

## Vapor pressure of water from -2.5 to 20 °C†

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*(Received 20 August 1970)*

The vapor pressure of water has been measured in the range -2.5 to 20 °C. The results are in good agreement with other experimental values, particularly those by Scheel and Heuse, but are higher than those in the International Steam Tables. A direct measurement of the triple-point pressure of water,  $(612.1 \pm 0.4) \text{ N m}^{-2}$  or  $(4.591 \pm 0.003) \text{ Torr}$ , was obtained.

### 1. Introduction

Recently, Stimson<sup>(1)</sup> published precise measurements of the vapor pressure of water from 25 to 100 °C which showed that the correlated values of the International Steam Tables (IST)<sup>(2,3)</sup> were 37 to 57 mTorr too low in this temperature range. The measurements reported by Stimson, which had remained unpublished during the past 20 or more years, were nevertheless quite generally known as the Cragoe-Stimson corrections, having been accepted as standard values by Rossini *et al.*<sup>(4)</sup> in the calibration of boiling-point apparatus, by Gibson and Bruges<sup>(5)</sup> for the derivation of a new equation for the thermodynamic properties of water, by Zwolinski in the preparation of the MCA Tables,<sup>(6)</sup> and also by Ambrose<sup>(7)</sup> in a new correlation of the vapor pressure of water as standard reference values in comparative ebulliometry.

The Cragoe-Stimson measurements did not go below 25 °C; however, vapor pressures published by Scheel and Heuse<sup>(8)</sup> and new vapor pressure measurements reported here in the range -2.5 to 20 °C indicate that IST values are also low over the range from 0 to 20 °C.

### 2. Experimental

Pressure measurements were made with the inclined-piston gage described by Douslin and McCullough<sup>(9)</sup> and Douslin and Osborn.<sup>(10)</sup> A schematic drawing (figure 1) shows sample and vacuum connections to the gage and the heights at various points along the vapor column. Since complete descriptions of the construction, operation, precision, and accuracy of the gage are in the above references, the gage will be described only briefly here; however, the apparatus used for measurement and control of the temperature of the water sample will be described in detail.

† Contribution No. 182 from the thermodynamics laboratory of the Bartlesville Petroleum Research Center.

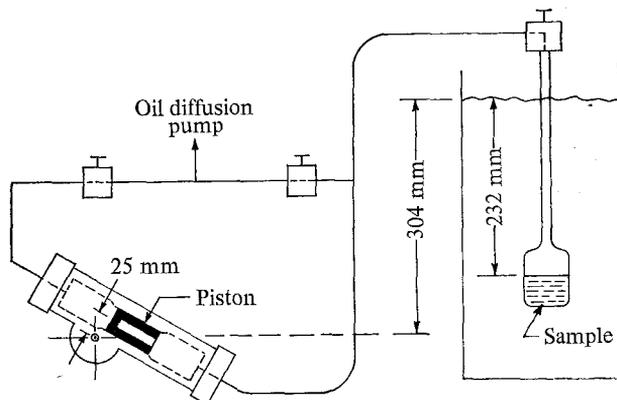


FIGURE 1. Schematic arrangement of the inclined-piston gage and sample bulb.

The inclined-piston pressure gage consisted of a sensitive piston-cylinder combination within an enclosing cylinder that terminated in a chamber at either end; one chamber was connected to the vapor space in the sample bulb and the other chamber was connected to a high-vacuum source.

Because the piston was eccentrically weighted about a diameter, a steady rotation of the piston-cylinder produced an oscillatory rotation of the piston that reduced friction and made the gage responsive to small pressure changes.

When the longitudinal axis of the cylinder was declined from the horizontal, with the vapor chamber placed below the vacuum chamber, an angle of declination  $\theta$  was found which brought the axial component of the weight of the piston into equilibrium with the vapor pressure of the sample.

At equilibrium, the vapor pressure  $p$  was calculated from the relation

$$p = (g/g_{\text{std}})(W/A) \sin \theta,$$

in which  $W$  and  $A$  were the weight and the effective area of the piston, respectively, and  $g/g_{\text{std}}$  was the ratio of the actual to the standard acceleration of free fall. The angle of declination, as read on a goniometer, was located by trial and error at the midpoint of the smallest angular increment  $\Delta\theta$  which reversed the direction of axial travel of the piston. The pressure head of vapor between the sample surface and the face of the piston was applied, when significant, as a correction to the nominal vapor pressure. Although small changes in the level of the gage-support occurred infrequently, the horizontal or null angle was determined at the beginning of each day following the evacuation of both chambers of the enclosing cylinder overnight through an oil diffusion pump.

In the present measurements, the water vapor contacted the piston directly. A positive seal between the vapor chamber and the vacuum chamber was provided by the lubricating oil† on the piston-cylinder, and the enclosing cylinder.

† Welsch 'Duo-Seal' vacuum pump oil was used; however, this use does not necessarily imply endorsement by the U.S. Bureau of Mines.

The effective area of the piston at  $20^{\circ}\text{C}$  was  $(5.0868 \pm 0.0005) \text{ cm}^2$ ;  $g/g_{\text{std}}$  was  $979.817/980.665 = 0.999135$ . The effective area  $A(t)$  of the piston at temperature  $t$  was calculated from the formula:

$$A(t) = A(20^{\circ}\text{C})\{1.0 + 2.09(t/^{\circ}\text{C} - 20)\}.$$

Gold fillers were used to increase the mass of the piston, when required, from 183.635 to 294.770 g and also to increase proportionately the equilibrium pressure at the same angle of declination. Thus, the use of weights in the piston increased the upper pressure range and provided for duplicate and overlapping pressure measurements.

The sample was contained in a Pyrex glass bulb which was enclosed in a plastic cup filled with mercury, controlled to  $\pm 0.001 \text{ K}$  in a thermostatted oil bath (figure 2).

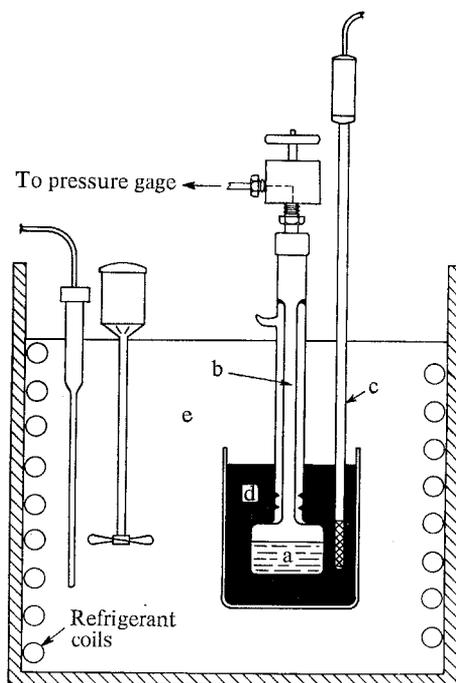


FIGURE 2. Apparatus for temperature measurement and control of the sample: a, water sample; b, Dewar tube; c, platinum resistance thermometer; d, mercury cup; e, thermostat light oil.

The temperature of the mercury, free of gradients or variations greater than  $\pm 0.0005 \text{ K}$ , was taken as the temperature of the water sample. Cold spots along the tube from the bulb to the valve were prevented by double-wall, evacuated construction that maintained a positive temperature gradient from the top of the bulb to the valve. Heat leak down the tube to the sample was prevented by contact with mercury at the top of the bulb. The valve was connected to the piston gage by a flexible metal hose also at ambient temperature. Cooling of the thermostatted bath was provided by a controlled refrigerant in coils regularly spaced on the inner wall. Electrical control heat was applied, through a thyatron-tube proportional controller, by a 125 W

blade heater placed near the vortex of the stirrer and well away from the sample bulb. Vigorous stirring of the oil bath prevented the formation of temperature gradients that might otherwise have caused measurable temperature changes throughout the mercury cup.

Temperatures were measured on the International Practical Temperature Scale of 1968 to the nearest 0.001 K with a 25  $\Omega$  platinum resistance thermometer calibrated with a continuous current of 2.0 mA at the oxygen, steam, and sulfur normal boiling temperatures by the National Bureau of Standards. Resistance readings with a current of 2 mA were made with a Mueller G-2 bridge and moving coil galvanometer. The resistance coils in the bridge were intercalibrated and normalized against a 100  $\Omega$  standard resistor that had been calibrated and certified to 0.002 per cent by the National Bureau of Standards. The ice-point resistance of the thermometer was determined with a reproducibility of  $\pm 0.0002$  K before and after the vapor pressure measurements with a current of 2 mA by direct immersion in a pure ice + slush bath. Water drained from the ice bath had an insignificant level of impurity as indicated by its low electrical conductivity, less than  $0.2 \mu\Omega^{-1} \text{ cm}^{-1}$ . The sum of the corrections to the ice-bath temperature for effects of impurity, barometric pressure, and depth of immersion of the thermometer was only 0.00002 K. A bridge zero-point correction of  $-0.00016 \Omega$  was determined and applied to the resistance readings.

#### SAMPLE

About 1 dm<sup>3</sup> of pure water (electric conductivity  $0.1 \mu\Omega^{-1} \text{ cm}^{-1}$ ), which had been deionized or softened by an exchange resin and distilled from potassium permanganate, was placed in a 2 dm<sup>3</sup> pyrex flask which had been washed with distilled water and was connected by manifold to the sample bulb and valve and to a diversion valve. Before the sample bulb and valve were connected to the manifold, they were cleaned by boiling with distilled water followed by repeated washing until the wash water indicated no significant conductivity, and then they were outgassed and evacuated.

Half of the water in the 2 dm<sup>3</sup> flask was then boiled off to remove dissolved gases, after which the flow was diverted to the cleaned evacuated sample bulb. When 25 cm<sup>3</sup> of sample had been collected in the bulb, the sample valve was closed, and the valve with sample bulb was placed in the thermostatted oil bath. The flexible line to the piston was connected to the valve and then the line and piston chamber were evacuated to  $1 \times 10^{-6}$  Torr through an oil diffusion pump before the valve on the sample was opened.† Thus, all sources of non-condensable gas were removed except, possibly, desorption from the line and the gage walls by water vapor. To remove any residual gas the gage, connecting line, and the vapor space over the sample were pumped through an auxiliary high-vacuum system before each vapor pressure was measured.

### 3. Results and discussion

The temperature and pressure measurements obtained with the piston unweighted, series I, and with the piston weighted, series II, are given in table 1. Series I measurements were begun in the supercooled region (in order to bracket the triple point) and

† Torr = (101.325/760) kN m<sup>-2</sup>.

TABLE 1. Vapor pressure  $p$  of water.

Series	$t_{\text{es}}/^\circ\text{C}$	$p/\text{Torr}$	$p/\text{N m}^{-2}$
I	$-2.500$ (supercooled)	$3.816 \pm 0.0023$	508.8
	$0.000$ (supercooled)	$4.586 \pm 0.0024$	611.4
	$+0.010$	$4.591 \pm 0.0025$	612.1
	$1.000$	$4.930 \pm 0.0026$	657.3
	$2.000$	$5.296 \pm 0.0026$	706.1
	$3.000$	$5.691 \pm 0.0027$	758.7
	$4.000$	$6.103 \pm 0.0028$	813.7
	$5.000$	$6.548 \pm 0.0029$	873.0
	$7.500$	$7.780 \pm 0.0032$	1037.0
	$10.000$	$9.219 \pm 0.0034$	1229.1
	$15.000$	$12.801 \pm 0.0043$	1706.6
II	$7.500$	$7.777 \pm 0.0032$	1037.0
	$12.500$	$10.865 \pm 0.0046$	1448.5
	$17.500$	$15.007 \pm 0.0055$	2000.7
	$20.000$	$17.548 \pm 0.0061$	2339.5

were overlapped at  $7.5^\circ\text{C}$  by series II measurements. The overlapping measurements provided a check of the internal consistency in the measured values of  $\theta$  and  $W$ .

The results were analyzed individually for maximum accumulative error based on the specifications for  $g/g_{\text{std}}$ ,  $\theta$ ,  $\Delta\theta$ ,  $W$ , and  $A$  (see references 9 and 10), and the presumed measurement and control of the temperature ( $\pm 0.001$  K) of the sample. Therefore, the calculated maximum systematic errors (column 3, table 1) include all known sources of error except possible non-equilibrium in the sample and gage.

Comparison of present values with experimental values and correlations from the literature were made in terms of residuals from the arbitrary fiducial relation $\dagger$  (see figure 3). The present results are in reasonably good agreement with the experimental values of Scheel and Heuse,<sup>(8)</sup> the  $25^\circ\text{C}$  point by Stimson,<sup>(1)</sup> the triple-point pressure measurement by Prytz,<sup>(11)</sup> and equation (2) of Smith, Keyes and Gerry.<sup>(12)</sup> The correlated vapor pressure values from "Warmetabellen"<sup>(13)</sup> were not included because they are based, in this temperature range, solely on the experimental data of Scheel and Heuse<sup>(8)</sup> which were preferred. Also, "Warmetabellen" values in the neighborhood of  $0^\circ\text{C}$  seem arbitrarily selected (see comments by Smith, Keyes, and Gerry, reference 12, page 151, and figure 3 of Osborne and Meyers, reference 2) and are suspected of being unreliable. Consequently, Osborne and Meyers'<sup>(2)</sup> selection of 4.584 Torr for the triple point of water must be considered in the same context. Measurements reported by Douslin and McCullough,<sup>(9)</sup> on the identical inclined-piston gage used for the present measurements, are as much as 30 mTorr higher at some temperatures than the present results and are not consistent. This variation did not previously involve a malfunction in the gage but rather was caused by incomplete degassing of the sample in the earlier work. Pertinent features of the present improved design of the

$\dagger$  The fiducial relation,  $\log_{10}(p/\text{Torr}) = 9.203001 - 2333.102 \text{ K}/T_{\text{es}}$ , was selected rather arbitrarily as a simple device for emphasizing differences in various sets of data by displaying residual quantities, and must not be mistaken as a satisfactory equation for the vapor pressure of water itself.

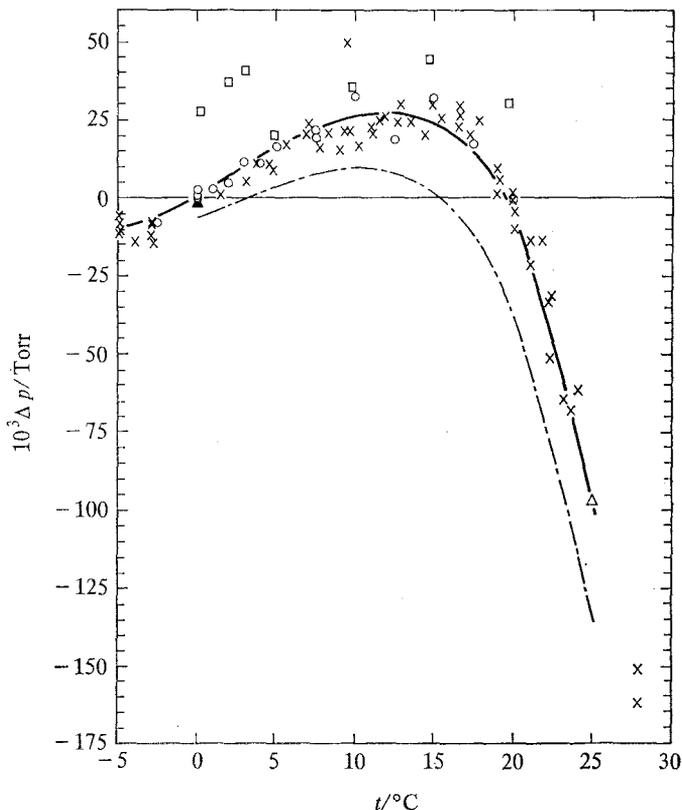


FIGURE 3. Vapor pressure of water showing deviations from a fiducial relation given in a footnote in section 3.  $\times$ , Scheel and Heuse<sup>(8)</sup>;  $\Delta$ , Stimson<sup>(1)</sup>;  $\blacktriangle$ , Prytz<sup>(11)</sup>;  $\square$ , Douslin and McCullough<sup>(9)</sup>;  $\circ$ , present measurements; —, Smith, Keyes, and Gerry,<sup>(12)</sup> equation (2); - - -, Osborne and Meyers, IST.

sample-bulb and thermostat which have led to significantly better vapor pressure measurements are discussed in section 2.

#### 4. Conclusion

On the basis of the new vapor pressures and the above comparisons with previous work, the following conclusions seem reasonable. (1) The International Steam Tables values are low by 7 to 37 mTorr in the range 0 to +20 °C; (2) the present results, in good agreement with Scheel and Heuse, and with Smith, Keyes, and Gerry, do indeed join smoothly with the +25 °C point of Stimson; and (3) the triple-point pressure is  $(612.1 \pm 0.4) \text{ N m}^{-2}$  or  $(4.591 \pm 0.003) \text{ Torr}$ .

The author thanks A. G. Osborn and P. H. Clopp for assistance in preparing the sample and in making the temperature measurements.

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