60% acid is used and the latter when 40% acid is used. Under the same experimental conditions the same products can be obtained in roughly the same proportions from both nitrosoanisole and from anisole. This fact strongly indicates that the nitrosoanisoles are intermediates in the nitrite-catalyzed nitration of anisole.

CHICAGO, ILLINOIS RECEIVED DECEMBER 13, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Vapor Pressures and Some Related Quantities of Pentene-1 from 0 to 200°

BY H. O. DAY AND D. E. NICHOLSON WITH W. A. FELSING

Introduction

The determination of the thermodynamic properties of hydrocarbons has been a part of the research program of this laboratory for a number of years. Thus, heat capacities, heats of vaporization, and compressibilities for a number of hydrocarbons have been determined and reported.[1] The increasing importance of olefinic hydrocarbons has indicated a study of the pentenes and this report covers a portion of the work on pentene-1. In determining *p-v-t* data on both gaseous and liquid pentene-1, it was found that adequate data on vapor pressures over the range of temperatures from room temperature to the vicinity of its critical temperatures were lacking. This paper, hence, reports the experimentally determined vapor pressures for the range 0 to 200°.

Previous Investigations

The existing vapor pressure data have been examined critically by Stull[2] and he has reported the most probable values for the temperature range of −80.4 to 30.1°.

The normal boiling points, as recorded in the literature, differ considerably, due probably to differences in the purity of the samples of pentene-1 used. The most probable value, as selected by Stull[2] and as reported by Sherrill and Walter[3] is 30.1°, though the value of 29.97° was chosen by the A.P.I. Project No. 44.[4]

Methods and Apparatus

The dead-weight piston gage apparatus used in this Laboratory in *p-v-t* investigations was limited to a low pressure value of about 5 atmospheres, as determined by the weight of the piston and scale pan. Hence, vapor pressures up to 7.5 atmospheres were determined by means of a glass-contained compound mercury manometer, as described by Wilson,[5] attached to a static vapor pressure determining apparatus used by Felsing and Thomas.[6] The loading device employed by Felsing and Durban[7] was used to introduce pure, air-free pentene-1 into the piezometer at about −65°. A reasonable fraction, usually one-third, of the liquid was then evaporated out of the piezometer into the vacuum system to insure complete freedom from dissolved gases. An internal stirrer, actuated by a solenoid and metronome, served to prevent temperature gradients in the liquid. The entire apparatus was constructed of Pyrex glass. Mercury levels in the manometer were determined by means of a Gaertner cathetometer which could easily be read to 0.05 mm. Temperatures within the Dewar-flask bath were measured by short range mercurial thermometers calibrated by the National Bureau of Standards. The overall precision of these measurements was ±0.3%.

For vapor pressures from about 6 to 40 atmospheres, a dead-weight piston gage previously described,[8] was employed. Thermostat temperatures were controlled to ±0.005° by means of a platinum resistance thermometer in conjunction with a Mueller bridge and a photoelectric cell relay. The actual thermostat temperature was simultaneously determined by the resistance thermometer (calibrated by the National Bureau of Standards). In determining the vapor pressures, the volume of the vapor phase was varied from 0.2 to 15 cc.; this change in vapor volume had no effect on the observed pressures, indicating a high purity of the pentene-1. Three separate runs on three separate fillings gave closely agreeing values; the precision of the measurements was within ±0.1%.

The region above 200° is *not* considered in this paper, since the critical pressure is in the neighborhood of 201°; this critical region and liquid and vapor compressibilities will be reported in a later paper.

Material Used

The pentene-1 for this investigation was obtained from the Phillips Petroleum Company. The National Bureau of Standards, from freezing point data on representative samples of this lot, reported a purity of 99.34 ± 0.40 mole per cent. The most probable impurity was isopentane. The densities of the liquid under its own vapor pressure as a function of the temperature over the range 0–50° are represented by the equation

$$d(\text{g./cc.}) = 0.6630 - 0.001034t$$

where *t* is in degrees centigrade. The normal boiling point, as calculated from the vapor pressure equation, was found to be 30.07 ± 0.02°.

Treatment of Data

The experimental data were plotted to large scale as log *p* (mm.) against the reciprocal of the absolute temperature. Three linear equations were fitted by the method of least squares to separate portions of the line

(1) 0– 35°: $\log_{10} p\ (\text{mm.}) = 7.40607 - 1372.194/T$

(2) 40– 95°: $= 7.31561 - 1342.407/T$

(3) 100–170°: $= 7.26782 - 1324.730/T$

The ice-point was taken as 273.16°K.

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[1] (a) Lemons with Felsing, THIS JOURNAL, **65**, 46 (1943); (b) Dailey with Felsing, *ibid.*, **65**, 42 (1943); (c) Felsing and Watson, *ibid.*, **64**, 1822 (1942); **65**, 1889 (1943); **65**, 780 (1943); (d) Templeton and Davies with Felsing, *ibid.*, **66**, 2033 (1944); (e) Felsing, Cuellar and Newton, *ibid.*, **69**, 1972 (1947).

[2] Stull, *J. Ind. Eng. Chem.*, **39**, 517 (1947).

[3] Sherrill and Walter, THIS JOURNAL, **58**, 742 (1936).

[4] A.P.I. Res. Project 44 at NBS; "Selected Values of Properties of Hydrocarbons" Table 8a, dated May 31, 1947.

[5] Wilson, *Univ. of Illinois Eng. Exp. Sta. Bull.*, No. 146 (1925).

[6] Felsing and Thomas, *J. Ind. Eng. Chem.*, **21**, 1269 (1929).

[7] Felsing and Durban, THIS JOURNAL, **48**, 2885 (1926).

[8] Kelso with Felsing, *ibid.*, **62**, 3132 (1940).

From 170 to 200°, as the critical region was approached, the logarithm of the vapor pressure no longer could be represented by a linear function of the reciprocal of the absolute temperature. The equation, derived by aid of a central difference table, was found to be

(4) 170–200°: $\log_{10} p$ (mm.) $= -2089.553682 + 233{,}084.9289/T + 7034.8267 \times 10^{-3}\ T - 1049.16605 \times 10^{-5}\ T^2 + 5868.8889 \times 10^{-3}\ T^3$

Equations (1) and (2) reproduce the data to within ±0.3%, while equations (3) and (4) are reliable to a mean deviation of ±0.1 per cent.

The vapor pressures calculated by means of these equations at a few selected rounded temperatures are given in Table I.

The latent heats of vaporization were calculated for 0 and 30.07° by means of the exact Clapeyron equation; the vapor volume was calculated by means of the van der Waals equation, the constants of which for pentene-1 were derived from critical data. These values are 6225 and 6117 calories per gram mole for 0 and 30.07°.

TABLE I

SOME VAPOR PRESSURES OF PENTENE-1 FROM 0 TO 200°

Temp., °C.	Vapor pressure, mm.	Temp., °C.	Vapor pressure, mm.
0	241.3	100	5,221
5	297.1	120	7,913
10	363.1	150	13,717
20	531.3	170	19,055
30.07[a]	760	180	22,233
40	1069	190	25,850
60	1933	195	27,902
80	3269	200	30,203

[a] Normal boiling point.

Summary

1. The densities of liquid pentene-1 under its vapor pressure were determined from 0 to 50°.
2. The vapor pressures of pentene-1 were determined from 0 to 200°;
3. Calculated heats of vaporization are reported at 0 and 30.07°.

AUSTIN, TEXAS RECEIVED JANUARY 14, 1948

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1]]

Densities and Liquid–Vapor Equilibria of the System Ethanol–Isoöctane (2,2,4-Trimethylpentane) between 0 and 50°

BY CARL B. KRETSCHMER, JANINA NOWAKOWSKA AND RICHARD WIEBE

The present investigation is part of a systematic program in progress at this Laboratory to determine certain physical properties of ethanol–hydrocarbon systems. A considerable amount of experimental and theoretical material on solutions of aliphatic alcohols in non-polar solvents has been published and will be referred to in its proper place.

Density Measurements

Commercial absolute ethanol was fractionated in a 5-foot column packed with glass helices and then treated with magnesium ethylate.[2] The final product of $d^{25}{}_4$ 0.78506 was kept under its own vapor pressure in a sealed container over magnesium ethylate and samples were withdrawn by vacuum distillation. Certified isoöctane (2,2,4-trimethylpentane) was fractionated in the same column. The middle fraction taken was filtered through a column of silica gel to remove the small content of olefins.[3] The final density was found to be $d^{25}{}_4$ 0.68777.

The 13-ml. pycnometer shown in Fig. 1A was used for measuring the densities of the air-saturated liquids and solutions at 25°. No noticeable loss of liquid through evaporation was experienced during weighing because of the smallness of the capillaries (0.3 mm.). By applying gentle suction at the top, filling was accomplished by means of a device shown in Fig. 1B, and the turned-down tip[4] greatly facilitated the adjustment of volume. The accuracy of measurement was estimated to be 2×10^{-5} g./ml. or better.

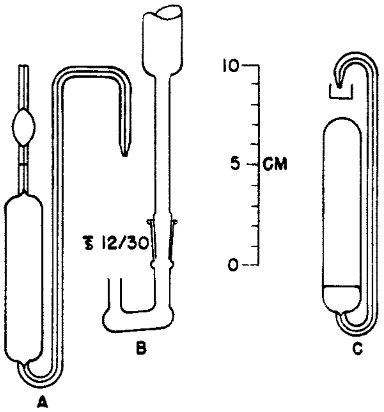

Fig. 1.—A, pycnometer; B, filling device; C, weight dilatometer.

The densities of the two pure liquids at 0 and 50° relative to their values at 25° were measured in a 14-ml. Pyrex weight dilatometer (Fig. 1C). Both apparatus and method were similar to those

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

[2] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[3] B. J. Mair and A. F. Forziati, *J. Research Nat. Bur. Standards*, **32**, 151, 165 (1944).

[4] G. F. Hennion, *Ind. Eng. Chem., Anal. Ed.*, **9**, 479 (1937).