Table II. Derived Coefficients for Vapor Pressure Equation of Cesium

$\log p = A + B/T + C \log T$

Data Used in Deriving Coefficients[a]	Coefficients			Deviations of Composite Data	
	A	B	C	Std Dev, $\log p$	Std %, Dev/p
X	5.87055	−7036.2	−0.5329	0.0035	0.80
X	3.84993	−6516.8	0	0.0046	1.06
Y	5.87303	−7040.7	−0.5329	(0.0035)	(0.81)

[a] X, Composite of low temperature data (*9*) and high temperature data (this publication); Y, low temperature data (*9*).

results since no equation of state has been obtained for this range.

A review of a previous paper, where a closed-chamber diaphragm method (*10*) was also used, suggested that the depression phenomenon observed at the intersection of the saturation and superheat curves might be explained by a combination of effects—an undetected temperature gradient along the axis at the lower extremity of the measurement chamber (at the filling tube) and the diminishing amount of liquid phase. This possibility was checked experimentally in the low temperature system (*10*) by making saturation measurements in this region with a thick metal cap installed over the filling tube and by inducing large temperature gradients along the axis of the chamber. The results of these tests showed conclusively that the vapor pressure lowering was not associated with thermal gradients on the apparatus. It is believed that the pressures are lowered by some physical phenomenon in combination with the diminishing liquid phase and that they do not represent true saturation values.

A discussion of the diaphragm method using columbium alloy for measuring vapor pressures at temperatures to 2400° F was presented by Stone *et al.* (*10*). The present study has shown that this method may be successfully extended to at least 3400° F with use of tantalum alloys. The 5-ml-thick diaphragms used in this study had free diameters of 1.25 inches and were found to perform reproducibly with high sensitivity for at least two full temperature cycles. Since one possible source of error was the diffusion of argon through the thin diaphragms at higher temperatures, it was demonstrated experimentally (by checking the chamber for gas content at the conclusion of each experiment and by the reproducibility of observed pressures at lower temperatures) that no significant diffusion had taken place.

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Vapor Pressure of D_2O from 106 to 300° C

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Although there have been many measurements of the vapor pressure of heavy water, the data in a substantial middle range of temperatures appear to be of lower precision and more questionable accuracy than the data at higher or lower temperatures. Figure 1 shows ranges covered by several of the better known investigations (*1, 2, 4, 9–15*). Although Miles and Menzies (*9*) and Riesenfeld and Chang (*13*) obtained results below 100° C in reasonable accord with a recent, careful study (*2*), their work at higher temperatures has several disturbing features. For example, in extending their measurements to pressures over 1 atm, Miles and Menzies used a cruder apparatus and techniques subject to greater error. Also, the Riesenfeld and Chang data scatter a good deal more at the higher temperatures than below 150° C. Finally and most importantly, both these early studies seem to have been subject to some systematic error at higher temperatures, for they both gave estimates of the crossover temperature (at which the vapor

The vapor pressure differences between pure H_2O and pure D_2O were measured at 12 temperatures from 106 to 300° C. These measurements include a substantial middle range of temperatures where previously existing data are unsatisfactory. The results agree favorably with the best investigations at higher and lower temperatures. The crossover temperature is estimated as 220.77 ± 0.05° C. Vapor pressure data for heavy water now appear to be in a satisfactory state over essentially all the liquid range.

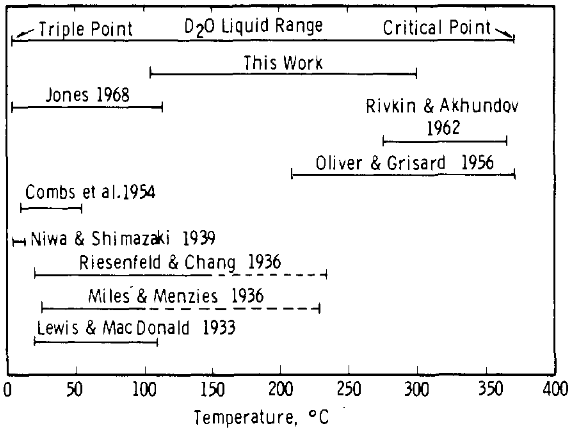


Figure 1. Temperature ranges covered by experimental investigations of D_2O vapor pressure

pressures of light and heavy water are equal) that are incorrect by several degrees.

Recently, Jones (*2*) has published differential tensimeter measurements that are probably the most precise data yet obtained at temperatures from the triple point to 114° C. The careful ebulliometric measurements by Oliver and Grisard (*12*) cover temperatures from 208° C to the critical point. We report the results of a series of precision differential vapor pressure measurements from 106 to 300° C, thus filling the middle range gap and overlapping somewhat the last two investigations.

EXPERIMENTAL

The measurements used differential vapor pressure equipment designed and used for osmotic coefficient determinations on dilute salt solutions at elevated temperatures. The apparatus and methods of that work have been described (*5–7*). This work followed the same general procedures.

Briefly, the fluid with the unknown vapor pressure and the reference fluid were contained in platinum cups within two similar but separate pressure cells that were held at constant and identical temperatures. A "double thermostatting" system was used to attain this objective, with the two cells symmetrically installed in a massive aluminum block, the block itself immersed in a vigorously stirred oil bath regulated to ±0.001° C. The bath fluid temperature was measured by a Leeds & Northrup Model 8163 platinum resistance thermometer calibrated against the laboratory standard thermometer. The resistance thermometer bridge was a Leeds & Northrup Model 8067, Type G-2 Mueller bridge, calibrated periodically against NBS-certified standard resistors.

Pressure differences between the vapor pressure cells were determined by balancing internal steam pressures with inert gas by the use of a sensitive arrangement of bellows and differential transformers, with the differences in gas pressure measured by a mercury-filled differential manometer. Manometer readings were corrected to mercury at its 0° C density. The correction to standard gravitational acceleration was of the order of or much smaller than experimental uncertainty and was not applied.

Palladium-silver diffusers were used to remove any hydrogen generated within the cells by corrosion reactions. Also, as the vapor pressure cells used in this work for H_2O and D_2O contained only the pure fluids, it was possible to bleed steam from the vapor space of each cell and repeat the measurements, thus obtaining extra assurance that noncondensable gases were not a source of systematic error.

The heavy water was obtained from Bio-Rad Laboratories, Richmond, Calif., and was reported as 99.85% isotopically pure. All glassware used for processing or transfer of D_2O first was carefully rinsed with heavy water of comparable isotopic purity. A polyethylene bottle used in the initial degassing procedure was soaked and steamed in heavy water for an extended period of time before use. The vapor pressure cell for heavy water was cleaned, rinsed, and steamed with heavy water. The interior of this cell was additionally conditioned by exposure to D_2O vapor at 700 to 800 psi and 300° C for several days just before final evacuation, baking, and injection of the liquid sample. The heavy water used for the measurements was redistilled in a preconditioned apparatus, with discard of the first and last portions of the distillate. Conductivity measurements were used to check the chemical purity of the distillate.

RESULTS AND DISCUSSION

The results are given in Table I. The pressure differences shown in column 2 are averages of from 5 to 20 individual measurements at the indicated temperatures. The vapor pressure differences between D_2O and H_2O are illustrated by Figure 2a for the temperature range where $P_{D_2O} - P_{H_2O}$ is negative and by Figure 2b for positive differences.

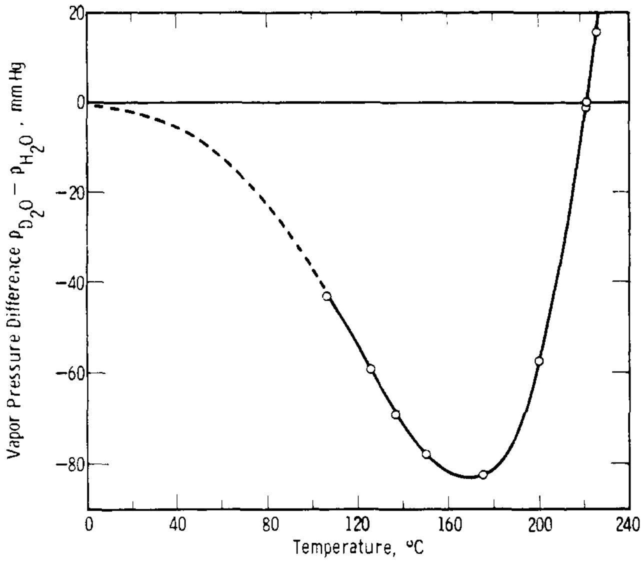
The vapor pressures for H_2O were calculated for each temperature from the analytical expressions given by Keenan and Keyes (*3*) and Smith *et al.* (*16*). Heavy water vapor pressures are based on the observed pressure differences and the Smith, Keyes, and Gerry correlating equation for the H_2O reference pressure. Note that the saturation vapor pressure expression adopted for H_2O in 1967 by the International Formulation Committee (*8*) deviates sufficiently from the Smith, Keyes, and Gerry correlation to affect slightly the absolute values of the vapor pressures given in columns 5 and 6 of Table I. However, the magnitudes of the deviations are too small to affect any of the significant figures given for the vapor pressure ratios in column 7. We have used the Smith, Keyes, and Gerry correlation for convenience because of its widespread general use for many years. Persons concerned in detail with absolute rather than relative vapor pressures can readily convert columns 5 and 6 to the basis of the alternative reference correlation.

The vapor pressure ratio is a much simpler function of temperature than the vapor pressure difference. Figure

Table I. Vapor Pressure Differences between Pure D_2O and Pure H_2O. Vapor Pressure of D_2O

	Vapor Pressure Difference			Vapor Pressures		Vapor Pressure Ratio
Temp., °C	$P_{D_2O} - P_{H_2O}$, Torr	No. of Observations	Std Dev, Torr	P_{H_2O}[a], Torr	P_{D_2O}, Torr	P_{H_2O}/P_{D_2O}
106.00	−42.78	8	0.10	937.92	895.14	1.04779
125.00	−59.03	7	0.03	1740.96	1681.93	1.03510
136.33	−68.77	6	0.03	2441.14	2372.37	1.02899
150.00	−77.92	20[b]	0.07	3570.68	3492.76	1.02231
175.00	−82.39[c]	7	0.02	6695.13	6612.74	1.01246
200.00	−57.28[c]	12	0.18	11664.93	11607.65	1.00494
220.00	−3.10	5	0.04	17402.67	17399.57	1.00018
221.00	+0.91	9	0.08	17738.01	17738.92	0.99995
225.00	+15.88	9	0.24	19129.53	19145.41	0.99917
250.00	+164.35[c]	17	0.43	29832.76	29997.11	0.99452
275.00	+409.81[c]	10	0.26	44615.23	45025.04	0.99090
300.00	+789.44	9	0.46	64432.36	65221.80	0.98790

[a] Calculated from Formula 1 of Keenan and Keyes (*3*) and Smith *et al.* (*16*). [b] Includes a second series of measurements. [c] These four reported values include calculated experimental corrections as follows: 0.12 torr at 175° C; 0.24 torr at 200° C; 1.0 torr at 250° C; 3.0 torr at 275° C. Error of ±50% in the corrections would change P_{H_2O}/P_{D_2O} by ±0.00001 at 175 and 200° C; ±0.00002 at 250° C; ±0.00003 at 275° C.



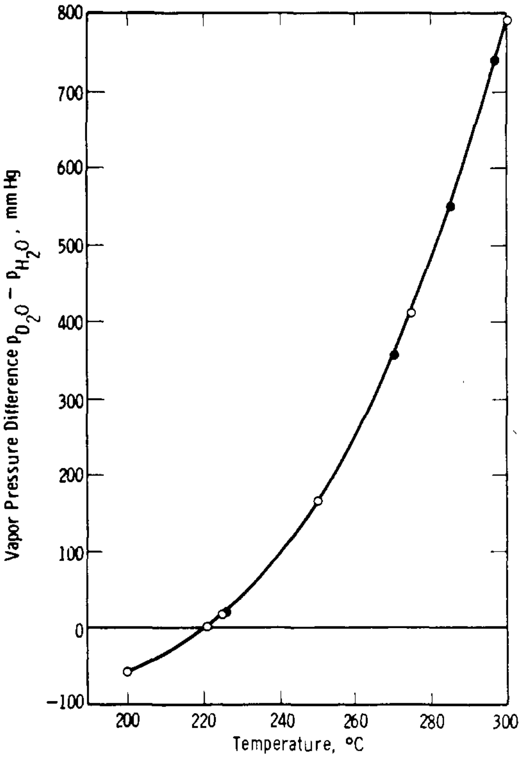


Figure 2. Vapor pressure difference, $P_{D_2O} - P_{H_2O}$, at lower and higher ranges of temperatures

○ This work

● Oliver and Grisard (*12*) (recalculated)

3 shows generally how the data of Table I compare on this type of plot with the higher and lower temperature data of Oliver and Grisard (*12*) or Jones (*2*). We have used the Smith, Keyes, and Gerry equation for reference in this comparison, calculating the D_2O pressures from this equation and the reported original data for Δp (Jones) or Δt (Oliver and Grisard). Solid lines on Figure 3 are smooth curves drawn through the high and low temperature data. Points are shown only for our measurements.

The much larger scale plots of Figures 4 and 5 show the data overlap regions more clearly. Here, the solid lines are extensions of a smooth curve drawn through only our results. The data from the other investigations scatter about this in excellent accord for both magnitude of the pressure ratio and its trend with temperature. Such good agreement suggests that all three investigations (this work, Jones, Oliver and Grisard) are free of any substantial systematic error. The points shown on Figure 5 for Riesenfeld and Chang indicate a definite discrepancy between their results and both our work and Oliver and Grisard's at these temperatures.

The crossover temperature was estimated by interpolation between our measurements at 220.00 and 221.00° C, giving 220.77 ± 0.05° C. This result is in essential agreement with the value of 220.68 ± 0.1° C reported by Oliver and Grisard. Crossover temperature estimates of 225 ± 1° C by Riesenfeld and Chang and 224.3 ± 0.5° C by Miles and Menzies are incorrect, illustrating the lower accuracy and precision at the high temperature end of the early investigations.

The results reported here for the middle range of temperatures are consistent with the best measurements made

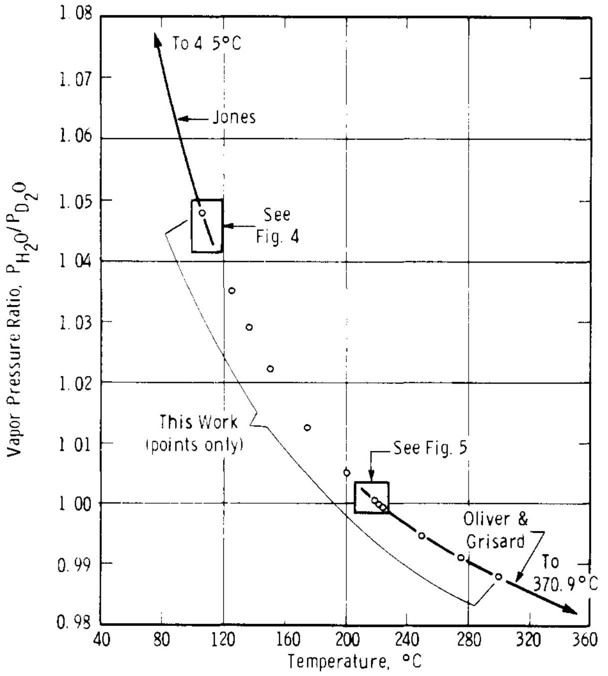


Figure 3. Vapor pressure ratio, P_{H_2O}/P_{D_2O}, as a function of temperature

○ This work

— Jones and Oliver and Grisard data (2, 12)

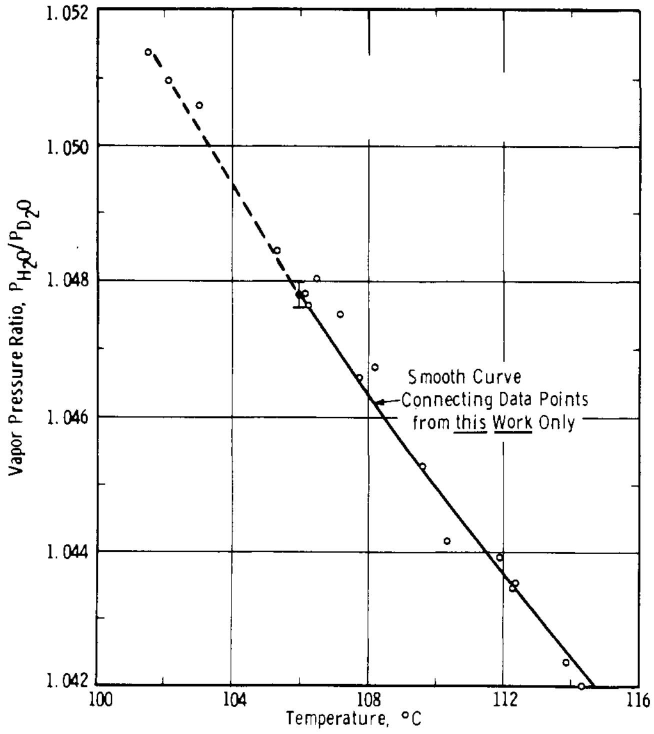


Figure 4. Vapor pressure ratio, P_{H_2O}/P_{D_2O}, vs. temperature in lower data overlap region

○ Jones (2)

● This work (95% confidence limits indicated)

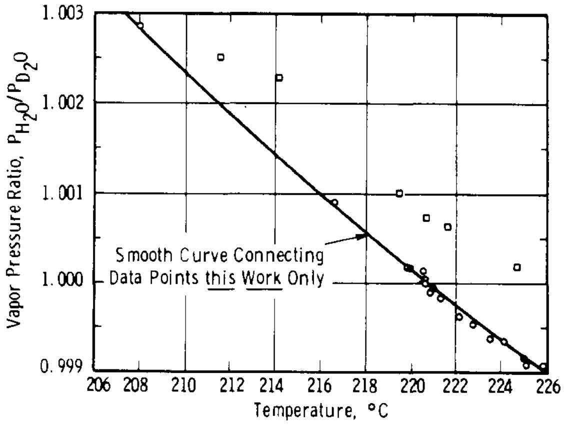


Figure 5. Vapor pressure ratio, P_{H_2O}/P_{D_2O}, vs. temperature in upper data overlap region

○ Oliver and Grisard (12)

● This work (95% confidence limits smaller than circle diam)

☐ Riesenfeld and Chang (13)

in the high and low temperature regions. Vapor pressure data for heavy water now appear to be in a satisfactory state over essentially the complete liquid range. A succeeding paper will deal with means for correlation of all these data by analytical representation over the complete range.

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