of $(C_4F_9)_3N$ used as well as for the data supplied. We also wish to thank Professor Joel H. Hildebrand for constructive criticisms of this paper

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Physical and Thermodynamic Properties of Terpenes.[1] III. The Vapor Pressures of α-Pinene and β-Pinene[2]

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RECEIVED JANUARY 21, 1954

The vapor pressure–temperature relations for α-pinene and for β-pinene between 15° and their normal boiling points are recorded. Equations to express these relations are presented. The data indicate the normal boiling points to be 155.9 ± 0.1° for α-pinene and 166.0 ± 0.1° for β-pinene.

A survey of the literature discloses considerable uncertainty in the vapor pressure–temperature relations of α-pinene and β-pinene. In some cases compounds used for the determinations were of doubtful purity, and in other cases the data cover only relatively short ranges of temperature and pressure.

Pickett and Peterson[3] used α-pinene, of which 5% boiled below 155° and 95% below 158°. They measured the vapor pressures from 4 to 623 mm. The same workers made similar measurements between 3 and 381 mm. with β-pinene of which 5% boiled below 160.2° and 95% below 163.8°. They measured the pressures to 0.1 mm. below 432 mm. and apparently to only 1.0 mm. at the higher pressures. The temperatures were measured to 0.1° over the whole range. E. G. Linder[4] measured the vapor pressures of α-pinene at three temperatures between −6 and 13.25°. The α-pinene used in this case was of unstated purity. Rudakov and Korotov[5] twice distilled crude turpentine, *Pinus sylvestrus*, through a two-meter du Pont column and obtained α-pinene for which they claimed a high degree of purity. They measured the vapor pressures of the pinene between 49 and 200 mm. and determined the boiling point at atmospheric pressure. Fuguitt, Stallcup and Hawkins[6] determined the boiling points of α-pinene and β-pinene at pressures from 15 to 76 mm. Both compounds were fractionated to a high degree of purity.

The uncertainty in the normal boiling points is indicated by the wide range of temperatures reported.[7] In the case of α-pinene these temperatures range from 154.5–155°, as determined by Nametkin,[8] to 158.5–159°, as found by Perkin.[9] For β-pinene the normal boiling point ranges from 156–157°, as determined by Slawinski, Piliczewski and Zacharewicz,[10] to 164–166°, as reported by Schorger[11] and Wallach.[12]

In view of the existing situation, the determination of the temperature–vapor pressure relations over a wide range for α-pinene and β-pinene of a high degree of purity was undertaken. The method used was essentially that devised by Ramsay and Young[13] and modified by Ryan and Lantz.[14]

Preparation of Materials

α-Pinene and β-Pinene.—These materials were prepared from the commercial products by the procedure previously described.[6] The constants of α-pinene were: $n^{25}{}_D$ 1.4631–1.4632, $d^{25}{}_4$ 0.8539, $[\alpha]^{25}{}_D$ +29.12. The constants of β-pinene were : $n^{25}{}_D$ 1.4768, $d^{25}{}_4$ 0.8667, $[\alpha]^{25}{}_D$ −18.54. Recent cryoscopic measurements on pinenes having these physical constants indicate a purity of approximately 99.6 and 98.7 mole %, respectively. It is believed that the impurities are of a nature that would not significantly affect the vapor pressures.

Other Materials.—The substances used for the calibration of the thermo-element were recrystallized sodium sulfate decahydrate, a National Bureau of Standards sample of tin, and highly purified water which contained about 2.3 parts per million of dissolved solids. This amount of solids would not affect the ice point as much as 0.001°.

A series of commercial grade liquids whose boiling points ranged from 46 to 170° was used to provide a constant temperature vapor-bath at the various pressures at which measurements were made.

Apparatus

In general, the apparatus was of conventional design.

Pressure Regulation and Measurement.—A constant pressure was maintained by use of a manostat of the type designed by Hershberg and Huntress.[15] The pressure fluctuation was reduced by the 18-liter reservoir placed in series between the pump and manostat and the boiler and the manometer. Below 400 mm. the pressure variations were not observable and at higher pressures were within 0.1 mm. The manometer was constructed and operated according to the directions of Germann.[16] The mercury levels were determined by a cathetometer reading to 0.01 mm. The adjustment of the cross-hair on the meniscus of the mercury was simplified by placing a piece of black paper a few millimeters above and behind the surface of the mercury. The pressures were corrected to correspond to the density of mercury at 0° and the value of gravity at 45° latitude and sea level on the basis that Gainesville is at

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(1) For the first article in this series see footnote 6, and for the second see THIS JOURNAL, **76**, 2669 (1954).

(2) The material included in this publication is based upon a thesis presented by George T. Armstrong to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Master of Science, February, 1943.

(3) O. A. Pickett and J. M. Peterson, *Ind. Eng. Chem.*, **21**, 325 (1929).

(4) E. G. Linder, *J. Phys. Chem.*, **35**, 531 (1931).

(5) G. A. Rudakov and S. Ya. Korotov, *J. Applied Chem.* (*USSR*), **10**, 312 (1937).

(6) R. E. Fuguitt, D. W. Stallcup and J. E. Hawkins, THIS JOURNAL, **64**, 2978 (1942).

(7) Gustav Egloff, "Physical Constants of Pure Hydrocarbons," Vol. II, Reinhold Publ. Corp., New York, N. Y., 1940, pp. 267, 459.

(8) S. Nametkin, *J. Russ. Phys. Chem. Soc.*, **54**, 177 (1922).

(9) W. H. Perkin, Jr., *J. Chem. Soc.*, **81**, 292 (1902).

(10) K. Slawinski, J. Piliczewski and W. Zacharewicz, *Roczniki Chem.*, **11**, 763 (1931).

(11) W. A. Schorger, THIS JOURNAL, **35**, 1896 (1913).

(12) O. Wallach, *Ann.*, **363**, 1 (1908).

(13) William Ramsay and Sydney Young, THIS JOURNAL, **47**, 42 (1885).

(14) R. W. Ryan and E. A. Lantz, *Ind. Eng. Chem.*, **20**, 40 (1928).

(15) E. B. Hershberg and E. H. Huntress, *Ind. Eng. Chem., Anal. Ed.*, **5**, 344 (1933).

(16) A. F. O. Germann, THIS JOURNAL, **36**, 2456 (1914).

29.66° N latitude and 200 ft. elevation. No correction was made for capillary effects as the manometer tubes were large and of the same diameters.

Temperature Measurement.—The temperatures at which the vapor and liquid were in equilbrium were measured by a thermocouple in conjunction with a Leeds and Northrup Type K potentiometer and a galvanometer having a sensitivity of 0.000047 microampere per millimeter.

In order to determine temperature differences as small as 0.01° a copper–constantan thermo-element of 24 junctions was used. This conveniently had a sensitivity of approximately one millivolt per degree, so rapid estimation of the temperature was possible.

The thermo-element was constructed essentially according to the recommendations of White[17] except that the wire was not tested for homogeneity. The wires were number 30, B. & S. gage, enameled copper and number 28, B. & S., constantan which had a layer of glass fiber insulation. The melting point of ice was used as a reference temperature.

Calibration of the Thermo-element.—The thermo-element was calibrated by measuring the e.m.f. at three fixed points, namely, the transition point of $Na_2SO_4 \cdot 10H_2O$ (32.38°), the boiling point of water at atmospheric pressure and the melting point of tin (231.87°). These measurements were used to determine the equation which would correct voltages to the data of Adams.[18] At 32.38° the deviation of the e.m.f. from Adams' data was in agreement to within 0.003° for two determinations. The boiling point of water was determined with the Ramsay and Young boiler[13] and also with a modified Othmer still.[19] Four determinations, made on different days, gave a calibration point with a maximum deviation of 0.007° and a mean deviation of ±0.003°.

Calibration at the melting point of tin was made by an indirect method. The tin was melted in a small, insulated clay crucible and a Beckmann thermometer was set. A repetition of the reading of the thermometer in melting tin gave values differing by 0.04°. Following this the thermocouple and the Beckmann thermometer were immersed in a well-stirred oil-bath and heated to approximately 235°. The bath was allowed to cool at a rate of 1° in about 12 minutes, and a series of e.m.f.'s and corresponding temperatures was recorded. This process was repeated by starting with the bath several degrees below the melting point of tin and heating the bath at about the same rate and recording the corresponding e.m.f.'s and temperatures. The calibration obtained as the average of these measurements is believed to have eliminated any error due to the lag of the thermometer temperature behind the temperature of the bath.

Potentiometric Standard.—A Weston cell was used for this purpose in all measurements. This cell was checked both at the beginning and at the end of the complete series of measurements against another Weston cell.

Experimental Procedure

To make a measurement the reservoir was filled with pinene and the system evacuated to the desired pressure. The heating liquid in the boiler was gently refluxed to provide a constant temperature bath slightly hotter than the expected boiling point of the pinene. When the inner chamber had become well heated the pinene was allowed to enter slowly from the reservoir through a stopcock and was spread over the thermometer well by cotton gauze or Pyrex fiber glass which was wrapped around the lower 15 cm. of the thermometer well. Equilibrium conditions were considered to have been obtained when the pinene dripped occasionally from the thermometer well but did not accumulate in the bottom of the inner chamber. The vapor which distilled was collected in an ice trap. Temperature changes of the thermocouple were followed by means of the galvanometer–potentiometer system. When the temperature became constant the e.m.f. and the pressure were recorded.

To ensure rapid heat transfer to the thermo-element the well was filled with an oil, "Muresol," to the level where the pinene came in contact with the well.

In most cases a series of measurements was made on a single day. This was accomplished by evacuating to the lowest desired pressure, making the determination and then introducing air to the apparatus to increase the pressure to the next desired point. By using pressures sufficiently close together two or three measurements could be made with the same vapor-bath. To change the vapor-bath the apparatus was cooled and a stopcock was opened to the outside air. The boiler was removed, emptied and refilled with the liquid of the desired boiling temperature. The steps were reversed, and the vaporizing chamber was quickly evacuated. This procedure avoided pumping out the large reservoir each time.

To check the accuracy of method and technique a series of measurements was made, using water as the test liquid. The results are listed in Table I in which the third column is interpolated from data compiled and smoothed by Washburn.[20]

TABLE I

THE VAPOR PRESSURE OF WATER

P, mm.	t, °C. Obsd.	t, °C. Washburn	Deviation, °C. Obsd.-calcd.
760.68	100.03	100.025	0.005
345.10	79.22	79.29	− .07
174.69	63.39	63.42	− .03
102.31	52.01	52.09	− .08
48.97	37.71	37.73	− .02
31.28	29.70	29.70	.00

Experimental Results

TABLE II

THE OBSERVED VAPOR PRESSURE–TEMPERATURE DATA FOR α-PINENE AND β-PINENE

α-Pinene				β-Pinene			
p, mm.	T, °K.	p, mm.	T, °K.	p, mm.	T, °K.	p, mm.	T, °K.
3.06	292.60	66.79	352.90	1.89	291.87	30.11	341.90
3.43	294.45	81.45	357.86	2.13	293.20	35.08	345.38
4.91	300.40	86.53	359.38	2.59	296.24	40.38	348.58
5.93	302.87	93.85	361.57	3.35	299.97	46.06	351.74
9.01	310.22	107.25	365.16	3.88	302.60	51.08	354.03
15.11	320.07	121.24	368.42	4.44	304.83	52.12	354.38
21.24	326.84	155.39	375.40	4.44	305.18	62.00	359.01
21.58	327.33	175.74	379.05	5.95	309.93	74.88	363.95
24.26	329.72	181.64	379.91	6.03	310.24	85.10	367.27
24.82	330.24	205.80	383.68	6.97	312.56	96.22	370.48
25.45	330.68	226.03	386.65	7.78	314.49	119.62	376.56
31.66	335.43	238.48	388.22	9.67	318.67	144.67	381.96
36.44	338.68	296.11	395.26	11.85	322.56	180.89	388.65
38.41	339.69	322.25	398.17	12.33	323.26	209.81	393.21
41.66	341.42	371.35	403.02	13.59	325.47	248.11	398.48
45.55	343.60	440.12	408.87	17.01	329.72	298.24	404.54
55.73	348.25	605.53	420.63	17.56	330.09	338.32	409.17
57.74	349.19	754.57	428.92	19.13	332.01	488.06	422.70
60.25	350.27	756.01	428.91	19.65	332.63	672.31	434.37
				22.92	335.77	755.97	438.95
				23.13	336.13	759.02	439.07
				26.51	339.07		

The data for α-pinene may be expressed over the entire range by the equation

$$\log_{10} P \text{ (mm.)} = 26.40174 - 3134.525/T - 6.16045 \log T$$

with an average deviation from the measured values of 0.4% and a maximum deviation of 4.1% at 175.74 mm.

For β-pinene the equation

$$\log_{10} P \text{ (mm.)} = 28.77768 - 3318.845/T - 6.94243 \log T$$

expresses the relation, over the entire range, with an average deviation of 1.1% and a maximum deviation of 4.8% at 1.89 mm.

The calculations of the parameters of these two equations, by the method of least squares, were carried out through the coöperation of Dr. Herbert A. Meyer, Director, Statistical Laboratory, University of Florida.

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(17) W. P. White, THIS JOURNAL, **36**, 2292 (1914).

(18) L. H. Adams, "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 58.

(19) D. F. Othmer, *Ind. Eng. Chem.*, **35**, 614 (1943).

(20) E. W. Washburn, ref. 18, Vol. III, p. 210.

Because the functional form of these equations makes interpolation difficult and also because the equations deviate somewhat from the data near the normal boiling points, the data were further treated in the following way. A large-scale plot of log P *vs.* T^{-1} was constructed for each compound. These graphs showed a mild but definite curvature. These curves were approximately fitted by four straight lines which covered successive portions in such a manner that the entire range was included. An equation of the type $\log p = A - B/T$ then represented each straight line. The range of each equation and the parameters for these equations are listed in Table III.

TABLE III

RANGES AND PARAMETERS FOR THE EQUATION $\log p = A - B/T$

Pressure range, mm.	B	A	L_v, cal./mole
	α-Pinene		
3–15	2435	8.806	11,140
15–110	2210	8.089	10,110
110–215	2130	7.871	9,747
215–760	2072	7.712	9,482
	β-Pinene		
2–23	2270	8.120	10,390
23–50	2250	8.060	10,300
50–175	2210	7.947	10,110
175–760	2100	7.663	9,610

By use of these equations the average heat of vaporization for each range was calculated from the Clapeyron equation. These values are shown in Table III.

A study of the data indicates that the normal boiling points of α-pinene and β-pinene are 155.9 ± 0.1° and 166.0 ± 0.1°, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Statistical Mechanics of Dilute Polymer Solutions. VI. Thermodynamic Parameters for the System Polystyrene–Cyclohexane

BY W. R. KRIGBAUM

RECEIVED JANUARY 15, 1954

Accurate osmotic pressure measurements are reported for five polystyrene fractions, ranging in molecular weight from 5×10^4 to 2×10^5, in cyclohexane at 30, 40 and 50°. Evaluation of these data yields for the thermodynamic parameters $\Theta = 307.6$°K. and $\psi_1 = 0.36$. Experimental values for the factor $F(X)$ appearing in the expression for the second virial coefficient confirm the previous conclusion that the $F(X)$ function deduced theoretically is only qualitatively correct. Such defects in the theoretical $F(X)$ function should not, however, vitiate the evaluation of the thermodynamic parameters at the Θ temperature, where the molecules assume random flight configurations and $F(X) = 1$. Although the Θ value stands in good agreement with that deduced from precipitation temperature measurements, the values obtained for the entropy parameter, ψ_1, from measurement of osmotic pressure, precipitation temperature and intrinsic viscosity are not in agreement, indicating the need for further revision of the existing theories of dilute polymer solutions.

The osmotic pressure of a dilute polymer solution may be expressed in virial form, *i.e.*

$$\pi = RT[A_1c + A_2c^2 + A_3c^3 + \ldots] \qquad (1)$$

where the first coefficient, A_1, is given by $1/\bar{M}_n$. Making use of the standard procedures for treating imperfect gases, a theoretical expression for the second virial coefficient

$$A_2 = (\bar{v}^2/V_1)(1 - \Theta/T)\,\psi_1\,F(X) \qquad (2)$$

was obtained[1–3] on representing each molecule by a Gaussian distribution of segments about its center of gravity. Here $\bar{v}$ and V_1 are the partial specific volume of polymer and the molar volume of solvent, respectively, Θ is the (absolute) temperature at which the second virial coefficient vanishes, and ψ_1 is the pair interaction entropy parameter.[2]

The function $F(X)$ occurring in equation 2 expresses the dependence of the second virial coefficient upon the average configuration of the individual polymer molecules; $F(X)$ depends upon the ratio, α, of the root-mean-square distance between the ends of the polymer coil to the corresponding dimension of the random flight counterpart. At the temperature Θ for which the second coefficient vanishes, the molecules assume their random flight configurations, hence $F(X) = 1$ at this unique temperature. The expression for the second virial coefficient given by the earlier statistical treatments of polymer solutions,[4,5] which disregarded the effects of molecular configuration on the long-range intramolecular interactions, differs from equation 2 through omission of the factor $F(X)$. The results of the two treatments therefore coincide only at the Θ temperature. In general, $F(X)$ depends upon the molecular weight, temperature and the thermodynamic parameters characterizing the polymer–solvent interaction; it is this factor which imparts to the second virial coefficient a dependence upon molecular weight and molecular weight heterogeneity. The dilute solution treatment has recently been extended to apply to ternary mixtures of two chemically-dissimilar polymers and a solvent.[6]

Turning now to a comparison of theory with the experimental evidence, the osmotic measurements of Bawn, Freeman and Kamaliddin,[7] and of Frank

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(1) P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949).

(2) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950).

(3) Equation 2 gives the second coefficient corresponding to concentration expressed in g./cc. For c in the units g./100 cc., $A_2 = 10^2(\bar{v}^2/V_1)(1 - \Theta/T)\psi_1 F(X)$.

(4) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(5) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **12**, 425 (1944).

(6) W. R. Krigbaum and P. J. Flory, *ibid.*, **20**, 873 (1952).

(7) C. Bawn, R. Freeman and A. Kamaliddin, *Trans. Faraday Soc.*, **46**, 862 (1950).