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Vapor Pressures of Some Nitrogen-Containing, Coal-Derived Liquids

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Vapor-pressure data were obtained for four heterocyclic, nitrogen-containing compounds. A gas-saturation apparatus was used to measure the vapor pressures of quinaldine, quinoline, 5-ethyl-2-methylpyridine, and *N*-ethylcarbazol. The range of pressures measured was 10^{-3}–10^{-1} mmHg.

Much attention is now being directed at obtaining gaseous and liquid fuels from coal. For design of coal-conversion processes, it is necessary to know the physical properties of the products. This work reports vapor-pressure data for four nitrogen-containing, heterocyclic compounds found in coal-derived liquids, including tars.

It is difficult to measure vapor pressures at elevated temperatures where thermal degradation of the compound may occur. In this work, vapor pressures are measured at near-ambient temperatures, where measurements are relatively simple. By use of knowledge of the molecular structure and low-temperature vapor-pressure data, the vapor pressure at high temperatures can be predicted by using a semiempirical correlation, as discussed elsewhere (*1*, *5*, *6*).

Experimental Apparatus and Procedure

Vapor pressures were measured for high-molecular-weight organic compounds with a nitrogen atom as part of a ring. For these measurements, the gas-saturation method described below is suitable. Following the procedure of Sinke (*4*) as developed by Macknick (*2*, *3*), pressure can be measured from 10^{-1} to 10^{-3} torr, and temperature may be varied from −30 to 150 °C. Oxygen is slowly passed over the sample until saturated. The resulting organic–oxygen stream is burned in a catalyst bed and the concentration of carbon dioxide is determined by an infrared analyzer. Using this method, it is possible to measure vapor pressures of complex organic compounds at moderate temperatures, thus avoiding degradation. The infrared analyzer allows determination of the small vapor pressures with high accuracy. Since measurement of pressure is continuous, there is no need for a collection method with its attendant inaccuracies. Figure 1 shows a schematic diagram of the process.

The sample is packed in a cell constructed of $^3/_8$-in. i.d. stainless-steel tubing. Figure 2 shows that there are three legs to this cell. Two contain the sample; the third and final leg contains glass packing to eliminate entrainment. If the sample is a liquid, it is poured over glass packing; if measurements are to be made in the temperature range where the substance is solid, the loose crystals are packed into the tubing. The three legs of the cell are connected in series. All connections and seals are metal-to-metal because materials used for other sealing methods (e.g., Teflon O-rings) have vapor pressures of the same order of magnitude as those being measured.

Oxygen is introduced into the system at 5–10 psig. Trace impurities are removed by passing the oxygen over a hot catalyst and then through Ascrite and Drierite to remove CO_2 and H_2O. The purified oxygen stream enters the constant-temperature bath and, after thermal equilibration, enters the sample cell. After saturation, the gas stream enters the catalyst bed. The entry and the bottom third of the catalyst bed are immersed in the constant-temperature bath to prevent condensation of the sample on the walls of the apparatus.

The catalyst is 0.5% palladium on $^1/_8$-in. alumina pellets. Catalyst temperature is 600–650 °C. With the large excess of oxygen, every organic molecule is combusted completely to CO_2, NO_2, and H_2O:

$$C_nH_mN_y + (n + y + m/4)O_2 \rightarrow nCO_2 + (m/2)H_2O + yNO_2 \qquad (1)$$

After combustion in the catalyst bed, the stream is sent to a Beckman Model 865 infrared analyzer tuned to detect carbon dioxide. The analyzer's working range is 100–2500 ppm of CO_2. Neither water nor NO_2 interferes with accurate determination of CO_2 concentration. Since the cell is loaded with a pure compound, the carbon number (number of carbon atoms per molecule) is precisely known, and the vapor pressure of the substance can be easily calculated:

$$P(\text{sat}) = \frac{(\text{ppm CO}_2)P(\text{atm})}{n}\left[\frac{P(\text{sample})}{P(\text{atm})}\right] \qquad (2)$$

where P(sat) is the vapor pressure of the sample and ppm CO_2 (molar concentration) is the experimentally determined composition of CO_2 in the effluent. The carbon number of the compound is represented by n; P(atm) is atmospheric pressure measured with a mercury barometer and a cathetometer and P(sample) is the pressure within the sample cell. Since the cell is exhausted to the atmosphere, the correction [P(sample)/P(atm)] is close to unity and can often be neglected.

After passage through the infrared analyzer, the gas stream passes through a flowmeter and then to exhaust.

The infrared analyzer was calibrated with standardized gases to determine the response curve for each scale. The curves thus generated allow conversion from the experimentally determined scale reading into parts per million of CO_2. Daily the calibration is checked with high-purity nitrogen as a zero standard and with a standardized gas whose CO_2 concentration corresponds to 75% of full scale.

A main concern is the purity of the sample. First, the empty sample cell is baked overnight in an oven at 400 °C. The sample is loaded into the cell and then the whole apparatus (sample cell and catalyst bed) is inserted into the constant-temperature bath. For several days the sample is held at an elevated temperature with oxygen flow to allow outgassing of light impurities; during this time, IR readings are approximately 150–200% of full scale. The temperature is gradually lowered and data collection begins when the system has reequilibrated.

Saturation of the oxygen stream with the sample can be checked by varying the flow rate; the vapor-pressure readings should remain unchanged. As a check that combustion within the catalyst bed is complete, IR readings should remain unaffected by changes in catalyst temperature.

The temperature of the bath is maintained by continuous cooling and on–off heating. Cooling is provided by a refrigeration system (−30 to +20 °C), cooling water (20–40 °C), or losses to the atmosphere (greater than 40 °C). Heating is provided by a knife heater controlled by a Thermotrol connected to a platinum resistance thermometer. Different fluids are used in

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Table I. Summary of Experimental Results

compd	a	b	temp range, °C	pressure range, mmHg	av % dev
quinaldine	21.55	−7365.2	8.75–39.49	1.07×10^{-2}–1.35×10^{-1}	1.91
5-ethyl-2-methylpyridine	20.94	−6204.4	−20.39 to +2.70	2.70×10^{-2}–2.05×10^{-1}	1.62
quinoline	20.96	−6993.2	12.62–35.90	2.89×10^{-2}–1.82×10^{-1}	2.80
N-ethylcarbazol	21.92	−9010.4	74.66–100.65	1.85×10^{-2}–1.10×10^{-1}	2.17

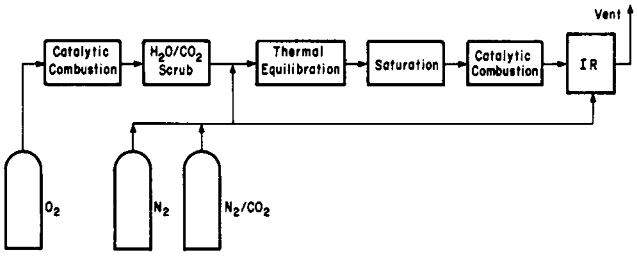

Figure 1. Schematic diagram of gas-saturation apparatus.

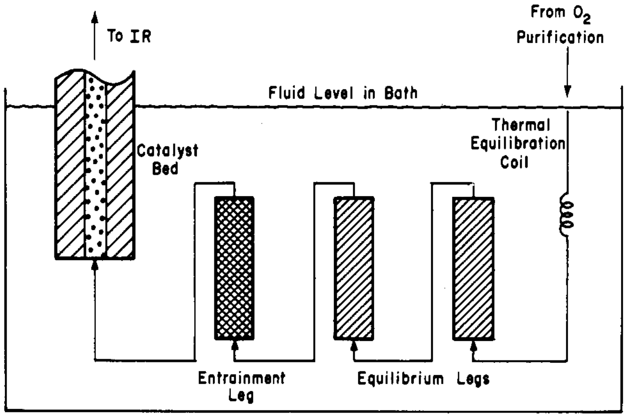

Figure 2. Oxygen saturated with organic vapor is combusted to carbon dioxide, water, and nitrogen dioxide.

the bath for each temperature range: below 10 °C, a mixture of 50% ethylene glycol and 50% water; for 10–35 °C, water; and for high temperatures (35–150 °C), Dow silicon oil.

All organic chemicals are from Aldrich Chemical Co. in the purest form possible; they are purified further before loading into the sample cell. High purity is important since small amounts of volatile impurities can cause large errors in observed vapor pressures.

Quinaldine was obtained at 98% purity and distilled in a Perkin-Elmer spinning-band column at 5 mmHg. The top cut (5% by volume) was discarded, as were the bottoms (15% by volume). Quinoline (96% initial purity) was purified by boiling under vacuum until 5% by weight of the sample was boiled off. A vacuum oven was used to purify *N*-ethylcarbazol (98.5%) which is solid at room temperature (mp 60 °C). The sample was baked at about 125 °C for several days. 5-Ethyl-2-methylpyridine required no further purification at 99+% purity.

To establish confidence, we first made vapor-pressure measurements for naphthalene. Results agreed to within 2% with those of Sinke (*4*).

Results and Discussion

Vapor pressures were obtained for quinaldine, 5-ethyl-2-methylpyridine, quinoline, and *N*-ethylcarbazol. All compounds were liquids in the temperature range used. The experimental scale readings from the infrared analyzer were converted to parts per million (molar) CO_2 by previously determined calibration curves. The vapor pressure is then easily calculated by eq 2. Vapor pressures were fit by the least-squares method to a straight line of the form

$$\ln P = a + b/T \qquad (3)$$

Table II. Quinaldine Vapor Pressures

t, °C	P_{exptl}, mmHg	P_{calcd}, mmHg	% dev
8.75	1.07×10^{-2}	1.03×10^{-2}	+3.54
12.18	1.35×10^{-2}	1.42×10^{-2}	−5.20
16.16	2.02×10^{-2}	2.02×10^{-2}	+0.25
20.18	2.90×10^{-2}	2.86×10^{-2}	+1.38
23.96	3.99×10^{-2}	3.94×10^{-2}	+1.30
27.85	5.33×10^{-2}	5.43×10^{-2}	−3.49
31.69	7.52×10^{-2}	7.38×10^{-2}	+1.78
35.58	1.00×10^{-1}	1.00×10^{-1}	0
39.49	1.35×10^{-1}	1.35×10^{-1}	+0.22

Table III. 5-Ethyl-2-methylpyridine Vapor Pressures

t, °C	P_{exptl}, mmHg	P_{calcd}, mmHg	% dev
−20.39	2.70×10^{-2}	2.71×10^{-2}	−1.54
−14.79	4.63×10^{-2}	4.61×10^{-2}	+0.39
−10.72	6.68×10^{-2}	6.70×10^{-2}	−0.21
−6.35	1.01×10^{-1}	9.87×10^{-2}	+2.40
−2.84	1.36×10^{-1}	1.33×10^{-1}	+2.00
+2.70	2.05×10^{-1}	2.12×10^{-1}	−3.15

Table IV. Quinoline Vapor Pressures

t, °C	P_{exptl}, mmHg	P_{calcd}, mmHg	% dev
12.62	2.89×10^{-2}	3.00×10^{-2}	−3.98
16.71	4.27×10^{-2}	4.23×10^{-2}	+0.98
21.35	6.12×10^{-2}	6.22×10^{-2}	−1.60
22.42	7.17×10^{-2}	6.76×10^{-2}	+5.76
25.16	8.40×10^{-2}	8.40×10^{-2}	0
28.25	1.11×10^{-1}	1.07×10^{-1}	+4.23
29.10	1.12×10^{-1}	1.14×10^{-1}	−2.15
35.90	1.82×10^{-1}	1.89×10^{-1}	−3.67

Table V. *N*-Ethylcarbazol Vapor Pressures

t, °C	P_{exptl}, mmHg	P_{calcd}, mmHg	% dev
74.66	1.85×10^{-2}	1.86×10^{-2}	−0.38
79.11	2.52×10^{-2}	2.57×10^{-2}	−1.94
83.81	3.57×10^{-2}	3.62×10^{-2}	−1.40
89.23	5.47×10^{-2}	5.24×10^{-2}	+4.19
93.26	7.17×10^{-2}	6.92×10^{-2}	+3.35
96.69	8.55×10^{-2}	8.67×10^{-2}	−1.17
100.65	1.10×10^{-1}	1.13×10^{-1}	−2.74

where P is in mmHg and T is in K. The assumption of a straight line fit is valid due to the short temperature range used here.

Table I summarizes the data. Temperature and pressure ranges and average percent deviation are also presented. The percent deviation is defined by

$$\%\ \text{dev} = ([P_{\text{exptl}} - P_{\text{calcd}}]/P_{\text{exptl}})100$$

where P_{exptl} is the experimentally determined value and P_{calcd} is from the straight-line fit.

Also

$$\text{av}\ \%\ \text{dev} = \sum_i |\%\ \text{dev}|/i$$

where i is the number of data points. The average percent deviation ranges from 1.62 to 2.80 for the four data sets.

The data used in preparing Table I are shown in Tables II–V. Each of these presents temperature, experimental vapor pressure, calculated vapor pressure, and percent deviation.

Although the exact freezing point of 5-ethyl-2-methylpyridine is not known, a small sample (~2 mL) immersed for 5 min in a −25 °C bath did not freeze, ensuring that the reading at −20.39

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°C is still well within the liquid range.

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Zinc Activity Measurements in Thallium–Zinc Alloys by the Torsion–Effusion Technique

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Zinc activities in liquid Tl–Zn alloys were determined at 730 K from vapor-pressure measurements carried out by the torsion–effusion technique. The corresponding values for thallium were derived by the Gibbs–Duhem equation. Since the system shows a large miscibility gap at the operating temperature, constant activity values for both components in the alloy with variable composition were found in this range. A special procedure was used for the zinc measurements over the Tl-rich alloy out of the gap (0–18 atom % of zinc).

Activities of the components for Tl–Zn alloys are not well-known. Calorimetric data of the mixing process[1] and zinc activity data measured in two dilute solutions at 625 K by the Knudsen effusion method[2] and by a comparative vapor pressure method[3] at 1000 and 1100 K have been reported in literature. Apparently no other direct determination of activity is reported. Therefore, we thought it useful to carry out measurements of this parameter by means of a torsion–effusion technique.

Experimental Section

The principle of the technique and details of the apparatus have been described elsewhere.[4,5]

The relation between the pressure and the cell deflection is given by:

$$P = 2K\alpha/(a_1l_1f_1 + a_2l_2f_2)$$

where α is the torsion angle, K is the torsion constant of the tungsten wire (30 μm in diameter, 35 cm length) from which the cell is suspended, a_1 and a_2 are the areas of the two effusion holes, l_1 and l_2 are their respective perpendicular distance from the rotation axis, and f_1 and f_2 are the corresponding geometrical correction factors.[6] In this work cells similar to the one illustrated in Figure 1 were used. The cell constants are given in Table I. The temperature of the operating cell was measured by a calibrated chromel–alumel thermocouple placed inside an identical cell directly beneath the operating cell.

In order to check that thermodynamic equilibrium conditions existed in each of the operating cells, we measured the absolute vapor pressures of pure zinc and thallium. The corresponding heats of vaporization $\Delta H°_{298}$ obtained from second- and third-law treatments of the data (32.8 ± 0.9 and 30.9 ± 0.7 kcal mol^{-1} for zinc and 41.9 ± 1.5 and 42.2 ± 0.5 kcal mol^{-1} for thallium) were in good agreement within the experimental errors and with the values selected by Hultgren et al.[7]

Table I. Constants of the Used Cells

		cell A (graphite)	cell B (pirophyllite)	differential cells (pirophyllite)
orifice area, $\times 10^{-3}$ cm[a]	(1)	7.39 ± 0.05	7.90 ± 0.07	7.85_5 ± 0.05
	(2)	7.09 ± 0.05	8.70 ± 0.07	7.85 ± 0.05
moment arm, cm (±0.01)	(1)	0.85	0.84	0.85
	(2)	0.88	0.87	0.90
force correction factor[b]	(1)	0.464	0.558	0.521
	(2)	0.410	0.570	0.530

[a] Measured by photographic enlargement. [b] Calculated by the equation[6] $1/f = 0.0147(L/r)^2 + 0.3490(L/r) + 0.9982$, where r and L are the radius and the thickness of the effusion hole, respectively.

Three Tl–Zn alloy samples of different compositions within the miscibility gap,[8] and six thallium-rich samples outside of this range at the operating temperature 700–750 K were prepared by melting required quantities of high-purity elements under vacuum in a quartz tube. The samples were kept for several hours at about 1100 K and then quenched in a water bath. The composition and the homogeneity of the alloys were evaluated by polarographic analysis for both the constituents (Zn, Tl) by testing different portions of each sample. The error in the composition has been evaluated to be not larger than 0.1–0.2 atom % of zinc.

Particular care was taken in the preparation and in the filling of the thallium-rich samples in the assembly.

The study of this system was performed in two steps. In the first step measurements were made on pure zinc and on the three Tl–Zn alloys (35, 51, and 87 atom % of Zn) inside the miscibility gap.[8] In Table II the constants of the straight lines log α vs. $1/T$ derived by least-squares treatment of the experimental data are summarized for each sample investigated.

Only the points taken at temperatures higher than 690 K, where the two solutions are molten, were considered. One alloy (35 atom % of Zn) was also studied by using a particular cell (called "differential cell") similar to the one described in a previous article[9] in which one semicell can be rotated around its axis (see Figure 2). In the first part of the experiment two sets of measurements were carried out by using this cell with the two semicells loaded with pure zinc: in the first set the semicells were placed in the conventional way and the temperature dependence of $\alpha°$ was measured; in the second set a semicell was placed in the differential way (two orifices in the same direction) for calibration purpose. Over the entire calibration

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