

## RESEARCH PAPER RP1088

Part of *Journal of Research of the National Bureau of Standards*, Volume 20,  
April 1938

## WATER AS A REFERENCE STANDARD FOR EBULLIOMETRY

By Wojciech Świątosławski<sup>1</sup> and Edgar Reynolds Smith

### ABSTRACT

The properties of water are discussed with reference to its suitability as a primary standard for comparative ebulliometric measurements. The influence of small natural or accidental differences in isotopic composition with respect to the oxygen as well as to the hydrogen isotopes is shown to be negligible. The equation of Beattie and Blaisdell is suitable for obtaining the boiling point of water to 0.001° C or better at any pressure between 660 and 860 mm, and an equation, based on the data of the same authors, is given for obtaining the pressure in an apparatus from the measurement of boiling point.

The establishment of a universally recognized primary reference standard for ebulliometric investigations is necessary because comparative measurements of boiling points and condensation temperatures of liquids can be made with high precision. Numerous measurements made during recent years have demonstrated that modern ebullioscopic methods easily permit the attainment of a precision of the order of magnitude of 0.001° C in relative boiling point or condensation temperature. These methods also permit the measurement of pressure in a closed system with a relative precision of about 0.03 mm of mercury. However, such precision can be obtained with ease only by the use of comparative measurements, which require that the value determined be related directly to that of the standard reference substance. For reasons to be discussed, it appears that water is the only liquid substance possessing the characteristic properties required of a primary reference standard for such measurements, and the desirability of its adoption has been the subject of a report presented to the Committee for Physico-Chemical Data of the International Union of Chemistry.<sup>2</sup>

The ebullioscopic constant of water is exceptionally small, so that a content of even several thousandths percent of electrolyte has a very small effect on the boiling point. For example, the addition of 0.006 percent of sodium chloride increases the boiling point by only 0.001° C, although the electrical conductivity of such a solution is considerably increased over that of pure water. Because of this circumstance, the substances that water extracts from the walls of the container have, in practice, insignificant influence on its boiling point.

<sup>1</sup> Professor of Physical Chemistry at the Polytechnic Institute of Warsaw, President of the Committee for Physico-Chemical Data of the International Union of Chemistry, Minister of Education for Poland.  
<sup>2</sup> W. Świątosławski. *Comptes Rendus de la XII Conférence de l'Union Internationale de Chimie*, p. 89. (1936).

Measurements, as well as theoretical considerations, demonstrate that the presence of isotopes of hydrogen and oxygen in ordinary water does not have a measurable influence on its boiling point. The boiling points of dilute aqueous solutions of deuterium water<sup>3</sup> in the range from 0.3 to 7 mole percent of D<sub>2</sub>O have been shown to increase linearly with increase in D<sub>2</sub>O, according to the equation

$$\text{Mole percent D}_2\text{O} = 70.9 \Delta T,$$

where  $\Delta T$  is the boiling point in degrees centigrade minus 100. It is obvious from the equation that an increase of 0.071 mole percent in the content of deuterium water, corresponding to an increase in density of 74 ppm, is required for an increase of 0.001° C in boiling point. No such concentration of D<sub>2</sub>O has been found in any water from natural sources. Fluctuations in the isotopic composition of ordinary surface water from different sources and the slight fractionation which occurs during purification by simple distillation may cause differences in the boiling point of the order of 0.00005° C, which at present certainly may be neglected when using water as the primary standard for precise ebulliometric measurements.

The effect of small differences in the isotopic composition of oxygen was tested experimentally in the following way. Water having a density of 438 ppm greater than normal, prepared by electrolysis, was normalized<sup>4</sup> with respect to the hydrogen isotopes. The remaining difference in density was 19 ppm, due to an increase in the proportion of the heavy isotopes of oxygen, this excess being about three times as much as corresponds to the difference in atomic weight of oxygen from air and from ordinary water. A series of measurements of the differences between the boiling point and condensation temperature of this water in a differential ebulliometer of standardized dimensions,<sup>5</sup> as well as of the differences between its boiling point and that of normal water in a second ebulliometer, gave values always less than 0.001° C, measured with a platinum resistance thermometer. Thus the influence of naturally occurring or of small artificial differences in isotopic composition of water with respect to the oxygen isotopes, as well as to the hydrogen isotopes, is negligible.

Considering that the precision required for contemporary ebulliometric measurements is of the order of 0.001° C, water of the purity used in determinations of electric conductivity, which is readily prepared, can be regarded as suitable.

The relation between the temperature of boiling water and the pressure has been investigated a number of times by different experimenters. Ordinarily it has been customary to use the data contained in *Wärmetabellen*,<sup>6</sup> which are based on the determinations of Holborn, Scheel, Henning, Wiebe, and others. During the past 5 years, the measurements of Zmaczynski and Bonhoure<sup>7</sup> and of Moser<sup>8</sup> have also been considered excellent for comparative ebulliometric work.

<sup>3</sup> Edgar R. Smith and Mieczysław Wojciechowski. *J. Research NBS* **17**, 841 (1936) RP947.

<sup>4</sup> Edgar R. Smith and Harry Matheson. *J. Research NBS* **17**, 625 (1936) RF9 32.

<sup>5</sup> W. Świętosławski. *Ebulliometry*, p. 16 (Chemical Publishing Co. of New York, Inc. 1937).

<sup>6</sup> *Wärmetabellen*, (Friedr. Vieweg & Son, Braunschweig, 1919).

<sup>7</sup> A. Zmaczynski and A. Bonhoure. *Compt. rend.* **189**, 1069 (1929); *J. Phys.* **1**, 285 (1930). The results of these measurements have been recalculated recently by Zmaczynski and the figures obtained are given in table 1.

<sup>8</sup> H. Moser. *Ann. Phys.* [5] **14**, 790 (1932).

More recently, however, the results of particularly careful measurements of the temperature-pressure relation for water, made with the highest accuracy attainable, have been published by two separate laboratories, the National Bureau of Standards<sup>9</sup> and the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.<sup>10</sup> The measurements of the latter include a special study of the range 660 to 860 mm, which ordinarily is of most value for ebulliometry. The data of several investigators over this range are shown in table 1. The values of the National Bureau of Standards and the Massachusetts Institute of Technology as well as those obtained recently by Zmaczynski at the Physikalisch Technische Reichsanstalt are in agreement to better than 0.001° C. Their maximum deviation from the recalculated data of Zmaczynski and Bonhoure and from the values of Wärmetabellen over the smaller range of the latter (680 to 800 mm) is 0.002° C.

TABLE 1.—Boiling point of water between 660 and 860 mm pressure

Pressure	Wärmetabellen	Zmaczynski and Bonhoure <sup>1</sup>	Moser	Zmaczynski 1937 <sup>2</sup>	Osborne and Meyers	Smith, Keyes, and Gerry	Beattie and Blaisdell
mm	° C	° C	° C	° C	° C	° C	° C
660	-----	-----	-----	96.095 <sub>5</sub>	96.0954	96.0967	96.0964
680	96.916	96.913 <sub>2</sub>	96.910	96.913 <sub>8</sub>	96.9138	96.9144	96.9141
700	97.714	97.711 <sub>4</sub>	97.709	97.712 <sub>6</sub>	97.7125	97.7128	97.7124
720	98.494	98.491 <sub>5</sub>	98.490	98.493 <sub>6</sub>	98.4925	98.4926	98.4924
740	99.255	99.254 <sub>2</sub>	99.254	99.254 <sub>4</sub>	99.2547	99.2548	99.2546
760	100	100	100	100	100	100	100
780	100.728	100.729 <sub>9</sub>	100.729	100.729 <sub>2</sub>	100.7293	100.7292	100.7292
800	101.442	101.444 <sub>5</sub>	-----	101.443 <sub>2</sub>	101.4432	101.4431	101.4430
820	-----	102.144 <sub>5</sub>	-----	102.142 <sub>5</sub>	102.1425	102.1426	102.1424
840	-----	102.830 <sub>1</sub>	-----	102.827 <sub>9</sub>	102.8279	102.8285	102.8279
860	-----	-----	-----	103.500 <sub>6</sub>	103.5004	103.5017	103.5004

<sup>1</sup> During his work at the PTR, Zmaczynski has found the temperature coefficient of the resistance of the Smith bridge, as given by the constructor of the apparatus, to be erroneous. Since the same bridge had been used by Zmaczynski at Paris in 1929, the data obtained by him in collaboration with Bonhoure proved to be erroneous too and had to be recalculated. Zmaczynski has made these calculations now. A note with the corresponding corrections will appear shortly in the Comptes Rendus de l'Académie des Sciences.

<sup>2</sup> In consequence of the understanding maintained between the President of PTR, Prof. J. Stark, Charlottenburg, and Prof. W. Świętosławski, Warszawa, Drs. H. Moser and A. Zmaczynski have carried out measurements of the boiling point of water under various pressures in the limits from 270 to 2,200 mm of mercury, using two different methods. This work is not yet finished. The above table contains some of the data obtained by A. Zmaczynski by the ebulliometric method, for pressures from 660 to 860 mm of mercury.

Beattie and Blaisdell have expressed their data precisely over the range of 660 to 860 mm by the equation

$$t = 100 + 0.0368578(p - 760) - 0.000020159(p - 760)^2 + 0.00000001621(p - 760)^3,$$

which is apparently reliable to better than 0.001° C on the International Temperature Scale for nearly 4° above and below the fixed reference point of 100° C. This precision is sufficient for every kind of comparative ebulliometric measurement, and is a potent reason for the adoption of water as a primary standard.

<sup>9</sup> N. S. Osborne and C. H. Meyers. J. Research NBS 13, 1 (1934) RP 691.

<sup>10</sup> L. B. Smith, F. G. Keyes, and H. T. Gerry. Proc. Am. Acad. Arts Sci. 69, 137 (1934); J. A. Beattie and B. E. Blaisdell. Proc. Am. Acad. Arts Sci. 71, 361 (1937).

For calculations of pressure from measurements of temperature, it is more convenient to have the pressure expressed as an explicit function of the temperature. For this purpose, the original data of Beattie and Blaisdell, consisting in 4 separate runs having a total of 38 determinations of temperature and corresponding pressure between 660 and 860 mm, were treated by the method of least squares to obtain the equation

$$p = 760 + 27.1313 (t - 100) + 0.40083 (t - 100)^2 + 0.003192 (t - 100)^3$$

This equation was found to fit the MIT data with an average deviation of 0.012 mm and a greatest deviation of 0.031 mm, and to agree with the NBS data with equal precision. It may be well to point out that the equation fails rapidly above and below the range for which it was obtained.

To avoid the use of logarithms, the power series type of equation was chosen. When the use of logarithms is convenient, the following equation, suggested by N. S. Osborne and C. H. Meyers of the heat measurements section of this Bureau, is recommended.

$$\log_{10} p = 5.053988 - \frac{1647.6}{t + 226}$$

In this equation  $p$  is expressed in standard atmospheres and  $t$  in degrees centigrade. Between 80 and 120° C, or from about  $\frac{1}{2}$  to 2 atmospheres, it reproduces the data tabulated by Osborne and Meyers with a precision of 0.001° C or better. In addition to validity over a greater range than the power series equation, it has the advantage of being explicit in either pressure or temperature.

In the paper by Osborne and Meyers there is given a table of the boiling point of water (table 8, condensation temperature of steam) at pressure intervals of 1 mm between 500 and 799 mm. Linear interpolation from this table is convenient, rapid, and reliable for comparative ebulliometric measurements when it is desired to avoid the use of an equation and when pressures lower than 660 mm are encountered.

When employing water as a standard, it is desirable to use a differential ebullimeter, or one having several stages<sup>11</sup> in order to be able, at any given moment, to compare the boiling point with the temperature of condensation of the vapor. This is of essential importance when the ebullimeter containing water is connected to another containing the liquid studied and when these two form, together with a manostat and manometer, an isolated system. This is because, in spite of all precautions, the vapors of the liquid may penetrate the ebullimeter filled with water and vice versa. By using differential ebullimeters, the purity of the water (primary standard) and of the substance studied can be verified at any time. Usually if the difference between the boiling point and temperature of condensation of the vapor does not exceed 0.001° C, contamination has not occurred to an extent which will affect the boiling point by more than a few thousandths of a degree.<sup>12</sup>

<sup>11</sup> W. Świątoślowski. *Ebullimetry*, p. 16. (Chemical Publishing Co. of New York, Inc. (1937).)

<sup>12</sup> It is possible, however, that this test can fail in case of the formation of an ideal solution between two components having nearly equal boiling points. To take an extreme case, for example, the boiling point of water containing 1 mole percent of deuterium oxide is increased over that of ordinary water by 0.014° C, although the difference between the boiling point and condensation temperature is only 0.001° C.

By the use of the comparative ebulliometric method of measurement, the value of  $T = T_{\text{subst.}} - T_{\text{H}_2\text{O}}$ , the difference between the boiling point of the given substance and that of water boiling under the same pressure is obtained. When this difference is large, both convenience and precision would be enhanced if suitable secondary standard liquids of reliably known boiling points, covering the range of 25 to 250° C were available for the comparison. Although encouraging progress has been made,<sup>13</sup> the problem of establishing a series of satisfactory secondary standards for ebulliometry requires further experimental study and consideration.

WASHINGTON, January 18, 1938.

<sup>13</sup> W. Świątosławski. Comptes Rendus de la XII Conférence de l'Union Internationale de Chimie, p. 89 (1936).