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BOILING POINT OF ETHYL ETHER AND ITS RELATION TO PRESSURE

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ABSTRACT

Ethyl ether of a high degree of purity was prepared, and its boiling point was found to be 34.481 ± 0.003° C. The $\frac{dt}{dp}$ ratio of ethyl ether (degrees per mm at 760 mm of Hg) is 0.0372.

Many attempts have been made to determine the exact boiling point of ethyl ether. The large discrepancies in the results reported are on the one hand due to difficulties connected with the purification of this important substance and on the other hand to a lack of ebulliometric technic adequate to insure high precision of the determination of the boiling point and $\frac{dt}{dp}$ ratio.

The impurities in ethyl ether are partly the products of side reactions in its manufacture, and are partly connected with its chemical nature, as it tends to decompose somewhat, especially when exposed to light or when heated with drying agents. The most persistent impurity is water. A mixture of ethyl alcohol and ether shows very marked positive deviations from Raoult's law, especially for small concentrations of ethanol. This indicates that it is difficult to prepare ether free from alcohol by distillation, even in an efficient column, and therefore the ethanol should be carefully washed out with water.

According to the nomenclature of Swietoslawski,[2] water forms with ether a homoazeotropic-heterozeotropic system, the boiling points of which are slightly below that of ether. For this reason small amounts of water in ether to be used for the determination of its boiling point and related properties are best removed by digestion with phosphorus pentoxide in the pot of an efficient still, after which the ether should be distilled directly into the ebulliometer to avoid any contact with moist air. For this purpose an efficient 40-bulb Swietoslawski [3] distilling column was used in this work. To control the purity of the substance under investigation, Swietoslawski's sensitive ebulliometric test of purity was used. In principle it is based on the measurement of the difference, Δt, between the boiling point and condensation temperature in an ebulliometer of standardized dimensions.[4] The

[1] Guest worker from Polytechnic Institute, Warsaw, Poland.
[2] W. Swietoslawski, Bul. Int. Acad. Polonaise [A] 1934, 472.
[3] W. Swietoslawski, J. chim. phys. 27, 329 (1930); Bul. Soc. Chim. France [4] 49, 1563 (1931).
[4] W. Swietoslawski, Bul. Int. Acad. Polonaise [A] 1929, 434; Bul. Soc. Chim. France 49, 1563 (1931); Z. phys. Chem. [A] 160, 259 (1932).

purer the substance is the smaller will be Δt, and for an absolutely pure substance or an azeotropic mixture, the boiling point and temperature of condensation are equal, thus giving Δt equal to zero.

For determining the boiling point and $\frac{dt}{dp}$ ratio of ether, Swietoslawski's ebulliometric technic [5] and the comparative method of measurements with water as a reference liquid were used. The measurements of temperature were made with a potential terminal, strain-free platinum resistance thermometer [6] having a coiled filament, and calibrated in the Heat Division of the National Bureau of Standards. The normal boiling point was calculated by the use of a formula previously reported,[7] in which t_s represents the normal boiling point

$$t_s = t'_s + \frac{dt_s}{dt_w}(100 - t'_w)$$

of the substance under investigation, t'_s the boiling point of the substance actually measured, t'_w the boiling point of water actually measured under the same pressure as t'_s, and $\frac{dt_s}{dt_w}$ the ratio of the coefficients $\frac{dt}{dp}$ for the given substance and water.

The ratio $\frac{dt}{dp}$ for the substance under investigation was calculated from the data on $\frac{dt_s}{dt_w}$ by multiplying the latter by the $\frac{dt}{dp}$ ratio of water at the same pressure.

$$\left(\frac{dt}{dp}\right)_s = \frac{dt_s}{dt_w}\left(\frac{dt}{dp}\right)_w$$

In these measurements, pressure is defined by the boiling point of water.

Two kilograms of nearly anhydrous ether, kindly furnished by the Mallinckrodt Chemical Works, through the courtesy of H. V. Farr, for a related investigation on the determination of water in ether, was boiled for 12 hours over phosphorus pentoxide in the 40-bulb distilling column under total reflux, and then slowly distilled, the first 400 ml of distillate being removed. Then a 50-ml sample was distilled directly into the ebulliometer, and its ebullioscopic properties determined at once. The difference, Δt, between the boiling point and condensation temperature of this sample was 0.001° C. The substance therefore was of the fifth or highest degree of purity on Swietoslawski's scale.[8] The measurement of Δt was repeated after the determination of the boiling point. No change in the purity of the substance was detected.

The ratio $\frac{dt_s}{dt_w}$ was measured for the pressures corresponding to

[5] W. Swietoslawski, Ebuljometrja, Warszawa (1935); J. chim. phys. **27**, 496 (1930); Roczniki Chem. **9**, 266 (1929).
[6] C. H. Meyers, BS J. Research **9**, 807 (1932) RP508.
[7] M. Wojciechowski, BS J. Research **17**, 453 (1936) RP921.
[8] W. Swietoslawski, IX Congreso Int. Quim. Pura Aplicada, Madrid, **1934**, 13.

those of water when boiling at 100.962° C and 97.749° C, and this ratio for any pressure included in these limits may be calculated by interpolation. The numerical data on the dt_s/dt_w ratio are presented below.

$\frac{dt_s}{dt_w}$	Boiling point of water
1. 0063	100. 962
1. 0067	97. 74

The normal boiling point of ether was found to be 34.48$_1$° C, and $\frac{dt}{dp}$ at 760 mm, calculated from the above data, equals 0.0372, taking $\frac{dt}{dp}$ of water as 0.0370.

Table 1 contains a comparison of the results obtained by the author with values previously reported in the literature.

TABLE 1.—*Comparison of the results with the data of previous observers*

Author	Boiling point	$\frac{dt}{dp}$
	°C	°C/mm
E. Beckmann and P. Fuchs [1]	34. 6	0. 0398
H. H. Perkin [2]	34. 60	.37 (10 mm)
S. Young [3]	34. 6	.37 (10 mm)
J. Wade and H. Finnemore [4]	34. 5	
B. H. Carroll, G. K. Rollefson, and J. H. Mathews [5]	34. 0	
J. Timmermans and F. Martin [6]	34. 60	.036
J. H. Mathews [7]	34. 66	
Calculated from temperature vapor pressure curve reported by E. A. Louder, T. R. Briggs, and A. W. Browne [8]	34. 45	
Author	34. 481 + 0. 003	.0372

[1] Z. phys. Chem. **18,** 495 (1895).
[2] J. Chem. Soc. **45,** 430 (1894).
[3] Distillation, Dublin, 1903; J. Chem. Soc. **85,** 933 (1904).
[4] J. Chem. Soc. **95,** 1840 (1909).
[5] J. Am. Chem. Soc. **47,** 1785 (1925).
[6] J. chim. phys. **23,** 411 (1926).
[7] J. Am. Chem. Soc. **48,** 569 (1926).
[8] Ind. Eng. Chem. **16,** 932 (1929).

The purity of the ether used in this investigation, as indicated by the value of 0.001° for Δt, was such that the accuracy of the boiling point can hardly be in question by more than 0.003°, allowing 0.001° for possible error caused by the use of the method of comparative measurements.

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