Vapor Pressure of Naphthalene

New Measurements between 40° and 180° C.

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The vapor pressure of solid naphthalene was measured between 40° and 80° C. An Antoine equation: log P = 9.58102 − 2619.91/(t + 220.651) was fitted with a standard deviation of 0.033 torr. Measurements of liquid between 81° and 180° C. gave: log P = 7.03382 − 1756.91/(t + 204.937), with a standard deviation of 0.088 torr. These results were compared with existing data and conformity shown.

ALTHOUGH various series of measurements of the vapor pressure of naphthalene have been summarized in the literature (*5-7*), there is a paucity of measurements in the vicinity of the melting point, 80.29° C.—i.e., between 50° and 120° C. Some preliminary experiments in this laboratory by evaporation loss methods indicated that extrapolations of the best available data were unsatisfactory. Discrepancies between previously reported data are also large in this region. A new group of measurements has been made.

EXPERIMENTAL

The naphthalene used was zone-refined material of a reported purity of 99.99% (J. Hinton, Valparaiso, Fla.). Examination by gas chromatographic and mass spectrometric techniques, using a variety of configurations of requisite sensitivity, could find no impurities above a level of 0.01% total. The melting point was 80.282° ± 0.005° C. Using the cryoscopic data of Mastrangelo (*3*), this implies an impurity level of 0.01 mole %.

The samples were contained in a bulb which, after conventional out-gassing by successive heating and cooling under vacuum, was sealed to a quartz helix (Texas Instruments, Inc.) of a sensitivity of about 50 torr for 100 degrees rotation. A mirror, lamp, and split photocell assembly on the helix enabled it to be used as a null-detector of better than 0.02 torr long-term sensitivity and stability. The sample bulb was immersed in a bath; the connecting tubing and null-detector were maintained at a stable temperature above the maximum measurement temperature.

The outer chamber of the null-detector was connected to a measurement manifold which provided the null-balance air pressure. The balancing pressure measuring elements comprised a high precision mercury manometer (Hass Instrument Corp., Type DMS-1) of a range of 100 torr and a quartz helix gage (Texas Instruments, Inc., Model 140) of 800 torr range. The legs of the mercury manometer are 85-mm. diameter; the levels are measured with screw micrometers reading to 2.5×10^{-3} mm. The manometer was checked by the manufacturer at three points with a maximum correction of 8×10^{-3} mm. In use, the manometer base was releveled before each reading, and appropriate corrections were made for temperature and the acceleration of gravity. Reproducibility of the manometer system was about 0.02 torr. The quartz helix gage is equipped with a counter to display the degrees of rotation required to restore a mirror-photocell system to balance. Least count is equivalent to 8×10^{-3} torr. Reproducibility was about 0.02 torr in 1 day and less than 0.05 torr over several days. The gage was compared with the mercury manometer to 100 torr and to 800 torr with an auxiliary mercury manometer and cathetometer assembly of a precision of 0.05 torr. A calibration chart was prepared.

The bath temperature was measured with a platinum resistance thermometer (Leeds and Northrup Model 8163-B), manufacturer's four-point calibration, confirmed at the triple point of water, and a Mueller bridge (Leeds and Northrup Model 8069-B). The combined error is less than 0.01° C.

The expected precision of measurement, with only instrumental sources of error considered, is equal to or better than 0.03 torr below 100 torr and 0.1 torr between 100 and 300 torr.

RESULTS

The combined results of several independent runs are shown in Table I. The data for the liquid region were fitted by a nonlinear regression least-squares method (computer program available on request from the authors) to an Antoine equation:

$$\log P = 7.03382 - 1756.91/(t + 204.937) \tag{1}$$

with a residual standard deviation of ± 0.088 torr, where P is in torr and t is degrees Celsius.

Camin and Rossini (*1*) reported data for the liquid from 126° to 218° C. and gave the interpolating equation:

$$\log P = 6.84577 - 1606.529/(t + 187.227) \tag{2}$$

for which a residual standard deviation of 0.348 torr was calculated. To evaluate continuity and agreement, their data were pooled with the authors' and an interpolating equation was developed:

$$\log P = 7.01065 - 1733.71/(t + 201.859) \tag{3}$$

with a residual standard deviation of 0.395 torr.

The solid region data were fitted to the following interpolation equation:

$$\log P = 9.58102 - 2619.91/(t + 220.651) \tag{4}$$

with a residual standard deviation of 0.033 torr.

Gil'denblat, Furmanov, and Zhavoronskov (*2*) reported data from 16° to 50° C. Their equation:

$$\log P = 11.424 - 3722.5/T \tag{5}$$

gives a standard deviation of 0.0052 torr. Their data were recalculated to give the following equation:

$$\log P = 12.8612 - 4577.47/(t + 303.544) \tag{6}$$

with a residual standard deviation of 0.0026 torr. Reconciling the present data with theirs gave a pooled equation:

$$\log P = 10.0896 - 2926.61/(t + 237.332) \tag{7}$$

with a residual standard deviation of 0.022 torr.

No trends assignable to any set of data were found.

Table I. Experimental Data for Naphthalene Vapor Pressure

Liquid		Solid	
t, ° C.	*P*, torr	*t*, ° C.	*P*, torr
80.33_4	7.51_9	40.33_7	0.35_4
82.88_8	8.55_7	49.45_1	0.74_1
83.35_6	8.80_0	54.17_0	1.11_4
85.69_7	9.71_8	60.22_7	1.83_6
88.85_2	11.30_2	61.20_0	1.90_8
92.74_6	13.58_1	65.05_8	2.54_1
93.28_2	13.85_8	66.35_8	2.88_6
94.31_9	14.64_7	70.18_7	3.75_9
98.66_5	17.67_5	70.98_1	3.91_4
102.93_7	21.25_7	75.61_4	5.44_8
106.19_6	24.33_5	76.70_6	5.92_0
109.23_0	27.73_1	79.34_4	6.99_5
109.49_4	27.88_0		
109.80_9	28.28_6		
115.55_9	35.63_9		
115.57_1	35.67_3		
119.22_2	41.03_1		
124.44_9	50.05_6		
124.91_8	50.98_7		
125.91_2	52.95_2		
133.28_1	69.06_8		
133.69_4	69.97_0		
138.48_3	82.63_4		
139.61_0	86.08_3		
140.83_8	89.64_3		
149.64_8	120.0_1		
150.38_0	122.8_6		
158.01_2	155.7_0		
159.08_8	161.3_1		
159.54_0	163.6_2		
168.70_4	214.8_0		
179.51_5	290.9_5		

At the triple point, 80.27° C. (*4*), Equations 1 and 4 give values of 7.47_7 and 7.49_4 torr, respectively. These values agree within the calculated precision. The use of a nonlinear regression and minimization of the deviation of *P* rather than of log *P* is feasible only with the aid of the computer. This method was chosen because it fits the experimental condition of a relatively constant error in the measurement of *P*, rather than the constant percentage error in *P* implied in the minimization of the deviation of log *P*. Trial calculations showed that the two methods do not lead to large differences in calculated values of the constants or of *P*. However, the authors believe there is a real gain in obtaining the value of the deviation in *P* directly from the calculation of the interpolating equation.

ACKNOWLEDGMENT

The authors acknowledge the assistance of R. F. Brooks and A. W. Dickinson for devising and implementing the computer programs.

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RECEIVED for review May 25, 1967. Accepted December 7, 1967.

Liquid Phase Density in the System Helium-Nitrogen

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Densities have been measured at 25 points in the compressed liquid region of the helium-nitrogen system at 77.38°, 100.61°, and 117.30° K. at pressures up to 544 atm. Density *vs.* pressure curves have been extrapolated to the saturation curves to obtain densities for the saturated liquid.

EXPERIMENTAL studies of liquid-vapor phase equilibria have been published for many low temperature binary systems; however, few of these include data on the densities of the coexisting phases. Such data are required for performing meaningful thermodynamic analyses and correlations of the phase data, but they are difficult to obtain because of the low temperature and sometimes high pressure at which these systems exist. Often the vapor phase density can be estimated from an equation of state, but estimates of the liquid density are far less reliable, especially when one of the pure components is a supercritical gas. In this paper, experimental measurements of densities in the compressed liquid region of the helium-nitrogen system are presented at temperatures of 77.38°, 100.61°, and 117.30° K. and at pressures from just above saturation to 544 atm. Density *vs.* pressure curves have been extrapolated to the saturation line to obtain saturated liquid densities.

EXPERIMENTAL

Liquid densities reported here have been measured by the method of gas expansion. In this method a small quantity of the fluid under study is confined in a cell of known volume at fixed pressure and temperature, and expanded into a large volume, thermostatically controlled at room temperature. The mass of gas is determined from known low pressure *PVT* relations in the large volume, and used to calculate the density under conditions in the cell. A detailed description of the experimental equipment and its

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