

9. The most convenient test of the quality of cells is the observation of the variation in apparent resistance with variation in frequency.

10. It has been shown experimentally that the ratio of the resistances of a pair of cells when filled with a common solution is independent of the electrolyte used for three different electrolytes. This does not confirm observations of earlier experimenters and removes the only experimental support for the hypothesis of Parker that adsorption is responsible for the Parker Effect.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF RUTGERS UNIVERSITY]

THE VAPOR PRESSURE OF PYRIDINE¹

BY P. A. VAN DER MEULEN AND RUSSELL F. MANN

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In the course of a study of certain complex compounds containing pyridine, a search made of the literature revealed that the vapor pressure curve of this substance below the normal boiling point has been only partially determined. Kahlbaum² determined the vapor pressure at six temperatures below 51°. Zawidzki³ reports a single value at 80°; the "International Critical Tables"⁴ give the boiling point as 115.3°, but the vapor pressure as 760 mm. at 115.50°. ^{5,6} The present study was undertaken to fill the gaps between these data.

Experimental Work

Pyridine c. p. brand of Baker was purified as recommended by Arndt and Nachtwey.⁷ This involves preparation of the pyridine perchlorate, purification of the perchlorate by crystallization, and liberation of the pyridine. The product was dried over solid potassium hydroxide, and was distilled with a fractionating column. The first and last quarters were rejected. The middle fraction, passing over between 115.1 and 115.3° was collected. This was redistilled as required.

The apparatus used was similar to that employed by Mortimer and Mur-

¹ This paper is based on a thesis submitted by Russell F. Mann to the faculty of Rutgers University in partial fulfilment of the requirements for the degree of Master of Science.

² G. W. A. Kahlbaum, "Siedetemperatur und Druck," Leipzig, 1885, p. 67.

³ J. v. Zawidzki, *Z. physik. Chem.*, **35**, 129-203 (1900).

⁴ "I. C. T.," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I, p. 190.

⁵ *Ibid.*, 1928, Vol. III, p. 219.

⁶ K. G. MacKensie, *Ind. Eng. Chem.*, **1**, 360-362 (1909); Robert Schiff, *Ber.*, **19**, 560-568 (1886); W. Louguinine, *Compt. rend.*, **129**, 366-369 (1899); H. Hartley, N. G. Thomas and M. P. Appleby, *J. Chem. Soc. (Trans.)*, **93**, 538-563 (1908); W. R. Innes, *ibid.*, **79**, 261-266 (1901); E. J. Constam and J. White, *Am. Chem. J.*, **29**, 1-49 (1903); J. v. Zawidzki, *Chem.-Ztg.*, **30**, 299 (1906).

⁷ F. Arndt and P. Nachtwey, *Ber.*, **59A**, 448-455 (1926).

phy⁸ in their modification of the static isoteniscope method of Smith and Menzies.⁹ The apparatus was checked against the values for the vapor pressure of water given by Holborn and Henning.¹⁰

The isoteniscope was attached to the apparatus by means of a slip joint provided with a mercury seal, making possible the removal of this portion of the apparatus for the purpose of cleaning and filling. For temperatures above 25° a four-liter beaker surrounded by an asbestos sheath provided with peep holes was used as a constant temperature bath. A white mineral oil served as the bath liquid. Below 25° a wide-mouthed Dewar flask of clear glass was employed as a thermostat. The liquid was chilled ether. It was found necessary to use two high-speed propeller-type stirrers to maintain a uniform temperature throughout the bath. All thermometers used in this work were standardized by means of a Reichsanstalt standard thermometer. The manometer was of the ordinary open-end type, 7 mm. wide, securely mounted on a brick wall, and shielded from the heat of the bath. All manometer readings were made with a cathetometer, as were also readings of the levels in the U-arm of the isoteniscope. Manometer and barometer readings were reduced to mm. of mercury at 0°. A brass scale correction for the barometer was necessary.

Manipulation.—For each set of determinations the detachable isoteniscope arm was thoroughly cleaned, and pyridine was redistilled directly into this portion of the apparatus. The isoteniscope was then immersed in a bath of solid carbon dioxide and ether to chill the pyridine, and the apparatus was pumped out with a Hy-vac oil pump. Pumping was continued for one-half hour. A portion of the sample was then allowed to distil over into the U-tube. As an open-end manometer was used throughout the experiment, readings were not made below -15°, since at lower temperatures the pressure was less than 1 mm.

Determinations were continued up to and slightly above the normal boiling point of pyridine, a complete series of determinations being made at one time. Several samples of pyridine were used for the pressure determinations and a sufficient number of checks were made to insure the accuracy of the results.

Experimental Data.—In order to secure a suitable empirical equation we followed the lead of Antoine,¹¹ Cox,¹² and Davis,¹³ and adopted the empirical equation

$$\text{Log } p = A - \frac{B}{t + 205}$$

⁸ F. Spencer Mortimer and R. V. Murphy, *Ind. Eng. Chem.*, **15**, 1140-1142 (1923).

⁹ Alexander Smith and A. W. C. Menzies, *THIS JOURNAL*, **32**, 1412-1434 (1910).

¹⁰ L. Holborn and F. Henning, *Ann. Physik*, [4] **26**, 833-883 (1908).

¹¹ Chwolson, "H Lehrbuch der Physik," Vol. III, 3d German ed., 1905, p. 741.

¹² Edwin R. Cox, *Ind. Eng. Chem.*, **15**, 592-593 (1923).

¹³ D. S. Davis, *ibid.*, **17**, 735 (1925); **22**, 380-381 (1930).

The best values for A and B were then calculated by the method of least squares from our fifty vapor pressure determinations between -15 and $+116^\circ$. The resulting equation is

$$\text{Log } p = 6.8827 - \frac{1281.3}{t + 205}$$

where p is expressed in mm. of mercury and t is temperature in degrees centigrade.

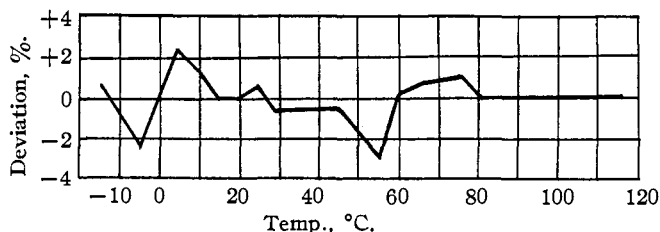


Fig. 1.

The deviations of our experimental results from this equation have been plotted in Fig. 1. The maximum deviation is 3.1%. Vapor pressures at round temperatures calculated from this equation are given in Table I.

TABLE I
VAPOR PRESSURE OF PYRIDINE AT ROUND TEMPERATURES

Temperature, °C.	Calculated pressure, mm.	Temperature, °C.	Calculated pressure, mm.
-20.0	0.91	60.0	111.6
-10.0	2.05	70.0	167.3
0.0	4.29	80.0	243.8
+10.0	8.38	90.0	346.3
+20.0	15.4	100.0	481
30.0	27.0	110.0	653
40.0	45.0	115.2	760
50.0	72.1	120.0	872

Summary

Pyridine has been purified by crystallization of the perchlorate, followed by redistillation. The vapor pressure of this purified pyridine has been determined by the isoteniscope method. The relation between temperature and vapor pressure between -20 and $+120^\circ$ is best represented by the empirical equation

$$\text{Log } p = 6.8827 - \frac{1281.3}{t + 205}$$

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