TABLE I

PHYSICAL CONSTANTS OF METHYLENECYCLOBUTANE, SPIROPENTANE AND 2-METHYL-1-BUTENE

Compound	F. p., °C.	B. p., °C., 760 mm.	$n^{20}D$	d^{20}_4	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methylenecyclobutane	−134.68	42.22	1.42087	0.7401	C_5H_8	88.17	87.94	11.83	11.61
Spiropentane	−107.05	39.03	1.41220	.7551	C_5H_8	88.17	87.95	11.83	11.88
2-Methyl-1-butene	−137.50	31.12	1.37781	.6504	C_5H_{10}	85.62	85.72	14.37	14.35

obtained according to the procedure of Rossini and co-workers.[4] Boiling points were determined at 760 mm. in a modified Willard and Crabtree apparatus.[5] All temperature measurements were made with a platinum resistance thermometer calibrated at the National Bureau of Standards. Index of refraction was determined with a precision-type refractometer thermostatically controlled to 20 ± 0.1°. Density was measured at 20° by use of a 5-ml. pycnometer.

Physical constants of the purified methylenecyclobutane, spiropentane and 2-methyl-1-butene are given in Table I.

The time–temperature freezing curves show that all these substances are very pure.

Summary

Reduction of pentaerythrityl tetrabromide in ethanol with zinc in the presence of sodium carbonate and sodium iodide was found to yield a mixture of hydrocarbons consisting of 56% methylenecyclobutane, 26% spiropentane, 15% 2-methyl-1-butene and 1–2% 1,1-dimethylcyclopropane.

The reaction procedure described is less troublesome for preparing large quantities of spiropentane than the molten acetamide reduction method previously reported.

The use of ethanol offers a means of preparing both methylenecyclobutane and spiropentane from the same reaction.

Methylenecyclobutane, spiropentane and 2-methyl-1-butene were obtained in a state of purity and their physical constants were determined.

CLEVELAND, OHIO RECEIVED FEBRUARY 11, 1946

[4] Mair, Glasgow and Rossini, National Bureau of Standards Research Paper RP 1397 (1941).

[5] Willard and Crabtree, *Ind. Eng. Chem., Anal. Ed.*, **8**, 79 (1936).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, STANDARD OIL CO. (IND.)]

The Vapor Pressures and Saturated Liquid and Vapor Densities of the Isomeric Hexanes

BY WEBSTER B. KAY

In connection with a study of the physical properties of petroleum hydrocarbons, the vapor pressures and saturated liquid and vapor densities of the five isomeric hexanes were determined over a temperature range from their atmospheric boiling points to their critical points. Previously, similar data have been reported in the literature on *n*-hexane[1] and 2,3-dimethylbutane[1] only.

Experimental

Method and Apparatus.—The static method of measuring vapor pressure was employed. The compressor, pressure gage[2] and method of temperature regulation and measurement[3] have been described. The pressure gage was calibrated with the aid of a pressure balance[4] and checked at 3 atmosphere intervals between 3 and 40 atmospheres, against the vapor pressure of pure water. The vapor pressure-temperature relations for pure water, as given in "International Critical Tables,"[5] were used to determine the true pressure from which the correction for the gage was calculated. For pressures below 3 atmospheres an open mercury column was used.

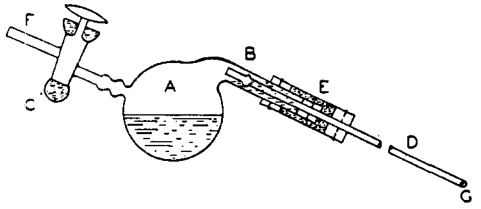

Fig. 1.—The loading apparatus.

Loading the Experimental Tube.—The method of loading the experimental tube with a pure air-free sample of liquid was a modification of that used by Young[6] in his classical vapor pressure studies. A sketch of the apparatus is shown in Fig. 1.

The apparatus was constructed from a 200-cc. Pyrex round-bottom flask A by bending the neck B at a 75° angle to the axis of the flask. A mercury sealed stopcock C was attached to the bottom, as shown. To avoid contamination of the hydrocarbon sample, the stopcock was not lubricated, the closed end of the barrel being filled with enough mercury so that the cock fitted snugly without sticking. Mercury in the cup surrounding the stem of the cock was prevented from spilling out by a rubber cap. The experimental tube D was held in B by a rubber stopper which was made vacuum tight by a mercury seal E. G was a small steel ball used for stirring the sample. The open arm F of the stopcock was connected to a cold trap by rubber tubing so that the apparatus could be manipulated during the filling operation.

The filling operation was carried out as follows: The apparatus was evacuated, C closed and disconnected from the pump and sufficient mercury admitted to A

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[1] Sidney Young, *Sci. Proc. Roy. Soc.* (Dublin), **12**, 374 (1910).

[2] W. B. Kay, *Ind. Eng. Chem.*, **28**, 1014 (1936).

[3] W. H. Bahlke and W. B. Kay, *ibid.*, **24**, 291 (1932).

[4] A Crosby fluid pressure scale, manufactured by the Crosby Steam Gage & Valve Co., was used.

[5] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 233.

[6] Sidney Young, "Stoichimetry," Longmans, Green & Co., New York, N. Y., 1918, p. 124.

TABLE I

BOILING POINTS, LIQUID DENSITIES AT 20° AND CRITICAL CONSTANTS OF THE ISOMERIC HEXANES

	Boiling point, °C.		Density at 20°, g./cc.		Critical constants		
		Lit.[7]		Lit.	Temp., °C.	Pressure, atm.	Density, g./cc.
2,2-Dimethylbutane	49.7	49.741	0.6503	0.6490[8]	216.2	30.67	0.240
2,3-Dimethylbutene	58.03	57.998	.6615	.6615[8]	227.1	30.99	.241
2-Methylpentane	60.13	60.271	.6536	.6532[9]	224.9	29.95	.235
3-Methylpentane	62.95	63.282	.6640	.6643[9]	231.2	30.83	.235
n-Hexane	68.70	68.740	.6591	.6594[9]	234.7	29.94	.233

through C to fill B and tube D. Connection was then remade with the pump and while the evacuation was continued the apparatus was tilted so that mercury spilled over into and filled B to within a few millimeters of the end of the tube D. Next, C was closed, the connection to the pump broken and a sample of the pure liquid distilled—in the presence of phosphorus pentoxide—and collected directly in F. By carefully manipulating C the distillate was made to flow continuously into A without admitting air into the apparatus. When about 40 cc. of liquid had been admitted, C was closed, the distillation stopped and the apparatus again attached to the vacuum pump and the liquid remaining in F pumped off and collected in the cold trap. C was then opened and the vapor-air mixture over the liquid pumped off until the liquid boiled vigorously, when C was closed and a piece of solid carbon dioxide was brought in contact with tube D so that the liquid distilled from A into the tube. The tube was then heated causing the liquid to boil vigorously while at the same time C was opened to the pump and a large volume of the vapor sucked off into the cold trap. C was again closed and the tube allowed to cool before another sample was distilled into the tube. The process was repeated 7 to 8 times in order to remove all traces of air from the liquid. Finally, the liquid in the tube was boiled away until the desired amount of sample remained in the end when the apparatus was quickly tilted and mercury entered and completely filled the remainder of the tube.

The tube, now in a vertical position, was allowed to cool to room temperature after which the tip was immersed in a carbon dioxide snow-acetone bath in order to freeze the mercury next to the liquid sample. C was then opened and the excess liquid in A distilled into the cold trap. Next, F was disconnected and C opened to bring the pressure in A to atmospheric. The mercury seal E was dismantled and the tube D removed from B. A rubber stopper was then fitted around the open end of D and D was again connected to B and held in a vertical position with the tip immersed in the Dry Ice-acetone bath. Enough mercury from A was spilled over into B to cover the end of tube D and the apparatus was again connected to the pump and evacuated. While the evacuation was taking place, tube D was heated with a torch beginning just above the section immersed in the cold bath and continuing up to the end of the tube, until all liquid occluded between the mercury and inner wall of the tube was removed. The tube was allowed to cool and was removed and the packing assembly for holding it in the compressor was put in place. Finally, with the end closed firmly with a finger the tube was turned up into the mercury-filled compressor block and fastened in place.

Next, the high temperature jacket was put in place and the tube heated to about 200°. During the heating the mercury level in the tube was lowered by reducing the pressure on the sample so that the trace of liquid which remained occluded between the mercury and inner wall near the top of the tube was freed and collected in the top of the tube with the main body of the sample. The tube was then allowed to cool and the high temperature jacket replaced with a tube filled with water at room temperature. Measurements of the distance between the top of the tube and the top of the mercury meniscus as well as the height of the meniscus were made using a cathetometer reading to 0.05 mm. From these data and the calibration of the tube the volume of the sample was calculated. The density of the liquid was then determined at the same temperature by means of pyknometer and from the volume and the density the weight of the sample was calculated.

Preparation and Purification of Materials.—*n*-Hexane, 2-methylpentane and 3-methylpentane were obtained from close-boiling fractions of petroleum naphthas by distillation using a 100-plate distilling column with a reflux ratio of 50:1. In addition to the distillation, the *n*-hexane fraction was further purified by passing it over silica gel to remove benzene. The benzene in the finished product was estimated by absorption spectra to be approximately 0.2 volume per cent. 2,3-Dimethylbutane was prepared by the catalytic alkylation of isobutane and ethylene. The product was purified by distillation in a 15-plate column using a high reflux ratio. 2,2-Dimethylbutane ("Pure Neohexane" grade) was obtained from the Phillips Petroleum Company and was further purified by sulfuric acid treatment and distillation in a 60-plate column.

The author is indebted to Dr. R. F. Marschner of this Laboratory and to Dr. D. R. Carmody and Mr. H. E. Huber formerly of this Laboratory for the preparation and purification of the hydrocarbon samples.

Results

In Table I the values of the liquid densities at 20°, which were read from plots of the density–temperature data, and the observed normal boiling points of all of the hexanes, with the exception of 2,2-dimethylbutane, are given and are compared with what are considered to be reliable values of these constants reported in the literature. The value of 49.7° given for the normal boiling point of 2,2-dimethylbutane was obtained by an extension of the log p *vs.* $1/T$ line to 760 mm.

The critical constants of the hexanes are also given in Table I. The critical points were determined by the disappearance-of-the-meniscus method and the temperature and pressure reported for each compound were those observed at the critical point while the density was obtained by extrapolating the mean density line to the critical temperature.

Measurements of the pressure and volume occupied by the sample at the boiling point and dew point were made at approximately 30 temperatures from near the standard boiling point to the critical point. The maximum difference

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(7) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *Bur. of Std. J. of Research*, **35**, 219 (1945).

(8) D. B. Brooks, F. L. Howard and H. C. Crafton, *ibid.*, **24**, 33 (1940).

(9) J. P. Wibaut, H. Hoog, S. L. Langediik, J. Overhoff and J. Smittenberg, *Rev. trav. chim.*, **58**, 329 (1939).

TABLE II

SUMMARY OF VAPOR PRESSURE AND DENSITY EQUATIONS FOR THE ISOMERIC HEXANES

	A	B	log k	m	n	α	β	γ	Average deviation: Vapor pressure Calcd.-obs., atm.	Average deviation: Liquid density Calcd.-obs., g./cc.	Average deviation: Vapor density Calcd.-obs., g./cc
n-Hexane	4.51628	−1543.94	0.21684	0.37757	1.3768	0.6779	-9.03×10^{-4}	0	0.016	0.0011	0.0003
2-Methylpentane	4.46335	−1487.59	.20094	.37083	1.4623	.6720	-9.05×10^{-4}		.015	.0013	.0003
3-Methylpentane	4.46416	−1500.45	.21016	.37692	1.3826	.6844	-9.84×10^{-4}	30×10^{-8}	.016	.0008	.0002
2,3-Dimethylbutane	4.41289	−1461.51	.20950	.38292	1.3425	.6800	-8.74×10^{-4}	0	.020	.0006	.0003
2,2-Dimethylbutane	4.36923	−1410.65	.19076	.36963	1.4272	.6692	-8.79×10^{-4}	0	.021	.0009	.0005

TABLE III

COMPARISON OF VAPOR PRESSURE AND DENSITY DATA CALCULATED FOR n-HEXANE AND 2,3-DIMETHYLBUTANE WITH DATA FROM THE LITERATURE

Temp., °C.	Pressure, atm. Calcd.	Pressure, atm. Lit.[1]	Pressure, atm. Diff.	Density, g./cc. Liquid Calcd.	Density, g./cc. Liquid Lit.[1]	Density, g./cc. Liquid Diff.	Density, g./cc. Vapor Calcd.	Density, g./cc. Vapor Lit.[1]	Density, g./cc. Vapor Diff.
					n-Hexane				
70	1.04	1.04	0.00	0.611	0.6122	−0.001	0.0035	0.0034	0.0001
100	2.43	2.42	.01	.580	.5814	− .001	.0077	.0075	.0002
150	7.37	7.38	.01	.520	.5207	− .001	.0230	.0230	.0000
200	17.79	17.57	.22	.435	.4365	− .002	.0621	.0633	−.0012
230	27.96	27.59	.37	.330	.3329	− .003	.1407	.1405	.0002
					2,3-Dimethylbutane				
70	1.44	1.44	.00	.614	.6144	.000	.0048	.0046	.0002
100	3.17	3.17	.00	.582	.5821	.000	.0102	.0099	.0003
150	9.06	9.06	.00	.520	.5199	.000	.0290	.0285	.0005
200	20.90	20.66	.24	.427	.4274	.000	.0782	.0783	.0001
220	28.03	27.63	.40	.354	.3565	− .003	.1343	.1321	.0022

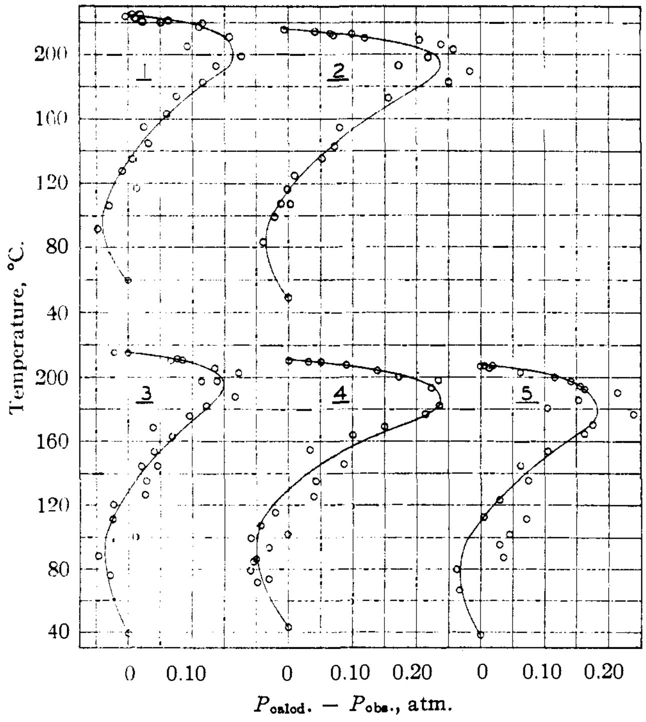

Fig. 2.—Deviations of the observed vapor pressures from the standard vapor pressure equation: 1, 2-methylpentane; 2, 2,2-dimethylbutane; 3, n-hexane; 4, 3-methylpentane; 5, 2,3-dimethylbutane.

in pressure between these two points, which is indicative of the purity of the material, amounted to about 0.040 atm.; this was within the experimental accuracy of the combined pressure reading, that is, 0.020 atm. for each reading. The average of the two pressures, therefore, was taken as the vapor pressure.

The vapor pressure data for each of the compounds have been represented by a combination of the standard vapor pressure equation, $\log P = A + (B/T)$, and a deviation curve. The constants, A and B, were evaluated using the coördinates of the pressure in atmospheres and temperature in °C. at the standard boiling point and the critical point and are given in Table II. The deviation curves, shown in Fig. 2, were obtained by plotting the pressure deviations of the experimental data from the vapor pressure equation against the temperature and drawing a smooth curve as nearly as possible through the points.

Fales and Shapiro[10] have shown that the ratio of the saturated liquid density to the saturated vapor density, ρ_L/ρ_V, can be calculated for a great many substances of the utmost diversity in physical and chemical properties by the following equation

$$\log \log \rho_L/\rho_V = \log k + m \log (1 - T_r^2) - n \log T_r$$

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[10] Fales and Shapiro, THIS JOURNAL, **58**, 2418 (1936).

where T_r is the reduced temperature, T/T_c. By combining this equation with the equation for the sum of the densities

$$\rho_L + \rho_V = \alpha + \beta t + \gamma t^2$$

the densities can be calculated from room temperature to within about 5° of the critical point. The values of the constants k, m, n, α, β, and γ evaluated for each of the compounds from the experimental data are given in Table II. Included in this table are the average deviations of the observed from the calculated values for both the vapor pressure and density. The agreement between the observed and calculated values is within the experimental error in the data.

A comparison of the vapor pressure and density data calculated for *n*-hexane and 2,3-dimethylbutane with data reported by Young[1] is shown in Table III.

Summary

1. The critical constants of all of the isomeric hexanes and the standard boiling points of all except 2,2-dimethylbutane were carefully determined. Values of the liquid density at 20° were obtained by interpolation of the density-temperature curves.

2. The vapor pressures and saturated liquid and vapor densities of the isomeric hexanes were determined from near their atmospheric boiling points to their critical points. The data have been represented by empirical equations: (a) the vapor pressure data by equations of the type log $P = A + (B/T)$ with the aid of deviation curves; (b) the density data by means of the equation of Fales and Shapiro, log log ρ_L/ρ_V = log k + m log $(1 - T_r^2)$ − n log T_r together with the equation for the sum of the liquid and vapor densities, $\rho_L + \rho_V = \alpha + \beta t + \gamma t^2$. Values of the constants in the equations are given for each hydrocarbon.

RECEIVED[11] NOVEMBER 5, 1942

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[11] This manuscript was originally received on November 5, 1942, and after examination by the Editorial Board was accepted for publication in the Journal. It was, however, referred to the National Defense Research Committee, and at their request was withheld from publication, in a confidential file, until clearance was granted on January 10, 1946.

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

The Composition, Optical and Crystallographic Properties of Two Calcium Oxalate–Chloride Double Salts

BY FRANCIS T. JONES AND LAWRENCE M. WHITE

When microscopical methods[1a] were employed for the identification of minute crystals of calcium oxalate found in asparagus juice and hemlock bark, two crystalline substances were observed whose optical properties indicated that they were probably new compounds. Analysis shows that these compounds are the double salts $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$ and $CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$.

A careful search of the literature failed to reveal any work on the calcium oxalate–chloride double salts later than that of G. Rainey[2] in 1865. He investigated the oxalate–chloride double salts of the alkaline earth elements and, among others, described the compound $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$ that appears to be the same as one of the two reported here in detail. This compound had been prepared earlier by Fritzsche,[3,4] who also described another double salt of the composition $3CaC_2O_4 \cdot CaCl_2 \cdot 8H_2O$. Souchay and Lensen[5] in 1856 reported a double salt having the formula $4CaC_2O_4 \cdot CaCl_2 \cdot 24H_2O$ the existence of which was later doubted by Fritzsche.[4]

Experimental

Microscopical Observations.—When crystals obtained from asparagus juice or hemlock bark were recrystallized on a microscope slide[6] from a drop of 3 *N* hydrochloric acid, a few relatively large plate-like crystals were obtained in addition to crystals characteristic of calcium oxalate monohydrate. On contact with water these plate-like crystals changed quickly to a fine grained mass. The behavior, shape and optical properties of the plate-like crystals could not be reconciled with any of the hydrates of calcium oxalate reported by Winchell[7] but references[2,3,4,5] found in Beilstein[8] indicated that the plate-like crystals might be a double salt of calcium oxalate–chloride, and analysis proves that they are $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$. Rainey's[2] method (reaction of saturated calcium chloride solution with solid calcium oxalate on a microscope slide) gave identical plate-like crystals after standing several days. During attempts to prepare large quantities of the new compound by recrystallizing calcium oxalate from 6 *N* hydrochloric acid, crystals of oxalic acid and of tetragonal $CaC_2O_4 \cdot 3H_2O$ were recognized by their optical properties as being mixed with the plate-like crystals of the new compound. A homogeneous preparation of the plate-like crystals was obtained by the method described below. When hot concentrated hydrochloric acid was saturated with calcium oxalate and cooled

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[1a] Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley & Sons, New York, N. Y., 1938.

[2] Rainey, *Proc. Roy. Soc.* (London), **14**, 144 (1865).

[3] Fritzsche, *Pogg. Ann. d. Physik u. Chemie*, **28**, 121 (1833).

[4] Fritzsche, *Jahresbericht uber de Fortschritte der Chemie*, **372** (1864).

[5] Souchay and Lensen, *Ann.*, **100**, 317 (1856).

[6] Chamot and Mason, ref. 1a, Vol. II, 1940.

[7] Winchell, "Optical Properties of Organic Compounds," University of Wisconsin Press, Madison, Wis., 1943.

[8] "Beilstein Handbuch," 4th ed., Vol. II, Julius Springer, Berlin, 1920, p. 515.