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Vapor Pressures of Tritium Oxide and Deuterium Oxide.
Interpretation of the Isotope Effect.*

W. M. Jones *University of California*
Los Alamos Scientific Laboratory, Los Alamos, New Mexico

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MASTER

Abstract

Measurements are reported on the difference in vapor pressures of H₂O and T₂O (264 to 387°K) and of H₂O and D₂O (277 to 387°K). The relative vapor pressures of the pure liquids are represented by $\ln (p_{\text{H}_2\text{O}}/p_{\text{T}_2\text{O}}) = (-103.87 \pm 0.57)/T + (46480 \pm 210)/T^2$ and $\ln (p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}}) = (-70.87 \pm 0.43)/T + (33630 \pm 160)/T^2$. The boiling points of T₂O and D₂O are 101.51 and 101.42°C. Isotopic differences in heats of vaporization are given from 10 to 120°C and triple point temperatures and pressures are summarized. The vapor pressure crossover temperatures are D₂O-T₂O, 116.2 ± 0.5°C; H₂O-T₂O, 190 ± 10°C (estimated); H₂O-D₂O, 220.7 ± 0.1°C. (previously determined). Estimates of the parameters in the above equation for H₂O-D₂O, using Raman and inelastic neutron scattering spectra and Bigeleisen's formulation of the vapor pressure isotope effect, agree satisfactorily with the experimental values. Ratios of corresponding parameters in the above two equations agree with theory.

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INTRODUCTION

This paper presents vapor pressure data on liquid and solid T_2O and on liquid D_2O . Some derived thermodynamic properties will be compared with those of H_2O . Ratios of isotopic vapor pressures are fitted to a two parameter theoretical equation which has been successfully used by Bigeleisen.¹ Estimates of these parameters which utilize Raman and inelastic neutron scattering data on liquid H_2O and D_2O agree satisfactorily with the experimental values. The work on D_2O was done to provide a check with previous work² and to obtain vapor pressure data on all three isotopes with the same apparatus. After completion of the present experimental work data on the vapor pressure of T_2O were reported by Popov and Tazetdinov.³

EXPERIMENTAL

Apparatus

The differences in vapor pressures of H_2O and T_2O and of H_2O and D_2O were determined in identical differential tensimeters (Fig. 1). The tensimeter limbs were made of 0.500 inch I.D. precision bore tubing. Tensimeters were conditioned at 100°C with preliminary samples of isotopic waters. In order to minimize radiolytic gas, only 0.07 cc T_2O was used; 0.07 cc of H_2O and D_2O were also used. An isotopic water was condensed into the 1 cc bulb on its side of the tensimeter through a silicone-greased stopcock. Mercury was pushed through the stopcock bore into a 5 cm length of 1 mm capillary tubing in order to isolate the isotopic water from the stopcock. The ground joints by which the tensimeter could be attached to the vacuum system were capped for protection against the thermostat mineral oil. Black-white interfaces (Lamicoid engraving stock), adjustable from

outside the thermostat, were located behind the menisci to facilitate their measurement. Illumination was through the transparent cover of the thermostat. Meniscus positions were estimated to 0.001-0.002 cm Hg with a Gaertner cathetometer through a double-windowed port in the thermostat. The temperature of the insulated 11 liter thermostat was constant to $\pm 0.003^{\circ}\text{C}$ and was measured with a G-2 Mueller bridge and a platinum resistance thermometer calibrated by the National Bureau of Standards. Measured temperatures were in $^{\circ}\text{C}$, International Temperature Scale of 1948, and were converted to the corresponding absolute scale by adding 273.15. The thermometer was located between the 1 cc bulbs of the tensimeter. For measurements below room temperature these bulbs were well-immersed in a single dewar vessel containing a suitable organic substance which was at its melting point and occasionally stirred.

Materials and Analysis

The H_2O had been distilled in all-quartz apparatus. D_2O vapor from a stock of liquid D_2O (Stuart Oxygen Co.) was condensed and distilled into the tensimeter. Portions of vapor from the stock in relative amounts 1:4:13, the last of which corresponded to the amount used in the vapor pressure measurements, were taken on separate occasions, completely reduced with magnesium (450°C) and analyzed on a Consolidated-Nier Model 201 Mass Spectrometer. The magnesium had been conditioned by repeated reductions of D_2O , and the mass spectrometer had been repeatedly baked and conditioned with D_2 . The deuterium atom fraction N_D was 0.9901 ± 0.0002 and showed no trend with sample size. Five fillings of D_2O were used. After one series, used for several measurements but not at high temperatures, the D_2O was

decomposed to give $N_D = 0.9893$. After another long series, with many high temperature runs, N_D was found to be 0.987. On the basis of these measurements and the history of each D_2O filling a value of N_D in the range 0.990-0.987 was assigned to each vapor pressure measurement, with an uncertainty of about 0.001. All the above values of N_D include a correction of 0.0007 for hydrogen introduced by the magnesium. This was estimated from a total drop of 0.0016 in N_D obtained when (1) mass spectrometrically analyzed D_2 was converted to D_2O with conditioned CuO , and (2) this D_2O was reduced with magnesium to D_2 which was reanalyzed. An error of 0.001 in N_D leads in the worst case (highest temperature) to an error of 0.005 cm Hg in $p_{H_2O}^O - p_{D_2O}^O$.

T_2O was prepared by oxidizing mass spectrometrically analyzed T_2 at $400^\circ C$ with iron oxide in an iron-iron oxide mixture which had been conditioned with T_2-T_2O . The reaction was brought to completion by trapping the T_2O with liquid nitrogen. At the end of a series of vapor pressure measurements the same system was used to reduce T_2O to T_2 for mass spectrometer analyses. The reduction was made complete by removing the T_2 through a palladium valve. N_T was found to decrease by 0.0028 ± 0.0006 when analyzed T_2 was converted to T_2O and the latter reduced to T_2 for reanalysis. Half of this decrease was assigned to the oxidation and half to the reduction step. The composition of the T_2O was thus known at the beginning and end of a series of vapor pressure measurements, and an N_T was assigned to each measurement with an uncertainty of about 0.001. The total range of N_T was from 0.994 to 0.986 but the range for any one of the three series was less than 0.003. The decrease in N_T in the oxidation or reduction step was later reduced from 0.0014 to 0.0009 by Maxwell Goldblatt of this laboratory in

connection with the measurement of the density of liquid T_2O .⁴ The absolute accuracy of the method in the analysis of liquid D_2O under carefully controlled conditions has been shown to be 0.01-0.02%.⁵

Procedure and Calculations

In H_2O - T_2O measurements the T_2O was freed from radiolytic gas before a run by cycles of melting, freezing at CO_2 temperature, and pumping. Check was frequently made for an essentially zero pressure difference when both waters were frozen with CO_2 . The tensimeter was then placed in the thermostat.⁶ Pressure measurements were usually continued for about an hour. The tensimeter was removed from the bath, the H_2O and T_2O were frozen in CO_2 , and the pressure of radiolytic gas was measured. This pressure, after correction to the bath temperature and the volume of the T_2O side of the tensimeter during the vapor pressure run, was added (since the vapor pressure of H_2O is greater than that of T_2O here) to the observed pressure difference extrapolated to the time of withdrawal of the tensimeter from the bath. The radiolytic pressure correction was usually less than 0.050 cm Hg but occasionally as large as 0.100 cm Hg.^{7, 8} Corrections were made for capillary depression⁹ and pressure differences were reduced to international cm Hg using the density of mercury¹⁰ at bath (or room) temperature and the local and standard gravitational accelerations, 979.132 and 980.665 cm sec⁻², respectively. This corrected Δp_c was divided by N_T to get Δp^0 , the difference in vapor pressures of pure H_2O and T_2O .¹¹ The effect of partial vaporization in changing the composition of the liquid was negligible.

Procedure and calculations for H_2O - D_2O experiments were similar but simpler.

Values of Δp° are given in Tables I and II and were combined with vapor pressures of H_2O^{13} to obtain the parameters in Eqns. (1) and (2)

$$\ln (p_{H_2O}/p_{T_2O}) = (-103.87 \pm 0.57)/T + (46480 \pm 210)/T^2 \quad (1)$$

$$\ln (p_{H_2O}/p_{D_2O}) = (-70.87 \pm 0.43)/T + (33630 \pm 160)/T^2 \quad (2)$$

The number of significant figures in the parameters corresponds to a precision of 0.002 cm Hg or less in a calculated Δp° . The parameters in Eqns. (1) and (2) were determined by a least squares procedure, programed for an IBM 7090 computer by Dr. Aaron Goldman and utilizing the generalized least squares code of Moore and Zeigler.¹⁴ Parameters were chosen by minimizing $\sum_1 (\Delta p^\circ_{\text{exp}} - \Delta p^\circ_{\text{calc}})^2$. This was done because Δp is the experimental quantity which is believed to be subject to greatest experimental error and because the uncertainty in Δp is roughly the same over the temperature range (actually the data scatter is greater at high temperatures, as shown by the magnitudes of $\Delta p^\circ_{\text{exp}} - \Delta p^\circ_{\text{calc}}$ in Tables I and II). If, rather than as above, the sum of the squares of the deviations of the left hand side of Eq. (1) or (2) is minimized, then relatively small errors in measured Δp 's at low temperatures become important in determining the parameters. The deviations in Tables I, II tend to be positive at low temperatures and more so for H_2O - T_2O . In part, this effect may be forced in the least squares procedure by the larger magnitude of the deviations at high temperatures and might be decreased by some (objective) weighting procedure. It is believed that the experimental data should be considered strongly and the deviation pattern used along with Eq. (1) when best values of p_{T_2O} are needed at low temperatures¹⁵ (cf. Table III).

Table III gives $p_{\text{H}_2\text{O}} - p_{\text{T}_2\text{O}}$, $p_{\text{H}_2\text{O}}/p_{\text{T}_2\text{O}}$, $L_{\text{T}_2\text{O}} - L_{\text{H}_2\text{O}}$, $p_{\text{H}_2\text{O}} - p_{\text{D}_2\text{O}}$, $p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}}$ and $L_{\text{D}_2\text{O}} - L_{\text{H}_2\text{O}}$, calculated from Eq. (1), (2) at rounded temperatures. L is the molal heat of vaporization. The ΔL 's do not include corrections for gas imperfection and molal volumes of the liquids. Estimates of these corrections (cal. mole⁻¹), based on the Berthelot equation of state, are: $L_{\text{T}_2\text{O}} - L_{\text{H}_2\text{O}}$, 0.8 (25°C), 2.0 (60°C), 3.1 (100°C); $L_{\text{D}_2\text{O}} - L_{\text{H}_2\text{O}}$, 0.6 (25°C), 1.7 (60°C), 2.9 (100°C). Table IV summarizes boiling points, triple point temperatures and pressures and cross-over temperatures (temperatures of equal vapor pressures).

Comparison with Other Work

The only other work on essentially pure T_2O is by Popov and Tazetdinov³ who directly (rather than differentially) measured the vapor pressures of 83.4 and 98.1 atom percent T_2O from 20 to 95°C and 12 to 95°C, respectively. Their errors are larger at the higher temperatures, but the results are in general agreement. The boiling point from their Antoine equation for 100% T_2O is 101.55°C (uncertainty apparently about 0.05°C). Their molal heat of vaporization of T_2O (given to nearest 100 cal/mole) exceeds that of H_2O by 0.3₈ kcal at 100°C and by 0.4₈ kcal at 25°C.

The vapor pressures and heats of vaporization of pure D_2O are in general agreement with the data summarized by Kirshenbaum.² The $\text{H}_2\text{O}-\text{D}_2\text{O}$ data of Lewis and MacDonald¹⁶ (10 points at rounded temperatures from 20 to 110°C) were fitted to an equation like Eq. (2) and gave $A = 70.67 \pm 0.85^\circ\text{K}$ and $B = 33618 \pm 338 (^\circ\text{K})^2$, in close agreement with our Eq. (2).

Smith and co-workers¹⁷ measured the vapor pressure of D_2O from 10 to 55°C by a dynamic method. As they point out, their ratios $p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}}$ are

higher than those in Kirshenbaum's summary², with which our data agree. This disagreement seems outside the combined errors at the higher but not at the lower temperatures. They also determined¹⁷ a separation factor, $\alpha = (H/D)_{\text{gas}} / (H/D)_{\text{liquid}}$, for an equimolal H_2O - D_2O mixture which is in reasonable agreement with the approximate¹² relationship $\alpha = (p_{H_2O}^0 / p_{D_2O}^0)^{\frac{1}{2}}$. Using tracer amounts of tritium, this group¹⁸ also measured values of $\alpha = (H/T)_{\text{gas}} / (H/T)_{\text{liquid}}$ from 20 to 60°C which, except for the 60° point, agree with $(p_{H_2O}^0 / p_{T_2O}^0)^{\frac{1}{2}}$ using our (Table III) or Popov and Tazetdinov's³ T_2O pressures.

DISCUSSION

General

Bigeleisen^{1, 19} has reviewed theoretical work on the vapor pressures of isotopic substances, extended the theory and put it into a form suitable for comparison with experiment.²⁰ The general procedure in obtaining a theory of vapor pressure is to equate the molal Gibbs free energy of the vapor, whose theoretical form is well known and involves the pressure, to the free energy of a model of the condensed phase. Similarly, and recognizing that the classical partition functions of isotopic substances are equal, expressions for the ratio of isotopic vapor pressures can be obtained. In practice a liquid is taken to be a collection of oscillators and use is made of the fact that the internal vibrations of a gas molecule maintain their identity (although with change in magnitude) in going to the condensed phase, while the free translation and rotation go over into corresponding hindered motions. Usually it is not possible to calculate the frequencies in the condensed phase with much accuracy, and it is more feasible to

compare the experimental vapor pressure results with predictions based on other types of information on the liquid, e.g. structural and spectroscopic. In our case the most suitable theoretical equation is^{1, 25}

$$\ln (p'/p) = -B/T + A/T^2 \quad (3)$$

$$\text{with } B = (hc/2k) \sum_i^{3n-6} [(\nu_i' - \nu_i)_g - (\nu_i' - \nu_i)_c] \quad (4)$$

$$\text{and } A = \frac{1}{8} (hc/k)^2 [(\mu_2' - \mu_2)_{tr} + (\mu_2' - \mu_2)_{rot}] \quad (5)$$

Primed quantities refer to the light isotope; c and g to condensed (liquid) and gas phases.

In Eq. (4) the summation is over the internal frequencies in the gas and the corresponding frequencies in the liquid. Strictly, B/T should be supplemented by an additive term D which is due to

$$D = \sum_i^{3n-6} \ln (u_i/u_i')_c (u_i'/u_i)_g \left[\frac{1 - \exp(-u_i')}{1 - \exp(-u_i)} \right]_c \left[\frac{1 - \exp(-u_i)}{1 - \exp(-u_i')} \right]_g \quad (6)$$

$$u_i = h\nu_i/kT$$

population in other than the ground state of the internal frequencies. If the u_i are large enough and the plausible assumption $(u_i/u_i')_c = (u_i/u_i')_g$ is made, D will be negligible (see footnote 38 for numerical estimates). While (4) and (6) are for harmonic frequencies in the liquid, (4) is also correct if B is the appropriate expression for zero point energy including anharmonic effects; D, including anharmonic corrections, will in general continue to be negligible for u_i sufficiently large.

In equation (5) the μ 's are the second moments of the frequency distributions in the hindered translation and hindered rotation regions of the

liquid. There is an assumption that these frequencies do not interact with the internal frequencies or with each other. Convergence of an expansion of partition functions, of which A/T^2 is the leading term, requires $u'_1 < 2\pi$ for the hindered frequencies. This condition is satisfied (see section on estimation of A_{12} , etc. below). The effect of higher terms is considered later.

Estimation of B_{12} and B_{13}/B_{12} from Raman Spectra

Much work has been done on the Raman and infrared spectra of liquid H_2O and D_2O which pertain to the internal vibrations contributing to B . A summary up to 1956, including work in the hindered region, was given by Giguère and Harvey.²⁶ We shall adopt the Raman results of Schultz and Hornig.²⁷ The bending frequencies of liquid H_2O and D_2O are 1636.5 cm^{-1} (average of 1633^{27b} and 1640^{27a}) and 1208 cm^{-1} ^{27a}. Schultz and Hornig fitted their Raman spectra of H_2O and D_2O in the region 3100 - 3700 cm^{-1} to three Gaussians, interpreted by them as belonging in order of increasing frequency to $2\nu_2$ (bend overtone), ν_1 (symmetric stretch) and ν_3 (assymmetric stretch).²⁸ In order to account for the intensity of $2\nu_2$ they concluded that $2\nu_2$ and ν_1 are in Fermi resonance. The unperturbed values of ν_1 are $3366.5 \pm 6.0 \text{ cm}^{-1}$ for H_2O and $2467.5 \pm 4.3 \text{ cm}^{-1}$ for D_2O (uncertainties in the unperturbed separation and in the Gaussian fit are 5.5 and 2.3 cm^{-1} for H_2O). For H_2O ν_3 was $3612.5 \pm 2.8 \text{ cm}^{-1}$ (minimum uncertainty, from Gaussian fit alone). Actually ν_1 and ν_3 overlap considerably, especially for D_2O , leading to an uncertainty in ν_3 and to what SH consider to be unreasonable relative intensities of $2\nu_2$, ν_1 and ν_3 for D_2O . A need for adjustment of ν_3 (D_2O), 2617 cm^{-1} from their fit, is also suggested by the comparison of $(\nu_H/\nu_D)_{liq}$ with $(\nu_H/\nu_D)_{gas}$ ³⁰ in Table V. These ratios

are about the same for ν_1 and ν_2 within the errors for the liquids (which are probably minimum estimates), but the ratio for ν_3 suggests that ν_3 (D_2O) is too low. This is consistent with the anomalously high intensity for the ν_3 (D_2O) band (see above). Considering the above, it seems best for our purposes to calculate the fundamentals for D_2O (ℓ) from those of H_2O (ℓ) and the corresponding ratios for the gases. S , defined as $\frac{1}{2} \sum_{i=1}^3 [(\nu_H - \nu_D)_{ig} - (\nu_H - \nu_D)_{i\ell}]$, is then $51.6 \pm 5.5 \text{ cm}^{-1}$ at an estimated 25°C (uncertainty based only on precisions in Table V). S should be essentially zero at the mean of the critical points of H_2O (374.1°C) and D_2O (370.9°C).³¹ Linear interpolation of S to 74°C , the average of the temperatures of our H_2O - D_2O measurements, gives $S = 44.4 \pm 4.7 \text{ cm}^{-1}$ at 74°C . Such interpolation is consistent within the uncertainties with Cross, Burnham and Leighton's measurements²⁹ on the temperature dependence of the frequency of maximum intensity in their main stretch band. The true difference in the zero point energies of gaseous H_2O and D_2O is 1.0516 times one-half the difference in the sums of the fundamentals³⁰ considered in S . With the same assumption for the liquids, S gives $B_{12} (74^\circ\text{C}) = 46.7 \pm 5 \text{ cm}^{-1}$ or $67.2 \pm 7.2^\circ\text{K}$, in satisfactory agreement with the experimental value 70.9°K from Eq. (2). The calculated B_{12} would be increased if the anharmonicity in the liquid were relatively greater than assumed.

If the harmonic and anharmonic parts of B_{12} are taken to be the same fractions of B_{12} as in the gas,³⁰ they are $B_{12} (h) = 48.0$ and $B_{12} (anh) = -1.3 \text{ cm}^{-1}$. In satisfactory approximation B_{13}/B_{12} is then $[48.0 (1.4297) - 1.3 (1.333)]/46.7 = 1.432$, compared to 1.466 ± 0.012 from the experiments, Eq. (1), (2). The factor 1.4297 is the weighted average ratio of the

zeroth order frequencies of H_2O^{30} to those for T_2O^{32} divided by the same ratio for H_2O^{30} to D_2O^{30} [gas values assumed; a ratio is weighted in proportion to the magnitude of the frequency; an approximate value of the double ratio is $(1-3^{-\frac{1}{2}})/(1-2^{-\frac{1}{2}}) = 1.441$]. The factor $1.333 = (1-1/3)/(1-1/2)$ is the corresponding anharmonic factor.

A more detailed estimate of the harmonic and anharmonic parts of B_{12} was attempted assuming that the observed fundamentals and vibrational energy of the liquid could be represented in the same way as in the gas, with zeroth order frequencies (harmonic part) and anharmonic constants. The calculation was made to see whether this approach could empirically take account of the complicated intermolecular interactions. Isotopic ratios of zeroth order frequencies and anharmonic constants in the liquids were taken to be the same as in the gas.³⁰ Zeroth order frequencies and certain combinations of anharmonic constants could then be obtained for each assumed δ (separation of unperturbed $2\nu_2$ and ν_1 ; known within limits^{27a}). One further and uncertain assumption about the ratio of two anharmonic constants of $\text{H}_2\text{O} (l)$ had to be made before B_{12} (and the full set of anharmonic constants) could be evaluated. The results for B_{12} (estimated to be roughly 65 cm^{-1} , or more, at 74°C) and the anharmonicity constants (some came out positive) are sensitive, as might be guessed, to some of the assumptions and to moderate variations in the primary data and are considered unreliable. A satisfactory treatment would probably have to take explicit account of the interaction among the internal frequencies, hindered translation and rotation (the prominent band around 2200 cm^{-1} in $\text{H}_2\text{O} (l)$ has generally been considered to be $\nu_2 + \nu_r$; two bands to the high frequency side of ν_2 in the Raman spectrum^{27a} of D_2O may be $\nu_2 + \nu_t$ and $\nu_2 + \nu_r$).

Estimation of A_{12} and A_{13}/A_{12} from Raman
and Inelastic Neutron Scattering Spectra

Work on the Raman and infrared spectra in the region associated with hindered translation and rotation in liquid (and solid) H_2O and D_2O was summarized by Giguère and Harvey,²⁶ who also contributed data of their own. The liquid spectra have not been systematically studied as a function of temperature. The bands overlap and difficulty in locating maxima has no doubt contributed to disagreement in frequencies reported. As reasonable a summary as can be given indicates that there are bands at about 60 cm^{-1} and at $160 \pm 40\text{ cm}^{-1}$ for H_2O and at essentially the same values for D_2O . The ratios of isotopic frequencies are not inconsistent with $(18/20)^{\frac{1}{2}}$. Hence these frequencies, ν_t , have usually been interpreted as corresponding to translational motions of the molecule as a whole.²⁸ A theoretical estimate of the higher frequency also suggests this conclusion.²⁹ A broad Raman band with frequency of maximum intensity at about 500 cm^{-1} for H_2O and about $2^{-\frac{1}{2}}$ times this for D_2O has generally been assigned to a hindered rotation with a frequency inversely proportional to a moment of inertia.²⁹ This identification is supported by a theoretical estimate²⁹ of the frequency of such a motion and by a correlation of the effects of corresponding frequencies in solid H_2O and D_2O with their heat capacities.³³ In solid D_2O and H_2O the evidence suggests that the three librational frequencies are about the same.³⁴ Blue³³ also gave a plausible argument for this conclusion. Some but not all observers²⁶ consider that there is a frequency around 700 cm^{-1} in the liquid; there is a similar indication from some of the neutron scattering data (see below). This might be a combination band, $\nu_t + \nu_r$.

Recently these hindered motions have been investigated by inelastic neutron scattering.³⁵ Larsson and Dahlborg³⁶ obtained approximate frequency distributions for the hindered translation and rotation region, for H₂O (l) at 275, 295, and 365°K and for D₂O (l) at 278, 295, and 368°K. These data are the most suitable for an estimate of A₁₂ for comparison with Eq. (2). The data for D₂O are in a region of better energy resolution than those for H₂O, especially for the hindered rotation band which mainly determines A₁₂. The frequencies for D₂O were therefore obtained from the neutron data and frequencies for H₂O were calculated from the D₂O values. This procedure is consistent with a comparison of the observed ratio of the hindered rotation frequencies of maximum intensity, $\nu_H/\nu_D = 1.34 \pm 0.11$,³⁶ with our estimate (see below) based on an average ratio of moments of inertia, $\nu_H/\nu_D = 1.380$. The D₂O frequency spectra (Ref. 36, Fig. 8) were fitted to the sum of three Gaussians using the least squares code of McWilliams, et al.³⁷ The frequencies (σ , standard deviation of a Gaussian in parentheses) for D₂O were $\nu_{t_1} = 45 (27) \text{ cm}^{-1}$ and $\nu_{t_2} = 121 (66) \text{ cm}^{-1}$ for the two lowest frequency peaks (average values taken to be independent of temperature within the uncertainties). Values for H₂O were obtained by multiplying by $(20/18)^{\frac{1}{2}}$. They are lower than the Raman values (especially ν_{t_2} , which is poorly resolved). The uncertain experimental values for ν_{t_2} do not conform very well to the above mass dependence. Fortunately, the lowness of these frequencies and their small mass dependence result in a small contribution to A₁₂. Similarly, it is unnecessary to compare the Gaussian with a Debye distribution for these frequencies. For definiteness ν_{t_1} was assumed to be a transverse frequency with weight 2/3 and ν_{t_2} to be longitudinal with

weight $1/3$ in computing the translational second moment, $234 (^{\circ}\text{K})^2$, even though the areas of these Gaussians were about equal within their appreciable uncertainty. The Gaussian of highest frequency ν_r (taken to correspond to all three librational modes) had an area about twice (rather than equal to) the sum of the two ν_t Gaussians. This may be due to inability to obtain the shapes of the Gaussians well enough (e.g. because of poor resolution of ν_{t_2}) and to uncertainties in the theoretical scattering cross sections, which do not take account of the detailed molecular motion and which are required to obtain frequency distributions from the observations.

A_{12} is almost completely determined by the hindered rotation frequencies which for D_2O were 455 (113), 407 (181), and 297 (100) cm^{-1} at 278, 295, and 368 $^{\circ}\text{K}$, respectively; σ , cm^{-1} , in parentheses. Interpolation to 347 $^{\circ}\text{K}$ (average of the temperatures of the H_2O - D_2O measurements) gave $\nu_r = 334 \text{ cm}^{-1}$ with $\sigma_r = 131 \text{ cm}^{-1}$ (average of the above three). A frequency squared for H_2O was taken to be greater than for D_2O by a factor 1.905, which is the average ratio of a moment of inertia of D_2O to the corresponding moment for H_2O , computed classically. Then, cf. Eq. (5), $\frac{1}{8} (\mu_2 - \mu_2)_{\text{rot}}$ is $\frac{1}{8} \nu_r^2 [1 + (\sigma_r / \nu_r)^2] [1.905 - 1] = (\frac{1}{8}) 1.116 \times 10^5 (1.154)(0.905) = 14,570 \text{ cm}^{-2}$ or 30,170 $(^{\circ}\text{K})^2$. This gives a total $A_{12} = 30,400 (^{\circ}\text{K})^2$, with a precision of roughly 10%, to be compared with $33,630 \pm 160$ from Eq. (2).³⁸

If there is actually a librational frequency around 700 cm^{-1} for H_2O , as well as the lower one we have used, then these have to be taken as singly and doubly degenerate, respectively, in order to explain $(A_{12})_{\text{exp}}$. Using Walrafen's⁴³ values of 780 and 450 cm^{-1} for H_2O at 40 $^{\circ}\text{C}$, we estimate 670 and 390 cm^{-1} at 74 $^{\circ}\text{C}$; $\frac{1}{8} (\mu_2 - \mu_2)_{\text{rot}}$ is then $\frac{1}{8} [(670)^2 (1/3) + (390)^2 (2/3)] [1 - 1/1.905] = 14,900 \text{ cm}^{-2}$ or 30,850 $(^{\circ}\text{K})^2$. With a Gaussian breadth factor

1.154 this becomes 35,600 ($^{\circ}\text{K}$)², also consistent with $(A_{12})_{\text{exp}}$.

The second moment for the H_2O hindered rotational moment is 2.728 times that for T_2O , based on moments of inertia. The translational second moment is 22/18 times greater for H_2O . From these numbers and the preceding numbers for $\text{H}_2\text{O}-\text{D}_2\text{O}$, A_{13}/A_{12} was calculated to be 1.337,⁴⁴ compared to the experimental value 1.382 ± 0.009 from Eqns. (1), (2).

Calculated and experimental parameters are tabulated in Table VI. The agreement is as good as could be expected, especially for A_{12} and B_{12} , considering the information available on water and the physical approximations.

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- 6 Immersion caused some distillation of the waters onto the Hg surface. If this was excessive the tensimeter was withdrawn, the mercury was heated with a light bulb, and the tensimeter was re-immersed. Frequently, especially at the highest temperatures, there was a ring of water between the mercury and glass (about 0.02 cm maximum depth on each side). Sometimes a small water droplet formed on the Hg surface. Waters also condensed on the walls throughout the tensimeter. These comments apply to the H_2O-T_2O , H_2O-D_2O , and also to the H_2O-H_2O blank measurements (which were satisfactory and show that the effects are not serious). The condensation of waters throughout the tensimeter was considered desirable in the T_2O measurements because (a) this helps ensure a uniform concentration of radiolytic gas, as assumed in the correction, and (b) a large surface was created for dissipation of radioactive heat (although distillation away from possible overheated areas should fix the vapor pressure at bath temperature).

Experiments at several temperatures with H_2O on both sides of a tensimeter tested over-all performance, including effects of inequalities in temperature. The results suggest that, even at the highest temperatures, a systematic error in measured Δp would not be more than about 0.01 cm Hg. Experiments with H_2O on both sides, but with heat introduced on one side at the same rate as in T_2O with a small coil of platinum wire, suggest that the effect of radioactive heating in T_2O could be as much as 0.01 cm Hg at the highest temperature. No correction was made since non-uniform introduction of heat in this test probably makes the case less favorable than with T_2O .

- 7 This procedure was tested in the $\text{H}_2\text{O}-\text{D}_2\text{O}$ run at 379.27°K (Table II). There was about 0.10 cm Hg inert gas on the D_2O side. The volume of the T_2O side of the tensimeter, about 24 cc with the mercury columns at equal height, was accurately determined by measuring the pressure due to a known amount of gas measured in another system. The known diameter of the limb allowed correction for other meniscus positions.
- 8 It was usually possible to extrapolate back to the time of immersion to obtain a pressure, requiring no correction for radiolytic gas, which agreed with the pressure obtained as described in the text to within 0.010 cm Hg. The latter method was always considered more accurate. On a few occasions, when a high temperature $\text{H}_2\text{O}-\text{T}_2\text{O}$ pressure measurement was made after several days storage of the T_2O in CO_2 (but with the usual purgings before the run), the pressure-time curve suggested that there was a small abrupt initial generation of gas from the T_2O which was followed by a normal relationship. Assuming the initial gas to be oxygen from decomposition of T_2O_2 , the initial (T_2O_2) was estimated to be roughly 0.005 mole/liter. This concentration of T_2O_2 , if it persisted, would cause the vapor pressure of T_2O to be low by about 0.008 cm Hg at 100°C . Values of Δp° from such experiments do not differ systematically from the results of experiments not showing the effect. The above estimate of initial (T_2O_2) may be compared with the concentration of 0.001-0.002 mole/liter found by Goldblatt,⁴ using ultraviolet spectrophotometry, in a 1 cc sample of T_2O at room temperature.
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- 11 The error made by taking $\Delta p^\circ = \Delta p_c / N_T$ is less than 0.001 cm Hg. Recognizing effects of HTO (HDO), which are significant at comparable values of N_H and N_T (N_D), one has¹² more generally but with some reasonable assumptions:

$$\Delta p^\circ = \Delta p_c / N_T - (1 - N_T) p_{\text{H}_2\text{O}}^\circ (1-a)^2, \text{ where } a = (p_{\text{T}_2\text{O}}^\circ / p_{\text{H}_2\text{O}}^\circ)^{\frac{1}{2}}.$$
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an atom by its neighbors enters. The existence of the vapor pressure isotope effect (and of a liquid phase) depends on the fact that these forces in the condensed phase include those between neighboring molecules, concerning which little is known. A very detailed approach is for this reason alone not possible at present. Wolfsberg²² recently demonstrated the magnitude of intermolecular interactions by useful approximation methods. Oppenheim²³ formally developed the theory of isotope effects in equilibrium processes along the lines of the Wigner method using pair potentials. Friedmann²⁴ has applied the quantum mechanical distribution method to the vapor pressures of isotopes and made correlations with experimental data which do not require knowledge of intermolecular potentials.

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As mentioned, data fitting did not permit evaluation of a term E/T^4 . The theoretical $1/T^4$ term for hindered rotation, evaluated at 74°C and assumed to contribute to $(A_{12})_{expt}$, contributes minus 5% to $(A_{12})_{expt}$. The contribution to $(A_{13}/A_{12})_{expt}$ is about 0.01. The numerical effects can at present be considered relatively small.

The breadth of the bands in water and in other hydrogen bonded substances is not well understood. We have assumed that the breadth is due only to a distribution of frequencies, associated with distributions in configurations, whereas anharmonicity, tunnelling, combination bands involving translation, etc. may also contribute.^{39, 40} Also, the experimental and calculated parameters for H_2O - D_2O were compared at the average of the experimental temperatures. A treatment based on the statistical mechanics of systems with temperature-dependent energy levels^{41, 42} would be worth while.

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LEGENDS FOR FIGURES

Fig. 1. Differential tensimeter

Table II. Vapor Pressure Differences for H₂O-D₂O

T, °K	$\Delta p_{\text{obs}}^{\circ}$ cm Hg	$\Delta p_{\text{obs}}^{\circ} - \Delta p_{\text{calc}}^{\circ}$ cm Hg	T, °K	$\Delta p_{\text{obs}}^{\circ}$ cm Hg	$\Delta p_{\text{obs}}^{\circ} - \Delta p_{\text{calc}}^{\circ}$ cm Hg
387.46	4.996	+0.005	351.02	2.247	+0.014
387.08	4.975	+0.015	348.08	2.063	+0.008
385.53	4.852	+0.021	345.00	1.880	+0.003
385.44	4.830	+0.001	342.07	1.729	+0.005
385.07	4.819	+0.025	341.18	1.682	+0.012
383.52	4.663	+0.003	337.34	1.485	+0.015
382.78	4.594	-0.011	334.45	1.349	+0.018
381.37	4.515	+0.026	328.84	1.118	+0.005
380.93	4.435	-0.018	328.66	1.113	+0.017
380.31	4.424	+0.022	323.40	0.912	+0.001
379.65	4.372	+0.024	322.90	0.899	+0.005
379.44	4.306	-0.024	319.53	0.784	-0.002
379.27	4.296	-0.020	318.11	0.749	+0.004
378.47	4.231	-0.020	317.75	0.728	-0.005
376.19	4.074	+0.009	312.62	0.599	-0.001
375.28	3.973	-0.017	312.01	0.587	+0.007
374.67	3.917	-0.025	311.69	0.571	-0.003
374.09	3.917	+0.022	311.09	0.562	+0.004
374.04	3.912	+0.020	302.74	0.388	+0.002
373.99	3.873	-0.014	302.35	0.377	-0.002
373.68	3.846	-0.017	295.19	0.280	+0.010
370.92	3.635	-0.009	293.40	0.254	+0.008
370.87	3.634	-0.006	287.83	0.189	+0.004
370.52	3.586	-0.027	283.20	0.153	+0.009
370.51	3.587	-0.025	282.05	0.155	+0.020
368.30	3.427	-0.013	278.11	0.112	+0.004
366.32	3.264	-0.025	277.65	0.118	+0.014
366.15	3.282	+0.005	276.95	0.097	-0.003
366.03	3.262	-0.005			
365.15	3.205	+0.004			
362.17	2.978	-0.005			
361.93	2.956	-0.010			
359.93	2.826	+0.003			
356.92	2.633	+0.018			
356.53	2.596	+0.006			
353.89	2.424	+0.009			

Table III. Smoothed Pressure Ratios, Differences
in Pressures and Heats of Vaporization

t °C	$p_{H_2O} - p_{T_2O}^a$ cm Hg	$p_{H_2O}/p_{T_2O}^a$	$(L_{T_2O} - L_{H_2O})^c$ cal mole ⁻¹	$p_{H_2O} - p_{D_2O}^b$ cm Hg	$p_{H_2O}/p_{D_2O}^b$	$(L_{D_2O} - L_{H_2O})^c$ cal mole ⁻¹
10	0.197	1.27	446	0.150	1.19	331
20	0.316	1.220	424	0.249	1.166	315
25	0.396	1.200	413	0.317	1.154	307 ^d
30	0.493	1.184	403	0.399	1.144	300
40	0.742	1.155	383	0.612	1.124	286
50	1.076	1.1317	365	0.903	1.1082	273
60	1.516	1.1129	348	1.289	1.0944	260
70	2.055	1.0964	332	1.776	1.0822	249
80	2.684	1.0817	316	2.367	1.0714	238
90	3.379	1.0687	302	3.054	1.0617	227
100	4.099	1.0570	289	3.821	1.0529	217
110	4.781	1.0466	276	4.635	1.0451	208
120	5.339	1.0372	263	5.452	1.0380	199

^a Δp° corresponding to Eq. (1) increased (see text) by 0.019 (10°), 0.018 (20°), 0.016 (25°), 0.014 (30°), 0.009 (40°).

^b Δp° corresponding to Eq. (2) increased (see text) by 0.006 (10°), 0.006 (20°), 0.005 (25°), 0.005 (30°), 0.004 (40°).

^c Uncertainties roughly 20 (25°C) and 10 (100°C) cal mole⁻¹.

^d $(L_{D_2O} - L_{H_2O}) = 331 \pm 8$ cal mole⁻¹ at 25°C from F. D. Rossini, J. W. Knowlton and H. L. Johnston, J. Research Natl. Bur. Standards 24, 369 (1940). This value refers to the vapors at zero pressure. About 1 cal mole⁻¹ should be added if the vapors are at their saturation pressures.

Table IV. Boiling Points, Triple Points, Cross-over Temperatures

	H ₂ O	D ₂ O	T ₂ O
Boiling pt, °C	100.00	101.42 ^a	101.51 ^b
Triple point temp., °C	0.010	3.82 ^c	4.49 ^d
Triple point pressure, cm. Hg.	0.458 ^e	0.502 ^f ±0.004	0.487 ^g ±0.007
Cross-over temperatures, °C: H ₂ O-D ₂ O, 220.7 ± 0.1 ^h ; H ₂ O-T ₂ O, 190 ± 10 ⁱ ; D ₂ O-T ₂ O, 116.2 ± 0.5 ^j			

^a From Eq. (2) and $p_{\text{H}_2\text{O}}$; also Ref. 2

^b From Eq. (1) and $p_{\text{H}_2\text{O}}$

^c From Ref. 2; also W. M. Jones, J. Am. Chem. Soc. 74, 6065 (1952)

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^e Calculated from Ref. 13b

^f Based on: 0.498 cm Hg from Eq. (1) of K. Niwa and E. Shimazaki, J. Chem. Soc. Japan 60, 985 (1939) and C. A. 34, 1537 (1940); 0.502 cm Hg from data of Ref. 16 fitted to equation like our Eq. (2); 0.503 cm Hg calculated from the vapor pressure and heat of sublimation measured at 0°C by E. Bartholome and K. Clusius, Z. physik. Chem. B28, 167 (1935); 0.504 cm Hg from Table II, 276.95°K; 0.502 cm Hg from Eq. (2).

^g Based on: 0.489 cm Hg, calc from Eq. (5) of Ref. 3 0.489 cm Hg from our Table I, $T = 277.65^\circ\text{K}$; 0.489 cm Hg from solid data (Table I) and estimated heat of sublimation of 12830 cal/mole; 0.502 cm Hg from Eq. (1), which with a correction of 0.020 (cf. Table III, footnote a) gives 0.482 cm Hg.

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ⁱ Estimated by comparison of the (too low) value 201.4°C calculated for H₂O-D₂O from Eq. (2) with the true value 220.7°C and from the (presumably too low) value 174.3°C for H₂O-T₂O from Eq. (1).

^j Calculated from Eq. (1), (2).

Table V. Fundamental Absorption Frequencies
of Liquid and Gaseous H₂O and D₂O

	^a H ₂ O(l), cm ⁻¹	^{a, b} D ₂ O(l), cm ⁻¹	^c H ₂ O(g), cm ⁻¹	^c D ₂ O(g), cm ⁻¹	(ν_{D_2O}/ν_{H_2O}) _l	(ν_{D_2O}/ν_{H_2O}) _g
ν_1	3366.5±6.0	2467.5±4.3	3651.7	2666	0.733±0.002	0.7301
ν_2	1636.5±4	1208±2	1595.0	1178.7	0.738±0.002	0.7390
ν_3	3612.5±2.8	2616.7	3755.8	2789	0.724	0.7426

^a Reference 27

^b Note that the frequencies actually used for D₂O(l) in the calculation of S are those for H₂O(l) multiplied by the last column of Table V. (see text).

^c Reference 30

Table VI. Calculated and Experimental
Parameters of Equations (1), (2)

	expt.	calc.
$A_{12}, (^\circ K)^2$	$33,630 \pm 160$	30,400
$B_{12}, (^\circ K)$	70.87 ± 0.43	67 ± 7
A_{12}/A_{13}	1.382 ± 0.009	1.337
B_{12}/B_{13}	1.466 ± 0.012	1.432