EBULLIOMETRIC AND TONOMETRIC MEASUREMENTS ON NORMAL ALIPHATIC HYDROCARBONS

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ABSTRACT

By the application of the precise method developed by W. Swietoslawski for measuring the boiling points and the differences between boiling point of liquids and the condensation temperature of their vapors, it is possible to determine several facts of interest to the chemist. Among these are the purity of the substance under investigation, its boiling point, and the relation of boiling point to pressure.

The normal hydrocarbons, pentane, hexane, heptane, and octane have been studied by this method. The ebulliometric control of purity of the preparations, the use of substances of high purity, and the application of a method of comparative measurements insure the accuracy of the results reported.

The numerical data are as follows: n-pentane, boiling point 36.077, $\frac{dt}{dp}=0.0391$; n-hexane, boiling point 68.733, $\frac{dt}{dp}=0.0420$; n-heptane, boiling point 98.365, $\frac{dt}{dp}=0.0449$; n-octane, boiling point 125.658, $\frac{dt}{dp}=0.0477$.

It was found that the introduction of a CH_2 group into the chain of each of the normal aliphatic hydrocarbons investigated has the specific effect of increasing the $\frac{dt}{dp}$ ratio by the amount 0.0029.

CONTENTS

I. INTRODUCTION

The development of W. Swietoslawski's precise ebulliometric technic [2] and application of the comparative method of measurements [3] offers an opportunity for systematic ebulliometric and tonometric studies. The present work was done to establish exact data

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[1] Guest worker from Polytechnic Institute, Warsaw, Poland.
[2] W. Swietoslawski, Ebuljometrja, Warszawa (1935).
[3] W. Swietoslawski, J. chim. phys. 27, 496 (1930), Roczniki Chem. 9, 266 (1929).

on boiling points and $\dfrac{dt}{dp}$ ratios, the rate of change of boiling point with change of pressure, as well as to investigate the relation between the *constitution* of a compound, and the value of its $\dfrac{dt}{dp}$ ratio for a series of normal aliphatic hydrocarbons.

The application of the sensitive ebulliometric test for purity makes it possible to select preparations of high purity and consequently to obtain results which approach very closely to the constants for substances of "absolute" purity.

II. METHOD OF MEASUREMENT

The method of measurement used in the present work has been described in detail by W. Swietoslawski.[4] The following are the principles of the method. A barometric ebulliometer [5] filled with water as a reference liquid, and a standard differential ebulliometer,[6] containing the substance under investigation, are connected to a manostat, and the boiling point of each liquid is measured at three or more different pressures. The ratio of the change in boiling point of the given substance to the change in the boiling point of water caused by the change in pressure is equal to the ratio between the $\dfrac{dt}{dp}$ coefficients of the given substance and that of water.

$$\frac{dt_s}{dt_w} = \frac{\dfrac{dt}{dp_s}}{\dfrac{dt}{dp_w}}$$

A. Zmaczynski [7] has carefully investigated the influence of pressure on the ratio $\dfrac{dt_s}{dt_w}$ for several substances, and found that the curve representing this relation has only a very small curvature and a relatively small slope, thus permitting interpolation of the data to the pressure at which the boiling point was determined.

Obviously, the correction for pressure to be introduced in calculating the normal boiling point of the substance investigated is equal to the correction for water multiplied by the ratio $\dfrac{dt_s}{dt_w}$. In this manner the boiling point of water serves as a barometric reading, and gives directly the value of the correction to normal pressure as the difference $100 - t'_w$, where t'_w is the boiling point of water actually measured.

The normal boiling point t_s of the substance under investigation may be calculated by the formula

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

[4] W. Swietoslawski, J. Chim. phys., also A. Zmaczynski, Roczniki Chem. **13**, 181 (1933); J. chim. phys. **27**, 503 (1930).
[5] W. Swietoslawski, Bul. int. Acad. Polonaise [A] **1929**, 434; Bul. Soc. Chim. France **49**, 1563; Z. phys. Chem. [A] **160**, 257 (1932).
[6] W. Swietoslawsi, I X Congreso Int. Quim. Pura Aplicada, Madrid **1934**, 13; J. Phys. Chem. **38**, 1169 (1935); Z. phys. Chem. [A] **160**, 257 (1932).
[7] A. Zmaczynski, J. chim. phys. **27**, 503 (1930); Roczniki Chem. **13**, 181 (1933).

where t'_s is the boiling point of the substance actually measured under the same pressure as t'_w, that of water.

A knowledge of the ratio $\dfrac{dt_s}{dt_w}$ for the given substance permits calculation of the value of the $\dfrac{dt}{dp}$ ratio, referred to that of water as the primary reference liquid.

$$\frac{dt}{dp_s} = \frac{dt}{dt_w} \frac{dt_s}{dp_w}$$

This method permits rapid and precise measurements of $\dfrac{dt}{dp}$ ratios.

The value 0.0370 for $\dfrac{dt}{dp}$ of water at normal pressure, found by Zmaczynski and Bonhour,[8] was used in calculating the $\dfrac{dt}{dp}$ ratios reported in this paper.

III. CONTROL OF PURITY OF SUBSTANCES

Swietoslawski's ebulliometric test [9] for the purity of liquid substances, as used in this work, is based on the measurement of Δt, the difference between the boiling and condensation temperatures in an ebulliometer of standard dimensions. For a pure substance or an azeotropic mixture, this difference is equal to zero, and increases with concentration of impurities. The magnitude of Δt depends also on the nature of the impurities.

To classify the purity of the preparations under investigation, Swietoslawski's scale of purity of liquid substances was used. According to this scale, substances are divided into five groups, as shown below.

Limits of Δt	Degree of purity
°C	
0.000 to 0.005	V
.005 to .020	IV
.020 to .050	III
.050 to .100	II
.100 to 1.000	I

IV. MEASUREMENTS OF TEMPERATURE

Boiling points were measured with a potential terminal platinum resistance thermometer with coiled filament,[10] calibrated at this Bureau, and kindly furnished by C. H. Meyers. The measurements of the degree of purity were made with a Beckmann-Swietoslawski mercury thermometer.[11]

[8] A. Zmaczynski and A. Bonhour, J. Phys. 1, 285 (1930).
[9] W. Swietoslawski, IX Congreso Int. Quim. Pura Aplicada, Madrid 1934, 13.
[10] C. H. Meyers, BS J. Research 9, 807 (1932) RP508 .
[11] W Swietoslawski, Roczniki Chem. 11, 545 (1931).

V. METHOD OF EXTRAPOLATION OF THE BOILING POINT

To calculate the normal boiling point of a substance not of high purity, a method of extrapolation related to that previously reported [12] was applied. The method is based on the correlation of the change of boiling point with the change of Δt, the difference between the boiling point and condensation temperature, when distilling through the side tube of the ebulliometer successive small portions, each of a few milliliters, of the preparation. This distillation partially removes the more volatile impurities, and the substance then behaves like a series of preparations containing different amounts of practically the same kind of impurities. By plotting boiling point T, T_1, T_2 . . . . against corresponding differences Δt, Δt_1, Δt_2 . . . one may easily extrapolate to the boiling point of the preparation having the difference Δt equal to zero, which is the boiling point of the pure substance.

VI. MATERIALS USED

In the present work there have been investigated the following hydrocarbons: n-pentane, n-hexane, n-heptane, and n-octane.

1. n-PENTANE

The n-pentane used was that prepared synthetically and purified by Mair.[13] The sample used had a difference between the boiling and condensation temperatures of 0.002° C, and was accordingly of the fifth (highest) degree of purity on Swietoslawski's scale.

2. n-HEXANE

Two preparations of n-hexane were used. One was prepared synthetically and purified by Mair;[14] the other was also synthetic. Mair's preparation, having Δt equal to 0.005° C, was of the fifth degree of purity. The second preparation investigated was of the fourth degree of purity, as indicated by a value of 0.010° C for Δt.

3. n-HEPTANE

A preparation of n-heptane obtained from Mair, distilled from Jeffrey pine oil, was used. This preparation, having a difference Δt between its boiling point and temperature of condensation equal to 0.013° C, was according to Swietoslawski's scale of the fourth degree of purity.

Another preparation of n-heptane from Jeffrey pine oil, purified by distillation in a locket chain column by F. W. Rose, Jr., was of the fifth degree of purity, having Δt equal to 0.005° C.

4. n-OCTANE

The preparation of n-octane used was prepared by B. J. Mair, and was found to be of the fourth degree of purity, having $\Delta t = 0.008°$ C.

[12] M. Wojciechowski and E. R. Smith, Nature 138, 30 (1936).
[13] B. J. Mair, BS J. Research 9, 457 (1932) RP482.
[14] See footnote 13.

VII. EXPERIMENTAL RESULTS AND CONCLUSIONS

The data on boiling points obtained in the present work are tabulated in table 1.

TABLE 1.—*Boiling points of four normal aliphatic hydrocarbons*

Substance	Δt	Degree of purity	Boiling point	Boiling point extrapolation
	°C		°C	°C
n-Pentane	0.002	V	36.077	
n-Hexane	.005	V	68.733	
	.010	IV	68.679	
n-Heptane	.013	IV	98.345	98.364
	.005	V	98.365	
n-Octane	.008	IV	125.655	125.658

In table 2 results for boiling points and $\dfrac{dt}{dp}$ ratios previously reported by other authors are compared with those given in table 1.

TABLE 2.—*Comparison of the data with those of other observers*

Observer	n-Pentane		n-Hexane		n-Heptane		n-Octane	
	Boiling point	$\dfrac{dt}{dp}$ p=760	Boiling point	$\dfrac{dt}{dp}$ p=760	Boiling point	$\dfrac{dt}{dp}$ p=760	Boiling point	$\dfrac{dt}{dp}$ p=760
	°C		°C		°C		°C	
Mair	36.06		68.70		98.38		125.59	
Shepard, Henne, and Midgley	36.00		68.71	0.042	98.38	0.045	125.59	0.048
Timmermans and Martin			68.80	0.42 (10 mm of Hg)			125.8	.47 (10 mm of Hg)
Timmermans	36.10	0.41 (10 mm of Hg)			98.35	.45 (10 mm of Hg)		
Young	36.3	.0388			98.43	.045		
Woringer			68.53	.418			124.32	.0478
Author	36.07₇	.0391	68.73₃	.0420	98.36₅	.0449	125.65₈	.0477

Table 3 contains the tabulated values of $\dfrac{dt_s}{dp_w}$ and $\dfrac{dt}{dp}$ ratios for the four hydrocarbons.

TABLE 3.—*Data on* $\dfrac{dt_s}{dt_w}$ *and* $\dfrac{dt}{dp}$ *ratios for four normal aliphatic hydrocarbons*

Substance	$\dfrac{dt_s}{dt_w}$	Corresponding temperature	$\dfrac{dt}{dp}_{p=760}$	Difference in $\dfrac{dt}{dp}$ ratios
		°C		
n-Pentane	1.0654 / 1.0407	100.836 / 98.032	0.0391	
				0.0029
n-Hexane	1.1383 / 1.1324 / 1.1271	101.075 / 97.948 / 94.035	.0420	
				.0029
n-Heptane	1.2149 / 1.2136	100.820 / 98.029	.0449	
				.0028
n-Octane	1.2976 / 1.2708	100.895 / 97.877	.0477	

From table 3 it is apparent that the introduction of a CH_2 group into the chain of the normal aliphatic hydrocarbon has a specific effect, increasing the $\frac{dt}{dp}$ ratio by a constant value of 0.0029. The data for *n*–octane may be slightly affected by impurities in the sample investigated. However, the $\frac{dt}{dp}$ ratio is not very sensitive to small amounts of contaminating substances, especially when of a nature similar to the main substance.

With the introduction of the method of comparative measurements into ebulliometry, the accuracy of determination of $\frac{dt}{dp}$ ratio is high enough to consider this constant as a fundamental one for characterizing liquid substances.

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