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BOILING POINTS OF *n*-HEPTANE AND 2,2,4-TRIMETHYLPENTANE OVER THE RANGE 100- TO 1,500-MILLIMETER PRESSURE

By Edgar Reynolds Smith

## ABSTRACT

By a comparative dynamic method, using water as the reference standard and ebulliometers of the Świątosławski type, data were obtained from which were developed the following equations to express the relationship between temperature and vapor pressure from 100 to 1,500 mm:

For *n*-heptane,

$$\log_{10} p = 6.905\ 113 - \frac{1269.821}{217.110 + t}$$

For 2,2,4-trimethylpentane,

$$\log_{10} p = 6.820\ 137 - \frac{1262.707}{221.307 + t}$$

In these equations,  $p$  is the vapor pressure in standard millimeters of mercury exerted by the substance at the temperature  $t$  in degrees centigrade.

## CONTENTS

	Page
I. Introduction.....	229
II. Apparatus and materials.....	231
III. Experimental results.....	232
IV. References.....	234

## I. INTRODUCTION

In the comparative dynamic method of measuring the boiling points of liquids, successive measurements are made of the boiling point of the substance under investigation and the boiling point of water, in ebulliometers connected to the same manostat by means of which the pressure can be varied. Thus the data are obtained in the form of a series of corresponding boiling points of the substance and of water under the same pressure [9].<sup>1</sup>

For pressures not far from 1 atmosphere, in particular over the range of 660 to 860 mm, the temperature-pressure relationships of water and

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

of other liquids [1, 4, 6, 10] can be expressed precisely by equations of the type

$$t - t_n = a(p - 760) + b(p - 760)^2 + c(p - 760)^3$$

and

$$p - 760 = q(t - t_n) + r(t - t_n)^2 + s(t - t_n)^3,$$

in which  $a$ ,  $b$ ,  $c$ ,  $q$ ,  $r$ , and  $s$ , are constants,  $t$  is the temperature in degrees centigrade at which the vapor pressure is  $p$ , and  $t_n$  is the normal boiling point. Over the range of pressures reported in this paper, an exponential type of equation represents the data better than a three-power series, and the following procedure for the computations was found convenient.

From the observations of  $t_s$ , the boiling point of the substance under consideration, and  $t_w$ , the corresponding boiling point of water, the derivatives,  $dt_s/dt_w$  and  $d^2t_s/dt_w^2$ , were expressed in the approximate form of finite increments. The former was found to be linear with respect to  $t_w$ , and the values of the latter were scattered about an average value and showed no trend, thus indicating that the second derivative was constant. Accordingly, an equation of the type

$$t_s = a + bt_w + ct_w^2 \quad (1)$$

has the proper form to represent the relationship between the corresponding temperatures,<sup>2</sup> and the constants  $a$ ,  $b$ , and  $c$  were evaluated next by the method of least squares. Using the equation thus obtained, values of  $t_s$  which correspond to a series of reference values of  $t_w$  in the measured range were computed. The reference values of  $t_w$  and the corresponding pressures taken as primary reference standards were chosen from the recent critical compilation by Osborne, Stimson, and Ginnings [5] and are given in table 1. The computed values of  $t_s$  were then tabulated with these corresponding pressures, and the constants  $A$ ,  $b$ , and  $c$  in the equation

$$\log p = A - \frac{b}{c + t} \quad (2)$$

were evaluated to fit the tabulated data and thus to obtain a relationship between temperature and pressure. The symbol "log" is used in this paper to denote the logarithm to the base 10. Equation 2 written in the form  $t = b/(A - \log p) - c$  is explicit in temperature. Also,

$$\frac{dp}{dt} = \frac{p(A - \log p)^2}{b \log e}; \quad (3)$$

and by integration of eq 3,

$$t_n - t = \frac{b(\log 760 - \log p)}{(A - \log 760)(A - \log p)}, \quad (4)$$

in which  $t_n$  is the normal boiling point and  $t$  is the boiling point at the pressure  $p$ . Equation 4 is useful for calculating the normal boiling point from a boiling point measured at any pressure within the range for which eq 2 is applicable.

<sup>2</sup> This equation has been found by A. Zmaczynski to express satisfactorily the same relationship for several substances [9, 11].

TABLE 1.—Reference values of the vapor pressure of water adopted for comparative ebulliometric measurements over the range of 100- to 2,000-mm pressure

Temperature	Pressure	Temperature	Pressure
°C	mm	°C	mm
50	92.52	95	633.99
55	118.06	100	760.00
60	149.40	105	906.06
65	187.57	110	1074.58
70	233.72	115	1268.03
75	289.13	120	1489.14
80	355.22	125	1740.77
85	433.56	130	2026.02
90	525.86		

## II. APPARATUS AND MATERIALS

Two simple barometric ebullimeters of the type developed by Świętosławski [9] were sealed to a manostat through drying tubes. These tubes contained phosphoric anhydride next to the ebullimeter containing the substance under investigation and calcium chloride next to the ebullimeter containing water. In addition to a tube for filling, a small condenser for distilling out a portion of the charge was sealed to the ebullimeter used to contain the liquid to be meas-

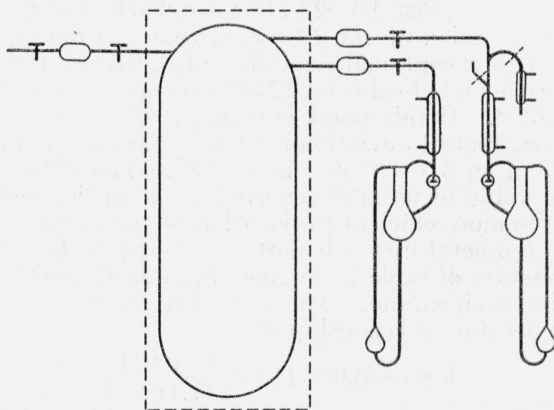


FIGURE 1.—Arrangement of ebullimeters and manostat.

ured. The manostat was a vessel of Pyrex glass with a volume of 25 liters and was placed in an insulated casing. The arrangement is shown diagrammatically in figure 1. All joints were of fused Pyrex glass tested for vacuum tightness. Pressures above atmospheric were obtained by the addition of nitrogen to the previously evacuated and nitrogen-filled manostat. After filling the ebullimeter with the liquid under investigation, the filling tube was sealed off, ice water was circulated through the condensers by means of a miniature centrifugal pump, and the boiling point was measured. A portion was then distilled out through the small external condenser, and the boiling point was measured again. No significant difference was detected in any case. The external condenser was then sealed off, and the comparative measurements of temperature were made with a platinum resistance thermometer (coiled-filament type) and a Mueller ther-

meter bridge, by the method described in other papers from this laboratory [6, 7]. It was unnecessary to thermostat the bridge, since the temperature corrections to the resistances were practically identical for the reference and the measured substance in these comparative measurements.

The temperatures were measured to  $0.001^\circ$  with an average reproducibility of  $0.002^\circ$  to  $0.003^\circ$  and an accuracy estimated at about  $0.005^\circ$  with respect to their values on the international temperature scale. Corrections for the difference in density of water vapor and hydrocarbon vapor in the column above the thermometer coil were estimated to be within the experimental error.

The *n*-heptane and 2,2,4-trimethylpentane were supplied by D. B. Brooks, of the Automotive Power Plants Section of this Bureau. Their preparation, purity, and physical properties have been described in a recent paper by Brooks, Howard, and Crafton, Jr. [2]. When tested in a differential ebulliometer [9], the difference between boiling point and condensation temperature of each substance was only  $0.002^\circ$ .

### III. EXPERIMENTAL RESULTS

*n*-Heptane.—The comparative boiling points of *n*-heptane and water are given in table 2. The expression obtained for the boiling point of *n*-heptane as a function of the corresponding boiling point of water is

$$t = -13.6536 + 1.025\,711\,t_w + 0.000\,950\,92\,t_w^2 \quad (5)$$

The average deviation of the 18 measurements from eq 5 is  $0.003^\circ$ ; and there is one exceptional deviation of  $0.015^\circ$  at the sixth point, for which the calculated value is  $62.754^\circ$  as compared with the observed value of  $62.739^\circ$ . If this point is omitted, the average deviation is  $0.002^\circ$  and the greatest deviation is  $0.005^\circ$ . The normal boiling point calculated from eq 5 ( $t_w=100^\circ$ ) is  $98.427^\circ$ . The difference between this and the value of  $98.413^\circ$  reported in an earlier paper [6] is attributed to the more efficient purification of the material used in this work. The temperatures calculated from eq 5 for the standard reference pressures of table 1 are given in table 4, together with those for 2,2,4-trimethylpentane. The equation found to represent the pressure-temperature relationship is

$$\log p = 6.905\,113 - \frac{1269.821}{217.110 + t} \quad (6)$$

This equation represents the data given in table 4 with an average deviation of 0.04 mm and one exceptionally large deviation of 0.14 mm at the highest pressure. The normal boiling point ( $p=760$  mm) calculated from eq 5 is  $98.428^\circ$ . Smyth and Engel [8] have measured the vapor pressure of *n*-heptane between  $22.7^\circ$  (41.4 mm) and  $98.4^\circ$  (760 mm). Considering that their measurements of temperature and pressure were made only to the nearest  $0.1^\circ$  and 0.1 mm, respectively, the agreement of their values with those calculated by eq 6 is within their experimental error and indicates that eq 6 can be used with confidence for extrapolation to pressures at least as low as 40 mm. The relationship

$$t_n = t + 315.538 \frac{(2.880\,814 - \log p)}{(6.905\,113 - \log p)}$$

from eq 4 is useful for calculating the normal boiling point from the boiling point at any pressure in the range of 100 to 1,500 mm.

TABLE 2.—Corresponding boiling points of *n*-heptane and water

Boiling point		Boiling point	
<i>n</i> -Heptane	Water	<i>n</i> -Heptane	Water
°C	°C	°C	°C
37.076	47.379	83.881	87.923
41.785	51.578	89.084	92.268
46.920	56.135	94.104	96.435
51.938	60.545	99.110	100.562
57.224	65.164	103.990	104.561
62.739	69.955	109.745	109.240
67.984	74.450	114.967	113.460
73.474	79.135	118.285	116.128
78.738	83.594	124.594	121.173

*2,2,4-Trimethylpentane (isooctane)*.—The corresponding boiling points of water and 2,2,4-trimethylpentane are given in table 3. The expression found for the boiling point of 2,2,4-trimethylpentane in terms of the corresponding boiling point of water is

$$t = -16.0924 + 1.044\ 559t_w + 0.001\ 086\ 89t_w^2. \quad (7)$$

The average deviation of the 16 measurements from eq 7 is 0.002° and the greatest deviation is 0.004°. The normal boiling point calculated from eq 7 is 99.232° as compared with 99.234 reported previously [6] from measurements over the range 660 to 860 mm. The temperatures calculated from eq 7 to correspond with the standard reference pressures are given in table 4, together with those for *n*-heptane. The equation found to represent these pressure-temperature data is

$$\log p = 6.820\ 137 - \frac{1262.707}{221.307 + t} \quad (8)$$

with an average deviation of 0.05 mm and one exceptional deviation of 0.16 mm at the highest pressure. No other data on 2,2,4-trimethylpentane could be found for comparison [3]. For calculating the normal boiling point from the boiling point at any pressure in the range of 100 to 1,500 mm, the equation

$$t_n = t + 320.539 \frac{(2.880\ 814 - \log p)}{(6.820\ 137 - \log p)} \quad (9)$$

may be used.

TABLE 3.—Corresponding boiling points of 2,2,4-trimethylpentane and water

Boiling point		Boiling point	
2,2,4-Tri-methyl-pentane	Water	2,2,4-Tri-methyl-pentane	Water
°C	°C	°C	°C
45.329	55.585	92.187	94.392
51.012	60.441	98.441	99.371
57.515	65.945	99.310	100.061
63.484	70.944	104.415	104.091
68.759	75.327	107.670	106.647
74.588	80.133	113.891	111.501
80.254	84.763	119.413	115.777
86.224	89.598	126.439	121.176

TABLE 4.—Boiling points of *n*-heptane and 2,2,4-trimethylpentane at standard reference pressures

Boiling point		Pressure	Boiling point		Pressure
<i>n</i> -Heptane	2,2,4-Trimethylpentane		<i>n</i> -Heptane	2,2,4-Trimethylpentane	
°C	°C	mm	°C	°C	mm
40.009	38.853	92.52	98.427	99.232	760.00
45.637	44.646	118.06	104.530	105.569	906.06
51.312	50.494	149.40	110.681	111.961	1074.58
57.035	56.396	187.57	116.879	118.406	1268.03
62.806	62.353	233.72	123.125	124.906	1489.14
68.624	68.363	289.13	129.418	131.460	1740.77
74.489	74.428	355.22			
80.402	80.548	433.56			
86.363	86.722	525.86			
92.371	92.950	633.99			

Values of the temperature and rates of change of pressure with temperature at even values of the pressure are given in table 5 for both *n*-heptane and 2,2,4-trimethylpentane.

An expression for the logarithm of the relative volatility, defined as the ratio of the vapor pressures of the two pure substances, may be obtained by subtracting eq 8 from eq 6.

TABLE 5.—Values of pressure, temperature, and rates of change of pressure with temperature for *n*-heptane and 2,2,4-trimethylpentane

Pressure	<i>n</i> -Heptane		2,2,4-Trimethylpentane	
	Temperature	$dp/dt$	Temperature	$dp/dt$
mm	°C	mm/°C	°C	mm/°C
50	<sup>a</sup> 26.80	<sup>a</sup> 2.46	<sup>a</sup> 25.26	<sup>a</sup> 2.39
100	41.767	4.363	40.658	4.237
200	58.693	7.688	58.109	7.448
300	69.661	10.666	69.438	10.319
400	77.988	13.430	78.049	12.978
500	84.787	16.040	85.089	15.485
600	90.679	18.530	91.091	17.875
700	95.653	20.923	96.352	20.169
760	98.428	22.319	99.232	21.507
800	100.185	23.234	101.055	22.383
900	104.293	25.474	105.321	24.528
1000	108.059	27.653	109.233	26.612
1200	114.789	31.851	116.229	30.624
1400	120.700	35.871	122.380	34.461
1600	125.993	39.740	127.892	38.150
1800	<sup>a</sup> 130.80	<sup>a</sup> 43.48	<sup>a</sup> 132.90	<sup>a</sup> 41.71

<sup>a</sup> Extrapolated value.

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