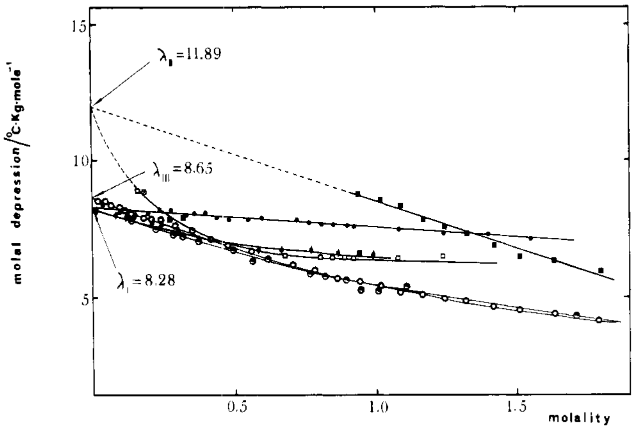

**Figure 5.** Molal depressions of binary solutions of carbon tetrachloride, sulfolane, and *n*-heptane in 2-methylpropan-2-ol vs. molality: solid phase, crystal I, (●) carbon tetrachloride, (⊖) sulfolane (⧫) *n*-heptane; solid-phase, crystal II, (□) carbon tetrachloride, (■) sulfolane, (⊠) *n*-heptane; solid phase, crystal III, (○) sulfolane.

are consistent with this extrapolated value, even if they may not be extrapolated themselves owing to the lack of low molality data. The cryoscopic constant $\lambda_{III} = 8.65$ may be calculated only from data of sulfolane solutions in which this form is stabilized preferably.

$\lambda_I$, $\lambda_{II}$, and $\lambda_{III}$ values are reported in Table IV and melting entalpies, $\Delta H_I$, $\Delta H_{II}$, and $\Delta H_{III}$, and melting entropies, $\Delta S_I$, $\Delta S_{II}$, and $\Delta S_{III}$, are derived and compared with previous literature.

The comparison is satisfactory in spite of the confusion arising from the fact that the existence of the third crystalline phase was ignored hitherto or, at least, regarded with some disbelief. Indeed data more frequently reported by literature refer to crystal I which is the more stable form, whereas, as it concerns crystal II and crystal III, some physical properties of crystal III have been erroneously ascribed to crystal II.

Nevertheless attention must be called on the fact that our value of $\Delta H_I$ (=1587 cal/mol) is in good agreement with previous data, ranging within 1555 and 1622 cal/mol, some of them obtained from calorimetric measurements, and also $\Delta H_{II}$ (=1100 cal/mol) is consistent with literature data (1026–1143 cal/mol) even if derived from cryoscopic measurements; obviously the comparison is quite lacking in the case of crystal III. Oetting reports indeed a value of 1721 cal/mol, which would be comprehensive of transition entalpy III → I, not measurable directly; furthermore, owing to the difficulty in establishing base curves of heat capacities in the premelting region, the value would be affected by noticeable incertainty.

Melting entalpies exceeding transition entalpies seem to preclude globular properties of 2-methylpropan-2-ol; neverthless if melting entropies are accepted as a valuable criterion of discrimination, the absence of globular character is not quite certain for 2-methylpropan-2-ol crystal II.

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(6) Carbon tetrachloride and sulfolane are "globular" molecules, very similar in size and shape with solvent; the former possesses an approximately central force field whereas the latter exibits a fairly high dipole moment, $\mu$ = 4.8 D, of which only the negative part is exposed; *n*-heptane molecules on the other hand differ noticeably in shape and size from the solvent.

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# Vapor Pressures of High-Molecular-Weight Hydrocarbons

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**A gas-saturation apparatus is used to obtain experimental data at near-ambient temperature; vapor pressures in the range $10^{-1}$–$10^{-3}$ torr are presented for the liquids *n*-octadecane, *n*-eicosane, 1-methylnaphthalene, and 2-ethylnaphthalene and the solids naphthalene, anthracene, and phenanthrene. Methods are recommended for extrapolating the data to higher temperature. These vapor-pressure data are useful for dew-point calculations in processing of gases containing heavy hydrocarbons such as those found in coal tars.**

## Introduction

In recent years, high-molecular-weight hydrocarbons have become increasingly important because of development of energy-related processes: coal liquefaction, oil shale, tar sands, and especially coal gasification. Gasification of coal often produces a byproduct tar which contains hydrocarbons in the boiling range 200–600 °C; to design efficient processes for tar-containing gases, it is essential to predict their vaporization/condensation characteristics.

Hot effluent gases from coal gasifiers, often as high as 1100 °C, are a significant source of sensible heat. Recovery of this energy is accompanied by cooling of the gas with subsequent condensation of the heavy components. To minimize condensate fouling or plugging, design of heat-recovery processes requires knowledge of the thermodynamic properties that govern dew points of gas streams from coal-gasification processes.

A heavy component (i) remains in the gas phase as long as its fugacity $f$ obeys the relation

$$f_i^{v} < f_i^{c} \qquad (1)$$

where superscript v stands for vapor phase and superscript c stands for condensed phase. These fugacities are related to composition by

$$f_i^{v} = y_i \phi_i P \qquad (2)$$

$$f_i^{c} = x_i \gamma_i f_i^{\circ} \qquad (3)$$

where, for component i, $y_i$ and $x_i$ are the mole fractions in the

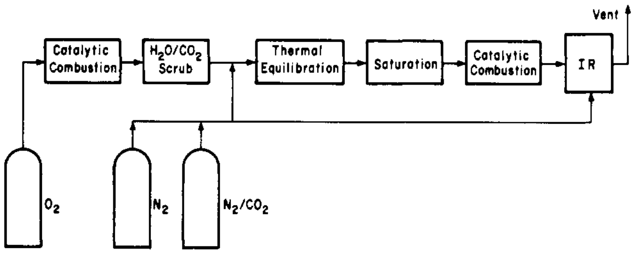

**Figure 1.** Gas-saturation apparatus for vapor-pressure measurements.

vapor and condensed phases, respectively, $\phi_i$ is the fugacity coefficient, $\gamma_i$ is the activity coefficient, and $P$ is the total system pressure. Reference fugacity $f_i^\circ$ is usually chosen to be the vapor pressure of pure i at system temperature.

The dew-point condition for component i occurs when the inequality in eq 1 is replaced by an equality. Therefore, to predict condensation conditions of a heavy component, we require accurate vapor-pressure data at temperatures normally encountered in coal-gasification effluents.

Experimental determination of vapor pressures near 800 °C is difficult because operation of experimental apparatus at such elevated temperatures is cumbersome. Also, since achieving thermodynamic equilibrium may take several hours, the hydrocarbon is susceptible to thermal degradation. (Degradation is often not severe in a gasification process because of the relatively short residence time from gasifier exit to cooling or condensation.)

In this work, we report experimental data at near-ambient temperatures. We then use semitheoretical correlations to extrapolate to normal-boiling-point temperatures.

A modification of Sinke's apparatus (*3*) was used to measure vapor pressures in the range $10^{-1}$–$10^{-3}$ torr. Vapor pressures were measured for the liquids *n*-octadecane, *n*-eicosane, 1-methylnaphthalene, and 2-ethylnaphthalene and for the solids naphthalene, anthracene, and phenanthrene. For liquids, extrapolation to higher temperatures is based on the modified SWAP method described by Macknick et al. (*1*). For solids, extrapolation is based on the Clapeyron equation and on the SWAP method of Smith et al. (*4*).

## Experimental Section

A modification of Sinke's gas-saturation method (*3*) was used; Figures 1 and 2 show schematic diagrams of the apparatus. An oxygen carrier gas at atmospheric pressure is saturated with a hydrocarbon in a thermostated bath. This mixture is then combusted completely to $CO_2$ and $H_2O$ over a hot catalyst. The amount of $CO_2$ produced is measured with a commercial infrared analyzer (IR), monochromatically tuned and calibrated for $CO_2$ detection. Upon knowing the carbon number $n$ of the hydrocarbon and the concentration of $CO_2$ after combustion, ppm($CO_2$), we can calculate the saturation pressure of the hydrocarbon $P$(sat) by the expression

$$P(\text{sat}) = \frac{[\text{ppm}(CO_2)]\,[P(\text{atmo})]}{n}\,[P(\text{sample})/P(\text{atmo})] \qquad (4)$$

$P$(sample) is the total pressure in the equilibrium cell. The pressure in the IR analyzer is equal to atmospheric pressure $P$(atmo) since the analyzer is vented directly to the atmosphere. The last term in eq 4, $[P(\text{sample})/P(\text{atmo})]$, is a correction for pressure drop through the system; this term is usually very close to unity at the low flow rates used. Equation 4 justifiably assumes ideal-gas behavior since operation is at low pressure and low hydrocarbon concentrations.

All connecting tubing in the system is 5-mm i.d. stainless steel. Metal-to-metal fittings are used since the analyzer detects also the vapor pressure of packing or sealing materials. The combustion catalyst, kept at 700 °C, is 20 g of 3.2-mm alumina pellets containing 0.5 wt % palladium. Oxygen carrier gas is purified prior to saturation by passage over a hot catalyst followed by a scrubbing section containing Ascrite and Drierite to remove any background $CO_2$ or $H_2O$.

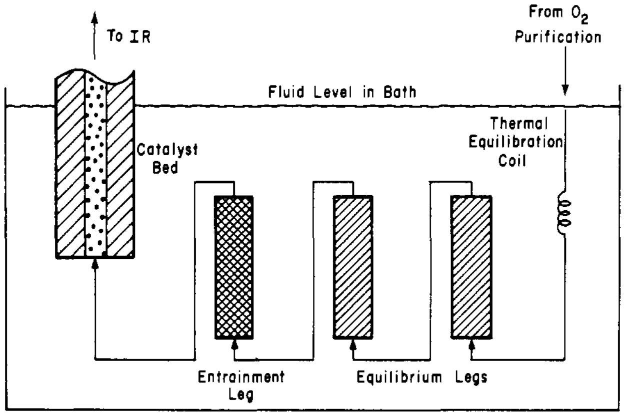

**Figure 2.** Saturation/combustion portion of gas-saturation apparatus.

The IR analyzer is calibrated for three ranges: 0–350, 0–800, 0–2500 ppm $CO_2$ by volume. Calibration is achieved by using eight Primary Standard gas mixtures from Matheson Gas Products Co. These range in concentration from 75 to 2350 ppm $CO_2$ by volume in nitrogen, certified to an accuracy of ±1% in $CO_2$. High-purity nitrogen is used for zero-gas calibration. Temperature measurements of the well-stirred, thermostated bath are made with a platinum-resistance thermometer coupled with a linearizing bridge to give direct readout on a digital volt meter. Temperature-measuring instruments are calibrated with NBS-traceable thermometers to an accuracy of ±0.05 °C. The bath fluid is water for 5–80 °C and silicon oil for 80–200 °C. Pressure measurements are made with a mercury manometer and cathetometer. The apparatus is constructed such that calibration checks can be made on the analyzer while bypassing the combusted $O_2$/hydrocarbon mixture to the atmosphere.

Sample cells are 8-mm i.d. stainless-steel tubing, 150 mm long. Before loading, all cells and all connecting tubing are washed with acetone and baked in an oxygen atmosphere at 400 °C for 12 h to remove impurities. Hydrocarbon sample sizes are approximately 5 g/cell. Liquid samples contain 2-mm glass helices as packing to enhance saturation rates. Solid samples are crushed prior to loading into the cells.

All samples are commercially available with purities of at least 99+%. Once the samples are loaded, each is run for a period of 24–72 h at a temperature higher than the highest operating temperature, to strip out any light impurities. Because of high initial purities and the method of measurement, the error introduced by trace heavy impurities is not significant.

Purified oxygen, at approximately 0.5 (NTP) $cm^3\ s^{-1}$, passes through a coil of tubing in the bath for thermal equilibration. The gas then flows through two equilibrium cells. A tandem-cell design is used to assure saturation. The saturated gas mixture then passes through a third cell containing spun glass to eliminate any entrained droplets or particulates. After passing through the cells, the gas flows directly into the combustion zone. The heavily insulated catalyst chamber is partially submerged in the bath fluid to eliminate any condensation of the gas mixture prior to reaching the catalyst. From the combustion zone exit, the $CO_2/H_2O/O_2$ mixture flows into the IR analyzer where the concentration of $CO_2$ is monitored.

Once the apparatus is functional, the IR reading reaches steady state in approximately 30 min. Since the $CO_2$ concentration should not be a function of flow rate, the flow rate was varied between 0.1 and 5.0 (NTP) $cm^3\ s^{-1}$. No flow-rate effect was observed.

Previous tests with catalyst-bed temperatures indicate that even at 300–400 °C complete combustion is achieved. All runs

Table I. Vapor Pressures of Four High-Molecular-Weight Liquid Hydrocarbons

| *n*-octadecane | | *n*-eicosane | |
|---|---|---|---|
| *t*, °C | $10^3P$(sat), torr | *t*, °C | $10^3P$(sat), torr |
| 45.00 | 1.65 | 71.15 | 3.08 |
| 51.45 | 3.00 | 79.90 | 7.30 |
| 54.50 | 4.26 | 86.70 | 12.7 |
| 54.85 | 4.43 | 90.35 | 17.5 |
| 59.85 | 7.01 | 94.50 | 24.5 |
| 65.50 | 11.4 | 102.95 | 50.4 |
| 71.25 | 18.7 | 107.30 | 68.5 |
| 80.85 | 43.7 | av error in *P*(sat) = 1.6% | |
| 84.10 | 53.6 | $A = 26.849$ | |
| 88.10 | 72.9 | $B = -11\,230$ | |
| av error in *P*(sat) = 2.2% | | | |
| $A = 25.548$ | | | |
| $B = -10\,165$ | | | |

| 1-methylnaphthalene | | 2-ethylnaphthalene | |
|---|---|---|---|
| *t*, °C | $10^2P$(sat), torr | *t*, °C | $10^2P$(sat), torr |
| 5.70 | 1.32 | 13.05 | 1.15 |
| 11.40 | 2.19 | 17.90 | 1.66 |
| 18.10 | 3.94 | 22.90 | 2.55 |
| 22.15 | 5.35 | 29.50 | 4.66 |
| 28.85 | 9.45 | 34.85 | 7.35 |
| 32.25 | 11.8 | 39.40 | 9.87 |
| 34.90 | 14.2 | 45.10 | 15.0 |
| 38.60 | 17.6 | av error in *P*(sat) = 2.7% | |
| av error in *P*(sat) = 2.0% | | $A = 21.485$ | |
| $A = 20.552$ | | $B = -7435.9$ | |
| $B = -6933.2$ | | | |

Table II. Vapor Pressures of Three High-Molecular-Weight Solid Hydrocarbons

| naphthalene | | anthracene | | phenanthrene[a] | |
|---|---|---|---|---|---|
| *t*, °C | $10^2P$(sat), torr | *t*, °C | $10^3P$(sat), torr | *t*, °C | $10^3P$(sat), torr |
| 7.15 | 1.32 | 85.25 | 6.69 | 51.60 | 3.49 |
| 12.80 | 2.35 | 90.15 | 10.2 | 57.00 | 6.10 |
| 18.40 | 4.19 | 95.65 | 16.4 | 61.85 | 9.91 |
| 18.85 | 4.45 | 100.70 | 24.9 | 67.35 | 15.9 |
| 26.40 | 9.44 | 104.70 | 34.4 | 71.80 | 23.2 |
| 31.85 | 15.4 | 111.90 | 60.3 | 78.90 | 42.4 |
| av error in *P*(sat) = 1.1% | | 116.40 | 85.2 | 83.40 | 66.7 |
| $A = 26.250$ | | 119.95 | 110.0 | 90.30 | 109.0 |
| $B = -8575$ | | av error in *P*(sat) = 0.8% | | av error in *P*(sat) = 2.3% | |
| | | $A = 26.805$ | | $A = 26.648$ | |
| | | $B = -11\,402$ | | $B = -10\,484$ | |

[a] Finke et al. [Finke, et al., *J. Chem. Thermodyn.*, 9, 937 (1977).] report a phase transition for solid phenanthrene with an enthalpy change of 52 cal/mol. That small change is within the experimental uncertainty of the data presented here.

are monitored for at least 2 h to check for steady-state operation. A slow, continuous drop in the $CO_2$ concentration indicates that light impurities are stripped and depleted from the sample. A steady $CO_2$ concentration, independent of flow rate and catalyst temperature, indicates complete saturation and combustion of the pure hydrocarbon.

## Results

Tables I and II present vapor pressures of four liquids and three solids. The indicated errors are average percent deviations of the experimental pressures from calculated pressures at the same temperature. The calculated pressures are calculated from the Clapeyron equation

$$\ln P(\text{sat}) = A + B/T \qquad (5)$$

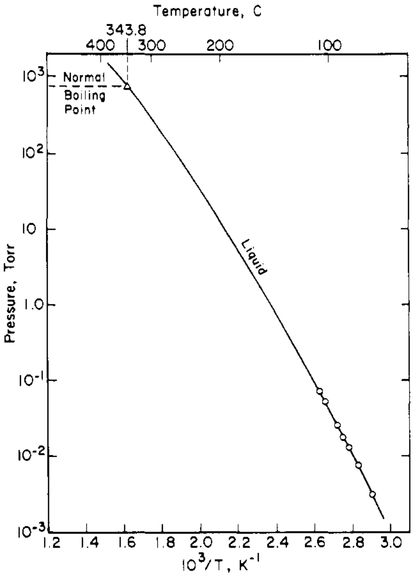

**Figure 3.** Extrapolation of vapor-pressure data for *n*-eicosane at near-ambient temperatures to the normal boiling point, by using the SWAP method ($t_{0.01}$ = 83.85 °C; $F_A = F_B = F_N = 0.0$).

where $P$ is in torr and $T$ is in kelvins. Constants $A$ and $B$ are determined from a least-squares fit of the experimental data. Over narrow ranges in temperature, the Clapeyron equation is valid; therefore, the percent deviation of the experimental data from the Clapeyron equation gives a good estimate of random experimental uncertainty. For the data reported here, an equation with more than two parameters is not suitable since such an equation would tend to fit the data scatter and not give a valid reflection of random experimental uncertainty.

Sinke (*3*) measured the vapor pressure of naphthalene in the same temperature range; for comparison, we interpolated his data using the Clapeyron equation. For six points, the average deviation between the two data sets is 1.4% in *P*(sat).

The triple-point pressure for phenanthrene reported here is in good agreement with that reported by Osborn and Douslin (*2*); the former is only 1.8% higher than the latter.

These errors are within the experimental uncertainty of the data presented here.

## Discussion

For liquids, the Clapeyron equation is used to find $T_{0.01}$, the temperature at which the vapor pressure is $10^{-2}$ torr. Using $T_{0.01}$ and the modified SWAP method of Macknick et al. (*1*), we report the data extrapolated to the normal boiling point $T_{760}$. Figure 3 shows the extrapolation for *n*-eicosane. Average error in estimating the four liquid $T_{760}$'s is 3.8 °C, which corresponds to an average error of 8.8% in pressure.

For solids, assuming no significant solid–solid phase transitions, the Clapeyron equation is used to extrapolate the experimental data to the known melting point. The SWAP method of Smith et al. (*4*) is then used to predict the liquid-phase vapor-pressure curve. This method requires either $T_{10}$ or $T_{760}$. (Many aromatics are solids at $T_{10}$; we have therefore chosen to use $T_{760}$.) The normal boiling point is not known but can easily be calculated. The liquid and solid vapor-pressure curves must intersect at the triple point which is here taken to be equal to the melting point. Therefore, a trial-and-error calculation yields $T_{760}$ which is then used to obtain the correct melting-point vapor pressure. The function of Smith et al. is well-behaved for convergence to the correct $T_{760}$; there is only one reasonable $T_{760}$ which gives the correct melting-point vapor pressure for each compound. Figure 4 shows this extrapolation for anthracene. For the three compounds which are solids at near-ambient temperature, the

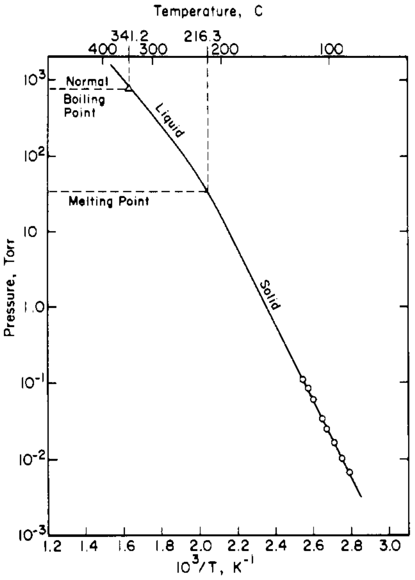

**Figure 4.** Extrapolation of vapor-pressure data for anthracene at near-ambient temperatures to the normal boiling point, by using the SWAP method ($t_{mp}$ = 216.3 °C; $P(\text{sat})_{mp}$ = 33.4 torr; $F_A$ = 1.0; $F_B$ = $F_N$ = 0.0).

average error in estimating $T_{760}$ is 5.2 °C, or 11.1% in pressure.

For extrapolation of solid data to the normal boiling point, the melting point temperature must be known. However, the SWAP method is not highly sensitive to small errors in melting point temperatures. For anthracene, if the melting point temperature used is in error by ±10 °C, the subsequent error in predicting $T_{760}$ is only ±4.7 °C.

## Conclusions

The experimental technique used here yields reliable vapor-pressure data near ambient temperatures. Since the experiment is performed at convenient temperatures and pressures, it is simple to operate and provides good-quality data easily and rapidly. Using the SWAP method, we estimate vapor pressures for high-molecular-weight hydrocarbons in the range $10^{-3}$–$10^3$ torr from experimental data at near-ambient temperature for both solids and liquids.

## Glossary

| | |
|---|---|
| $A$, $B$ | Clapeyron equation constants |
| $f$ | fugacity, torr |
| $F_A$, $F_B$, $F_N$ | SWAP parameters: fraction of carbon atoms per molecule which are aromatic, branched paraffin, and naphthenic, respectively |
| $n$ | number of carbon atoms per molecule of hydrocarbon |
| ppm-($CO_2$) | concentration of $CO_2$, ppm by volume |
| $P$(atmo) | atmospheric pressure, torr |
| $P$(sample) | total pressure in equilibrium cell, torr |
| $P$(sat) | vapor pressure, torr |
| $t$ | temperature, °C |
| $T$ | temperature, K |
| $x$ | mole fraction in condensed phase |
| $y$ | mole fraction in vapor phase |

*Greek Letters*

| | |
|---|---|
| $\phi$ | fugacity coefficient |
| $\gamma$ | activity coefficient |

*Subscripts*

| | |
|---|---|
| i | component i |
| mp | melting point |
| 0.01, 10, 760 | at pressures of $10^{-2}$, 10, and 760 torr, respectively |

*Superscripts*

| | |
|---|---|
| c | condensed phase |
| o | standard state |
| v | vapor phase |

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# Use of Rational Functions for Representing Data

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**The relative merits of polynomials and rational functions for the representation of data are illustrated by means of various fits to typical sets of physical data by using these two types of parameterization. In many situations rational functions provide superior fits with the same number of adjustable parameters (or fits with fewer parameters for the same degree of precision), greater stability of extrapolation to points outside the fitted range, and greater versatility in approximating diverse functional forms, including those showing singularities. A useful algorithm for the computation of rational fits is briefly discussed.**

One popular method for representing data is to use a simple polynomial. For example Prausnitz (*6*) represents Henry's constants as a function of the variable $\beta$ = 1000/$T$, where $T$ is the temperature in K, in the form

$$\ln H = a_0 + a_1\beta + \ldots + a_M\beta^M \qquad (1)$$

where $M$, in some instances, is as high as 5. Many other examples of this approach can be found in the chemical engineering literature.

Polynomial parameterizations have certain serious theoretical limitations (*1*). For example, a power-series expansion for a given function has a radius of convergence which is equal to the distance from the point of expansion to the nearest singularity in the function, so even the exact power series, if it were known, would be completely useless beyond that point. These theo-

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