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Vapor Pressure of Azulene between 114 and 261 °C

Edwin F. Meyer* and Timothy H. Gens

Chemistry Department, DePaul University, Chicago, Illinois 60614

The vapor pressure of a sample of azulene (99.8% purity by gas–liquid chromatography) has been measured between 114 and 160 °C using an oil manometer, and between 169 and 261 °C using comparative ebulliometry with water as reference. Cox and Frost–Kalkwarf equations fit the latter data with an average $\Delta p/p$ of 9.2×10^{-5}; the Antoine equation, 1.1×10^{-4}. When the oil manometer data are included, $\Delta p/p$ for the first two equations rises to 2.5×10^{-4}. Calculated vaporization properties (liquid → vapor) at 25 °C, $\Delta H° = 14.14$ kcal mol^{-1}, $\Delta S° = 28.64$ eu, do not agree with values in the literature.

There is serious disagreement among authors (*1, 4, 5, 8*) concerning the vaporization properties of azulene. Because of its interest as an aromatic, polar isomer of naphthalene, its standard thermodynamic properties ought to be at least as well known. Toward this end we have measured the vapor pressure of azulene from a temperature close to its triple point to about 10° above its normal boiling point, and have fitted the data to Antoine, Cox, and Frost–Kalkwarf equations.

Experimental Section

Azulene was purchased from Aldrich Chemical Co., and was 99.8% pure by gas–liquid chromatography, the only impurity found being naphthalene. It was used as received.

Measurements were made using the same apparatus as previously described (*7*). The sample was repeatedly rinsed with helium in an attempt to remove all traces of oxygen before any heating was done. Measurements started at 144 °C using an oil manometer. Pressure was decreased in intervals until a temperature of 108 °C was reached, when temperature instability was encountered. The pressure was then raised until the highest pressure compatible with the oil manometer was attained, corresponding to a temperature of 160 °C. The first stable comparative ebulliometric point was at 169 °C, and these data extend to 261 °C at intervals of about 8 °C. Once the azulene was heated, measurements were made continuously for 72 h, to avoid the unnecessary heating associated with shut-down and warm-up times.

Immediately after completion of the last data point, the pressure in the system was reduced to a value corresponding to the neighborhood of our fourth comparative ebulliometric point. (Lower pressures have sometimes led to uneven boiling, and a reliable check was desired.) The observed pressure was 0.018 cmHg above the originally measured one, a discrepancy ten times experimental error.

After removing the azulene from the boiler, another GLC analysis was run which indicated a slight increase in naphthalene content (to about 0.3%), consistent with the increase in vapor pressure during the experiment, but no other impurities were apparent. The presence of traces of another decomposition product, a brown residue, however, remained on the glass in the top part of the boiler. Attempts to evaluate its effect on the data are made in the discussion section.

The values for R_0 for both platinum resistance thermometers were checked using the triple point of water before and after the measurements.

Results

Table I presents the equilibrium temperatures and pressures for azulene, and includes the temperature of the water equilibrium for those points obtained using comparative ebulliometry. Table II presents constants for Antoine, Cox, and Frost–Kalkwarf (*3*) equations fitted to the comparative data only, and the last two equations fitted to both sets of data. The table includes average values of $\Delta p/p$ for each equation, where Δp is the absolute value of the difference between the observed and calculated values. Though the Frost–Kalkwarf is less convenient to work with, it has a basis in theory and was included to provide a check on the ability of the Cox equation to extrapolate to lower temperatures. All data fitting was accomplished using the rigorous, iterative least-squares method described by Wentworth (*10*), with weighting as previously discussed (*7*).

Discussion

There have been three studies of the vapor pressure of azulene published: Heilbronner and Wieland (*4*) (HW) used a static method, sealing their sample into one arm of a mercury manometer. They measured the vapor pressure of the solid from

Table I. Vapor Pressure Data for Azulene

t_{azulene}, °C	P_{azulene}, cmHg	t_{H_2O}, °C
114.360	1.201	—
121.536	1.630[a]	—
129.039	2.222	—
136.349	2.955	—
144.465	4.008	—
160.364	6.984	—
169.053	9.278	50.041
176.823	11.821	55.011
185.992	15.547	60.848
193.121	19.063	65.348
202.187	24.457	71.041
210.691	30.574	76.331
218.563	37.299	81.202
227.216	46.014	86.519
235.641	56.006	91.664
244.335	68.038	96.928
252.548	81.225	101.874
260.950	96.700	106.893

[a] Excluded when fitting data.

Table II. Constants for Vapor Pressure Equations

Comparative Ebulliometer Data Only; *t* range: 169–261 °C

Antoine Equation[a]

$A = 6.050\,943 \pm 0.000\,95$

$B = 1865.413 \pm 0.782$

$C = 197.895 \pm 0.019$

$\Delta p/p = 1.1 \times 10^{-4}$

Cox Equation[b]

$a = 0.846\,233 \pm 0.002\,13$

$b = (-0.462\,427 \pm 0.009\,05) \times 10^{-3}$

$c = (0.303\,692 \pm 0.009\,58) \times 10^{-6}$

$T_{bp} = 522.5815 \pm 0.0006$

$\Delta p/p = 9.2 \times 10^{-5}$

Frost–Kalkwarf Equation[c]

$A = 25.6708 \pm 0.274$

$B = -3794.258 \pm 16.88$

$C = -5.7169 \pm 0.0892$

$D = 3.5892 \pm 0.265$

$\Delta p/p = 9.2 \times 10^{-5}$

Oil Manometer plus Comparative Ebulliometer Data;
t range = 114–261 °C

Cox Equation[b]

$a = 0.863\,092 \pm 0.000\,742$

$b = (-0.533\,572 \pm 0.003\,30) \times 10^{-3}$

$c = (0.378\,526 \pm 0.003\,66) \times 10^{-6}$

$T_{bp} = 522.5834 \pm 0.0006$

$\Delta p/p = 2.5 \times 10^{-4}$

Frost–Kalkwarf Equation[c]

$A = 27.5177 \pm 0.0739$

$B = -3908.025 \pm 4.42$

$C = -6.318\,10 \pm 0.0242$

$D = 5.3643 \pm 0.0919$

$\Delta p/p = 2.7 \times 10^{-4}$

[a] $\log p\,(\text{cmHg}) = A - B/(C + t)$. [b] $\log p\,(\text{atm}) = A'(1 - T_{bp}/T)$, where $\log A' = a + bT + cT^2$. [c] $\log p\,(\text{mmHg}) = A + B/T + C \log T + Dp/T^2$.

47 to 98 °C, and the liquid from 102 to 155 °C. Bauder and Günthard (*1*) (BG) used the Knudsen effusion method for the solid vapor pressure between 20 and 50 °C, and the same method as HW between 50 and 150 °C. Hoyer and Peperle (*5*) (HP) used an effusion method for the solid vapor pressure between −20 and 20 °C.

Table III. Standard Vaporization Properties of Supercooled Azulene

	HW	BG	Present work Cox	Present work F–K
ΔH° (kcal mol^{-1})	13.26	15.24	14.26	14.14
ΔS° (eu)	25.99	32.01	28.99	28.64

The temperature range from 102 to 150 is common to the measurements of HW, BG, and the present work. The data of HW agree with the present work within about 0.1 mm up to 126 °C, but diverge seriously at higher temperatures, being 4 mm higher at 155 °C. The pressures of BG are systematically higher than ours by about 0.5 mm up to 135 °C, but become slightly lower by 150 °C. The fact that different temperature scales were presumably used in the three sets of experiments can account for a discrepancy of but 0.05 mmHg in the most extreme case (155 °C).

An important use for vapor pressure data is the estimation of standard enthalpies and entropies of vaporization at 298.15 K. The present data will provide these quantities for azulene only for the supercooled liquid; they are presented and compared with previous values in Table III. Coincidentally, the present results fall very nearly halfway between the two sets of previous values. The F–K equation provides values significantly lower than the Cox. This probably means it is more reliable, since, where comparisons are available, the Cox equation produces values which are slightly too high (*9*).

Combination of our vaporization enthalpy with the sublimation enthalpy of Morawetz (*8*) yields an enthalpy of melting of 4.22 kcal mol^{-1} at 298.15 K, in much more reasonable alignment with the value 4.28 kcal mol^{-1} for naphthalene (*6*), based on the data of Camin and Rossini (*2*), than the 2.89 kcal mol^{-1} obtained by HW for azulene.

After completion of the vapor pressure measurements, the brown residue mentioned earlier was discovered in the ebulliometer. It proved to be insoluble in organic solvents and inorganic acids. The residue was removed from the ebulliometer with dilute HF, though it did not dissolve in the process. Its insolubility gives us confidence that it did not have an effect on the vapor pressure measurements, and suggests that the slight change observed during the experiment was caused solely by the increase (from about 0.2 to 0.3%) of naphthalene impurity. The observed change is consistent with this interpretation. Using Raoult's law and the vapor pressure of naphthalene, we estimate that the observed pressure is lower than the true vapor pressure of azulene by at most 0.3%. The similar values of vaporization properties of azulene and naphthalene make errors in these properties due to the naphthalene impurity negligible.

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