[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

STUDIES ON THE POLYMETHYLBENZENES. III. THE VAPOR PRESSURES OF THE TETRAMETHYLBENZENES, AND OF PENTA- AND HEXAMETHYLBENZENE

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No data are recorded in the literature on the vapor pressures of any of the polymethylbenzenes containing four or more methyl groups, and the work reported in this paper deals with the determination of the vapor pressure curves of five polymethylbenzenes: the three tetramethylbenzenes, penta- and hexamethylbenzene. Only the vapor pressures of the liquid hydrocarbons have been measured: the lower limit is either around room temperature, or as close to the melting point of the hydrocarbon as could be obtained with the apparatus used.

The purification of all the materials is given in a previous paper.[1] In every case except one the purest materials at hand were used, judging by the freezing point curve. The one exception is in the case of prehnitene (1,2,3,4-tetramethylbenzene), the vapor pressure sample showing a freezing point of −6.8° as compared with a later sample purified through the picrate, and which showed a freezing point of −6.4°. However, the boiling point of this very pure sample was determined at two or three pressures and the results were found to check within the experimental error the values given by the sample freezing at −6.8°, so that it was not felt necessary to re-check the whole curve.

Apparatus and Procedure.—The procedure followed was to determine the boiling point under various pressures in a modified Claisen flask, arranged so that the distillate was returned to the flask. Superheating was avoided by passing a very fine stream of air through the boiling liquid, and the temperature of the outside (Wood's metal) bath was carefully regulated so that a nice even distillation resulted. The neck of the flask was made long enough so that the thermometer was completely immersed in the vapor, and was wide enough so that the thermometer did not touch the flask at any point. The thermometers used were all standardized. The pressure was read on a closed tube manometer, internal diameter about 7.5 mm., which had a range up to atmospheric, and which had been carefully checked against an accurately calibrated manometer. The accuracy of reading the manometer scale was about 0.3 mm., but since two readings were necessary in order to determine the pressure, the error in any given reading was double this, or about 0.5 mm. The pressure was varied by inserting a long tapering capillary into the line and cutting off small lengths in passing from one determination to the next.

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[1] Smith and MacDougall, THIS JOURNAL, **51**, 3001 (1929).

With a good pump having high capacity, this method permits the pressure to be changed easily and very constant readings were obtained. In every case the readings were checked: first the pressure was read, then the temperature, and after half a minute these readings were repeated in the reverse order.

Results.—The results are given in the tables and curves. Figure 1 is taken from the observed data directly, plotting alternate readings in order to simplify drawing these curves. In addition, the curves for durene and isodurene are so close together that only one of them has been drawn,

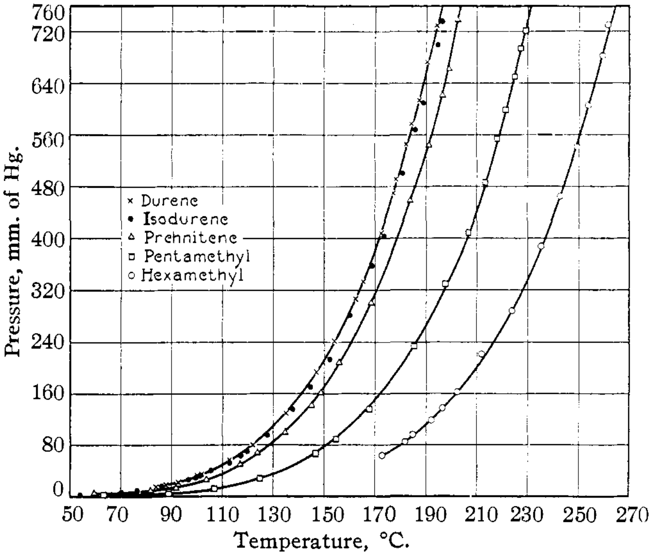


Fig. 1.—Vapor pressure curves of the polymethyl benzenes.

TABLE I

VAPOR PRESSURE EQUATIONS, $u = 1000/T$

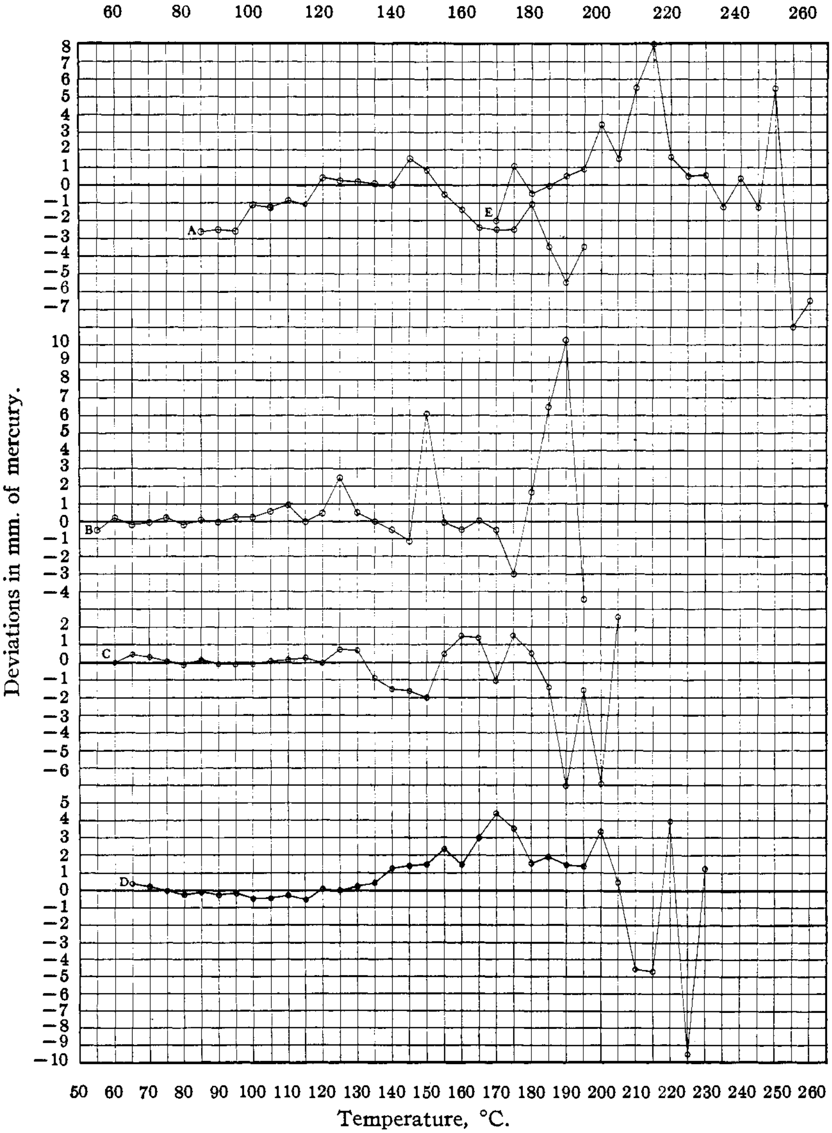
Durene	$\log_{10} P = 18.8224 - 3093/T - 3.499 \log_{10} T$
Isodurene	$\log_{10} P = 5.9514 - 0.6033\, u - 0.3972\, u^2$
Prehnitene	$\log_{10} P = 6.4470 - 1.0542\, u - 0.3099\, u^2$
Penta	$\log_{10} P = 6.7125 - 1.323\, u - 0.309\, u^2$
Hexa	$\log_{10} P = 7.7760 - 2.4394\, u - 0.1009\, u^2$

TABLE II

CONSTANTS

Substance	T_{760}	L_{760}	$\frac{L_{760}}{T_{760}}$
Durene	469.0	10,880	23.2
Isodurene	471.1	10,470	22.2
Prehnitene	477.6	10,760	22.5
Penta	505.0	11,650	23.1
Hexa	536.7	12,870	24 0

the points on the other merely being indicated. Table I gives the empirical equations for the vapor pressures. Figure 2 gives the deviations of the calculated pressures from the observed values. These deviations,



A, Durene; B, isodurene; C, prehnitene; D, pentamethylbenzene; E, hexamethylbenzene.

Fig. 2.—Deviation plots for the vapor pressures of the polymethylbenzenes. Positive deviations are to be added to the calculated to find the observed. Negative vapor pressures are to be added.

when positive, are to be added to the calculated pressures, and subtracted when negative. Table II gives the normal boiling point, the latent heats of vaporization, and L/T, or the "entropy of vaporization." All pressure readings are in mm. of mercury at 0°, and all temperatures are corrected.

Summary and Conclusions

1. The vapor pressures of all the polymethylbenzenes containing four or more methyl groups have been determined over a considerable range of temperatures, and the results are given in the form of tables and curves.
2. From these data, the latent heats of vaporization have been calculated.

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RESEARCHES ON PYRIMIDINES. CXV. ALKYLATION ON NITROGEN OF THE PYRIMIDINE CYCLE BY APPLICATION OF A NEW TECHNIQUE INVOLVING MOLECULAR REARRANGEMENTS

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That the *lactim* ethers I will undergo rearrangements to their isomeric and stable *lactam* configurations II has been known for a long time. These transformations are not reversible and are brought about by the application of heat or through the influence of special catalytic agents, and have been observed to take place in both the acyclic and cyclic series of organic compounds.[2]

$$\underset{\text{I}}{N{=}C{-}OCH_3} \longrightarrow \underset{\text{II}}{CH_3N{-}C{=}O}$$

The interesting data obtained by Knorr as a result of his study of molecular transformations in the pyrazolone and quinoline series suggested that corresponding changes might be brought about in pyrimidine combinations containing *lactim* ether groupings.[3] Knorr showed that certain α- and γ-alkoxyquinolines interact with methyl iodide with formation of addition products IV which are unstable and break down on heating to form N-alkylquinolones V. The transformation of the ethoxyquinoline

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[1] Sterling Research Fellow, 1928–1930.

[2] A review of the literature on imido-ester rearrangements has been recorded in the following publications: Johnson and Hahn, "Theories of Organic Chemistry (Henrich)," John Wiley and Sons, Inc., New York, **1922**, and in "Molecular Rearrangements," by C. W. Porter, American Chemical Society Monograph No. 45, The Chemical Catalog Company, Inc., New York, **1929**. See also Chapman, *J. Chem. Soc.*, 569 (1929).

[3] Knorr, *Ann.*, **293**, 5 (1896); *Ber.*, **30**, 922, 927, 937 (1897); see also Lieben and Haitinger, *Monatsh.*, **6**, 315 (1885). for rearrangement of alkoxypyridines.