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Vapor Pressures of Some Sulfur-Containing, Coal-Related Compounds

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A gas-saturation apparatus is used to measure vapor pressures in the range 10^{-2}–4 torr for four heterocycloaromatic compounds similar to those which might be found in coal tars: 2-propylthiophene, thionaphthene, dibenzothiophene, and thianthrene. For each compound, the SWAP method for estimating vapor pressures is used to extrapolate the low-pressure data to the normal boiling point.

Introduction

The need to find alternative energy sources has spawned intensive research and development of processes for coal liquifaction and gasification. Almost all processes, including those involving coal, expend large amounts of capital on separation. Reliable thermodynamic data are needed for efficient design of coal-processing and separation equipment. Vapor pressure is an important physical property required to perform calculations for the design of separation equipment.

It is desireable to calculate vapor pressures of all components from general correlations rather than to measure new data for each new situation. To generate these correlations, however, we require experimental data for model compounds which resemble molecules that might be found in typical coals and coal products. Coal is of complex structure containing large aromatic rings, some of which contain heteroatoms such as N, O, and S. Few data are available for these types of compounds, partly because vapor pressures of high-molecular-weight compounds may be too low for measurement by conventional means. Sinke (*1*) and Macknick et al. (*2*) have shown that a gas-saturation method is suitable for measuring vapor pressures of high-molecular-weight hydrocarbons. Van de Rostyne et al. (*3*) extended the use of this method to high-molecular-weight compounds containing nitrogen. This work reports vapor pressures of high-molecular-weight, coal-related compounds containing sulfur.

Experimental Apparatus and Procedure

Figure 1 shows a schematic of the apparatus, first proposed by Sinke (*1*). Ultrahigh-purity oxygen passes first through a high-temperature (400 °C) catalytic bed to convert any residual hydrocarbon to CO_2 and H_2O. The resulting CO_2 and H_2O are scrubbed from the oxygen stream by passing it over a packed bed of Ascrite and Drierite. The O_2 stream is slowly passed over the compound being studied so that it becomes saturated and then passes to a catalytic furnace. There, the sulfur-containing compound is combusted completely to CO_2, H_2O, and SO_2; the combustion products flow to a calibrated infrared analyzer where CO_2 concentration is measured. This technique can be used to measure vapor pressures of solids and liquids in the range 10^{-3}–10 torr. The lower end is limited by the accuracy of the infrared analyzer; generally, it is reliable to 100 ppm CO_2.

Since larger molecules generate a larger number of moles of CO_2 per mole of sample, lower vapor pressures of higher-molecular-weight compounds can be measured more accurately than those of lower-molecular-weight compounds.

Sample cells are arranged as shown in Figure 2. Ca. 5 g of sample are packed in each of two equilibrium cells constructed of $^3/_8$-in. diameter tubing. Liquid samples also contain glass helixes to enhance equilibration while solid samples are crushed before packing. The third cell is packed with glass helixes to eliminate entrainment. The three cells are connected in series by using metal-to-metal fittings since soft-seating materials can have vapor pressures of the same order of magnitude as those being measured.

Carrier-Gas Metering. Oxygen is metered into the system at 5–20 psig (depending on the range of vapor pressures being studied) by using valves A, B, and C, as shown in Figure 1. For system operation at low pressure, pressure regulator A is set at 5–10 psig and flow is regulated with valve B. For system operation at higher pressures, pressure regulator A is set at 10–20 psig and flow is regulated with valve C. System pressure is measured downstream of the H_2O/CO_2 scrubber by using a mercury manometer and a cathetometer.

Conversion of Sample to CO_2. Purified oxygen enters a constant-temperature bath where it becomes saturated with the vapor of the compound being studied and flows to the catalytic furnace. All tubing from the inlet of the thermal equilibrium coil to the inlet of the catalyst furnace is immersed in the constant-temperature bath to prevent condensation of the sample from the vapor phase.

Complete combustion of the organic sample saturating the oxygen-rich gas phase is accomplished by using a 0.5% Pd-on-$^1/_8$-in.-pelleted-alumina catalyst maintained at 700 °C. The products of the combustion are CO_2, H_2O, and SO_2. At the temperature used in the furnace, sulfur poisoning of the catalyst is not significant.

Measurement of CO_2 Concentration. After combustion, the gas flow enters a Model 865 Beckman infrared analyzer to measure CO_2 concentration accurate to ±0.1% of full scale. Neither H_2O nor SO_2 interferes in this measurement; their discrimination ratios are respectively 2500 ppm H_2O = 1 ppm CO_2 and 278 ppm SO_2 = 1 ppm CO_2. The IR analyzer is equipped with two cells: a low-concentration cell calibrated for a range of 0–2500 ppm CO_2, and a high-concentration cell calibrated for a range of 0–25000 ppm CO_2. Calibration is accomplished by using standard gases containing varying amounts of N_2 and CO_2 supplied by Matheson Gas Products.

Since chemical reaction of the sample is essentially complete, we assume stoichiometric production of CO_2 by eq 1.

$$C_nH_mS_y + (n + m/4 + y)O_2 = nCO_2 + (m/2)H_2O + ySO_2 \tag{1}$$

Assuming an ideal gas phase, we relate the measurement of CO_2 concentration to vapor pressure of the sample by eq 2,

$$P_{sat} = ((\mathrm{ppmCO_2})P_{sample,abs})/n \tag{2}$$

where ppmCO_2 = concentration of CO_2 measured by IR, $P_{sample,abs}$ = pressure of sample measured by using a cathetometer and a barometer, and n = carbon number of sample.

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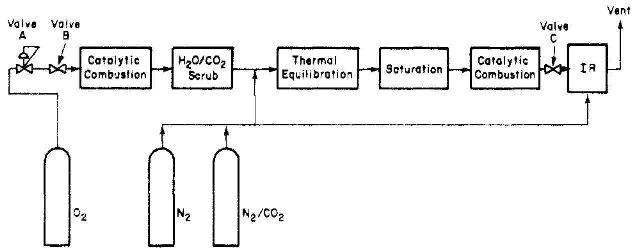

Figure 1. Gas-saturation apparatus for vapor-pressure measurements.

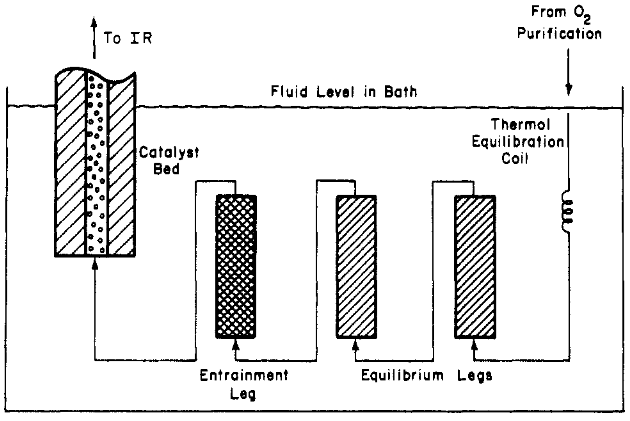

Figure 2. Saturation/combustion portion of gas-saturation apparatus.

Because of the low gas flows used in practice and the subsequent small pressure drop, P_{sample} is often nearly equal to atmospheric pressure. However, we can extend the range of our equipment to higher vapor pressures by increasing $P_{\text{sample,abs}}$. This increase dilutes the sample in the gas phase since the sample can only exist in the gas phase at its saturation pressure; thereby we attain a lower measured CO_2 concentration. In this way we can increase the range of the apparatus limited only by the assumption of gas-phase ideality.

After exiting the IR analyzer, the gas stream flows through a bubble flowmeter and then to the atmosphere. Accurate determination of vapor pressures using this method requires that the gas phase be saturated. To assure that this is the case, the flow rate should not affect measured vapor pressures. It is also important that complete combustion be attained in the catalytic furnace; furnace temperature should not affect measured vapor pressures.

Required Purity. Sample purity is of utmost importance in determining vapor pressures. Small amounts of light impurities can lead to large errors in measured vapor pressures. Therefore, sample compounds are obtained in as pure a form as possible. Samples used in this study are baked in a vacuum oven for 1–2 h at 125 °C after which they are checked for impurities by using gas-chromatographic analysis. This analysis showed no evidence of any impurities in any of the samples studied.

It is also important to avoid hydrocarbon impurities in the tubing used to construct the equilibrium cells. Before use, this tubing is rinsed with acetone and baked overnight in an oven at 400 °C.

As a final step to ensure purity, the constant-temperature bath surrounding the apparatus is operated at elevated temperatures for several days before taking data to allow outgassing of any remaining light material. For solids, this temperature is just below the melting point, while for liquids the temperature is ~15 °C greater than the maximum temperature at which data are to be taken.

Bath-Temperature Control. The constant-temperature bath fluid depends on the temperature range to be studied. Below 10 °C, a 50%-by-volume mixture of ethylene glycol and water is used. From 10 to 40 °C, pure water is adequate. Dow Corning 200 silicone heat-transfer fluid is appropriate from 40 to 200 °C. Bath temperature is maintained with continuous cooling and on–off heating. Cooling is provided by using refrigeration (below 25 °C), cooling water (25–40 °C), or losses to the atmosphere (above 40 °C). Bath temperature is monitored by using a platinum resistance thermometer connected to a linearizing bridge for direct readout on a digital voltmeter. The Pt resistance thermometer is calibrated vs. NBS traceable thermometers to within ±0.05 °C.

Table I. Comparison of Naphthalene Data with Those of Sinke (*1*)

temp, °C	press., torr: Sinke	press., torr: this work	% difference (based on data of Sinke)
26.26	0.0927	0.0892	−3.8
33.42	0.182	0.176	−3.3
38.99	0.302	0.306	1.2
45.04	0.513	0.514	0.3
49.70	0.760	0.746	−1.8
55.15	1.18	1.19	0.5

Table II. Summary of Experimental Results[a]

compd	constants for equation[a]: *a*	*b*	temp range, °C	press. range, torr	av % error
thianthrene					
solid	27.8	11790	85–155	0.005–1	3.5
liquid	20.3	8557	155–175	1.5–3.3	2.3
dibenzothiophene					
solid	27.9	10910	60–90	0.01–0.15	3.1
liquid	21.1	8353	100–130	0.3–1.5	1.9
thionaphthene					
solid	23.1	7349	0–30	0.02–0.3	3.1
liquid	20.2	6468	33–73	0.4–4.5	2.2
2-propylthiophene					
liquid	19.7	5534	−30–30	0.04–4	2.1

[a] $\ln P = a - b/T$. P is in torr and T is in K.

Sample Availability. Sample compounds were obtained from commercial chemical suppliers: dibenzothiophene (98%) and thionaphthene (98%) from Fluka AG, thianthrene (97%) and 2-propylthiophene (98%) from Aldrich Chemical Co.

Results

To assure proper operation of the apparatus, we determined vapor-pressure data for naphthalene over the range 30–60 °C and compared them to the data of Sinke (*1*). Our measurements were in good agreement with those of Sinke; deviations were less than 4%, as shown in Table I.

Vapor pressures are presented in Tables III–IX and are summarized in Table II. Generally, vapor pressures range from 0.01 to 4 torr for each of the four compounds studied: thionaphthene, dibenzothiophene, thianthrene, and 2-propylthiophene. Vapor pressures for both the solid and the liquid are reported for all compounds except 2-propylthiophene, which failed to freeze at the lowest temperature studied, −31.93 °C.

Because the temperature ranges are not large, the data were fit to a straight line of the form

$$\ln P = a - b/T \tag{3}$$

where P is in torr and T is in K. Constants a and b are shown in Table II. Errors were determined as relative deviations from the best-fit straight lines: error = $(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$. Errors are presented in Tables III–IX and summarized in Table II. Average errors range from 1.9% to 3.5% with maximum deviations of no more than 7.1%.

Experimental difficulties can arise in measuring vapor pressures of certain types of compounds by using the gas-saturation

Table III. Thianthrene (Solid) Vapor Pressures

	press., torr		
temp, °C	exptl	calcd	% error
84.90	0.00555	0.00573	−3.2
90.55	0.00999	0.00955	−4.4
93.02	0.0116	0.0119	−2.4
93.05	0.0117	0.0119	−1.8
97.85	0.0183	0.0181	1.3
99.24	0.0197	0.0203	−3.3
103.48	0.0294	0.0291	−1.2
112.09	0.0553	0.0585	−5.8
113.24	0.0670	0.0641	4.4
120.50	0.109	0.112	−3.2
121.92	0.130	0.125	3.7
128.13	0.206	0.199	3.5
128.29	0.209	0.201	3.8
134.14	0.323	0.307	5.1
134.81	0.334	0.322	3.7
139.90	0.487	0.459	5.7
139.91	0.485	0.459	5.3
153.50	1.12	1.14	−1.8

Table IV. Thianthrene (Liquid) Vapor Pressure

	press., torr		
temp, °C	exptl	calcd	% error
156.60	1.47	1.49	−1.4
157.64	1.60	1.56	2.3
158.28	1.62	1.61	0.6
164.25	2.17	2.11	2.7
164.75	2.08	2.16	−3.8
168.85	2.53	2.59	−2.3
169.74	2.62	2.69	−2.7
169.80	2.78	2.70	3.0
173.83	3.28	3.21	2.1

Table V. Dibenzothiophene (Solid) Vapor Pressures

	press., torr		
temp, °C	exptl	calcd	% error
62.92	0.0108	0.0100	6.9
63.85	0.0117	0.0110	6.0
66.97	0.0143	0.0148	−3.5
67.11	0.0149	0.0150	−0.7
67.75	0.0153	0.0159	−4.1
68.35	0.0166	0.0169	−1.5
71.00	0.0209	0.0215	−3.1
72.42	0.0244	0.0245	−0.6
72.61	0.0246	0.0250	−1.5
75.10	0.0294	0.0313	−6.4
76.59	0.0363	0.0358	1.5
76.78	0.0363	0.0364	−0.2
79.21	0.0441	0.0451	−2.3
80.71	0.0526	0.0514	2.3
80.89	0.0552	0.0522	5.4
83.10	0.0647	0.0632	2.3
84.10	0.0730	0.0689	5.6
84.96	0.0744	0.0741	0.4
87.16	0.0893	0.0893	0.0
91.10	0.116	0.124	−6.8
92.76	0.147	0.142	3.5

Table VI. Dibenzothiophene (Liquid) Vapor Pressures

	press., torr		
temp, °C	exptl	calcd	% error
100.60	0.282	0.276	2.1
101.36	0.314	0.307	2.3
104.60	0.335	0.350	−4.5
106.44	0.404	0.390	3.6
108.70	0.422	0.444	−5.1
110.96	0.513	0.505	1.6
112.62	0.554	0.554	0.0
115.21	0.642	0.640	0.7
116.69	0.669	0.695	−3.8
119.38	0.834	0.805	3.5
121.08	0.890	0.882	0.9
123.61	1.01	1.01	0.1
124.90	1.07	1.08	−1.0
127.74	1.26	1.25	0.5
130.24	1.42	1.43	−0.5
131.75	1.55	1.54	0.6

Table VII. Thionaphthene (Solid) Vapor Pressure

	press., torr		
temp, °C	exptl	calcd	% error
−0.34	0.0193	0.0207	−7.1
−0.23	0.0223	0.0209	6.3
6.02	0.0410	0.0382	6.8
7.66	0.0431	0.0445	−3.4
12.35	0.0692	0.0685	1.1
13.82	0.0772	0.0781	−1.2
18.30	0.117	0.116	1.0
20.21	0.134	0.136	−1.8
23.73	0.181	0.184	−1.5
25.35	0.208	0.210	−1.0
29.46	0.301	0.293	2.5

Table VIII. Thionaphthene (Liquid) Vapor Pressures

	press., torr		
temp, °C	exptl	calcd	% error
33.38	0.398	0.391	1.7
35.36	0.440	0.448	−1.8
40.75	0.636	0.642	−1.0
42.71	0.742	0.730	1.6
46.33	0.949	0.920	3.0
47.35	0.957	0.982	−2.6
52.84	1.34	1.38	−2.9
52.86	1.42	1.38	2.8
59.01	2.05	1.99	2.8
59.20	1.94	2.02	−3.9
64.66	2.81	2.76	1.7
65.42	2.84	2.88	−1.5
71.01	3.88	3.93	−1.3
73.14	4.51	4.41	2.2

Table IX. 2-Propylthiophene (Liquid) Vapor Pressures

	press., torr		
temp, °C	exptl	calcd	% error
−31.93	0.0402	0.0408	−1.6
−22.38	0.0992	0.0978	1.4
−22.04	0.104	0.101	3.1
−15.17	0.180	0.181	−0.7
−12.32	0.221	0.229	−3.7
−8.25	0.327	0.317	2.9
−1.72	0.542	0.525	3.2
−1.32	0.526	0.541	−2.8
7.32	1.02	1.01	0.8
9.24	1.11	1.16	−4.3
15.17	1.77	1.73	2.2
18.87	2.17	2.21	−1.8
22.60	2.79	2.80	−0.5
27.92	3.96	3.90	1.4
28.67	4.13	4.09	1.1

method. Edwards (*4*) provides a detailed critique of the use of the gas-saturation method for vapor pressures, especially with regard to sulfur-containing compounds.

Extrapolation of Data Using SWAP. Since the compounds studied are similar to sulfur-containing compounds which might be found in coal, we are interested in comparing our data with predictions of the SWAP method (*5*). The SWAP method is designed to estimate vapor pressures of coal-related liquids by using a minimum of experimental information, viz, one vapor-pressure datum and rough molecular characterization of the compound. The main advantage of the SWAP method over other methods for vapor pressures is that characterization is

Table X. Data Used for SWAP Predictions

				fractions			
	T, °C	P, torr	T_{760},[a] °C	aromaticity	naphthenicity	branching	heteroatomicity
thianthrene	173.83	3.28	327	1.0	0	0	0.143
thionaphthene	71.01	3.88	162	1.0	0	0	0.111
dibenzothiophene	131.75	1.55	287	1.0	0	0	0.0769
2-propylthiophene	28.67	4.13	136	0.625	0	0	0.125

[a] These are for the structural homomorph.

Table XI. Comparison of Measured and Calculated Normal Boiling Points for Coal-Related Liquids Using SWAP

	T_{760}, °C	
compd	measured	calcd
thianthrene	364-366	340
thionaphthene	221-222	220
dibenzothiophene	332-333	323
2-propylthiophene	157-160	158

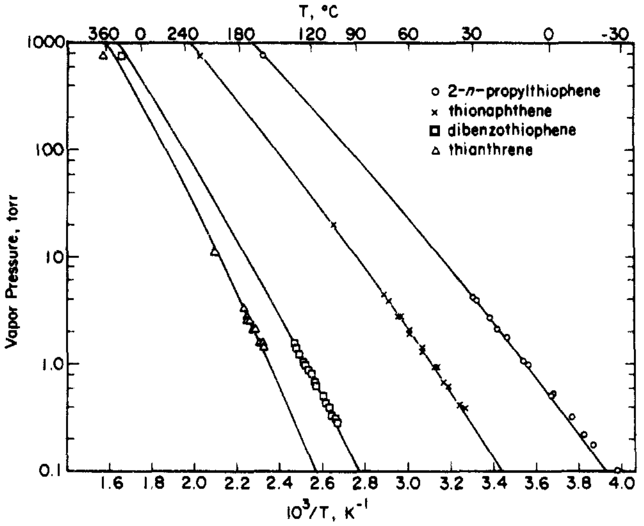

Figure 3. Experimental (points) and calculated vapor pressures using SWAP (lines). Calculations based on one (low) vapor-pressure datum.

achieved through easily measured fractions of aromaticity, naphthenicity, branching, and heteroatomicity instead of precise structural information. Therefore, the SWAP method is readily extended to complex mixtures (cuts or fractions) for which precise structural information cannot be determined. We are interested here in assessing the reliability of SWAP in extrapolating from the relatively low vapor pressures and temperatures reported in this work to the higher vapor pressures and temperatures found in most industrial processing equipment. Reliable vapor-pressure data at higher temperatures, however, are often difficult to obtain because of chemical decomposition.

The data used to determine the SWAP parameters for each of the four compounds studied in this work are presented in Table X. Calculated extrapolations are shown in Figure 3. SWAP is used to extrapolate the low-temperature data by ~3 orders of magnitude to 1000 torr.

For comparison, we also show normal boiling points and other available data in Figure 3 and Table XI for each of the compounds studied. These data were obtained from ref *6*. For both of the relatively low-boiling compounds (thionaphthene and 2-propylthiophene), SWAP predictions of normal boiling point are good while those for the relatively high-boiling compounds (thianthrene and dibenzothiophene) show considerably more error. However, we do not know the reliability of the published boiling points. It is possible that, because of the high temperatures at which these compounds boil, they may have fused or condensed during boiling-point determination, causing the measured boiling temperature to be too high.

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Ternary Phase Equilibria. Dichlorobenzene–*n*-Heptane–Solvent Systems

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Phase equilibrium and tie-line data for the ternary systems comprising *o*- and *p*-dichlorobenzene–*n*-heptane and the solvents nitromethane and aqueous methanol (95 vol %) determined at 20.5 °C are presented. The tie-line data are also correlated by Hand's method.

Introduction

Ternary phase equilibrium and tie-line data are essential for the understanding of solvent extraction and salting-out operations. The study of the phase equilibrium and tie-line data of *o*- and *p*-dichlorobenzene was undertaken with a view to