect the relatively high precision and good agreement from laboratory to laboratory for the high-temperature data (i.e., those above 100 °C (3-17)). At lower temperatures the measurements become more difficult. Scatter in the data increases markedly, and differences between laboratories become larger.

As a part of our program of measurement of the thermodynamic properties of solutions in HOH and DOD, we have recently noted small but significant differences between pure solvent calibrating runs for $\ln R$ and recommended smoothing equations (Table II), including the recent Hill-MacMillan equation (22). We have therefore made new measurements of $\ln R$. The object of the present paper is to review the available vapor-pressure data for liquid D_2O below the normal boiling temperature, report data complementing those already available, and present a correlating equation for the vapor-pressure isotope effect for temperatures up to 363 K.

Between the ice and normal boiling points the vapor pressure of D_2O or H_2O changes by more than 2 orders of magnitude. The vapor-pressure ratio, $P(\text{H}_2\text{O})/P(\text{D}_2\text{O})$, however, only varies from 1.2 to 1.06. For this reason, and also because it is convenient to present the molecular theory of condensed-phase isotope effects (1, 23) in a form which leads directly to the calculation of the logarithmic ratio, $\ln R = \ln [P(\text{H}_2\text{O})/P(\text{D}_2\text{O})]$, the data are reported in terms of $\ln R$. To anticipate, we find that our analysis establishes $\ln R$ with a precision of $\pm 0.2\%$ between 0 and 100 °C. Further we set unresolved systematic errors at no more than an additional $\pm 0.1\%$. In the range 25-90 °C the vapor pressure of water is known to better than 50 ppm (parts per million) (24, 25). Since $\ln R$ is ~ 0.1 over that range, the resulting uncertainty in $P(\text{D}_2\text{O})$ as calculated from ref 24 or 25 and in R is $\sim 0.03\%$.

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Table I. Measurements of $\ln [P(\text{HOH})/P(\text{DOD})]$

ref (year)	authors	temp range, K	method ^a
3 (1933)	Lewis and McDonald	293-383	M
4 (1936)	Miles and Menzies	293-510	DM
5 (1936)	Riesenfeld and Chang	293-500	DM
6 (1939)	Niwa and Shimazaki	277-286	DM
7 (1954)	Combs, Googin, and Smith	283-328	GS
8 (1956)	Oliver and Grisard	481-643	DM
9 (1962)	Rivkin and Akhundov	548-638	M
10 (1966)	Kiss, Jakli, and Illy	233-283	DM
11 (1968)	Jones	277-387	DM
12 (1970)	Liu and Lindsay	379-573	M
13 (1972)	Pupezin, Jakli, Jancso, and Van Hook	273-363	DC-I
14 (1973)	Besley and Bottomley	273-298	M
15 (1978)	Bottomley	261-275	DC-I
16 (1980)	Jakli and Jancso	280-361	DC-II
17 (1970)	Jakli and Van Hook	288-353	DC-I, -II
(1980)	Jakli and Van Hook (present work)	279-353	DC-II, -III

^a M = manometry, measurement of total pressure. DM = differential manometry, measurement of ΔP . GS = gas-saturation method. DC-*j* = differential capacitance manometry; calibration method *j* (see text).

Table II. Vapor-Pressure Equations for DOD

ref (year)	authors	temp range, K
18 (1957)	Whalley	293-401
19 (1959)	Baker	277-644
20 (1963)	Elliot	277-644
13 (1972)	Pupezin, Jakli, Jancso, and Van Hook	268-353
1 (1974)	Jancso and Van Hook	268-353; 353-623
21 (1974)	Tanishita et al.	277-644
22 (1979)	Hill and MacMillan	273-644
(1981)	Jakli and Van Hook (present work)	283-363

Experimental Section

Laboratory-distilled water was treated with basic potassium permanganate and then redistilled 2 times in a glass apparatus. Heavy water obtained from Merck and Co. (analytical grade) was used without further purification. H/D analysis was made from the densities by using a Mettler-Paar densitometer (26). Differential pressures $P(\text{HOH}) - P(\text{DOD})$ and the absolute H_2O pressures, $P(\text{HOH})$, were measured in the University of Tennessee differential vapor pressure apparatus previously described (13). In this apparatus in its 1980 configuration, the temperature is controlled to ca. ± 0.0003 K by using a Tronac PTC-40 controller. The temperature is measured by using a platinum resistance thermometer calibrated in our laboratories (27) and a G2 Mueller bridge and coincides with IPTS to within ± 0.005 K. That calibration is regularly checked. $P(\text{H}_2\text{O})$ and $\Delta P = P(\text{H}_2\text{O}) - P(\text{D}_2\text{O})$ are measured by differential capacitance manometry using Datametrix 521 and 531 transducers with a 1018 controller/readout unit. The precision of the measurement is determined by the capacitance manometry and is found to be $\sim 0.2\%$ of $\Delta P/P$. We have determined that the accuracy of the measurements is limited by the procedures employed to calibrate the capacitance manometers. Measurements of $P(\text{HOH})$ were consistent with the accepted values

within our precision; the smoothed literature values were used in the calculation of $\ln R$ from the observed pressure differences.

For the measurements reported in this paper, the capacitance manometer calibration was carried out in three independent ways. In method I the gages were calibrated by mercury manometry over the pressure range 1333 Pa to 101 kPa by using dry nitrogen gas as the pressure-transmitting fluid. The precision of the calibration, ca. ± 2 Pa, varies from $\sim 0.2\%$ (low-pressure end) to significantly less than 0.1% above 10 kPa. It was this calibration technique which was employed by Pupezin, Jakli, Jancso, and Van Hook (13) some years ago. Method I, however, fails to consider the effect of the dielectric constant of the vapor on the response of the differential capacitance manometers; therefore, in method II we calibrated the gages against the vapor pressure of water (i.e., in effect against our thermometer which was employed to define $P(\text{HOH})$) (24, 25). The calibration of the ΔP gage therefore ranges from 611.7 Pa (triple point) on up to a useful maximum around 4 kPa. We note several difficulties with method II. First the lower limit of the calibration is at an inconveniently high pressure (611 Pa). Second, there is a significant difference between the recently recommended triple-point pressure, 611.7 Pa (28), and that calculated from accepted equations defining the vapor pressure of water vs. temperature, 611.2 Pa (24, 25). The difference amounts to an uncertainty of 0.1% at the triple point. Finally the ΔP gage is exposed to water vapor on only one side of the membrane, while in the experiment it has water vapor on both sides, albeit at slightly different pressures. We therefore made an additional check on the calibration (method III) by measuring differences generated between water and aqueous solutions of NaCl at appropriate concentrations. The pressure differences can be calculated within the necessary precision from the well-established osmotic coefficients (29). Technique III has the advantage of exposing both sides of the gage to water vapor during calibration, just as they are in the experiments themselves.

Results

Values of $\ln R = \ln [P(\text{HOH})/P(\text{DOD})]$ at 57 temperatures as obtained from measured ΔP and $P(\text{HOH})$ values for three separate runs (using different samples of HOH and DOD) and corrected to the value expected for 100% DOD using Raoult's law are reported in Table III.

In the data analysis we made least-square fits of the information in Table III by using the functional form

$$\ln R = A/T^2 + B/T + C \quad (1)$$

A , B , and C are constants which can be interpreted in terms of the molecular theory of isotope effects in condensed phases (1, 23). Large-scale deviation plots of the present data and that previously reported (especially ref 7, 11, 13, 14, 16, 17) demonstrated that the present data joined smoothly with the Besley-Bottomley (BB) data (14) which are over the range 4–25 °C. The BB data show excellent precision (ca. $\pm 0.2\%$) across this entire temperature range. In contrast, the data that we report, which show a precision of ca. $\pm 0.2\%$ above 30 °C, degrade somewhat toward lower temperatures; at 10 °C the precision is more nearly 0.5% . At any rate, because of the excellent agreement between the two data sets in the region of overlap, we have elected to report a single smoothing equation obtained by least-squares analysis of the 37 BB data points together with the 57 points from Table III. Each data point was assigned unit weight. The correlating equation, eq 2, is valid over the range $10 < t < 90$.

$$\ln R = (4.422 \pm 0.095) \times 10^4 / T^2 - (124.9 \pm 6.1) / T + (0.0684 \pm 0.0098) \quad (2)$$

Table III. Vapor-Pressure Isotope Effects; $\ln R = P(\text{HOH})/P(\text{DOD})$

t , °C	$\ln R$	t , °C	$\ln R$
Sample 1			
6.88	0.1862	42.70	0.1162
10.94	0.1759	46.86	0.1099
15.00	0.1670	51.07	0.1039
19.03	0.1588	55.07	0.0984
23.06	0.1505	59.27	0.0928
26.98	0.1432	63.46	0.0877
30.98	0.1357	67.58	0.0827
34.91	0.1289	71.71	0.0782
38.95	0.1221		
Sample 2			
10.07	0.1812	48.07	0.1081
10.15	0.1807	52.30	0.1021
14.30	0.1698	56.35	0.0965
18.42	0.1608	60.58	0.0912
22.49	0.1522	64.53	0.0863
26.82	0.1438	68.50	0.0817
31.08	0.1358	72.37	0.0773
35.40	0.1283	76.27	0.0732
39.54	0.1215	80.06	0.0690
44.02	0.1143		
Sample 3			
12.36	0.1724	54.78	0.0989
12.36	0.1730	58.82	0.0935
16.50	0.1635	62.81	0.0885
20.69	0.1555	66.81	0.0839
24.98	0.1470	70.74	0.0792
29.39	0.1388	74.67	0.0751
33.58	0.1312	78.47	0.0711
38.10	0.1238	82.27	0.0674
42.25	0.1170	85.82	0.0639
46.34	0.1107	89.54	0.0606
50.43	0.1049		

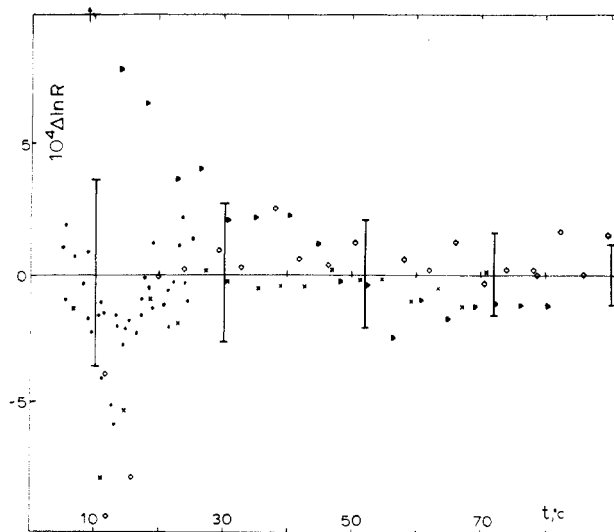


Figure 1. Difference plot of eq 2 and data in Table III or from Besley and Bottomley (14): (●) Besley and Bottomley (14); (×) present data—run 1; (▽) present data—run 2; (◇) present data—run 3; (I) $\pm 0.2\%$.

For this fit, $\sum_{i=1}^{94} \sigma_i^2 = 1.9 \times 10^{-7}$. A deviation plot of the present data points and those of BB is given in Figure 1. It is clear from the figure that our estimate of precision for this fit ($\pm 0.2\%$) is reasonable. When one uses the Wexler-Greenspan (24) equation for $P(\text{HOH})$, a relation for the vapor pressure of $P(\text{DOD})$ is readily obtained

$$\ln P(\text{DOD}) = -A/T^2 + (D - B)/T + (E - C) + FT + GT^2 + H \ln T \quad (3)$$

where $A-C$ are taken from the present work ($A = 4.422 \times 10^4$, $B = -124.9$, and $C = 0.0684$) and $D-H$ are from ref 24

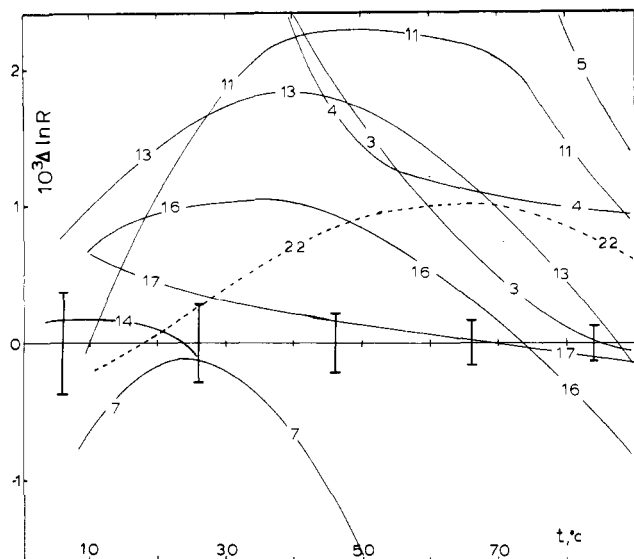


Figure 2. Difference plot of eq 2 and literature vapor-pressure isotope effects. The numbers on the lines refer to literature citations at the end of the text. The dotted line is for the correlating equation recently presented by Hill and MacMillan (22). The error bars indicate $\pm 0.2\%$.

($D = 6898.2434$, $E = 59.38385$, $F = -5.797662 \times 10^{-3}$, $G = 6.2223854 \times 10^{-6}$, and $H = -4.7406885$). Pressures calculated from eq 3 have units of pascals. The expression is limited to the same range of temperatures as eq 2.

In Figure 2 we present a difference plot between eq 2 and our fits of eq 1 to various experimental data in the literature. Because $P(\text{HOH})$ has been established with much higher precision than the ratio R , the deviations also measure the logarithmic differences of $P(\text{DOD})$ which are nearly equal to the fractional deviations. The 0.2% error bars are also shown, as are the differences between the recent Hill-MacMillan (22) correlating equation and eq 2. We have already referred to the excellent agreement between the present data and those of Besley and Bottomley (14). It is interesting to note that agreement between eq 2 and Combs, Googin, and Smith (7) is excellent (within 0.3%) between 10 and 35 °C. These authors employed a vapor-saturation method (10–55 °C) which is expected to become less reliable toward the high-temperature end of the experiments. Excellent agreement (0.2–0.3%) is also displayed between the present fit and a fit to a single run (19 points) made by one of us in Knoxville in 1970 (17). This run employed differential capacitance manometry but with an entirely different set of transducers from those currently used in our apparatus. Agreement with the set of runs on the differential capacitance manometer in Budapest (16), while not quite as good, is within 0.5% over the bulk of the range from 0 to 90 °C and is never more than 0.8% anywhere in that range. The present experiments show that the smoothing equation given by Pupezin, Jakli, Jancso, and Van Hook (13) is as much as 2% low. Smoothed equations based on the data

of Jones (11), Miles and Menzies (4), Lewis and McDonald (3), and Riesenfeld and Chang (5) are even lower.

Remarks. Since isotopic substitution generally results in significant but small changes in physical properties, it is appropriate to express isotope effects experimentally and theoretically in terms of differences or ratio equations. The equation that we present as eq 2 predicts a vapor-pressure isotope effect higher than all previous work with the exception of ref 7 and 14. However, since H_2O is nearly ubiquitous in laboratory air, apparatus walls, etc., most common systematic errors will tend to lower $\ln R$ from its true value. The present correlating equation shows internal consistency at $\sim 0.2\%$ precision. We are aware of no possible source of systematic error which should increase this by more than an additional 0.1%. We therefore conclude that the vapor-pressure isotope effect for the system $\text{H}_2\text{O}/\text{D}_2\text{O}$ is now established over the range 10–90 °C (283–363 K) with an accuracy of 0.3%.

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