

# Some Precise Measurements of the Vapor Pressure of Water in the Range From 25 to 100 °C

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(May 29, 1969)

The vapor pressure of water was measured at seven temperatures in the range from 25 to 100 °C using the boiler and precision manometer with which standard resistance thermometers were calibrated at the NBS in the 1940's. A table gives measured values of pressure, adjusted to even degrees, and indicates estimates of the standard deviations of pressure and of the corresponding temperatures. Except for the measurement at 25 °C, the values of pressure were consistent within one part in 50 000. The temperature measurements had an estimated standard deviation of 0.000 40 degree.

Key words: Manometer; precision manometer; pressure;  $p$ - $t$  relation;  $p$ - $t$  relation of water; standard resistance thermometers; temperature; vapor pressure; vapor pressure of water;

## 1. Introduction

One of the fundamental fixed points on the International Temperature Scale of 1948 [1]<sup>1</sup> was the steam point, defined as the temperature of equilibrium between liquid water and its vapor under the pressure of 1013250 dynes per square centimeter. To realize this fixed point precisely at the NBS, the equilibrium temperature was maintained in a boiler and the pressure measured with a precision manometer. The boiler was developed in 1940 by N. S. Osborne and D. C. Ginnings to boil water without bumping. The precision manometer, first made functional in 1941, was being developed for gas thermometry.

In their formulation and tables for the pressure of saturated water vapor, in 1934, N. S. Osborne and C. H. Meyers [2] stated, "In the range below 100 C, . . . , it appears that the spread of the individual results leaves considerable to discretion. . . ." In this range the steam point boiler and the precision manometer could also be used for making reliable measurements of vapor pressure. During January 1942, therefore, C. S. Cragoe and H. F. Stimson made some vapor pressure measurements near 50 °C, 25 °C, 80 °C, and 60 °C in that order. It had been intended to extend the range of these measurements; in particular to obtain reliable values near the ice point, but war emergencies prevented this being done.

The four values obtained in 1942 were used by several authors in compiling tables. These values were known as the Cragoe-Stimson corrections to the Osborne-Meyers formulation and have been mentioned

as from a private communication. These corrections were finally published, however, by M. R. Gibson and E. A. Bruges in 1967 [3].

When work was resumed in 1946, a new boiler had to be made for the calibration of standard resistance thermometers at the steam point. This arrangement of the boiler and manometer is shown in part of figure 5 on page 156 of the book *Temperature*, Vol. 2 [4], and is essentially the same as that used in 1942. The descriptions of the manometer and boiler which follow that figure (*q.v.*) furnish many of the details which are relevant here.

From the ice point to 630.5 °C, the International Temperature Scale of 1948 was defined by standard resistance thermometers using the formula which, in the Callendar form, is

$$t = \frac{1}{\alpha} \left( \frac{R_t}{R_0} - 1 \right) + \delta \left( \frac{t}{100} - 1 \right) \left( \frac{t}{100} \right)$$

where  $\alpha = \frac{1}{100} \left( \frac{R_{100}}{R_0} - 1 \right)$  and  $R_0$ ,  $R_{100}$ , and  $R_t$  were

measured resistances at the ice point, steam point, and temperature,  $t$ . The  $\delta$  was to be found from added measurements near the sulfur point.

For certain special thermometers which could not be heated above the steam point, the  $\delta$  could be found well enough from added measurements at an intermediate temperature which could be determined with standard resistance thermometers.

One place to maintain the intermediate temperature was in the boiler, using the manometer as an indicator for the control of pressure. The manometer at the same time could also furnish data from which to determine

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

additional values of the vapor pressure of water. Accordingly six series of calibrations were made this way during 1947-1949 by R. E. Wilson, J. L. Cross, and H. F. Stimson. The data relevant to pressure were recorded but the necessary corrections were not applied at that time.

In recent years the author has received urgent requests from several sources for a formal publication of the values of the Cragoe-Stimson corrections. To make such a publication more useful, the values of pressure have now been computed from the 1947-1949 data and are included herein. Some statements are given with these values which may help one to make estimates of their accuracy.

## 2. Procedures

For the determinations made in January 1942, values of temperature from four platinum resistance thermometers were used. These thermometers were C-21 and C-22, which are known to have been made by H. K. Griffin about 1915; thermometer A-1, which probably was one of that same epoch; and M-2, which was a coiled filament thermometer described by C. H. Meyers in 1932 [5]. All four of these thermometers had alpha coefficients greater than 0.00390, which was considered good at that time. The bridge carried the designation L&N 50953 but it had been rebuilt at the NBS in 1932 by E. F. Mueller and C. H. Meyers with smaller coils thermostated in a metal block of high thermal diffusivity instead of a stirred oil bath. This rebuilt bridge was the prototype for the L&N G-2 bridge.

In the final computation single values of temperature were used from two thermometers near 50 °C, from four thermometers near 25 °C, from three thermometers near 80 °C, and from three thermometers near 60 °C. All values of temperature were actually below the even degrees but none by as much as 0.015 deg. Estimates of the standard deviations of these values are 0.000 28 deg at 50 °C, 0.000 75 deg at 25 °C, 0.000 27 deg at 80 °C, and 0.000 35 deg at 60 °C. The values of pressure have been adjusted to even temperatures by using the slopes,  $dp/dt$ , given in the Osborne-Meyers table.

For the determinations made in 1947-1949, four thermometers were used of an improved type which C. H. Meyers developed in 1943. This type is described briefly on page 149 of *Temperature*, Vol. 2 [4]. Their numbers were S-13, S-14, S-15, and S-17 and all had alpha coefficients between 0.003 9256 and 0.003 9261. (Values greater than 0.003 910 were specified in the International Temperature Scale of 1948.)

Six series of measurements were made, each series taking about two days. The first three series were made near 50 °C during May 1947, October 1947, and January 1948. The fourth series was made near 40 °C in July 1948. The fifth series was made near 60 °C in April 1949, and the sixth series was made near 70 °C in July 1949. The values of the actual temperatures were as near the even degrees as those in 1942.

The same bridge, 50953, that had been used in 1942 was used for the first five series. For the sixth series in July 1949 a new bridge, L&N 752448, was used. This bridge was designed by E. F. Mueller after he retired and is described briefly on page 151 of *Temperature*, Vol. 2 [4]. Twenty calibrations of bridge 50953 were made during the interval from April 1947 to May 1949. At no time did the calibrations change enough to affect the values of temperature by more than a few ten-thousandths of a degree.

Calibrations of standard resistance thermometers involve determining the three coefficients,  $R_0$ ,  $\alpha$ , and  $\delta$ , in the Callendar formula. The  $\delta$  does not change significantly and in fact all good thermometers have a  $\delta$  about 1.491 degrees. In some fifteen sets of calibrations of these thermometers during this two year interval, each  $R_0$  was found to increase, the greatest being for S-14, which increased by the equivalent of about 0.01 degree. Some years later, it was demonstrated to the author that a shock, such as letting the thermometer tube hit the table, increases its  $R_0$ . This helps to explain why the  $R_0$  increased for all the thermometers and implies that S-14 had a more shocking history than the others.

The values of individual alpha coefficients, on the other hand, were essentially constant and did not vary more than the equivalent of a few ten-thousandths of a degree in a hundred degrees; except for one set of calibrations in late March 1948, where values of all four thermometers were low by the equivalent of over 0.0015 degree. No certain explanation has been offered for this one set but the discrepancy is so large that the values from this set have been discarded from the averages.

To determine a value of an intermediate temperature, a common practice is to compute the value of temperature using the alpha obtained nearest the time when the measurements were made. Because the values of alpha were essentially constant over this period it is now believed that the averages of these alphas are preferable for use here; hence all steam point data in this period were recomputed and the averages taken.

The alpha coefficient for each of the four thermometers was determined at least six times during the two year period. The average values are given in table 1 and also estimates of their standard deviations. A change of  $39 \times 10^{-9}$  in the alpha coefficient corresponds to a change of 0.001 deg in 100 deg. The estimate of the standard deviation of the 100-deg interval with these four thermometers is thus 0.000 44 deg.

TABLE 1.

Thermometer	Alpha	Std. dev.
S-13	0.003 925 678	$5 \times 10^{-9}$
S-14	0.003 926 086	$27 \times 10^{-9}$
S-15	0.003 926 080	$12 \times 10^{-9}$
S-17	0.003 925 907	$23 \times 10^{-9}$

Immediately following the vapor pressure measurements made in January 1942 a triple-point cell was

developed at the NBS to furnish a more reproducible fixed point than the ice point. These cells were used in all subsequent measurements.

All bridge measurements were made with four readings, N-R-R-N (normal and reversed leads), with the thermometer current at 2 milliamperes (mA) and again at 1 mA. These measurements were then extrapolated to get the values of thermometer resistance at zero current. Corrections were made for the bridge zero, the bridge calibration, and, when using the triple point cell, for the extrapolation to 0 °C. Triple-point measurements were made at the end of each day's series and sometimes also during the middle of the day. This practice helped to minimize the errors from changes in  $R_0$  and in part for drifting of the bridge calibrations.

Using the alpha coefficient and the values obtained from  $R_t$  and  $R_0$ , values of the first term in Callendar's formula were computed and the delta term added. (At 50 °C the delta term is just  $-0.25 \delta$ . At 40 and 60 °C the term is  $-0.24 \delta$  and at 70 °C it is  $-0.21 \delta$ .) These computations gave values of temperature on the International Temperature Scale of 1948, at the level of the thermometer coils in the boiler.

To determine the pressure at this level an account was made for all fluid (both liquid and gas) heads contributing to the pressure. Above the thermometer coils was a head of steam up to the ice-water condenser. Above the condenser up to the dry ice trap was helium with some of the water vapor at the 0 °C saturation pressure. From the dry ice trap down to the laboratory floor was helium at 25 °C. From the floor down to the lower mercury meniscus of the manometer in the cellar there was helium at 20 °C. From the lower meniscus to the upper meniscus was liquid mercury at 20 °C. Finally above the upper meniscus there was mercury vapor pressure at 20 °C (about 1.6 dynes/cm<sup>2</sup>).

The values for these head corrections were computed for the expected pressure at the even ten degree temperatures, on the assumption that everything in the cellar below the laboratory floor was at 20 °C. This temperature is the temperature at which the gage blocks were calibrated and also was near the temperature of the earth surrounding the cellar. A platinum thermometer and thermocouples were used to measure the departures from 20 °C, several times a day. A "cellar-factor" was applied to these departures to account for the thermal expansion of the gage blocks and for the thermal expansion of all the fluid columns in the cellar contributing to the pressure head. These corrections were small, seldom exceeding a few dynes per square centimeter.

Table 2 gives the values used for these factors, and

TABLE 2. Correction factors in dynes/(cm<sup>2</sup> deg)

Temperature	Cellar-factor	$dp/dt$
40 °C	12.57	3931
50 °C	21.01	6121
60 °C	33.93	9220
70 °C	53.12	13481

also values from the Osborne-Meyers table for the  $dp/dt$  used to adjust values of pressure to the even temperatures.

### 3. Results

Table 3 gives the values of the vapor pressure of water obtained in 1942, adjusted to the even temperatures. The number of determinations of temperature is given in column 2. Column 3 gives the values of pressure in dynes per square centimeter and column 4 gives them in newtons per square meter, which is the unit of pressure in the International System of Units.

TABLE 3. 1942 values for the vapor pressure of water

Temperature	Number	Dynes/cm <sup>2</sup>	N/m <sup>2</sup>
25 °C	4	31 670	3 167.0
50 °C	2	123 386	12 338.6
60 °C	3	199 243	19 924.3
80 °C	3	473 639	47 363.9

Table 4 gives the average values for the vapor pressure of water obtained from each of the six series of measurements made in 1947-1949. The second column gives the month of the series. Column 3 gives the number of computed values of pressure contributing to the average. Column 4 gives the average values of pressure in dynes per square centimeter, and column 5 gives estimates of the standard deviations of these values of pressure.

TABLE 4. 1947-1949 values for the vapor pressure of water

Temperature	Date	Number	Pressure	Std. dev.
50 °C	May 1947	16	dynes/cm <sup>2</sup> 123 393.7	dynes/cm <sup>2</sup> 2.7
50 °C	Oct. 1947	8	123 381.6	1.0
50 °C	Jan. 1948	7	123 383.7	0.3
40 °C	July 1948	24	73 772.7	1.5
60 °C	Apr. 1949	20	199 241.5	1.6
70 °C	July 1949	18	311 661.5	2.2

In this table the value for pressure at 50 °C in the May 1947 series is seen to be higher than the later two. This series took three days. During this time the values of temperature, at the level of the thermometer coils, rose by over a thousandth of a degree but on the third day were still a thousandth of a degree below the values in the October 1947 and the January 1948 series. If it is true that the temperature was low, it should indicate that the pressure was also lower than that computed from the measured height of the mercury column. When adjusted to the even temperature, therefore, the value for pressure would be too high.

It now seems plausible that a bubble of gas was in the mercury column to the upper cell, thus decreasing the fluid head and giving too low a pressure and temperature. A note added to the record book, soon after the May 1947 series, suggests to the author that a gas bubble was suspected then. A similar explanation

might also account for the low values of alpha in the late March 1948 set, mentioned above. The value from the May 1947 series, therefore, has not been included in the final table of values of the vapor pressure of water at 50 °C.

Table 5 gives the combined results from the 1942 and the 1947-1949 periods. In column 4 are the estimated standard deviations of pressure in dynes per square centimeter. Using values for  $dp/dt$  gives the corresponding deviations of temperature in the next column. The last column gives the values in newtons per square meter. From the estimates of the standard deviations in table 5 it appears that (except for the 25 °C measurement) the pressure measurements were consistent with each other to one part in 50 000. It also appears that temperatures in this range were

measured with a standard deviation estimated to be 0.000 40 degree.

The International Practical Temperature Scale of 1968 (IPTS-68) [6] now replaces the International Temperature Scale of 1948, which has been used for all foregoing temperature computations. In the range between 0 and 100 °C the values of temperature on the new scale are smaller than on the 1948 scale. This makes the values of pressure larger, when adjusted to the corresponding even temperatures. Table 6 gives the even temperatures on the 1968 scale in the first column, the temperature correction in the second column, and the values of pressure adjusted to the even temperatures in the third column.

In conclusion, it appears that the earlier and later measurements agree within experimental error.

TABLE 5. Summary of measured values for the vapor pressure of water

Temperature ITS-48	Years	Pressure	Std. dev.	Std. dev.	Pressure
°C		<i>dynes/cm<sup>2</sup></i>	<i>dynes/cm<sup>2</sup></i>	<i>degrees</i>	<i>N/m<sup>2</sup></i>
25	1942	31 670.	1.4	0.000 75	3 167.0
40	1948	73 772.7	1.5	0.000 41	7 377.3
50	1942, 1947, 1948	123 383.0	1.8	0.000 19	12 338.3
60	1942, 1949	199 242.2	1.6	0.000 17	19 924.2
70	1949	311 661.5	2.2	0.000 16	31 166.2
80	1942	473 639.	5.2	0.000 27	47 363.9
100	1947-1949	1013 250.	15.9	0.000 44	101 325.0

TABLE 6. Values of pressure at temperatures on the IPTS-68

Temperature IPTS-68	Correction $t_{68} - t_{48}$	Pressure
°C	<i>degrees</i>	<i>N/m<sup>2</sup></i>
25	-0.008 54	3 168.6
40	-0.010 34	7 381.3
50	-0.010 37	12 344.6
60	-0.009 57	19 933.0
70	-0.008 05	31 177.0
80	-0.005 89	47 375.2
100	0.000 00	101 325.0

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(Paper 73A5-567)