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BOILING POINTS OF BENZENE, 2,2,3-TRIMETHYLBUTANE, 3-ETHYLPENTANE, AND 2,2,4,4-TETRAMETHYLPENTANE WITHIN THE RANGE 100 TO 1,500 MILLIMETERS OF MERCURY

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ABSTRACT

By the comparative method of Świętosławski, with water for the reference standard, data were obtained from which were developed the following equations to express the relationship between temperature and vapor pressure in the range of pressures from 100 to 1,500 mm Hg.

For benzene,

$$\log_{10}p = 6.905216 - \frac{1211.215}{220.870 + t}.$$

For 2,2,3-trimethylbutane,

$$\log_{10}p = 6.799682 - \frac{1204.997}{226.615 + t}.$$

For 3-ethylpentane,

$$\log_{10}p = 6.873058 - \frac{1249.825}{219.595 + t}.$$

For 2,2,4,4-tetramethylpentane, no convenient single equation was found to fit the data with satisfactory accuracy over the entire range of pressures. By dividing the data into two ranges, satisfactory reproduction was obtained with the following equations:

(a) From 100 to 450 mm,

$$\log_{10}p = 6.643408 - \frac{1231.620}{204.975 + t}.$$

(b) From 430 to 1,500 mm,

$$\log_{10}p = 6.860684 - \frac{1368.925}{221.679 + t}.$$

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

The method, apparatus, and procedure used in this work have been described in a previous paper [5].[1]

From observations at various pressures of t_s, the boiling point of the substance under consideration, and t_w, the corresponding boiling point of water, the constants of equations of the type

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

were determined by the method of least squares. For 2,2,4,4-tetramethylpentane, however, the simple quadratic form of equation was insufficient and an additional cubic term was found necessary to

[1] Figures in brackets indicate the literature references at the end of this paper.

reproduce the data with adequate accuracy. Using the equations thus obtained, values of t_s corresponding to a series of reference values of t_w in the measured range were computed. The reference values of t_w and the corresponding reference pressures adopted for comparative ebulliometric measurements over the range of 100- to 2,000-mm pressure have been previously tabulated [5] and were taken from the compilation by Osborne, Stimson, and Ginnings [3].

The computed values of t_s at these reference pressures were used to obtain a relationship of the form

$$\log p = A - \frac{b}{C+t}, \tag{2}$$

which is explicit in either temperature or pressure. The symbol "log" is used to denote the logarithm to the base 10. Also

$$t_n - t = \frac{b(\log 760 - \log p)}{(A - \log 760)\,(A - \log p)}, \tag{3}$$

in which t_n is the normal boiling point and t is the boiling point at the pressure p. Equation 3 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.

The benzene used for the measurements was the fifth fraction from a fractional distillation described in a former paper [6]. The 2,2,3-trimethylbutane, 3-ethylpentane, and 2,2,4,4-tetramethylpentane were supplied by D. B. Brooks, of the Automotive Power Plants Section of this Bureau. Their preparation and properties have been described in other papers [1, 2].

Temperatures were measured to 0.001° C., and the equations expressing the data are given so that calculations may be made with them to that precision. The accuracy of the results, however, depends on the purity of the measured substances as well as on the method of measurement, calibrations of instruments, and experimental technique. From the methods of preparation and the observations as to the behavior of the substances with respect to distillation and freezing, which are given in the references cited, it is evident that all the substances were of a high degree of purity. However, no quantitative estimates of their purities are possible and no exact measure of the accuracy of the results can be made. It is believed that the results are accurate to better than 0.01°.

Benzene.—The measured corresponding boiling points of benzene and water are given in table 1. The expression for the boiling point of benzene as a function of the corresponding boiling point of water is

$$t = -26.8739 + 0.979949 t_w + 0.00089772 t_w^2. \tag{4}$$

The average deviation of the 16 measurements from eq 4 is 0.004° and the greatest deviation is 0.009°. The normal boiling point calculated from eq 4 is 80.098°. The difference between this and the value of 80.094° reported in an earlier paper [6] on measurements over the more limited range of 660 to 860 mm is just equal to the average deviation of the experimental values from those calculated by eq 4. This agreement is adequate. The temperatures calculated from eq 4 for the standard reference pressures are given in the second column of table 5. The equation found to represent the pressure-temperature relationship is

$$\log p = 6.905216 - \frac{1211.215}{220.870 + t} \tag{5}$$

and reproduces the data given in the first and second columns of table 5, with an average deviation of 0.04 mm and a greatest deviation of 0.28 mm at the highest pressure. Values of the vapor pressure of benzene caculated by eq 5 for 30, 40, 50, 60, 70 and 80° C. yield an average deviation of 0.15 mm from the values tabulated by Scatchard, Wood, and Mochel [4] from their measurements on benzene over this range of temperatures. The equation

$$t_n = t + 300.968 \frac{(2.880814 - \log p)}{(6.905216 - \log p)}$$

may be used to calculate the normal boiling point of a sample of benzene from the boiling point measured at any pressure in the range of 100 to 1,500 mm.

TABLE 1.—*Corresponding boiling points of benzene and water*

Boiling point		Boiling point	
Benzene	Water	Benzene	Water
°*C*	°*C*	°*C*	°*C*
33.248	58.243	70.604	91.758
37.707	62.344	75.484	96.010
42.977	67.158	79.774	99.723
48.440	72.087	85.483	104.630
53.015	76.201	90.224	108.678
57.677	80.366	95.339	113.015
60.877	83.200	100.493	117.358
65.276	87.084	105.052	121.168

2,2,3-Trimethylbutane (*triptane*).—The measured corresponding boiling points of 2,2,3-trimethylbutane and water are given in table 2. The expression found for the boiling point in terms of the corresponding boiling point of water is

$$t = -30.1869 + 1.004715 t_w + 0.00105873 t_w^2. \tag{6}$$

The average deviation of the 17 measurements from eq 6 is 0.003° and the greatest deviation is 0.008°. The normal boiling point calculated from eq 6 is 80.872°. The temperatures calculated by eq 6 to correspond with the standard reference pressures are given in the third column of table 5. The equation found to represent these pressure-temperature data is

$$\log p = 6.799682 - \frac{1204.997}{226.615 + t}, \tag{7}$$

with an average deviation of 0.07 mm and one exceptionally large deviation of 0.48 mm at the highest pressure. For calculating the normal boiling point from the boiling point measured at any pressure in the range of 100 to 1,500 mm, the equation,

$$t_n = t + 307.486 \frac{(2.880814 - \log p)}{(6.799682 - \log p)}$$

may be used.

TABLE 2.—*Corresponding boiling points of 2,2,3-trimethylbutane and water*

Boiling point		Boiling point	
2,2,3-Trimethylbutane	Water	2,2,3-Trimethylbutane	Water
°C	°C	°C	°C
25.774	52.772	71.727	92.433
31.597	57.954	76.835	96.674
36.385	62.186	81.214	100.283
41.785	66.923	87.030	105.042
47.424	71.806	92.126	109.178
52.186	75.910	97.335	113.379
57.301	80.284	102.430	117.455
61.862	84.153	107.262	121.298
66.357	87.941		

3-Ethylpentane.—The comparative boiling-point data for 3-ethylpentane and water are given in table 3. The equation found for the boiling point of 3-ethylpentane in terms of the corresponding boiling point of water is

$$t = -18.2932 + 1.019200\, t_w + 0.00098408\, t_w^2. \tag{8}$$

The average deviation of the 17 measurements from eq 8 is 0.002° and the greatest deviation is 0.005°. The normal boiling point calculated from eq 8 is 93.468°. The temperatures corresponding to the standard reference pressures are given in the fourth column of table 5. The equation representing the pressure-temperature relationship is

$$\log p = 6.873058 - \frac{1249.825}{219.595 + t}, \tag{9}$$

which reproduces the data for 3-ethylpentane given in table 5 with an average deviation of 0.03 mm and a greatest deviation of 0.09 mm at the highest pressure. The normal boiling point of a sample of 3-ethylpentane may be obtained from a boiling point measured at any pressure between 100 and 1,500 mm by the equation

$$t_n = t + 313.063\, \frac{(2.880814 - \log p)}{(6.873058 - \log p)}.$$

TABLE 3.—*Corresponding boiling points of 3-ethylpentane and water*

Boiling point		Boiling point	
3-Ethylpentane	Water	3-Ethylpentane	Water
°C	°C	°C	°C
37.486	52.103	86.992	94.652
43.732	57.652	91.730	98.571
49.337	62.576	94.846	101.134
54.572	67.141	100.618	105.851
60.567	72.324	104.967	109.384
65.592	76.635	110.175	113.589
70.493	80.806	114.899	117.379
75.785	85.282	120.047	121.486
81.541	90.113		

2,2,4,4-Tetramethylpentane.—The measured corresponding boiling points of this substance and water are given in table 4.

TABLE 4.—*Corresponding boiling points of 2, 2, 4, 4-tetramethylpentane and water*

Boiling point		Boiling point	
2,2,4,4-Tetramethylpentane	Water	2,2,4,4-Tetramethylpentane	Water
°C	°C	°C	°C
60.711	51.938	111.630	91.991
67.256	57.285	117.434	96.368
72.665	61.653	122.436	100.115
78.581	66.389	128.684	104.759
85.241	71.657	134.261	108.874
90.477	75.754	140.081	113.139
95.955	80.007	146.065	117.494
100.963	83.867	151.202	121.204
105.951	87.685		

The equation found to represent the corresponding data is

$$t=1.7064+1.049344t_w+0.00178137t^2_w-0.0000021712t^3_w, \qquad (10)$$

which shows an average deviation of 0.004° and a greatest deviation of 0.009° from the 17 experimental values. The normal boiling point calculated from eq 10 is 122.283°. The temperatures calculated from eq 10 to correspond with the standard reference pressures are given in the fifth column of table 5. A single equation of the form of eq 2 would not adequately reproduce these pressure-temperature data over the entire range. By dividing the data into two ranges, satisfactory reproduction was obtained with the following two equations:

(a) From 100 to 450 mm,

$$\log p=6.643408-\frac{1231.620}{204.975+t}, \qquad (11)$$

with average and greatest deviations of 0.02 and 0.04 mm, respectively.

(b) From 430 to 1,500 mm,

$$\log p=6.860684-\frac{1368.925}{221.679+t}, \qquad (12)$$

with average and greatest deviations of 0.06 and 0.13 mm, respectively. The equation

$$t_n=t+343.962\frac{(2.880814-\log p)}{(6.860684-\log p)}$$

may be used to obtain the normal boiling point from a boiling point measured at any pressure within the range of 430 to 1,500 mm.

TABLE 5.—*Boiling points of benzene, 2,2,3-trimethylbutane, 3-ethylpentane, and 2,2,4,4-tetramethylpentane at standard reference pressures*

Pressure	Boiling point			
	Benzene	2,2,3-Trimethylbutane	3-Ethylpentane	2,2,4,4-Tetramethylpentane
mm	°*C*	°*C*	°*C*	°*C*
92.52	24.368	22.696	35.127	58.356
118.06	29.739	28.275	40.740	64.448
149.40	35.155	33.907	46.402	70.611
187.57	40.616	39.593	52.113	76.844
233.72	46.121	45.331	57.873	83.145
289.13	51.672	51.122	63.682	89.511
355.22	57.267	56.966	69.541	95.943
433.56	62.908	62.863	75.449	102.438
525.86	68.593	68.813	81.406	108.994
633.99	74.323	74.816	87.412	115.610
760.00	80.098	80.872	93.468	122.283
906.06	85.918	86.981	99.572	129.014
1,074.58	91.783	93.142	105.726	135.799
1,268.03	97.693	99.357	111.929	142.638
1,489.14	103.647	105.625	118.182	149.528

Values of the temperature and rates of change of pressure with temperature at even values of the pressure are given in table 6 for all four substances.

TABLE 6.—*Values of pressure, temperature, and rates of change of pressure with temperature for benzene, 2,2,3-trimethylbutane, 3-ethylpentane, and 2,2,4,4-tetramethylpentane*

Pressure	Benzene		2,2,3-Trimethylbutane		3-Ethylpentane		2,2,4,4-Tetramethylpentane	
	Temperature	*dp/dt*	Temperature	*dp/dt*	Temperature	*dp/dt*	Temperature	*dp/dt*
mm	°*C*	*mm/°C*	°*C*	*mm/°C*	°*C*	*mm/°C*	°*C*	*mm/°C*
50	[a] 11.78	[a] 2.58	[a] 9.63	[a] 2.49	[a] 21.96	[a] 2.47	[a] 44.12	[a] 2.29
100	26.054	4.57	24.443	4.40	36.882	4.38	60.266	4.03
200	42.198	8.06	41.242	7.73	53.768	7.70	78.653	7.05
300	52.660	11.18	52.154	10.71	64.719	10.68	90.641	9.74
400	60.601	14.08	60.452	13.47	73.036	13.44	99.780	12.21
500	67.086	16.82	67.236	16.07	79.830	16.05	107.254	14.57
600	72.611	19.43	73.021	18.54	85.620	18.54	113.634	16.82
700	77.450	21.94	78.094	20.92	90.692	20.92	119.224	18.99
760	80.098	23.40	80.872	22.30	93.468	22.32	122.283	20.25
800	81.773	24.36	82.629	23.21	95.225	23.23	124.219	21.08
900	85.691	26.71	86.742	25.43	99.334	25.46	128.749	23.10
1,000	89.283	28.99	90.516	27.59	103.102	27.64	132.902	25.07
1,200	95.702	33.39	97.265	31.74	109.837	31.82	140.327	28.86
1,400	101.340	37.61	103.200	35.71	115.755	35.83	146.851	32.49
1,600	[a] 106.39	[a] 41.67	[a] 108.52	[a] 39.53	[a] 121.06	[a] 39.68	[a] 152.696	[a] 35.98

[a] Extrapolated value.

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