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BOILING POINTS OF BENZENE, ETHYLENE CHLORIDE, *n*-HEPTANE, AND 2,2,4-TRIMETHYLPENTANE OVER THE RANGE 660- TO 860-MM PRESSURE

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ABSTRACT

By the comparative ebulliometric method, using water as the reference standard and ebulliometers of the Świętosławski type, data were obtained from which were developed the following equations expressing the relation between temperature and vapor pressure from 660 to 860 mm:

For benzene

$$t=80.094+0.042683(p-760)-0.00002199(p-760)^2+0.0000000250(p-760)^3,$$

and

$$p=760+23.429(t-80.094)+0.2804(t-80.094)^2-0.000383(t-80.094)^3;$$

for ethylene chloride

$$t=83.483+0.042037(p-760)-0.00002201(p-760)^2+0.0000000180(p-760)^3,$$

and

$$p=760+23.789(t-83.483)+0.2946(t-83.483)^2+0.00156(t-83.483)^3;$$

for *n*-heptane

$$t=98.413+0.044849(p-760)-0.00002344(p-760)^2+0.0000000145(p-760)^3,$$

and

$$p=760+22.297(t-98.413)+0.2599(t-98.413)^2+0.00246(t-98.413)^3;$$

for 2,2,4-trimethylpentane (isooctane)

$$t=99.234+0.046511(p-760)-0.00002374(p-760)^2+0.0000000182(p-760)^3,$$

and

$$p=760+21.500(t-99.234)+0.2348(t-99.234)^2+0.00126(t-99.234)^3.$$

In these equations, t is the temperature in degrees centigrade at which the substance exerts the vapor pressure p in standard millimeters of mercury. The use of these substances as reference standards for boiling-point measurements is discussed. Equations for the relative volatilities of the two pairs, benzene-ethylene chloride and *n*-heptane-2,2,4-trimethylpentane, are given. The data show that Dühring's rule and the corresponding reciprocal temperature relationship hold accurately over a limited range of pressures, even for substances of different types.

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I. INTRODUCTION

The comparative method of measuring vapor pressures of liquid substances requires a primary standard reference liquid for which the

relation between temperature and pressure is known with satisfactory precision. Undoubtedly, water is the best available liquid for a primary standard, for reasons which have been discussed by Świętosławski.[1 2] Recent measurements of the temperature-pressure relations of water between 660 and 860 standard mm pressure [3] are of adequate precision for a reference standard, and cover a most convenient and useful range of pressures for ebulliometric measurements. According to these measurements the boiling point of water between 660- and 860-mm pressure is given by the equation

$$t=100+0.0368578(p-760)-0.000020159(p-760)^2+0.00000001621(p-760)^3, \quad (1)$$

in which t is expressed in degrees centigrade (Int.) and p in millimeters of mercury (standard). This equation is in excellent agreement with the data of the National Bureau of Standards [4] as well as with those obtained recently by Zmaczynski [5] at the Physikalisch-Technische Reichsanstalt, and is apparently reliable to better than 0.001° on the International Temperature Scale for nearly 4° above and below the fixed reference point of 100°.

For comparative measurements of pressure, it is desirable to have an equation in which pressure is an explicit function of temperature. To obtain such an equation, the data of Beattie and Blaisdell were treated by the method of least squares to obtain the constants in the following equation

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

which is valid over the same range of pressures. Equation 2 reproduces the 38 experimental points from which it was obtained with an average deviation of 0.012 mm and a greatest deviation of 0.031 mm, and agrees with the NBS data with equal precision over the range in which the two sets of data overlap. It may be well to mention that the equation fails rapidly above and below the range for which it was obtained.[6]

In the experimental procedure, successive measurements were made of the boiling point of one of the substances under investigation and the boiling point of water, in ebulliometers connected to the same manostat, by means of which the pressure was varied in steps from 660 to 860 mm. The pressures were calculated from the measured boiling points of water by eq 2 and tabulated with the corresponding boiling points of the substance. From the data tabulated for each substance, the constants were evaluated, by the method of least squares, for equations of the type

$$t=t_B+a(p-760)+b(p-760)^2+c(p-760)^3 \quad (3)$$

and

$$p=760+q(t-t_B)+r(t-t_B)^2+s(t-t_B)^3, \quad (4)$$

[1] W. Świętosławski, Comptes Rendus de la XII Conférence de l'Union Internationale de Chimie, p. 89 (1936).
[2] W. Świętosławski and E. R. Smith, J. Research NBS **20**, 549 (1938) RP1088.
[3] J. A. Beattie and B. E. Blaisdell, Proc. Am. Acad. Arts Sci. **71**, 361 (1937).
[4] N. S. Osborne and C. H. Meyers, J. Research NBS **13**, 1 (1934) RP691.
[5] Zmaczynski's data over this range are given in the reference under footnote 2.
[6] In the reference of footnote 2, there is given an alternative equation involving the logarithm of the pressure, which is valid over a greater range. The additional alternative of interpolation from the table of Osborne and Meyers, footnote 4, is also pointed out.

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_B is the normal boiling point, which is determined as one of the computed constants.

II. APPARATUS AND MATERIALS

For the determination of boiling points two ebulliometers were used. One of these was a simple barometric ebulliometer containing redistilled water for the reference standard. The other was a standard differential ebulliometer containing the substance under investigation. These ebulliometers were of the Świętosławski type [7] and have been described in other papers from this laboratory.[8] They were connected through drying tubes to a manostat, which was an 18-liter carboy placed in an insulated wooden case to insure uniformity of temperature. The pressure in the system was increased by the addition of nitrogen from a cylinder connected through a stopcock to the manostat, and decreased by evacuating through the same stopcock. The changes in pressure were adjusted roughly according to the levels of mercury in an open-arm manometer, also connected to the manostat through a stopcock, final adjustments being made as indicated by observations of the boiling point of water. The procedure involved the approximate adjustment of the pressure to a desired value, say about 660 mm, followed by three temperature measurements. The temperature of the water boiling in one ebulliometer was first measured. The thermometer was then transferred, at equal short time intervals, from the ebulliometer containing water to the one containing the substance under examination and then back to the water, a temperature measurement being made in each position. Averaging the temperature readings of the water corrects for any possible slight drift in pressure in the manostat during the operation. Thus when water boils at this average temperature, t_w, the substance boils at the measured temperature, t_s, under the same pressure. This pressure is calculated from eq 2, and thus there are obtained a series of temperatures and corresponding vapor pressures for the substance relative to water, as the primary standard.

A calibrated platinum resistance thermometer (coiled-filament type)[9] and a calibrated Mueller thermometer bridge were used to measure the temperatures.

Water.—For the ebulliometric reference standard, distilled water from the laboratory supply was distilled from alkaline permanganate and again distilled shortly before use.

Benzene.—The initial material was benzene which conformed to the specifications adopted by the American Chemical Society for the reagent grade of this substance.[10] Two liters of this material was distilled fractionally in a 40-bulb vacuum-jacketed column of the Świętosławski type [11] equivalent to about 25 theoretical plates. The distillate was collected in eight fractions, each of about 250 ml. The normal boiling points of the third and fifth fractions were meas-

[7] W. Świętosławski, Ebulliometry, p. 7 and 16. (Chemical Publishing Company of New York, Inc., 1937).
[8] M. Wojciechowski, J. Research NBS 17, 453 (1936) RP921.
E. R. Smith and M. Wojciechowski, J. Research NBS 17, 841 (1936) RP947.
[9] C. H. Meyers, BS J. Research 9, 807 (1932) RP508.
[10] Ind. Eng. Chem., Anal. Ed. 4, 347 (1932).
[11] W. Świętosławski, Ebulliometry, p. 27 (Chemical Publishing Company of New York, Inc., 1937).

ured by the comparative method and found to be 80.093 and 80.094°, in agreement with the value of 80.094° reported by Wojciechowski [12] for benzene of high purity. The difference between the boiling point and the temperature of condensation of these fractions, measured in the differential ebulliometer, was 0.001°, which also indicated high purity. Since these fractions were of satisfactory purity, they were used for the measurements and the other fractions were not tested.

Ethylene chloride.—About 2 kg of this substance, obtained from Eastman Kodak Co., was distilled in the 40-bulb column and collected in a series of fractions, each of about 150 ml. Fractions 5, 7, and 10 had normal boiling points of 83.478, 83.481, and 83.482° C, respectively, according to single measurements, and each showed in the differential ebulliometer a difference of 0.002° between boiling point and temperature of condensation. Fraction 7 was used for the measurements.

n-Heptane.—The initial material obtained from the Eastman Kodak Co. showed in the differential ebulliometer a difference between boiling-point and condensation temperature of 0.04°. After fractionation in the 40-bulb column, this difference was reduced to 0.001° for fraction 3, which was used for the measurements. A preliminary measurement of its boiling point gave 98.413° C. Since this result is slightly higher than the value of 98.365° obtained by Wojciechowski,[13] and lower than the value of 98.52° found by Beattie and Kay,[14] a sample of synthetic *n*-heptane made by the California Chemical Co., was obtained through the kindness of F. W. Rose, Jr., Research Associate of Project 6 of the American Petroleum Institute. This sample had been prepared by fractionation of the initial synthetic material through a 2.5-m locket-chain column, equivalent to about 60 theoretical plates. The difference between its boiling point and condensation temperature was 0.001°, and its boiling point in the differential ebulliometer was 98.413°, in complete agreement with the sample used for this work.

2,2,4-Trimethylpentane (isooctane).—The sample used for measurement was a portion of material made by Röhm and Haas, which was further purified by successive fractional distillation. The sample was kindly supplied by D. B. Brooks, of the automotive power plant section of this Bureau, who will describe its preparation and properties in detail in a subsequent paper. This sample had a freezing point of −107.31° C, and a difference of 0.001° between boiling point and condensation temperature in the differential ebulliometer.

III. EXPERIMENTAL RESULTS AND CONCLUSIONS

Benzene.—The comparative boiling point data for benzene and water are given in table 1. The boiling point of benzene is shown in column 1, and the corresponding boiling point of water in column 2. The corresponding pressure, calculated from the boiling point of water by eq 2, is given in column 3.

[12] M. Wojciechowski, J. Research NBS **19**, 347 (1937) RP1029.
[13] M. Wojciechowski, J. Research NBS **17**, 453 (1936) RP921. The material used in Wojciechowski's determination had a difference of 0.013° between boiling point and temperature of condensation.
[14] J. A. Beattie and W. C. Kay, J. Am. Chem. Soc. **59**, 1586 (1937).

TABLE 1.—*Boiling points of benzene between 660- and 860-mm pressure*

Boiling point		Pressure
Benzene	Water	
°C	°C	mm
75.532	96.053	658.96
76.261	96.685	674.35
76.841	97.188	686.81
77.430	97.697	699.60
78.015	98.204	712.55
78.606	98.714	725.77
79.201	99.230	739.35
79.796	99.744	753.08
80.299	100.178	764.84
80.822	100.628	777.20
81.417	101.140	791.46
82.022	101.662	806.21
82.606	102.163	820.59
83.285	102.745	837.56
84.079	103.427	857.82

The expression obtained for the boiling point of benzene as a function of pressure is

$$t=80.094+0.042683(p-760)-0.00002199(p-760)^2+0.0000000250(p-760)^3 \quad (5)$$

The average deviation of the 15 measurements from this equation is 0.001° and the greatest deviation is 0.003°. The normal boiling point is 80.094°, in agreement with a previous determination in this laboratory by Wojciechowski.[15] It is interesting that the value obtained by Wojciechowski is an average for several samples of benzene purified by different methods and measured at pressures within a few millimeters of normal, while in this work the boiling point is obtained as a constant to fit the equation according to measurements on one sample from 100 mm below to 100 mm above normal pressure. The expression obtained for pressure as a function of temperature is

$$p=760+23.429(t-80.094)+0.2804(t-80.094)^2-0.000383(t-80.094)^3, \quad (6)$$

which reproduces the measurements with an average deviation of 0.03 mm and a greatest deviation of 0.05 mm. General expressions for the values of dt/dp and dp/dt may be obtained easily from eq 5 and 6.

Ethylene chloride.—The data for ethylene chloride are given in table 2. The equations for the temperature-pressure relations of this substance are

$$t=83.483+0.042037(p-760)-0.00002201(p-760)^2+0.0000000180(p-760)^3 \quad (7)$$

with an average deviation of 0.001° and a greatest deviation of 0.002°, and

$$p=760+23.789(t-83.483)+0.2946(t-83.483)^2+0.00156(t-83.483)^3 \quad (8)$$

with an average deviation of 0.01 mm and a greatest deviation of 0.04 mm from the experimental values.

[15] M. Wojciechowski, J. Research NBS 19, 347 (1937) RP1029.

TABLE 2.—*Boiling points of ethylene chloride between 660- and 860-mm pressure*

Boiling point		Pressure
Ethylene chloride	Water	
°C	°C	mm
79.325	96.129	660.80
79.628	96.613	672.57
80.100	97.029	682.84
80.644	97.509	694.85
81.209	98.004	707.42
81.556	98.309	715.24
82.273	98.939	731.66
82.898	99.487	746.19
83.487	100.004	760.11
83.494	100.011	760.30
84.065	100.511	773.97
84.638	101.012	787.86
85.198	101.504	801.72
85.782	102.014	816.29
86.358	102.518	830.90
86.912	103.000	845.10
87.486	103.502	860.06

n-Heptane.—The equations for *n*-heptane, based on the data given in table 3, are

TABLE 3.—*Boiling points of n-heptane between 660- and 860-mm pressure*

Boiling point		Pressure
n-Heptane	Water	
°C	°C	mm
93.432	95.893	655.11
94.046	96.400	667.38
94.675	96.920	680.15
95.341	97.468	693.82
95.650	97.725	700.31
96.005	98.018	707.83
96.634	98.536	721.13
96.946	98.795	727.88
97.251	99.046	734.48
97.748	99.456	745.36
99.020	100.500	773.67
99.672	101.034	788.49
100.480	101.696	807.18
100.870	102.016	816.35
101.504	102.537	831.46
102.121	103.045	846.42
102.740	103.551	861.54

$$t=98.413+0.044849\ (p-760)-0.00002344\ (p-760)^2+0.0000000145\ (p-760)^3 \tag{9}$$

which reproduces the 17 experimental values with an average deviation of 0.001° and a greatest deviation of 0.003°, and

$$p=760+22.297\ (t-98.413)+0.2599\ (t-98.413)^2+0.00246\ (t-98.413)^3 \tag{10}$$

with an average deviation of 0.02 mm and a greatest deviation of 0.07 mm.

2,2,4-Trimethylpentane (*isooctane*).—The data for 2,2,4-trimethylpentane are given in table 4.

TABLE 4.—*Boiling points of 2,2,4-trimethylpentane between 660- and 860-mm pressure*

Boiling points		Pressure
2,2,4-Trimethylpentane	Water	
° C	° C	mm
94.318	96.090	659.86
94.949	96.592	672.08
95.471	97.007	682.31
96.088	97.501	694.64
96.706	97.992	707.10
97.111	98.318	715.47
97.860	98.912	730.94
98.598	99.496	746.44
99.310	100.061	761.65
99.869	100.503	773.74
100.501	101.003	787.61
101.117	101.491	801.36
101.768	102.003	815.99
102.404	102.506	830.57
103.005	102.980	844.50
103.642	103.481	859.45

The equations obtained from the data are

$$t=99.234+0.046511(p-760)-0.00002374(p-760)^2 +0.0000000182(p-760)^3 \quad (11)$$

with average and greatest deviations of 0.001 and 0.003°, respectively, and

$$p=760+21.500(t-99.234)+0.2348(t-99.234)^2 +0.00126(t-99.234)^3 \quad (12)$$

with average and greatest deviations of 0.02 and 0.07 mm, respectively.

In table 5 are listed the normal boiling points and the values of $(dt/dp)_{760}$ for the four substances studied. It is noteworthy that these values have not been obtained from single measurements in the vicinity of normal pressure, but have been calculated as constants in the equations which reproduce 15 to 17 experimental values over the range 660- to 860-mm pressure. Of these four substances, benzene is the only one which would be suitable for a secondary ebulliometric reference standard. On prolonged boiling ethylene chloride undergoes a slight hydrolysis if a trace of water is present, while *n*-heptane and 2,2,4-trimethylpentane have boiling points within the range where a secondary standard is superfluous.

TABLE 5.—*Normal boiling points and values of dt/dp*

Substance	Normal boiling point	$(dt/dp)_{760}$
	°C	°C/mm Hg
Benzene	80.09_4	0.0426_8
Ethylene chloride	83.48_3	$.0420_4$
n-Heptane	98.41_3	$.0448_5$
2,2,4-Trimethylpentane	99.23_4	$.0465_1$

Relative volatility.—For calculating the number of theoretical plates required in a fractionating column to obtain a given separation of an ideal two-component mixture, the equation [16]

$$n=\frac{\log \frac{x_0(1-x_n)}{x_n(1-x_0)}}{\log R} \tag{13}$$

is often useful. In this equation, n is the number of plates, R is the ratio, assumed constant, of the vapor pressures of the two pure constituents, and x_0 and x_n are the mole fractions corresponding to $n=0$ and $n=n$, x_0 being greater than x_n. Beatty and Calingaert have shown that the mixture n-heptane-2,2,4-trimethylpentane is very nearly ideal from the standpoint of vapor pressure, and also that in any case where R is nearly unity, a change in the value of R creates a marked difference in the calculated value of n, but that in such a case the boiling range is small, so that the absolute change in R is also small over the boiling range. The effect on n of a change in R is thus considered negligible. The values of R at the normal boiling points of n-heptane (98.413°) and 2,2,4-trimethylpentane (99.234°) can be calculated accurately by eq 10 and 12 to be 1.02356 and 1.02432, respectively, for this pair. The corresponding values of n, from eq 13, for a change in mole fraction from 0.05 to 0.95 are 252.9 and 245.1, respectively, the difference over this range of temperature being negligible for practical purposes. Values of R for the systems n-heptane-2,2,4-trimethylpentane and benzene-ethylene chloride over a range of temperature are given in table 6. For these two pairs the relative volatilities are expressed by the following equations:

TABLE 6.—*Values of R*

n-Heptane-2,2,4-trimethylpentane		Benzene-ethylene chloride	
Temperature	R $\frac{p(n\text{-heptane})}{p(2,2,4\text{-trimethylpentane})}$	Temperature	R $\frac{p(\text{benzene})}{p(\text{ethylene chloride})}$
°C		°C	
94.5	1.01995	79.0	1.11464
95.5	1.02089	80.0	1.11334
96.5	1.02181	81.0	1.11203
97.5	1.02272	82.0	1.11071
98.5	1.02364	83.0	1.10935
99.5	1.02456	84.0	1.10796
100.5	1.02550		
101.5	1.02647		
102.5	1.02746		

For n-heptane and 2,2,4-trimethylpentane between 94.5 and 102.5° C

$$R=1.02088-0.0008783t+0.000009198t^2,$$

where $R=p(n\text{-heptane})/p(2,2,4\text{-trimethylpentane})$. For benzene and ethylene chloride between 79.0 and 84.0° C

$$R=1.14596+0.0004845t-0.000011152t^2,$$

where $R=p(\text{benzene})/p(\text{ethylene chloride})$.

[16] H. A. Beatty and G. Calingaert, Ind. Eng. Chem. 26, 504 (1934).

Dühring's rule.—An empirical relationship between the temperatures at which two liquids have equal vapor pressures, known as Dühring's rule, has found considerable use for the interpolation of data. The relationship is expressed by the equation

$$T_A = k_1 T_B + C_1, \tag{14}$$

where k_1 and C_1 are constants, and T_A and T_B are the temperatures at which the liquids A and B have the same vapor pressure. A similar relationship with a better claim to some theoretical basis involves the reciprocal temperatures

$$1/T_A = (k_2/T_B) + C_2 \tag{15}$$

Although these two relations have been tested before,[17] the relative vapor pressure data of this investigation afford a more precise comparison than has hitherto been made, over the short range of 200 mm, of the relative validities of eq 14 and 15.

In preference to an algebraic elimination between equations of type 3, the temperatures at which water, benzene, ethylene chloride, *n*-heptane, and isooctane exert the 11 vapor pressures of 660, 680, 700, ... 840, 860 mm were calculated from eq 1, 5, 7, 9, and 11. From these 11 sets of values the constants of eq 14 and 15 were found for each of the 10 possible pairs of the 5 substances. The accuracy with which these linear equations of types 14 and 15 hold is illustrated by the example of benzene and water given in table 7.

TABLE 7.—*Comparison of temperatures calculated from eq 12 and 13 for the pair benzene-water*

Pressure	Temperature of—			Δt eq 1−eq 16	Temperature of water, eq 17	Δt eq 1−eq 17
	Benzene, eq 5	Water, eq 1	Water, eq 16			
mm	°C	°C	°C	°C	°C	°C
660	75.581	96.096	96.102	−0.006	96.098	−0.002
680	76.526	96.914	96.917	−.003	96.916	−.002
700	77.448	97.712	97.713	−.001	97.714	−.002
720	78.350	98.492	98.491	+.001	98.494	−.002
740	79.231	99.255	99.251	+.004	99.255	.000
760	80.094	100.000	99.995	+.005	99.999	+.001
780	80.939	100.729	100.724	+.005	100.728	+.001
800	81.767	101.443	101.439	+.004	101.441	+.002
820	82.581	102.142	102.141	+.001	102.141	+.001
840	83.380	102.828	102.830	−.002	102.829	+.001
860	84.167	103.500	103.509	−.009	103.505	−.005
Average deviation				0.004		0.002
Greatest deviation				0.009		0.005

The equations for this pair are

$$t_w = 0.86268 t_s + 30\,900, \tag{16}$$

in which t is expressed in degrees centigrade, and

$$\frac{1}{T_w} = (0.772945/T_s) + 0.00049175, \tag{17}$$

[17] For example, see E. F. Linhorst. J. Am. Chem. Soc. **51**, 3262 (1929); A. M. White. Ind. Eng. Chem. **22**, 230 (1930); J. H. Perry and E. R. Smith. Ind. Eng. Chem. **25**, 195 (1933).

in which $T=t+273.160$. Without tabulating the results of the tests with the other nine pairs, an idea of the relative accuracy of eq 14 and 15 can be gained from the statement that for all pairs the average of the average and greatest deviations was found to be 0.002 and 0.004° from eq 14, and 0.001 and 0.003° from eq 15, respectively. Thus, in regard to accuracy there is very little choice between the two, though the reciprocal temperature relation seems to be slightly better, on the average, for the 10 pairs that were tested.

WASHINGTON, January 18, 1938.