about a similar equilibrium followed by hydrolysis of the methyl group and peracetylation to yield aldehydo-*d*-arabinose hexaacetate.

The isomeric pentaacetyl-*d*-arabinose hemi-acetals have been converted to two isomeric chloro derivatives, which by the usual methods are converted into the same tetraacetyl-*d*-arabinose dimethyl acetal.

d-Arabinose dimethyl acetal has been synthesized in crystalline condition by deacetylation of its tetraacetate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Densities and Vapor Pressures of Some Alkylbenzenes, Aliphatic Ketones and *n*-Amyl Chloride[1]

BY J. C. RINTELEN, JR., J. H. SAYLOR AND P. M. GROSS

During the course of an investigation of the solubility of some organic compounds being carried out in this Laboratory, it became necessary to know the vapor pressures and densities of these compounds at 10, 30 and 50°. An examination of the literature showed that there were no available density and vapor pressure data for some of the substances and that there were rather serious discrepancies in the vapor pressure data for ethylbenzene, the xylenes and mesitylene. Therefore, their vapor pressures together with the vapor pressures and densities of *n*-amyl chloride and some ketones were determined. After the experimental part of this work was completed, Kassel[2] called attention to the erroneous data of Woringer[3] for the vapor pressures of the xylenes and mesitylene that are given in the "International Critical Tables." Kassel redetermined the vapor pressures of these compounds.

Experimental

Materials.—The ethylbenzene and the dibutyl ketone were prepared in this Laboratory. The other substances were the best grades commercially available. All were subjected to a careful purification by successive fractionation using efficient stills and calibrated thermometers. Boiling points were corrected to 760 mm. by means of Craft's rule whenever the value of d*T*/d*P* could not be found in the literature. The boiling ranges of the samples used are given in Table I.

TABLE I

BOILING POINT RANGES OF THE COMPOUNDS

Substance	B. p. range, °C.	Previously observed b. p., °C.	Ref.
Ethylbenzene	136.13–136.18	136.15	4a
o-Xylene	144.0 –144.1	144.0	4b
m-Xylene	138.99–139.15	139.3 (139.00)	4b (6)
p-Xylene	138.27–138.37	138.4 (138.3)	5 (6)
Mesitylene	164.5 –164.6	164.6	4b
n-Amyl chloride	107.74–107.78	105.7 (106.6, 740 mm.)	6, (7)
Methyl isopropyl ketone	94.0 –94.52	95–96, 93–94, 95–95.3	8, 9, 10
Methyl isobutyl ketone	116.71–116.78	116.85	4c
Diethyl ketone	101.59–101.74	101.7	8
Dipropyl ketone	144.05–144.12	144.1	4b
Dibutyl ketone	187.4 –188.4	187.65	4d

Method.—The vapor pressures were measured by a differential static method. As the form of apparatus used has been found to be particularly convenient, it is shown in Fig. 1.

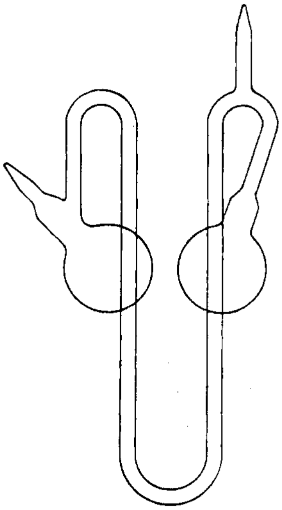

Fig. 1.—Vapor pressure apparatus.

Mercury was introduced into the manometer through the vertical tube, water placed in one bulb and the organic liquid in the other. The mercury in the manometer was

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(1) Taken in part from a thesis submitted by J. C. Rintelen, Jr., in partial fulfilment of the requirement for the degree of Doctor of Philosophy at Duke University, June, 1936.

(2) Kassel, THIS JOURNAL, **58**, 670 (1936).

(3) Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

(4) (a) Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911); (b) **30**, 62 (1921); (c) **27**, 334 (1913); (d) **36**, 506 (1927).

(5) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926).

(6) "International Critical Tables."

(7) Lieben and Rossi, *Ann.*, **159**, 72 (1871).

(8) Timmermans and Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).

(9) Henderson, Henderson and Heilbron, *Ber.*, **47**, 887 (1914).

(10) Clarke, THIS JOURNAL, **33**, 528 (1911).

heated and the water and organic liquid in the bulbs were boiled. Then both sides of the apparatus were evacuated simultaneously while gentle heating continued for thirty minutes. The capillaries were then sealed off.

Temperatures were controlled by thermostats regulated to within ±0.02°. The difference in the mercury levels in the arms of the manometer was read with a cathetometer and corrected to 0°. This added to or subtracted from the vapor pressure of water at the temperature in question, gave the vapor pressure of the liquid. Each apparatus was set up in duplicate for each substance and readings made at 10, 30 and 50°. The method was checked by carrying out the procedure with water in both sides of the apparatus. Several trials gave an average deviation from zero of 0.1 mm.

The densities were determined with a 10-cc. specific gravity bottle, in the same thermostats. These determinations were also made in duplicate at 10, 30 and 50°.

Results

Table II gives a summary of the vapor pressure and density data. Each result is the average of two independent determinations. The duplicate vapor pressure determinations agreed within 0.6 mm. in most cases and the density determinations to within less than 1 part in 10,000.

TABLE II

VAPOR PRESSURE AND DENSITY DATA

Substance	Vapor pressures, mm. 10°	30°	50°	Densities, d_4^t, g./ml. 10°	30°	50°
Ethylbenzene	2.9	11.6	34.6			
o-Xylene	1.6	7.4	25.1			
m-Xylene	2.2	9.1	29.3			
p-Xylene	2.3	10.7	32.3			
Mesitylene	0.6	3.8	11.5			
n-Amyl chloride	15.0	41.2	100.8	0.8940	0.8750	0.8544
Methyl isopropyl ketone	27.4	67.3	166.7	.8239	.8052	.7847
Methyl butyl ketone				.8198	.8025	.7845
Methyl isobutyl ketone	8.0	26.2	70.1	.8094	.7922	.7736
Diethyl ketone	16.9	46.1	117			
Dipropyl ketone	3.0	9.5	25.6			
Dibutyl ketone	1.5	4.7	12.6	.8296	.8148	.7981

The constants of the equation $\log_{10} P = (A/T) + B$ have been determined from a plot of the data for those substances for which no other vapor pressure data is known. While the limitations of such equations based on a few points is, of course, realized, they are given for convenience in interpolation. In these equations 0°C. = 273.16°K. The values of the constants are given in Table III. The average deviation of the observed values from those calculated is less than 1% in all cases.

TABLE III

CONSTANTS FOR THE VAPOR PRESSURE EQUATIONS

Substance	−A	B
n-Amyl chloride	1892	7.8573
Diethyl ketone	1926	8.0236
Dipropyl ketone	2126	7.9864
Dibutyl ketone	2101	7.6031

Kassel's values are in fair agreement with our own results although they are usually higher. Kassel points out that the accuracy of his data is limited by the fact that he did not purify his substances. Whether the differences noted here arise because of this or because of a small systematic error in our method or in his is not clear.

The results of Woringer used in the "International Critical Tables" are obviously wrong with the possible exception of those for *m*-xylene. This is probably attributable to a systematic error in method or more likely to the use of impure materials as he reported determinations by the same method for other compounds such as benzene and toluene which agree fairly well with the well established data of others.

Values for the vapor pressures of the hydrocarbons at 0° are given by Linder.[11] When our values are extrapolated to 0°, they are found to agree well with his except in the case of *m*-xylene and *p*-xylene. Values for *m*-xylene at higher temperatures given by Kudryavtzev[12] check with our results. Values for the vapor pressures for ethylbenzene at higher temperatures given by Kurbatov[13] check fairly well with our results while those given by Vvendenski[14] do not.

The values of Mayberry and Aston[15] for the vapor pressures of methyl isopropyl ketone and methyl isobutyl ketone given in Table III are only in fair agreement with ours.

Summary

The vapor pressures of ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-amyl chloride, methyl isopropyl ketone, methyl isobutyl ketone, diethyl ketone, dipropyl ketone and dibutyl ketone have been determined at 10, 30 and 50°. The densities of *n*-amyl chloride, methyl isopropyl ketone, methyl butyl ketone, methyl isobutyl ketone and dibutyl ketone have been determined at 10, 30 and 50°.

DURHAM, N. C. RECEIVED MARCH 20, 1937

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[11] Linder, *J. Phys. Chem.*, **35**, 53 (1931).

[12] Kudryavtzev, *J. Gen. Chem.* (U. S. S. R.), **4**, 563 (1934).

[13] Kurbatov, *Leningrad Tech. Inst.*, **1**, 32 (1927).

[14] Vvendenski, *J. Gen. Chem.* (U. S. S. R.), **2**, 826 (1932).

[15] Mayberry and Aston, THIS JOURNAL, **56**, 2682 (1934).