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PHASE-EQUILIBRIA FOR DESIGN OF COAL-GASIFICATION PROCESSES, DEW POINTS OF HOT GASES CONTAINING CONDENSIBLE TARS

Final Report

By
J. M. Prausnitz

May 1980

Work Performed Under Contract No. AC01-76ET10603

Chemical Engineering Department
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U. S. DEPARTMENT OF ENERGY

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FINAL REPORT

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Phase-Equilibria for Design of Coal-Gasification Processes.

Dew Points of Hot Gases Containing Condensible Tars

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May 1980

EXECUTIVE SUMMARY

This research is concerned with the fundamental physical chemistry and thermodynamics of condensation of tars (dew points) from the vapor phase at advanced temperatures and pressures. Fundamental quantitative understanding of dew points is important for rational design of heat exchangers to recover sensible heat from hot, tar-containing gases that are produced in coal gasification.

This report includes essentially six contributions toward establishing the desired understanding.

1. Characterization of Coal Tars for Dew-Point Calculations.

   Effluent gases from coal-gasification processes often contain high-molecular-weight hydrocarbons (tars) which, upon condensation, may foul heat exchangers needed to recover sensible heat. A method is given for the characterization of these tars to facilitate dew-point calculations. Small quantities of tar samples are fractionated in a spinning-band column; each fraction is then chemically classified with elemental analysis and proton NMR. Based on approximate chemical classification, methods are given for the estimation of vapor pressures and molecular weights, required for predicting tar-condensation conditions. For illustration, results are given for two tars; one is from a Wyoming subbituminous coal and the other from an Illinois No. 6 coal.

   Details are in Appendix I.

2. Fugacity Coefficients for Dew-Point Calculations in Coal-Gasification Process Design.

   Hot gases from coal gasification processes often contain tars and water which may condense upon cooling in heat exchangers. To calculate dew-point conditions at advanced pressures, vapor-phase fugacity coefficients must be known. Toward that end, this work presents an estimation procedure; it is based on the virial equation of state and the squarewell potential for calculating second virial coefficients. Techniques are given for estimating required potential parameters for identifiable components and for tar cuts obtained from tar fractionation. At pressures above 10 bars, where fugacity coefficients may be well removed from unity, gas-phase nonideality may have an appreciable influence on dew-point calculations.

   Details are in Appendix II.

3. Vapor Pressures of High-Molecular-Weight Hydrocarbons.

A gas-saturation apparatus is used to obtain experimental data at near-ambient temperature; vapor pressures in the range 10^{-1} to 10^{-3} Torr are presented for liquids n-octadecane, n-eicosane, 1-methyl-naphthalene, 2-ethylnaphthalene, and 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.

Details are in Appendix III.

4. Estimation of Vapor Pressures of High-Boiling Fractions in Liquefied Fossil Fuels Containing Heteroatoms Nitrogen or Sulfur.

The SWAP correlation is extended to include the effect of bound nitrogen and sulfur. Also, evidence is presented showing that the correlation is applicable to narrow-boiling petroleum fractions, heavy coal-derived liquids and tars. The extended correlation is for the region 10-2,000 torr. Using a minimum of experimental information including approximate characterization and one vapor-pressure datum, vapor pressures can be calculated within $\pm$ 10%.

Details are in Appendix IV.

5. Vapor Pressures of Heavy Liquid Hydrocarbons by a Group-Contribution Method.

The group-contribution method gives parameters for a vapor-pressure equation based on a kinetic theory of fluids. All parameters are obtained from molecular structure only. Good representation is obtained for vapor-pressure data for 67 hydrocarbon liquids in the region 10-1500 mm Hg. This group-contribution method is useful for estimation of vapor pressures and enthalpies of vaporization for those heavy hydrocarbons where no experimental data are available.

Details are in Appendix V.

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

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-methyl pyridine, and N-ethyl carbazol.

The range of pressures measured was 10^{-3} to 10^{-1} mm Hg.

Details are in Appendix VI.

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Introduction

The long-range goal of this research is to obtain fundamental physico-chemical data which, when coupled with theoretical results from molecular thermodynamics, will enable engineering calculations of dew points in tar-containing gas mixtures at advanced temperatures and pressures.

This research, initiated a few years ago, is continuing with DOE support under a new contract number.

The following have been achieved:

1- A thermodynamic analysis has been made of the dew-point phenomenon at high pressures. To calculate dew points under equilibrium conditions, we require

A- Characterization of the tar by considering it to be a mixture of pseudo-components called tar fractions.

B- Characterization of each tar fraction to estimate its vapor pressure as a function of temperature.

C- Estimates of fugacity coefficients to calculate the effect of vapor-phase nonideality.

D- Construction of a computer program to solve the non-linear equations of equilibrium applied to a flow system such as may be encountered in industrial practice, e.g. a constant-pressure heat exchanger where the temperature of the coal-derived, tar-containing gas falls as the gas proceeds through the exchanger.

2- To achieve 1A, we have successfully fractionated several actual tars, including one from Research Triangle Institute and one from the Synthane process. Fractionation is achieved with a Perkin-Elmer spinning-band apparatus operating at low pressure and high reflux. Details are given in Appendix I.

3- To achieve 1B, we have established that the following serve adequately to characterize tar fractions for our purposes:

A- One vapor-pressure datum for each fraction is found from the spinning-band distillation procedure.

B- The aromaticity of each fraction is determined from NMR spectra.

C- The hetero-atomicity of each fraction (presence of

sulfur, nitrogen or oxygen atoms) is determined by elemental analysix.

D- The molecular weight of each fraction is determined by vapor-pressure osmometry or by freezing-point depression in benzene.

Details are given in Appendix I.

4- We want to use tar-fraction-characterization data to calculate the vapor pressure of each fraction as a function of temperature. To do so, we require a vapor-pressure correlation based on experimental data for model compounds, i.e. compounds typically found in tars. We have established such a correlation, called SWAP (1,2) and we have extended it so that, in addition to paraffinic and strongly aromatic hydrocarbons, it may also be applied to hydrocarbon derivatives containing nitrogen or sulfur (3). Details are in Appendix IV.

5- Good vapor-pressure data are scarce for high-boiling fluids such as those found in tars. We have therefore constructed a vapor-pressure apparatus for measuring vapor pressures of selected model compounds. Since these compounds tend to decompose at higher temperatures, equilibrium measurements are best made at modest temperatures where the vapor pressures may be extremelv low. Therefore. a standard experimental method is not suitable. Our apparatus, applicable to pressures in the ranges 10^{-4}-10^{0} torr is similar to that of Sinke (4). We have measured vapor pressures of a number of model compounds as reported in two publications (5,6). This work has also led to a group-contribution method for estimating vapor pressures from molecular structure only (7). Details are in Appendices III, V and VI.

6- To achieve 1C, we use an equation of state for gas mixtures at advanced pressures. The necessary coefficients are determined by a molecular-thermodynamic method. (8) Special attention is given to coefficients describing gas-phase interactions when the hot gas contains water as well as condensible hydrocarbons and hydrocarbon derivatives.

7- To achieve 1D, we have developed a preliminary version of a computer program, suitable for engineering design, for an isobaric heat exchanger which recovers the sensible heat from a hot, tar-containing, coal-derived gas. To design such an exchanger, one must know the dew-point characteristics of the gas. These, coupled with heat and material balances, give the heat exchanger profile: percent condensed as a function of

temperature or, alternatively, distance in the exchanger.

Some details are given in Appendix II.

8- To test the dew-point calculations, we have built an equilibrium apparatus for measuring the solubilities of selected tar fractions in compressed gas (typically, methane) at high temperatures and pressures. We lost much time with an apparatus which did not give reproducible results. Therefore, we have entirely rebuilt the apparatus in such a way that we eliminate the need for bothersome chemical-analysis measurements which, we are quite sure, caused our major difficulties with the earlier apparatus. The new apparatus is now operating and we expect meaningful data to emerge soon.

The achievements listed above serve as a sufficient foundation to suggest that the goals of this research project can be attained in the extension of this contract which started October 1, 1979.

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APPENDICES

I Characterization of Coal Tars for Dew-Point Calculations

II Fugacity Coefficients for Dew-Point Calculations in Coal-Gasification Process Design

III Vapor Pressures of High-Molecular-Weight Hydrocarbons

IV Estimation of Vapor Pressures of High-Boiling Fractions in Liquefied Fossil Fuels Containing Heteroatoms Nitrogen or Sulfur

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APPENDIX I

CHARACTERIZATION OF COAL TARS

FOR DEW-POINT CALCULATIONS

Introduction

Coal gasification often produces by-product tar which can constitute as much as 5 weight percent of the coal feed (Institute of Gas Technology, 1975). While the nature of the tar varies from one gasification process to another, typical tars contain mostly hydrocarbons in the normal-boiling-point range 100-700 C.

Hot effluent gases from coal gasifiers provide a significant source of sensible heat whose recovery is achieved by cooling in a heat exchanger with possible subsequent condensation of heavy components. Design of coal gasifiers, therefore, requires calculation of dew points of gas streams containing high-molecular-weight hydrocarbons. This work discusses a technique for characterizing tars to facilitate such calculations.

Thermodynamic Analysis

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

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

$$f_i^c = x_i \gamma_i f_i^0 \qquad (3)$$

where y and x are the mole fractions in the vapor and condensed phases, respectively; ϕ is the vapor-phase fugacity coefficient; γ is the condensed-phase activity coefficient, and P is the total pressure. Reference fugacity f_i^0 is determined primarily by the vapor pressure of pure, condensed (i) at system temperature.‡

The dew-point condition for component (i) occurs when the inequality in Equation (1) is replaced by an equality.

In a typical application, the total pressure is known. Fugacity coefficients can be estimated using a suitable equation of state (Kaul and Prausnitz, 1978; Plöcker et al., 1978; El-Twaty, 1979) and activity coefficients can be assumed to equal unity as a good first approximation. However, reference fugacity (vapor-pressure data) and mole fractions must also be available for each component.

Coal tars are complex mixtures of many components; it is not economically feasible to establish the exact composition of the mixture or to determine the vapor pressure of each component as a function of temperature. The work presented here provides a classification of heavy hydrocarbon mixtures such that dew-point properties can be estimated with minimum experimental effort.

The tar is fractionated into narrow-boiling-point cuts, and each cut is analyzed for approximate chemical

‡At low total pressure, f_i^0 is usually set equal to the vapor pressure of pure, condensed (i); at elevated pressures, the Poynting correction must be added [Prausnitz, 1969].

structure. The cuts are assumed to be pseudo-pure components which constitute the tar mixture.

Using experimental data from fractionation and from chemical analysis, the SWAP method (Smith et al., 1976) is used to determine the vapor-pressure-versus-temperature relation for each cut. The SWAP method is useful because it requires minimal experimental information and because it is reliable for hydrocarbons containing large molecules from the melting point to 1500 mm Hg.

Molecular weights, needed to calculate x and y, are determined from a correlation based on predicted normal boiling point and approximate chemical structure.

Tar Fractionation

Heavy hydrocarbons may undergo chemical reactions at room temperature (i.e., polymerization). To prevent molecular rearrangements, tar samples were analyzed within a few days of their manufacture. Also, samples were kept in a dark, oxygen-free atmosphere and under refrigeration (5 C) whenever possible.

Two tar mixtures were analyzed: one was produced at Research Triangle Institute (RTI) in their bench-scale gasification unit (Mixon, 1978) and the second was produced by the SYNTHANE demonstration unit of the Pittsburgh Energy Technology Center (Institute of Gas Technology, 1975; Gasior, 1978).

Both "as-received" tar samples contained the total

condensate from a particular run. Therefore, these samples contained significant quantities of water. Since the purpose here is to analyze the heavy hydrocarbon portion of the condensate, the light components, including water, were distilled off prior to tar analysis.

Distillation and fractionation were achieved in a Perkin-Elmer adiabatic, spinning-band still (Model 251). Instead of trays or packing, this type of distillation column uses a helical band rotating at a high RPM. The rotating band gives high efficiencies, low pressure drops, and low liquid holdup while allowing operation at high temperature and high vacuum. To avoid thermal cracking, vacuum distillation is used to keep pot temperatures low.

Approximately 100 gm of "as-received" tar were used. The still was run with a monel band at 1800 RPM, a reflux ratio of 20:1, and a liquid holdup in the column of about 0.5 ml. Under these conditions, there exist about 50 theoretical plates in the column.

Temperature in the still pot and reflux head were monitored with thermocouples calibrated to ±0.1 C. Vacuum operation from 1 atm to 0.1 mm Hg was maintained with a Perkin-Elmer vacuum regulator (Model 086-0241). Vacuum operation from 0.1 to 0.01 mm Hg was achieved manually with a vacuum pump and bleed valve. Above 0.1 mm Hg, vacuum could be regulated to ±2%; below 0.1 mm Hg, control was ±10%. For pressure measurements, a manometer and cathetometer were used

above 1 mm Hg and a McCloud gauge below 1 mm Hg. Since fractionation cuts have boiling-point ranges of approximately 25 C, small errors in measurement of temperature or pressure are not significant for our purposes.

"As-received" tar samples were charged to the still pot. Initial overhead distillate, taken off at atmospheric pressure and reflux-head temperatures of 25-105 C, contained all light components and water. The remaining tar in the pot (25-75 gm) was then fractionated into pseudo-pure-component cuts.

Several experimental criteria were used to establish divisions between fractions. Since narrow-boiling-point cuts are desired, the boiling-point range for a cut was kept at 25 C or less. When distilling, it was often possible to identify obvious break points between cuts by observing a sharp decrease in the boilup rate and a sharp increase in the pot temperature. For example, several grams of material were taken off at a boilup rate of 20 drops/minute with an almost constant pot temperature. After 45 minutes, the boilup rate dropped to 5 drops/minute and the pot temperature started to increase at a rate of 2 C/minute. This behavior indicated that significantly heavier material started to come up the column and that the material being taken off at the reflux head was almost fully removed from the pot.

Sometimes it was also possible to make divisions between cuts by observing physical changes in the overhead

distillate. Variations in color or viscosity were sometimes used to decide where cuts should be made. In general, the division between cuts was not a difficult decision, and the total number of cuts was determined by what appeared to be the obvious breaking points between fractions. Not including light fractions, the RTI tar was divided into 8 cuts and the SYNTHANE tar into 12 cuts. At room temperature, the physical nature of the tar cuts varied from colorless, light oils to black, solid waxes.

The final cut was residual material in the still pot which would not boil at 350 C and 0.05 mm Hg. The residual tar was treated as the heaviest pseudo-pure component, with a boiling point determined by the conditions where it was no longer possible to obtain boilup. Upon cooling to room temperature, this residual tar was a brittle, glossy-black substance, similar in appearance to coal. Since the initial samples contained total condensate, the residual tar contained particulate matter or inorganic fly-ash produced during gasification.

Chemical Characterization

To calculate the vapor-pressure curve of each pseudo-pure component, the SWAP method requires one temperature/pressure datum and approximate chemical structure. (The SWAP method is only applicable to liquid hydrocarbons; in the tar fractionation described above, each cut was distilled as

a liquid.) The one temperature/pressure datum is obtained from the overhead distillation conditions.

The chemical structure information required is the distribution of carbon atoms by chemical type: aliphatic or aromatic. In this work, no distinction is made among aliphatic carbons; all aliphatics, including naphthenes, are treated alike. Macknick et al. (1978) showed that vapor pressures calculated with SWAP are only a weak function of molecular structure. Therefore, classification of carbon atoms as either aromatic or aliphatic is adequate for good vapor-pressure estimation for tar cuts.

To calculate F_A, the fraction of carbon atoms which are aromatic, we use a relation proposed by Brown and Ladner (1960):

$$F_A = \left[(C/H) - \frac{\alpha}{(H/C)_{ali}}\right] / (C/H) \qquad (4)^{\dagger}$$

where, for the particular cut, α is the ratio of aliphatic hydrogen atoms to total hydrogen atoms and (C/H) is the atomic carbon-to-hydrogen ratio. For large molecules, $(H/C)_{ali}$ (the hydrogen-to-carbon ratio for aliphatic structures) is 2.0.

Retcofsky et al. (1977) showed that Equation (4) is reliable for a wide variety of complex mixtures, including coal extracts, coal-tar pitches, and coal-carbonization products. The ratio (C/H) is obtained by standard chemical

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†Brown and Ladner (1960) use the notation H^*_{ali} instead of α.

analysis (Weissberger, 1954), and α is obtained from proton magnetic resonance (^{1}H NMR) (Dyer, 1965); Retcofsky compared carbon aromaticities calculated from Equation (4) to determinations by proton-coupled ^{13}C nuclear magnetic spectra and showed that agreement is excellent for coal-derived products.

In this work, carbon, hydrogen and nitrogen content were determined for each tar fraction using a Perkin-Elmer 240 C/H/N analyzer. Sulfur content was determined by the combustion method of Sundberg et al. (1946), converting sulfur dioxide from combustion to sulfur trioxide in a peroxide solution. Sulfur trioxide was then precipitated with barium ion for gravimetric determination of sulfur. Oxygen content was calculated by difference.

The ratio α was determined by ^{1}H NMR using a Varian T-60 spectrometer operating at 60 MHz. Experimental studies were performed at room temperature by dissolving 0.2 gm of sample in 1 ml of pyridine-d_5 (99 atom % deuterium). Tetramethyl siloxane (TMS) was used as an internal stnadard to set zero-chemical shift. Down-field shifts from TMS of 0-250 Hz were attributed to aliphatic hydrogen; down-field shifts of 300-500 Hz were assumed to be aromatic hydrogen. Since the samples were distillation products, there was no spectral interference from water or particulates. (It was not possible to dissolve residual tar from the still pot in carbon tetrachloride, deuterochloroform, or deuterated pyridine for ^{1}H NMR studies; for these cuts, chemical structure is

estimated from elemental analysis alone.) Figure 1 shows representative ^1H NMR spectrum for a tar fraction.

Table 1 gives the atomic (C/H) ratio and α along with aromaticities calculated by Equation (4). All fractions contained approximately the same quantities of nitrogen, sulfur, and oxygen: 0.5, 0.5, and 2.5 atom per cent, respectively. Since oxygen content was calculated by difference, small mass losses during analysis and the presence of trace elements may cause oxygen values to be erroneously high. In general, the tar fractions were over 95 atom per cent hydrocarbon.

Vapor-Pressure Calculation

Using the single temperature/pressure datum from distillation and the structural information from elemental and NMR analysis, the SWAP method (Smith et al., 1976) was used to calculate the vapor-pressure curves for the pseudo-pure components.

For vapor pressures below (about) 1500 mm Hg, the SWAP function relates vapor pressure P_i^S (mm Hg) to temperature T (K).

$$\ln \frac{P_i^S}{P_i^*} = A + B\left(\frac{T_i^*}{T}\right) + C\left(\frac{T_i^*}{T}\right)^2 \qquad (5)$$

Characteristic molecular parameters T_i^* and P_i^* are, respectively, in kelvins and in mm Hg. Parameter P_i^* is calculated from simple functions given by Smith et al. (1976) and Macknick et.

al. (1978); it is a function of approximate chemical structure and one boiling-point datum. In this work, we characterize chemical structure by F_A (carbon aromaticity as determined by the Brown-Ladner method) and for the boiling-point datum we choose $T_{0.01}$ or T_{10} or T_{760} (the temperature where the vapor pressure is 10^{-2}, 10, or 760 mm Hg, respectively). For a particular cut, the choice is that which is closest to the distillation temperature at which the cut was obtained. For example, if a cut was distilled at 5 mm Hg, T_{10} is used to calculate P_i^*.

Like P_i^*, coefficients A, B, and C are calculated from simple functions given by Smith et al. (1976) using F_A and $T_{0.01}$ or T_{10} or T_{760}. Once P_i^*, A, B, and C are known, Equation (5) along with $T_{0.01}$ or T_{10} or T_{760} are used to calculate T_i^*.

Final values of all parameters in Equation (5) are obtained by an iterative procedure.

For a particular cut, temperatures $T_{0.01}$, T_{10}, and T_{760} are not known, but they can easily be calculated since the vapor-pressure-versus-temperature curve must pass through the vapor-pressure point obtained during distillation. For example, if a cut was distilled at T = 500 K and a pressure of 5 mm Hg, a trial-and-error calculation for T_{10} is required which yields the correct distillation datum. Good <u>initial</u> guesses for $T_{0.01}$ or T_{10} or T_{760} can be obtained from the distillation datum by using the rough rule that the vapor

pressure doubles for each increase of 25 K.

As an example, take a cut obtained at a reflux condition of T = 500 K and P_i^s = 5 mm Hg. As determined from experimental NMR and elemental analysis, F_A = 0.5. To find P_i^*, A, B, and C, we choose T_{10} since it is closest to distillation conditions. For an initial value of T_{10}, we assume that the vapor pressure doubles for each increase of 25 K. Since P_i^s = 5 mm Hg at T = 500 K, $T_{10} \sim 525$ K.

Using T_{10} = 525 K and F_A = 0.5, we calculate P_i^*, A, B, and C. Once these are known, Equation (5), along with P_i^s = 10 mm Hg at T = 525 K, are used to calculate T_i^*.

Equation (5) is now checked at the distillation conditions. That is, at T = 500 K, does Equation (5) predict the observed result, P_i^s = 5 mm Hg? If not, successive iterations for T_{10} values are made until values for A, B, C, P_i^* and T_i^* are obtained such that Equation (5) gives the correct distillation datum.

Equation (5) is well-behaved for rapid convergence; there is only one reasonable $T_{0.01}$ or T_{10} or T_{760} which gives the correct distillation datum. For the tars analyzed here, the iteration method to calculate SWAP parameters was carried out on a programmable desk-top calculator. Figures 2 and 3 give representative vapor-pressure curves calculated with Equation (5). Table 2 gives SWAP parameters for two cuts from each tar.

Molecular-Weight Estimation

Weight fractions are obtained from experimental fractionation. However, the thermodynamic relations, Equations (2) and (3), require mole fractions. Therefore, estimates of molecular weights are required for each cut. Experimental techniques (Weissberger, 1959) are available to determine the molecular-weight distribution of the pseudo-pure components, but the large necessary experimental effort is not justified for our purposes here.

Figure 4 shows the dependence of molecular weight on structure and normal boiling point T_b. The heavy lines in Figure 4 represent extremes in aromaticity: normal paraffins and fused-ring aromatics. Figure 4 was constructed by plotting the molecular weight as a function of normal boiling point for normal paraffins C_5 - C_{50} and for aromatics benzene, naphthalene, anthracene, and chrysene. At a given T_b, linear interpolation between these extremes using aromaticity, F_A [as determined by Equation (4)], gives good estimates of molecular weight. For example, the molecular weight of 2,6-dimethyl-anthracene (F_A = 14/16, T_b = 643 K) is 206; using Figure 4, the estimated molecular weight is 207.

Since a tar fraction is a narrow-boiling-point cut, it does not have a single molecular weight, but rather a molecular-weight distribution. Figure 4 gives an average molecular weight using F_A, as determined from Equation (4),

and T_b, as determined from Equation (5). Table 3 gives normal boiling points estimated from the SWAP method and molecular weights calculated using Figure 4.

Conclusions

Upon cooling hot gases containing small amounts of tars produced during coal gasification, tar condensation can cause severe plugging and fouling problems. Therefore, the design of coal-gasification plants requires a reliable method to calculate the dew points of tar-containing gases.

Since tars are complex mixtures, it is not usually feasible quantitatively to identify each component. The method presented here supplies a simple technique for characterizing tars through fractionation into cuts or pseudo-components; each of these cuts is then subjected to approximate chemical analysis. The data obtained from fractionation and approximate chemical analysis are then used to estimate the molecular weight of each pseudo-component and its vapor pressure as a function of temperature. These are required for dew-point calculations. Since nitrogen, oxygen, and sulfur content was less than 5 atom per cent, the tars were classified as hydrocarbon liquids. However, inclusion of N, O, and S content in vapor-pressure and molecular-weight estimation methods is likely to improve the reliability of dew-point calculations.

As indicated in this work, small quantities of tar produced in bench-scale apparatus can be used to predict

equilibrium condensation conditions. Dew-point calculations assuming phase equilibrium predict the maximum condensation of tar. In practice, condensation depends also on mass transfer (i.e., kinetics of condensation and entrainment); however, thermodynamic calculations, as suggested here, facilitate prediction of potential fouling problems in large-scale installations.

Acknowledgment

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Nomenclature

A, B, C	Coefficients in the SWAP vapor-pressure equation
(C/H)	Atomic carbon-to-hydrogen ratio
f	Fugacity, mm Hg
F_A	Carbon aromaticity, fraction of carbon atoms per molecule which are aromatic
$(H/C)_{ali}$	Atomic hydrogen-to-carbon ratio for aliphatic structures
P	Total pressure, mm Hg
P^S	Saturated vapor pressure, mm Hg
P*, T*	Characteristic molecular parameters in the SWAP vapor-pressure equation; mm Hg and K respectively
t	Temperature, C
T	Temperature, K
x, y	Mole fractions in the condensed and vapor phases, respectively

Greek Letters

α	Fraction of hydrogen atoms per molecule which are aliphatic

ϕ	Vapor-phase fugacity coefficient
γ	Condensed-phase activity coefficient

Subscripts

0.01, 10, 760	At pressures of 0.01, 10, and 760 mm Hg, respectively

Superscripts

c	Condensed phase
o	Standard state
v	Vapor phase

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List of Figure Captions

Figure 1. Representative ^{1}H NMR Spectrum: Cut #6, RTI Tar; $\alpha = 74/(135 + 74) = 0.35$

Figure 2. Representative Vapor-Pressure Curves for RTI Tar Fractions

Figure 3. Representative Vapor-Pressure Curves for SYNTHANE Tar Fractions

Figure 4. Molecular Weight Estimation as a Function of Normal Boiling Point and Approximate Chemical Structure

Table 1. Fractionation Conditions and Chemical Characterization for Tar Fractions

Tar	Cut No.	Distillation Conditions t C	Distillation Conditions P mm Hg	Composition, Weight %	C/H	α	F_A
RTI	1	110	23	11.2	0.87	0.51	0.71
	2	140	24	15.7	0.92	0.56	0.70
	3	93	0.19	11.9	1.07	0.42	0.80
	4	122	0.20	12.3	1.17	0.38	0.84
	5	147	0.20	11.6	1.17	0.38	0.84
	6	152	0.02	4.6	1.19	0.35	0.85
	7	170	0.04	6.7	1.20	0.38	0.84
	Residual	330	0.03	26.0	1.48	--	0.9
SYNTHANE	1	115	33	3.0	0.85	0.35	0.80
	2	114	18	9.2	0.82	0.63	0.62
	3	135	20	5.7	0.81	0.73	0.55
	4	155	23	7.8	0.84	0.73	0.57
	5	177	24	7.8	0.89	0.69	0.61
	6	190	26	3.7	0.92	0.69	0.62
	7	130	0.15	9.8	0.94	0.66	0.65
	8	153	0.12	8.8	0.96	0.70	0.64
	9	179	0.13	11.1	0.94	0.70	0.63
	10	209	0.20	5.4	1.00	0.74	0.63
	11	220	0.30	4.2	1.02	0.71	0.63
	Residual	340	0.50	23.5	1.38	--	0.8

Table 2. Representative SWAP parameters for tar fractions.

Tar	Cut No.	P^*, mm Hg $\times 10^{-5}$	T^*, K	A	B	C
RTI	1	6.222	497.4	2.089	-6.272	-2.466
	7	6.340	635.1	1.608	-5.017	-5.342
SYNTHANE	1	6.291	521.8	2.056	-6.208	-2.681
	11	6.190	625.8	1.421	-4.405	-6.439

Table 3. Calculated normal boiling points, molecular weights, and molar compositions of tar fractions.

Tar	Cut No.	t_{760} C	Molecular weight	Composition, Mole %
RTI	1	222	146	16.8
	2	257	163	21.1
	3	319	188	13.9
	4	358	205	13.1
	5	395	224	11.3
	6	454	257	3.9
	7	461	263	5.6
	Residual	>688	398	14.3
SYNTHANE	1	217	140	5.1
	2	233	156	14.1
	3	255	171	8.0
	4	275	180	10.5
	5	302	193	9.7
	6	314	199	4.5
	7	373	234	10.0
	8	410	262	8.0
	9	445	292	9.1
	10	474	319	4.0
	11	479	324	3.1
	Residual	>624	406	13.9

Figure 1. Representative ^{1}H NMR Spectrum: Cut #6, RTI Tar;
$\alpha = 74/(135 + 74) = 0.35$

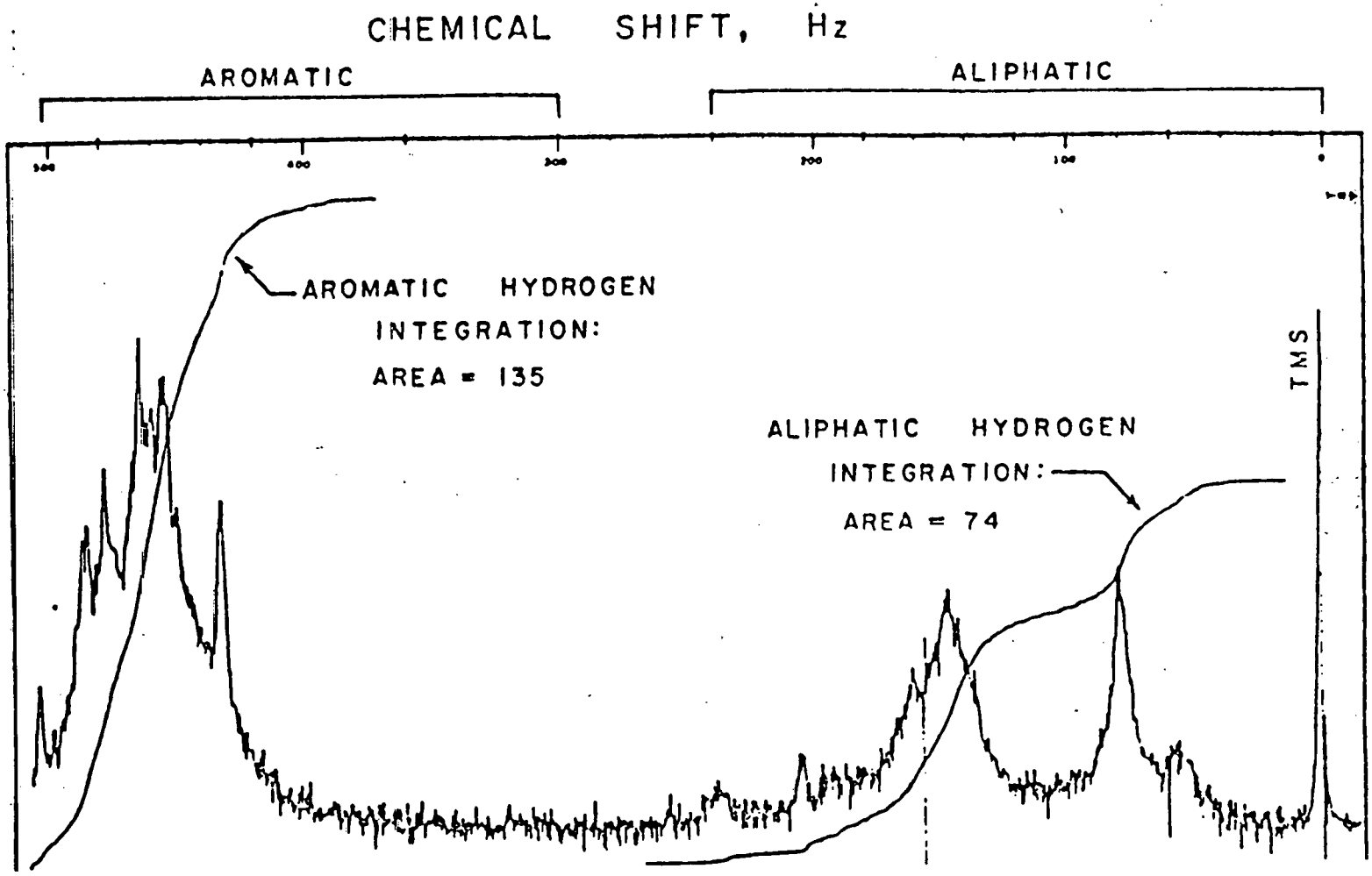


Figure 2. Representative Vapor-Pressure Curves for RTI Tar Fractions

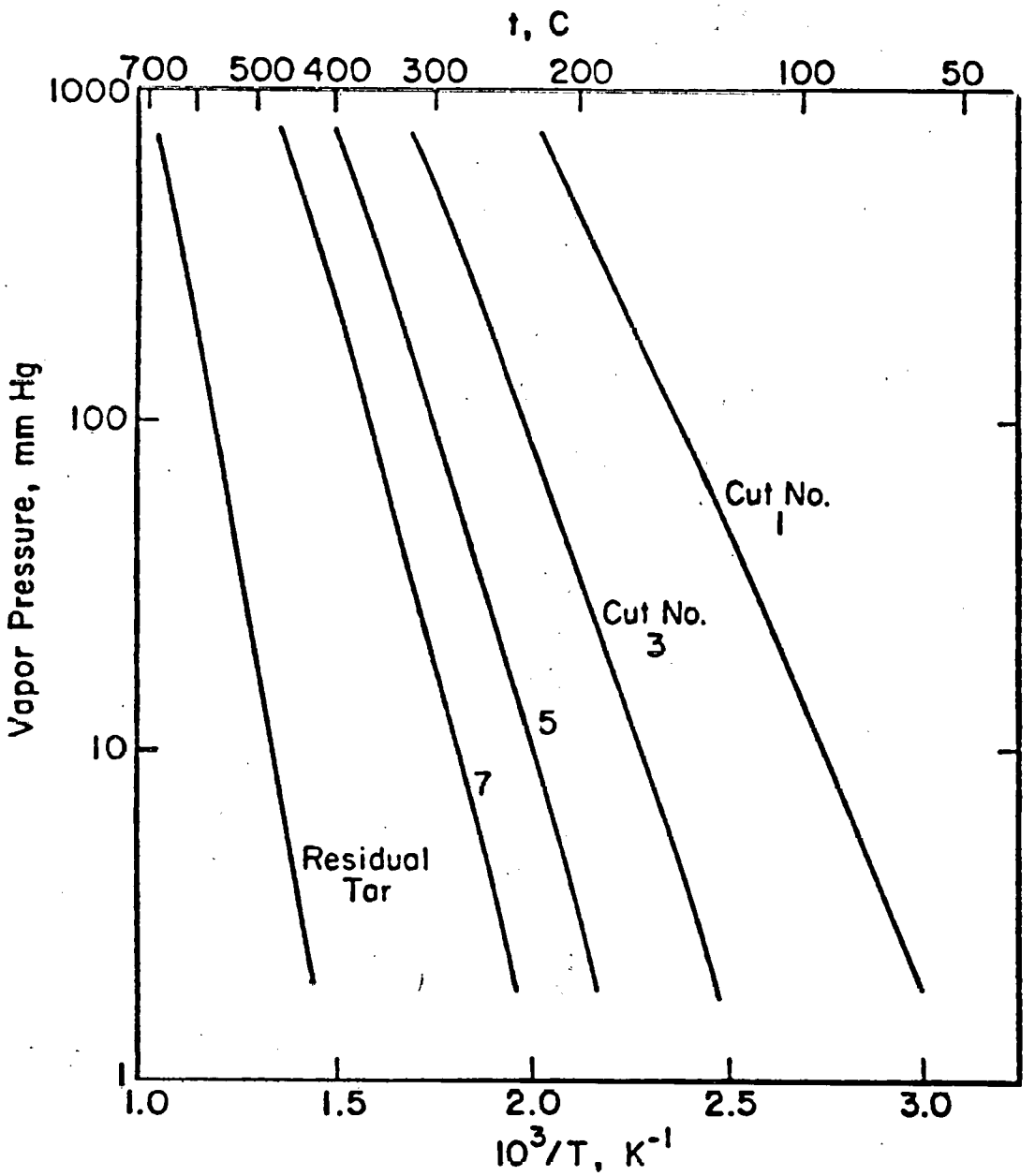


Figure 3. Representative Vapor-Pressure Curves for SYNTHANE Tar Fractions

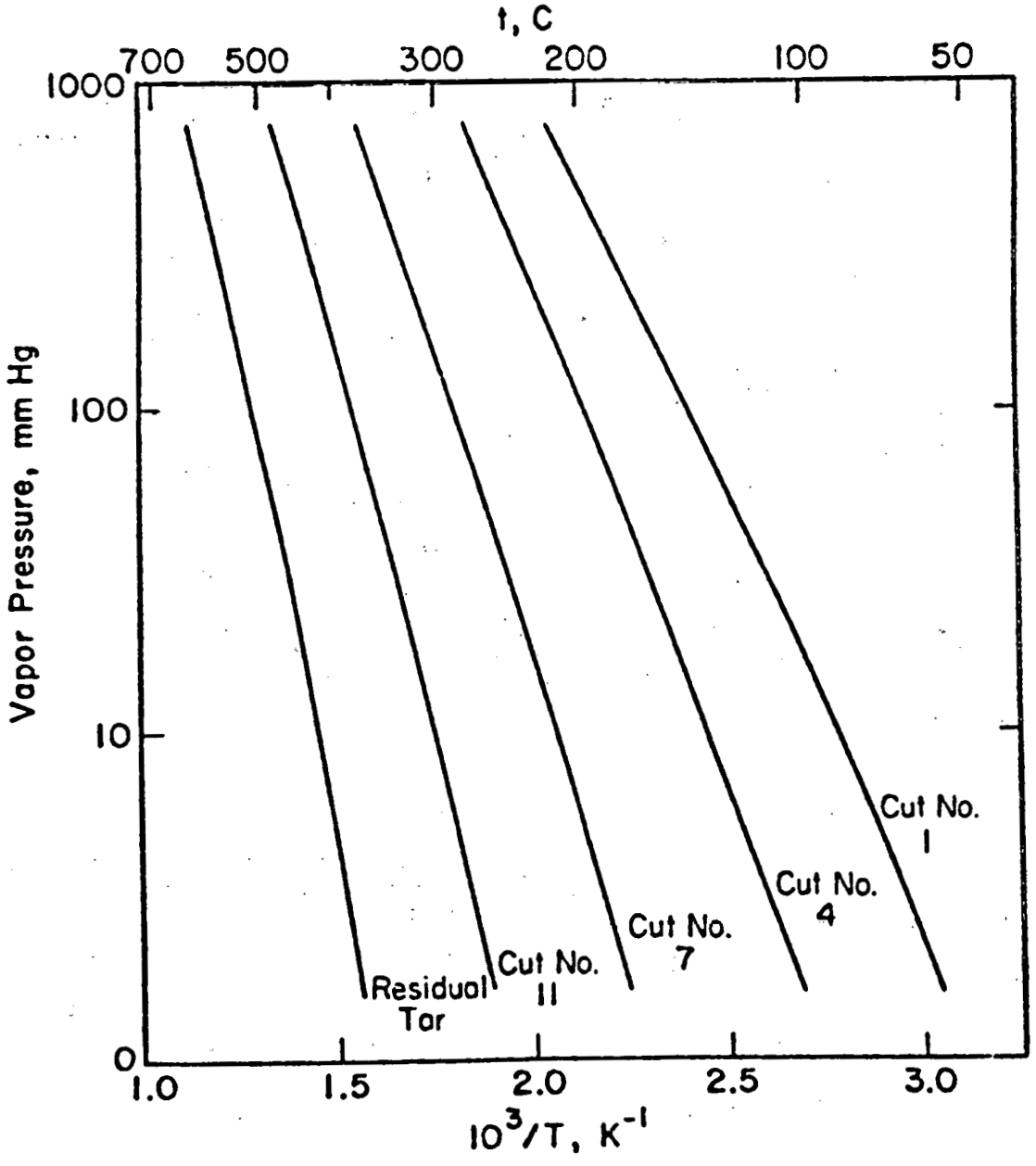
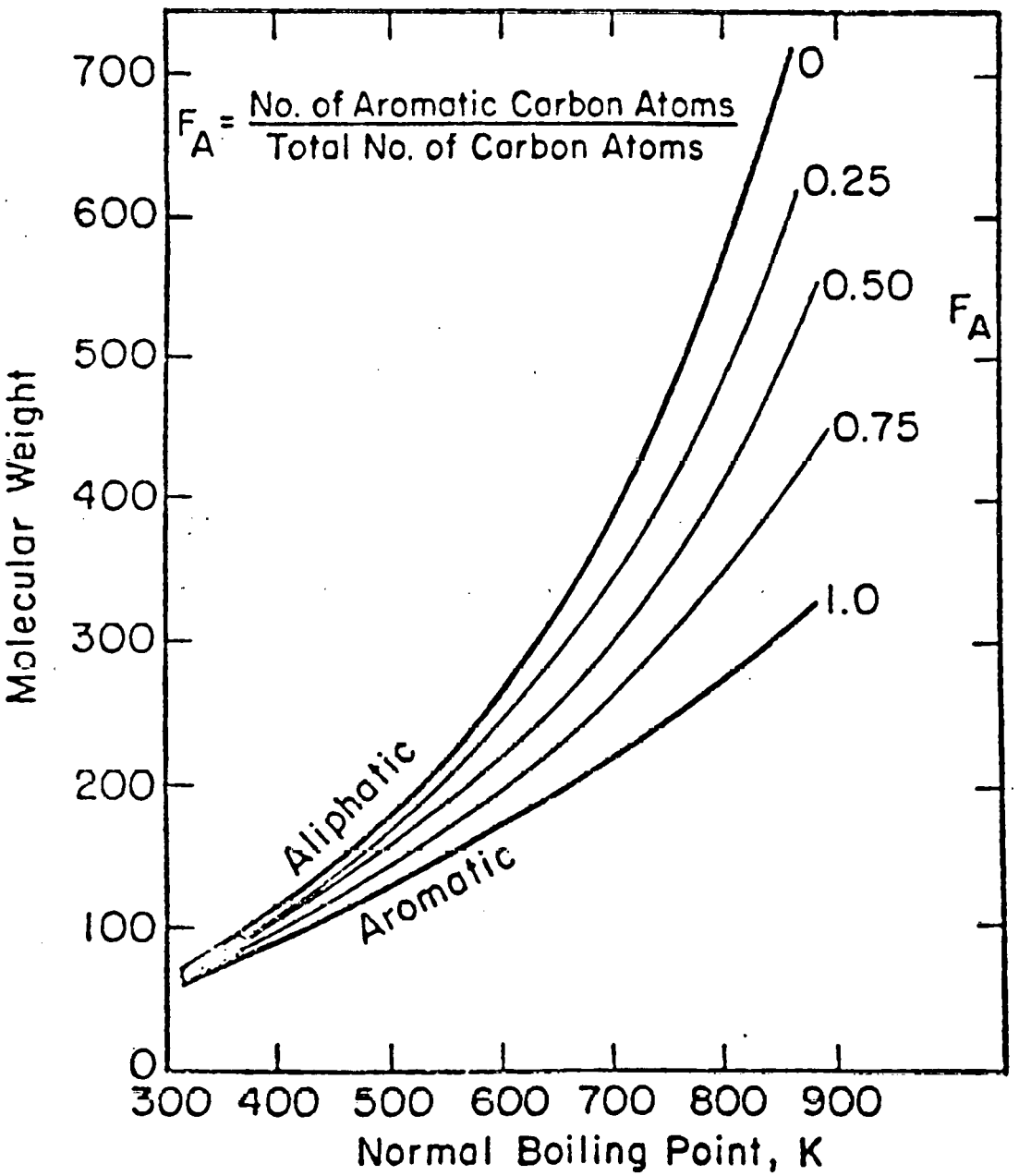


Figure 4. Molecular Weight Estimation as a Function of Normal Boiling Point and Approximate Chemical Structure



APPENDIX II

FUGACITY COEFFICIENTS FOR DEW-POINT CALCULATIONS IN COAL-GASIFICATION PROCESS DESIGN

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Coal-gasification processes produce hot gases that may contain small quantities of tar and water. The sensible heat of these hot gas streams is recovered by cooling in heat exchangers. For stable operation of these exchangers, it is necessary to prevent condensation of tars and water. Design of coal-gasification processes, therefore, may require quantitative estimates of dew-point conditions in tar-containing gases.

Consider a gaseous mixture at pressure P; the composition of the gas is given by mole fractions y_1, y_2...etc where the subscripts refer to components. For any component i, condensation does not occur as long as

$$\phi_i \, y_i \, P < \gamma_i \, x_i \, f_i^0 \qquad (1)$$

Where ϕ is the vapor-phase fugacity coefficient, γ is the liquid-phase activity coefficient and x is the liquid-phase mole fraction; the reference fugacity is denoted by f^0.

For typical tars, assuming immiscibility with water, we can assume that $\gamma_i \approx 1$ when f_1^0 is taken as the vapor pressure of pure liquid i at system temperature and pressure. The vapor pressure is strongly temperature dependent; as the temperature falls (at constant pressure), Equation 1 may no longer hold; the inequality becomes an equality. The temperature where this occurs is the dew-point temperature.

A typical tar is a mixture of many organic components and it is not feasible to identify each component through elaborate chemical analysis. It is far simpler to fractionate the tar into a set of pseudo-components whose vapor pressures can be estimated as a function of temperature, as discussed elsehwhere (Macknick and Prausnitz, 1979).

If water vapor is present in the hot gas, we assume that condensed water is immiscible with condensed tar. When i=water, we still use Equation (1) but in that case $\gamma_i x_i = 1$.

Depending on the particular coal-gasification process, total pressure P may vary from 1 to 80 bars. At low pressure, the gas phase is nearly ideal and therefore $\phi_i = 1$ for every component but, as the pressure rises, significant deviations from ideality are likely. This work is concerned with calculation of fugacity coefficients ϕ.

Fugacity Coefficients from the Virial Equation

The conditions of interest here are high temperatures (typically, 120-800°C) and moderate pressures; the gas composition is such that the mole fraction of methane (the desired product from coal-gasification) is always large. Therefore, the density of the gas is well below the critical and we may then describe gas-phase nonideality with the truncated virial equation of state:

$$z = \frac{Pv}{RT} = 1 + \frac{B_M P}{RT} \qquad (2)$$

Where z is the compressibility factor, v is the molar volume, T is the absolute temperature, R is the gas constant and B_M, the second virial coefficient of the mixture, is related to mole fraction by

$$B_M = \sum_i \sum_j y_i \, y_j \, B_{ij} \qquad (3)$$

where B_{ij}, a function of temperature, is determined by intermolecular forces between molecule i and molecule j.

From Equations (2) and (3), the fugacity coefficient is readily calculated using standard thermodynamics; for any component i,

$$\ell n \phi_i = \left[2 \sum_j y_j \, B_{ij} - B_M \right] \frac{P}{RT} \qquad (4)$$

In Equation (4), the summation is over all components, including component i.

Second Virial Coefficients

To use Equation (4), we require second virial coefficients for all i-j pairs, including most where i = j. Since the mole fractions of light components (especially methane) tend to be large, the main problem is to calculate those B_{ij} where i is a heavy (tar-like) component and j is a light component. This problem has been discussed by Kaul and Prausnitz (1977, 1978) who showed that good results for B_{ij} could be obtained when calculations are based on a square-well potential for describing intermolecular forces.

The square-well potential Γ_{ij} is a function of r, the center-to-center distance between a pair of molecules i and j:

$$\Gamma_{ij} = \quad \text{for } r \leq \sigma_{ij} \tag{5}$$

$$\Gamma_{ij} = -\varepsilon_{ij} \quad \text{for } \sigma_{ij} < r < \sigma_{ij} + \Delta_{ij} \tag{6}$$

$$\Gamma_{ij} = 0 \quad \text{for } r \geq \sigma_{ij} + \Delta_{ij} \tag{7}$$

Where σ is the collision diameter, ε is the characteristic potential energy of attraction and Δ is the well width.

Using the square-well potential, the second virial coefficient is given by

$$\frac{B_{ij}}{b_{0ij}} = 1 - \left[\left(\frac{\sigma_{ij} + \Delta_{ij}}{\sigma_{ij}}\right)^3 - 1\right]\left[\exp\left(\frac{\varepsilon_{ij}}{kT}\right) - 1\right] \qquad (8)$$

Where $b_{0ij} = \frac{2\pi}{3} N_{Av} \sigma_{ij}^3$; N_{Av} is Avogadro's number and k is Boltzmann's constant.

In their study of asymmetric mixtures (i.e. those where molecule j is much larger than molecule i), Kaul and Prausnitz (1978) found that Equation (8) gives a good representation of the limited experimental data, provided that σ_{ij} is calculated from the radii of gyration of molecules i and j.

In Kaul's work, Δ_{ij} is not set proportional to σ_{ij} (as is customary when molecules i and j are of similar size); instead, Kaul suggested that Δ_{ij} is a constant, reflecting the range of intermolecular attraction between small molecule i and the outer parts of large molecule j because small molecule i cannot "see" all of large molecule j. Kaul suggested that Δ_{ij} = 0.2 nm for all i-j pairs.

Figure 1 shows the reduced second virial coefficient as a function of reduced temperature for several values of σ_{ij} at fixed Δ_{ij}. As expected with a square-well potential, B_{ij} increases monotonically with temperature, asymptotically approaching b_{0ij}. However, Figure 1 also shows that at constant reduced temperature, B_{ij} becomes more positive as σ_{ij} rises. This increase in B_{ij} is due to the excluded volume effect as noted by Kaul and Prausnitz (1977).

In this work, following Kaul, we use Equation (8), re-

taining $\Delta_{ij} = 0.2$ nm for all i-j pairs.

For small molecules and their mixtures, we obtain parameters σ and ϵ/k from reduction of second virial-coefficient data. Table 1 gives these parameters for nine pure fluids containing small molecules.

For dissimilar pairs of small molecules, parameter ϵ_{ij}/k is given in Table 2.

For every cross-coefficient B_{ij} $(i \neq j)$, parameter σ_{ij} is found from

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \qquad (9)$$

Second Virial Coefficient of Water and Mixtures Containing Water

Since water is a common constituent in gases from coal gasifiers, it is important to include it in our correlation.

Equation (8) gives a good representation of the second virial coefficient of water when $\Delta = 0.2$ nm (as before) and $\sigma = 0.20$ nm. However, for polar water, the potential energy parameter is split into a nonpolar contribution, designated by superscript (0), and a polar contribution, designated by superscript (1):

$$\epsilon/k = \epsilon^{(0)}/k + \epsilon^{(1)}/kT \qquad (10)$$

When fit to experimental data for water, summarized by Dymond and Smith (1969), $\varepsilon^{(0)}/k = 186K$ and $\varepsilon^{(1)}/k = 1.67\ 10^5\ K^2$. Good agreement between calculated and experimental second virial coefficients is shown in Figure 2.

Reduction of pure-water data alone does not provide unique values for the three adjustable parameters σ, $\varepsilon^{(0)}/k$, and $\varepsilon^{(1)}/k$. The values chosen were those which first, give a physically reasonable σ and second, which are appropriate for calculating cross-virial coefficients for binary aqueous mixtures where the second component is a small, nonpolar molecule. For such mixtures we require that $\varepsilon_{ij} \approx (\varepsilon_i^{(0)} \varepsilon_j)^{1/2}$ where water is designated by subscript i.

Figure 3 shows calculated and experimental second virial cross coefficient B_{12} for three binary aqueous mixtures (Rigby and Prausnitz, 1968 and Coan and King, 1971). Calculations were made with the square-well potential using Equation (9) for σ; well width Δ_{12} was set equal to 0.2 nm and ε_{12} was calculated from

$$\varepsilon_{12} = (\varepsilon_1^{(0)} \varepsilon_2)^{1/2} (1-k_{12}) \qquad (11)$$

where k_{12} is a binary parameter, small compared to unity. (Here 1 refers to water and 2 refers to the second component.) Table 3 gives values of ε_{12}/k and corresponding values of k_{12}.

Figure 4 shows calculated and observed (Kobayashi and Katz, 1953) solubilities for water in compressed propane. Solubilities were calculated as described elsewhere (Rigby and Prausnitz, 1968) where the all-important second virial coefficient B_{12} was calculated using the square-well potential, as indicated above.

Because of experimental evidence of association between water and carbon dioxide in the gas phase (Coan and King, 1971), this binary is given special treatment. The cross virial coefficient B_{12} is split into two contributions (Nothnagel et al, 1973): B_{12} (chemical) and B_{12} (physical). For the chemical contribution to B_{12} we use the relation

$$B_{12}\ (\text{chemical}) = -\frac{1}{2} R\ T\ K_{eq} \qquad (12)$$

where K_{eq} is the equilibrium constant of the association reaction between water and carbon dioxide. De Santis et al (1974) have fitted K_{eq} as a function of temperature from experimental data in the temperature range 25-750 C:

$$\ln K_{eq} = -11.071 + 5953/T - 2746 \times 10^3/T^2 + 464.6 \times 10^6/T^3 \qquad (13)$$

where K_{eq} is in atmosphere and T is in K.

We use Equations (12) and (13) to calculate the chemical contribution to the cross virial coefficient for water-carbon

dioxide. Then, using experimental data of Coan and King (1971) for B_{12}, we found B_{12} (physical) which we fitted using the square-well potential with $\Delta_{12} = 0.2$ nm and using Equation (9) for σ_{12}. The optimum value of ϵ_{12}/k is 186.7 K. Figure 5 compares calculated and experimental cross virial coefficients for water and carbon dioxide.

Parameters for Mixtures Containing Large Molecules

Since tar-containing gases have only very small quantities of heavy hydrocarbons, we are not concerned with the second virial coefficients of pure heavy hydrocarbons. But we are much concerned with cross coefficients $B_{ij}(i \neq j)$ where j is a large molecule. These cross coefficients play a dominant role in Equation (4) for the fugacity coefficient of component j.

Since large molecules can adopt many configurations, the characteristic distance σ is related not only to molecular dimensions but also to molecular flexibility. For such molecules we calculate σ from the radius of gyration r_g as discussed by Kaul and Prausnitz (1977):

$$\sigma/2 = r_g + (\sigma/2 - r_g)_{\text{methane}} \qquad (14)$$

For methane, $\sigma/2 = 0.1675$ and $r_g = 0.0443$ nm.

Using molecular-structure data (Bower and Sutton, 1965), we have calculated radii of gyration for a number of heavy

hydrocarbons. Details are given elsewhere (Thompson and Braun, 1968 and Kaul, 1977) but some results are shown in Table 4. For σ_{ij} ($i \neq j$), we use Equation (9).

As before, we use Λ_{ij} = 0.2 nm. The remaining parameter is ϵ_{ij}/k. As discussed by Kaul and Prausnitz (1978), this parameter (for a fixed light component i) is related to the (Hildebrand) enthalpy of vaporization* of the heavy component j. Figure 6 gives a correlation for ϵ_{ij}/k as a function of Hildebrand enthalpy of vaporization for component j. For heavy components, whose Hildebrand enthalpy of vaporization ΔH is in excess of 10 K-cal/mole, Table 5 shows analytical correlations for ϵ_{ij}/k as a function of Hildbrand enthalpy of vaporization of component j.

Radius of Gyration for Tar Cuts

To calculate B_{ij} (where i is a small molecule and j is a large molecule), we use Equation (9) to find σ_{ij}. For small molecule i, Table 1 gives σ_i. We now discuss a procedure for calculating σ_j which is related to radius of gyration r_g through Equation (14), written below in a slightly different form

*The (Hildebrand) enthalpy of vaporization is defined as the enthalpy of vaporization at the temperature where the molar volume of the saturated vapor is 49.5 liters.

$$\frac{\sigma_j}{2} = 0.1232 + r_{g_j} \quad \text{(nm)} \qquad (15)$$

For convenience, we now drop subscript j, keeping in mind that the discussion below refers to large molecules.

We are concerned with a hydrocarbon tar cut which is characterized by a normal boiling point T_b (in Kelvins) and a hydrogen-to-carbon ratio, designated by H/C. These characterizing parameters can be obtained from distillation and elemental-analysis measurements as discussed by Macknick and Prausnitz (1979).

At one extreme, the tar cut may contain only saturated (alkane) hydrocarbons. In that case

$$(H/C)_{sat} = 2 + 2\,(n+1)^{-1} \qquad (16)$$

where n = number of carbon linkages.* For the radius of gyration (nanometers) of a saturated hydrocarbon

$$(r_g)_{sat} = 0.0637\, n^{0.6}\,(1+0.547/n)^{1/2} \qquad (17)$$

Equation (17) is based on the molecular-dynamic studies of Bellemans (1973).

The number of carbon linkages is given by

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*For example, in normal heptane, n = 6.

$$n = \exp\ (-0.128814+0.55811\times10^{-2}T_b-0.940000\times10^{-6}T_b^2) \qquad (18)$$

Equation (18) is based on boiling point data for normal alkanes from C_6 to C_{40}. It holds for the normal-boiling-point range 340-800 K.

At the other extreme, a tar cut may be completely aromatic in which case

$$(H/C)_{ar} = \frac{6 + 2\ (N-1)}{6 + 4\ (N-1)} \qquad (19)$$

where N is the number of fused rings in the aromatic.* N is related to the normal boiling point of fused-ring aromatics (benzene, naphthalene, anthracene, and chrysene) by

$$N = -\ 1.9256 + 8.124\ 10^{-3}\ T_b \qquad (20)$$

Using structural data, the radius of gyration of these aromatics was correlated with N by

$$(r_g)_{ar} = 0.0794 + 0.0389\ N \quad (nm) \qquad (21)$$

Equations (20) and (21) cover the normal boiling point range 350-720 K.

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*For example, N = 1 for benzene, 2 for naphthalene, 3 for anthracene.

A typical tar cut is neither completely saturated (alkane) nor completely aromatic. We define D, the fraction of the cut which is alkane, by

$$D \equiv \frac{(H/C) - (H/C)_{ar}}{(H/C)_{sat} - (H/C)_{ar}} \tag{22}$$

For any hydrocarbon cut whose carbon number is greater than 6 and where we know T_b and (H/C), we propose to calculate the radius of gyration by linear interpolation with respect to D

$$r_g = (r_g)_{ar} + D\,[(r_g)_{sat} - (r_g)_{ar}] \tag{23}$$

Figure 7 shows radius of gyration as a function of T_b and D.

Calculated radii of gyration for toluene and ethylbenzene using Equation (22) are in excellent agreement with values reported by Thompson and Braun (1968) after dividing by the appropriate factor $(2\ \text{Å})^{1/2}$.

Calculation of Parameter ε_{ij}/k for Mixtures where i is a Light Gas (or Water) and j is a Tar Cut

For a tar cut interacting with a light gas or water, ε_{ij}/k is calculated using Figure 6 or Table 5. To use the

results given here, we require the Hildebrand enthalpy of vaporization; we obtain this from vapor-pressure characteristics of the tar cut using the Clausius-Clapoyron equation. The vapor pressure characteristics of a tar cut are determined using the SWAP method as discussed by Smith et al (1976), Macknick et al (1978) and Macknick and Prausnitz (1979).

Illustrative Calculations for Fugacity Coefficients and Dew Points of Pseudo Components

Fugacity coefficients for two tar cuts were calculated, each at infinite dilution in methane, as a function of temperature for several isobars. The tar cuts were obtained by fractionation, as discussed by Macknick (1978), from coal tar obtained from the Synthane coal-gasification process. The average normal boiling point of the first cut is 528 K whereas that of the second is 747 K. Table 6 gives the properties of the two cuts. Figures (8) and (9) show that at pressures above 10 bars, significant deviations from ideal-gas behavior are likely, particularly as the temperature of the gas falls.

To demonstrate the effect of fugacity coefficients on phase equilbrium calculations, Table 7 presents calculations of condensation conditions for a mixture of two pseudo-components in methane. The mixture contains two tar cuts whose properties are listed in Table 6. Prior to condensation, the mole fractions of the cuts are, respectively, 2.0×10^{-4}

and 1.0×10^{-4}.

Table 7 shows that at 80 bars, failure to take fugacity coefficients into account introduces only a small error in dew-point temperatures. However, the corresponding error in percent condensed is large.

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Table 1

Square-Well Parameters for Nine Pure Fluids Containing Small Molecules (Well Width Δ = 0.2 nm)

Fluid	σ, nanometers	ε/k, K
1-Hydrogen	0.245	18.7
2-Nitrogen	0.327	89.1
3-Carbon Monoxide	0.325	92.6
4-Methane	0.335	141
5-Ethane	0.403	259
6-Carbon Dioxide	0.357	211
7-Hydrogen Sulfide	0.387	272
8-n-Propane	0.465	346
9-n-Butane	0.514	425

Table 2

Square-Well Parameters ε_{ij}/k for All Pairs of Small Molecules (i = j) Shown in Table 1

Pair	ε_{ij}/k, K	Pair	ε_{ij}/k, K
1-2	43.5	3-7	(127)
1-3	(43.5)*	3-8	(178)
1-4	50.3	3-9	(182)
1-5	59.5	4-5	197
1-6	(58.0)	4-6	171
1-7	(55.0)	4-7	154
1-8	79.7	4-8	231
1-9	84.0	4-9	258
2-3	(89.1)	5-6	222
2-4	106	5-7	237
2-5	151	5-8	295
2-6	141	5-9	331
2-7	127	6-7	245
2-8	178	6-8	251
2-9	182	6-9	272
3-4	(106)	7-8	(278)
3-5	(151)	7-9	(310)
3-6	145	8-9	379

*Quantities in parentheses are estimates.

Table 3

Square-Well Parameter ε_{12}/k for Water (1) and a Small Molecule (2)

Component (2)	ε_{12}/k, K	k_{12}
Hydrogen	(56)#	0.05
Nitrogen	131	0
Carbon Monoxide	(131)	0
Methane	162	0
Ethane	221	0
Hydrogen Sulfide	225	0
n-Propane	(245)	0.03
n-Butane	(304)	0.06

For Water-Carbondioxide see text.

#Quantities in parentheses are estimates.

Table 4

Radius of Gyration for Some Large Cyclic Molecules from Structural Data

Molecule	r_g, nanometers
Cyclohexane	0.1301
Benzene	0.1192
Naphthalene	0.1590
Anthracene	0.1896
Naphthacene	0.2253
Chrysene	0.2466

Table 5

Energy Interaction Parameter

for Coal Tar-Light Gas Binaries*

ε_{ij}/k is in K, ΔH^V is in Kcal/mole

Hydrogen Binaries

$$\varepsilon_{ij}/k = 146$$

Nitrogen and Carbonmonoxide Binaries

$$\varepsilon_{ij}/k = 266 - 603 \exp (-0.294 \Delta H_j^V)$$

Methane Binaries

$$\varepsilon_{ij}/k = 395 - 915 \exp (-0.224 \Delta H_j^V)$$

Ethane and Hydrogensulfide Binaries

$$\varepsilon_{ij}/k = 477 - 870 \exp (-0.255 \Delta H_j^V)$$

Carbondioxide Binaries

$$\varepsilon_{ij}/k = 437 - 915 \exp (-0.224 \Delta H_j^V)$$

n-Propane Binaries

$$\varepsilon_{ij}/k = 532 - 870 \exp (-0.255 \Delta H_j^V)$$

n-Butane Binaries

$$\varepsilon_{ij}/k = 576 - 870 \exp (-0.255 \Delta H_j^V)$$

Water Binaries

$$\varepsilon_{ij}/k = 420 - 915 \exp (-0.224 \Delta H_j^V)$$

---

*These correlations are valid only if ΔH_j^V, the (Hildebrand) enthalpy of vaporization, is greater than 10 Kcal/mole. For lighter second components, use either Tables 1, 2, 3 or Figure 6. ΔH_j^V is found from limited vapor-pressure data as discussed by Macknick and Prausnitz (1979).

Table 6

Properties of Two Tar Cuts from Synthane Process

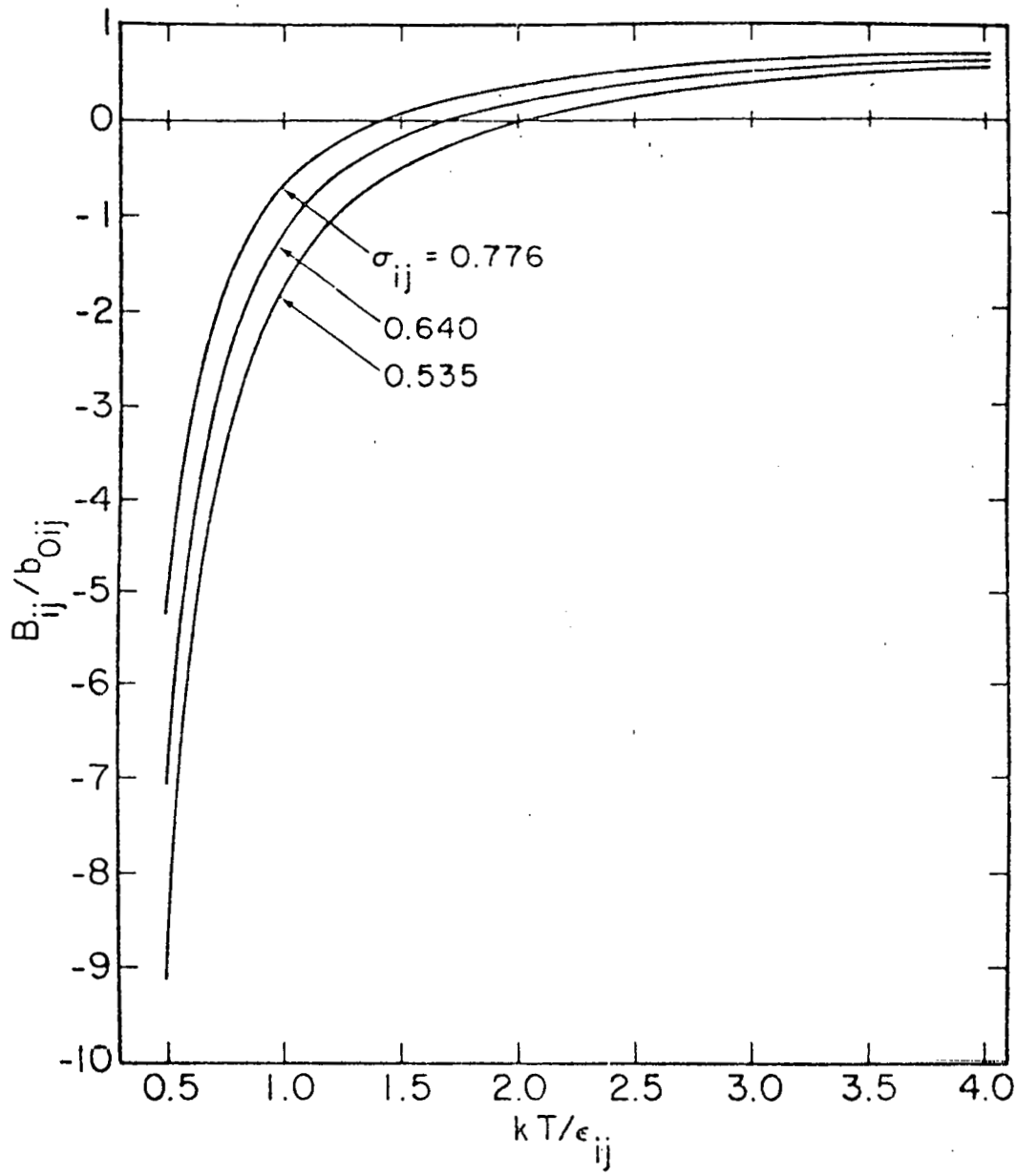
	Cut # 5	Cut # 12
T_b, K	528	747
N (equivalent aromatic)	2.364	4.143
$(H/C)_{ar}$	0.762	0.662
n (equivalent alkane)	12.88	33.64
$(H/C)_{sat}$	2.144	2.058
(H/C)	1.230	1.005
D	0.339	0.246
$(r_g)_{ar}$, nm	0.173	0.244
$(r_g)_{sat}$, nm	0.301	0.530
r_g, nm	0.216	0.314
σ_2, nm	0.680	0.875
σ_{12}, nm*	0.508	0.605
ΔH^V, Kcal/mole	12.13	18.41
ϵ_{12}/k, K*	334.5	380.1

*Component 1 is Methane

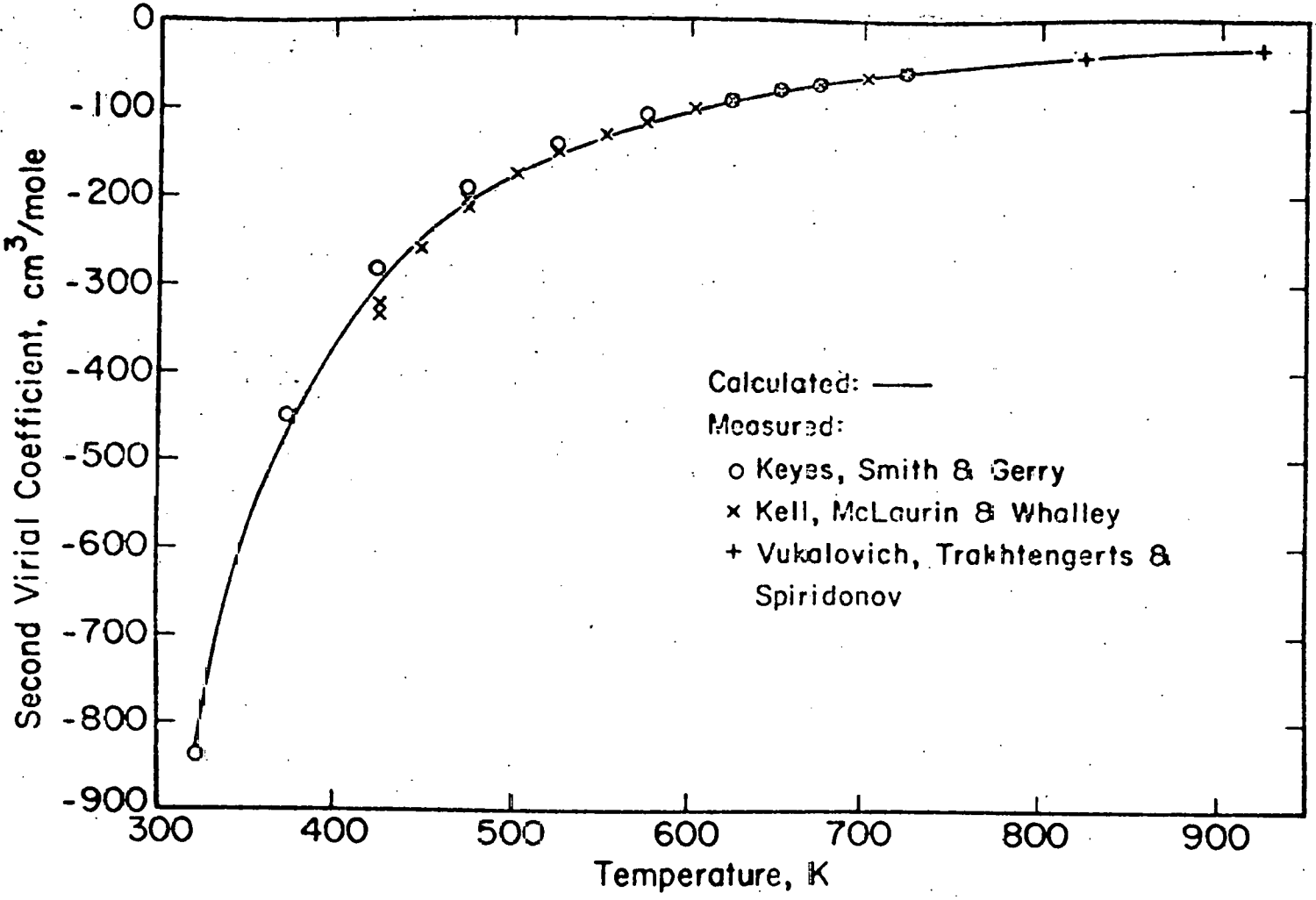
Table 7

Effect of Fugacity Coefficient on Condensation Conditions at 80 Bars Total Pressure

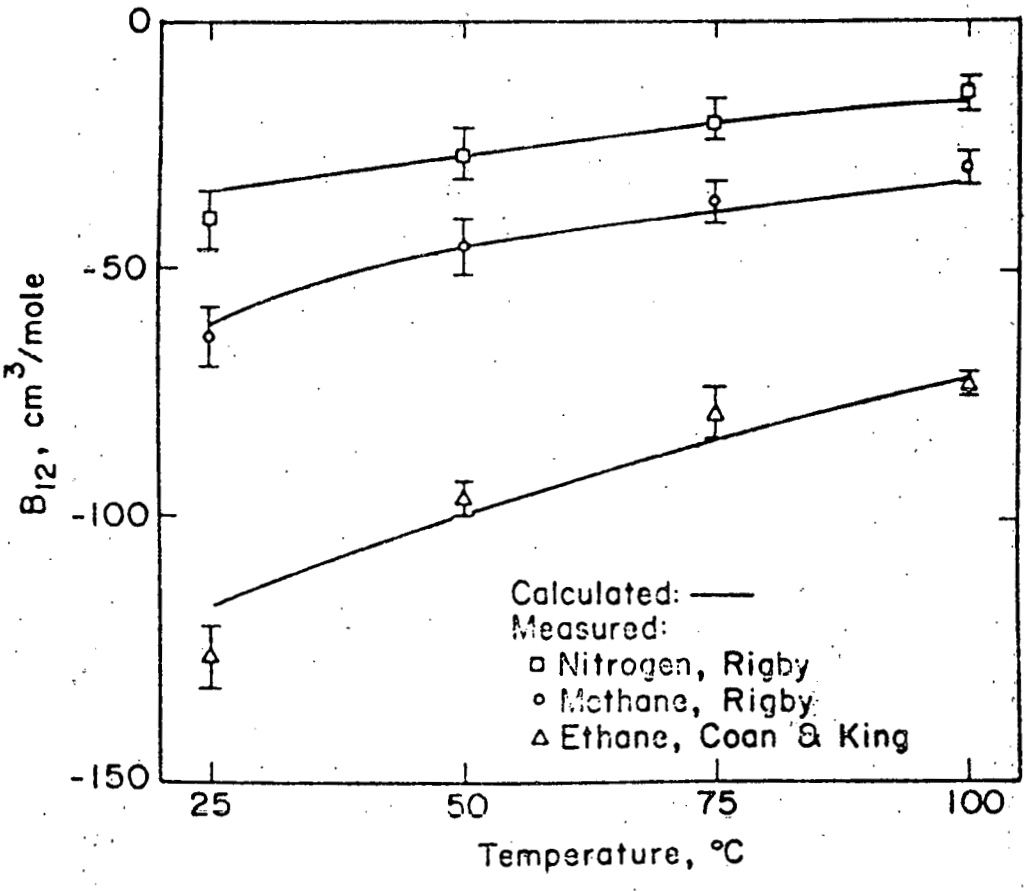
	Assuming Ideal Gas Phase $\phi = 1$	Correcting for Gas-Phase Nonideality $\phi \neq 1$
Dew Point Temperature, K	545	534
Mole Percent of Tar Condensed at T = 525 K	21.4	11.7



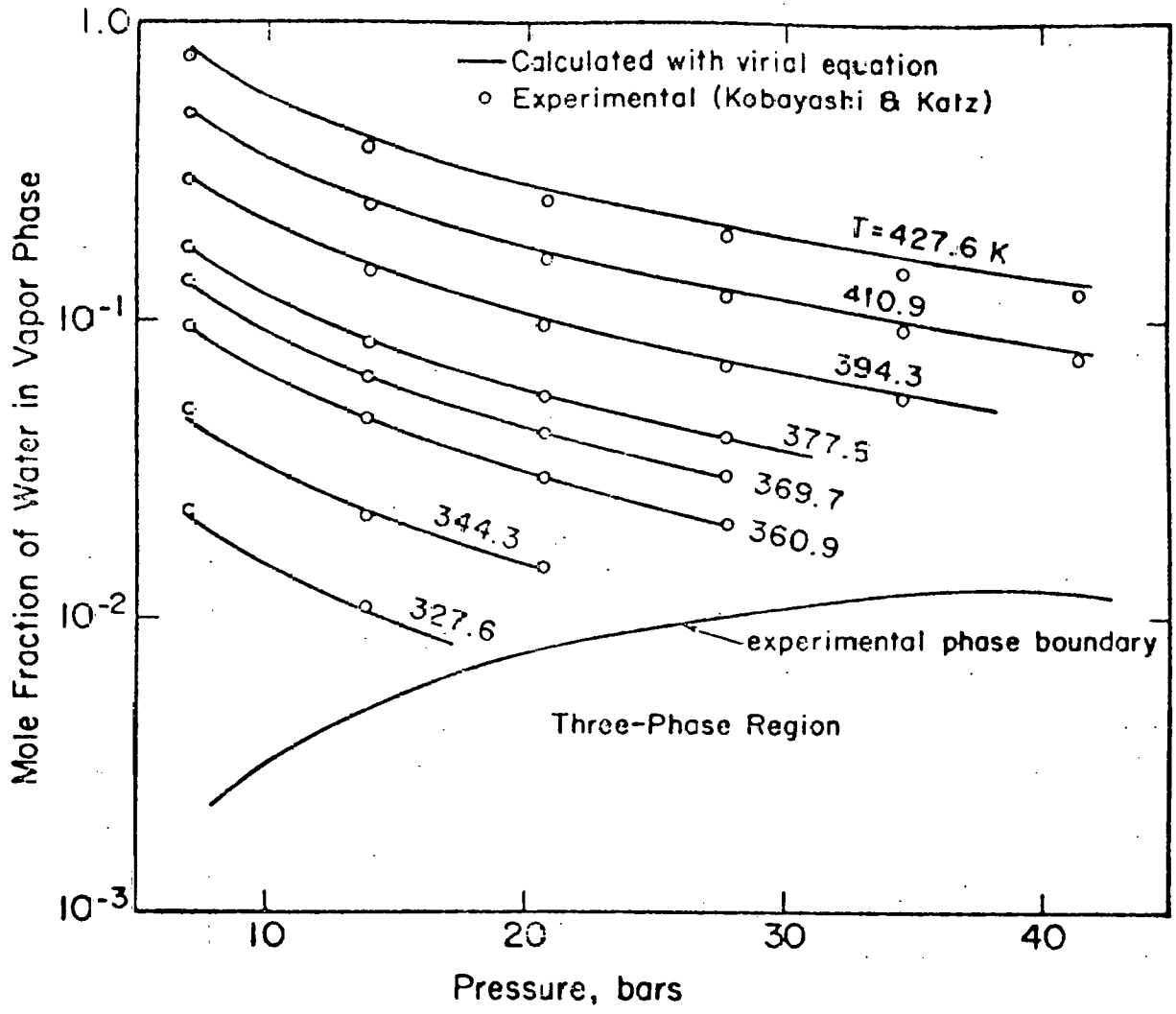
Reduced Second Virial Coefficient for a Pair of i-j Molecules Calculated from the Square-Well Potential with Well-Width Δ_{ij} = 0.2 nanometers. The units of σ_{ij} are nanometers. The values shown are for binary pairs containing methane and n-$C_{10}H_{22}$; n-$C_{16}H_{34}$; and n-$C_{30}H_{62}$.



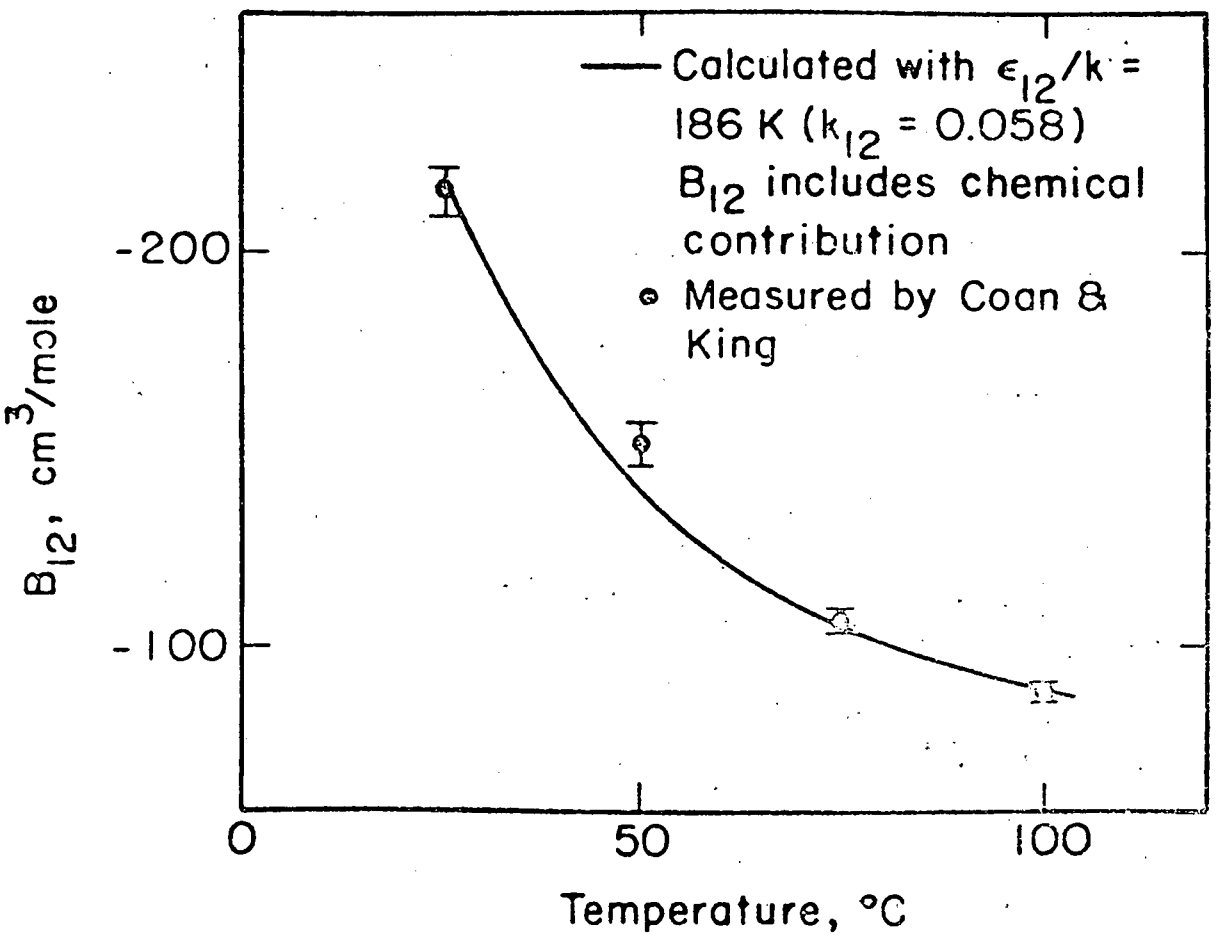
Calculated and Experimental Second Virial Coefficient for Water



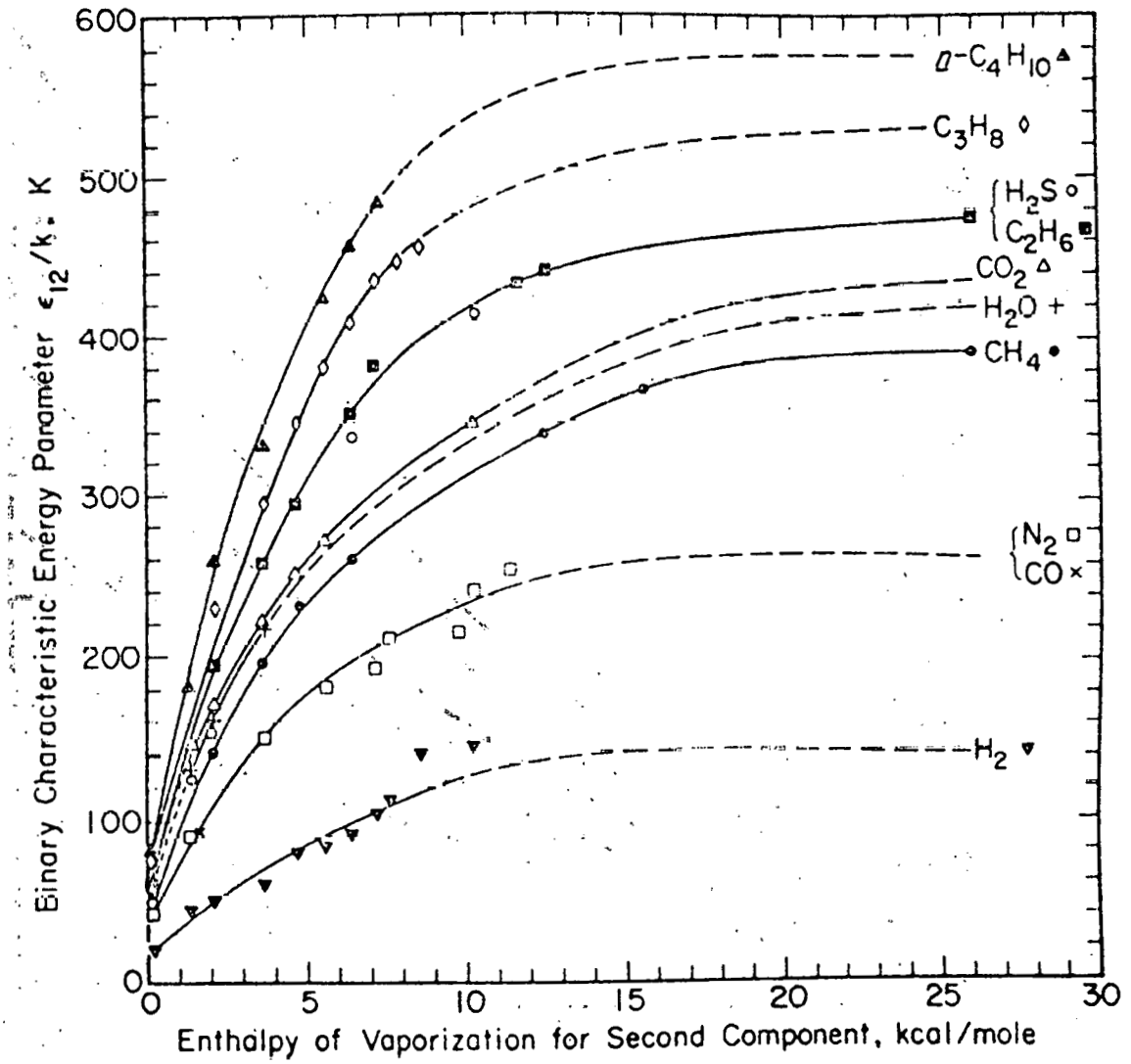
Calculated and Experimental Second Virial Cross Coefficients for Three Binary Aqueous Systems



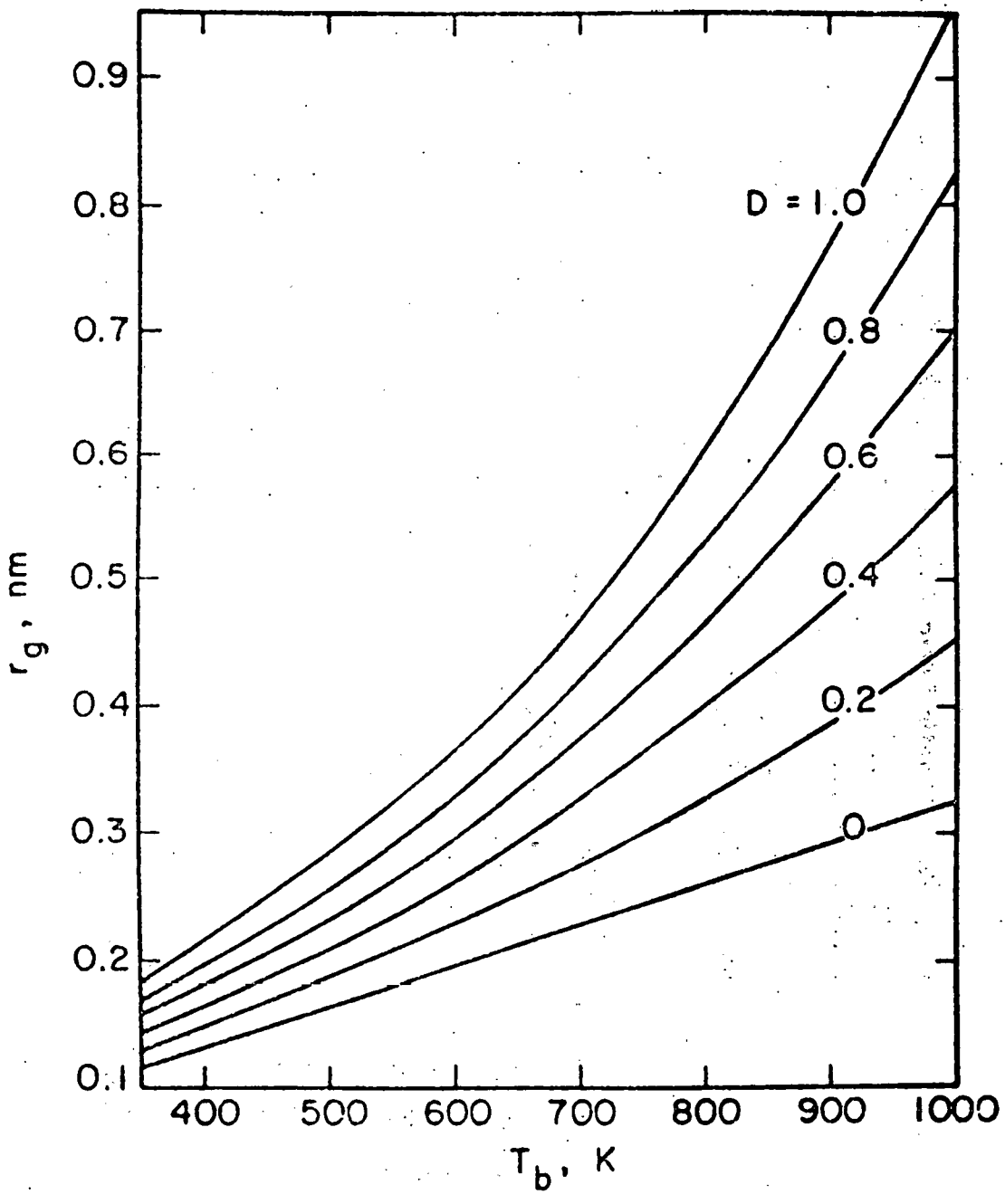
Calculated and Experimental Solubility of Water in Compressed Propane



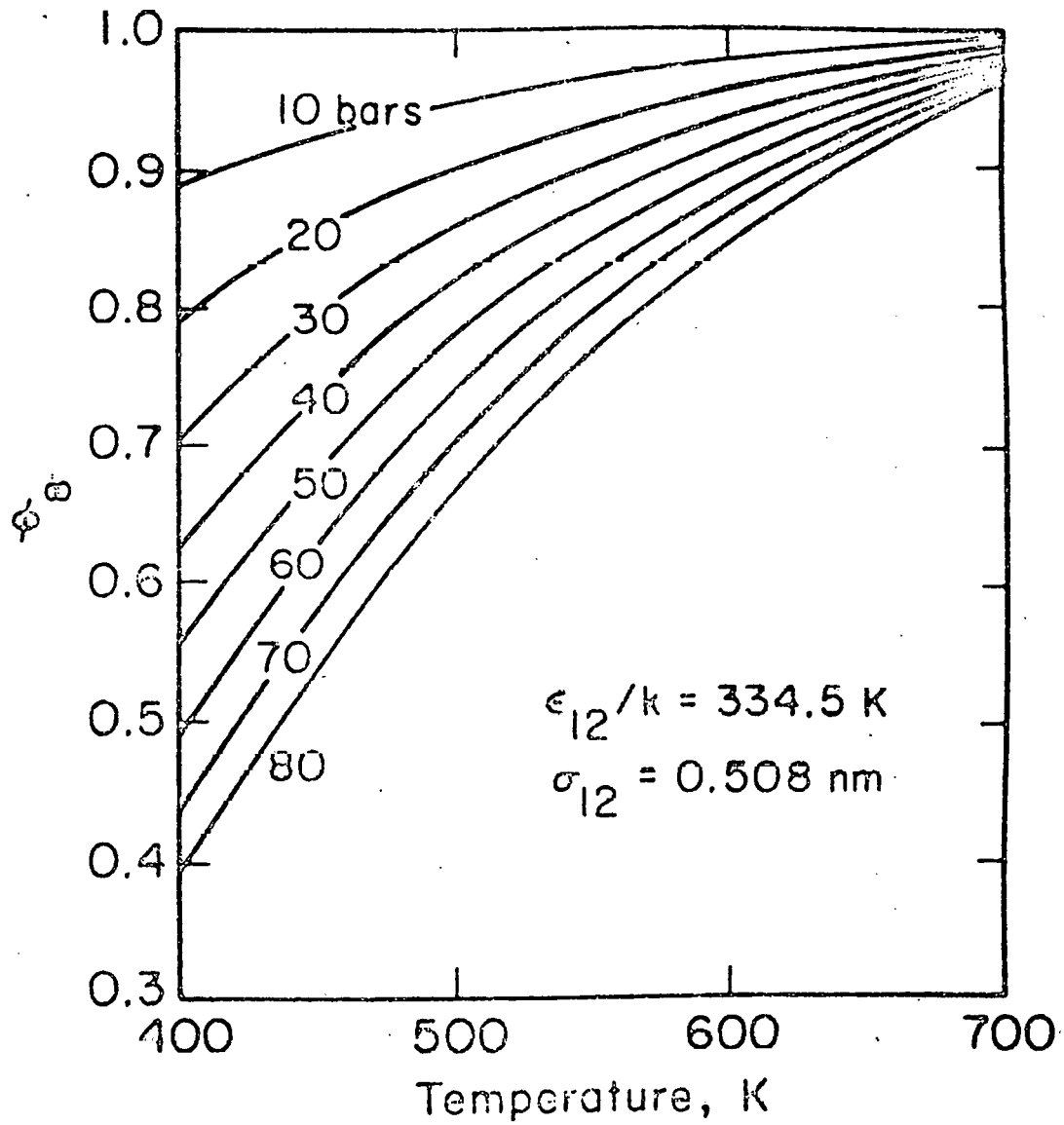
Calculated and Experimental Second Virial Cross Coefficients for Water—Carbon Dioxide



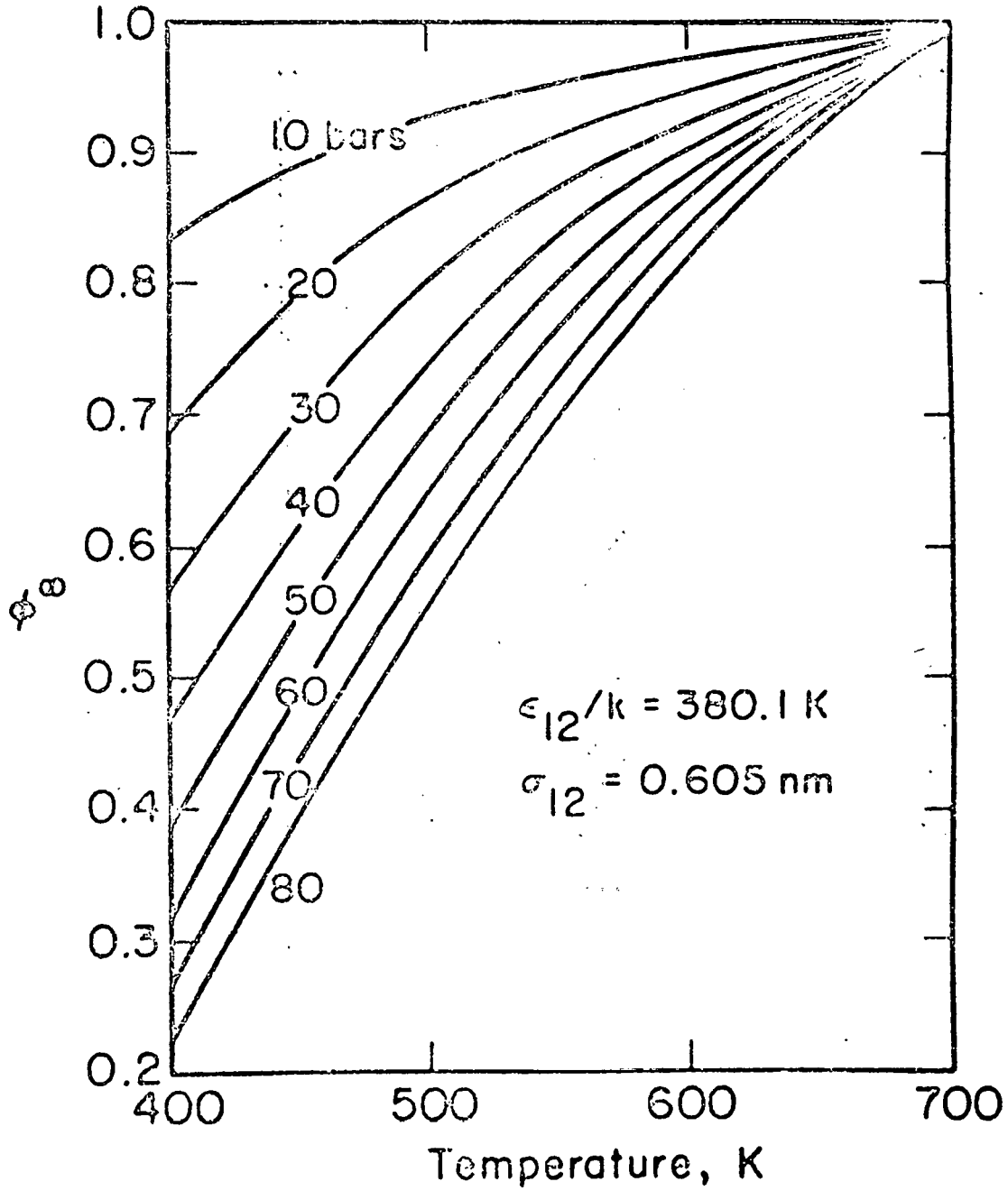
CHARACTERISTIC ENERGY PARAMETER ϵ_{12}/k FOR LIGHT-GAS (1)–HEAVY-HYDROCARBON (2) AS A FUNCTION OF (HILDEBRAND) ENTHALPY OF VAPORIZATION FOR COMPONENT (2).



Radius of Gyration for Tar Cuts as a Function of Normal Boiling Point and Fraction Saturated (Alkane)



Fugacity Coefficient of Synthane Tar Cut No. 5 in Methane at Infinite Dilution



Fugacity Coefficient of Synthane Tar Cut No. 12 in Methane at Infinite Dilution

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APPENDIX III

VAPOR PRESSURES OF HIGH-MOLECULAR-WEIGHT HYDROCARBONS

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 by-product 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

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

$$f_i^c = x_i \gamma_i f_i^0 \qquad (3)$$

where, for component (i), y_i and x_i are the mole fractions in the vapor and condensed phases, respectively; ϕ_i is the fugacity coefficient, γ_i is the activity coefficient and P is the total system pressure. Reference fugacity f_i^0 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 equation (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 semi-theoretical correlations to extrapolate to normal-boiling-point temperatures.

A modification of Sinke's apparatus (1974) was used to measure vapor pressures in the range 10^{-1} to 10^{-3} Torr.

Vapor pressures were measured for liquids n-octadecane, n-eicosane, 1-methyl-naphthalene, and 2-ethyl-naphthalene, and for solids naphthalene, anthracene, and phenanthrene. For liquids, extrapolation to higher temperatures is based on the modified SWAP method described by Macknick et al. (1978) For solids, extrapolation is based on the Clapeyron equation and on the SWAP method of Smith et al. (1976).

Experimental

A modification of Sinke's gas saturation method (1974) 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), the saturation pressure of the hydrocarbon P(sat) can be calculated by

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

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 equation (4),

[P(sample)/P(atmo)], is a correction for pressure drop through the system; this term is usually very close to unity at the low flowrates 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 gms of 3.2-mm alumina pellets containing 0.5 weight percent 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.

The IR analyzer is calibrated for three ranges: 0-350, 0-800, 0-2500 ppm CO_2 by volume. Calibration is achieved using eight Primary-Standard gas mixtures from Matheson Gas Products Company. 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 N.B.S.-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 by-passing 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 hours to remove inpurities. Hydrocarbon sample sizes are approximately 5 gm per cell. Liquid samples contain 2-mm glass helicies 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 to 72 hours 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^3s^{-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 minutes. Since the CO_2 concentration should not be a function of flowrate, the flowrate was varied between 0.1-5.0 (NTP) cm^3s^{-1}. No flowrate effect was observed.

Previous tests with catalyst-bed temperatures indicate that even at 300-400 C, complete combustion is achieved. All runs are monitored for at least two hours 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 flowrate and catalyst temperature, indicates complete saturation and combustion of the pure hydrocarbon.

Results

Tables 1 and 2 present vapor pressures for 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

$$\ell n\ P(sat) = A + B/T \qquad (5)$$

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 Claperyon equation gives a good estimate of random experimental uncertainty. For the data reported here, an equation using 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 (1974) 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). This error is approximately equal to the 0.8-2.7% 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. (1978), the data reported here are 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. (3) 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 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, vapor pressures for high-molecular-weight hydrocarbons in the range 10^{-3} to 10^{3} Torr can be estimated from experimental data at near-ambient temperature for both solids and liquids.

Nomenclature

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

ϕ	Fugacity coefficient
γ	Activity coefficient

Subscripts

i	Component (i)
m.p.	Melting point
0.01,10,760	At pressures of 10^{-2}, 10, and 760 Torr, respectively

Superscripts

c	Condensed phase
0	Standard state
v	Vapor phase

Literature Cited

Macknick, A. B., Winnick, J., Prausnitz, J. M., A.I.Ch.E. J., 24 (4), 731 (1978).

Sinke, G. C., J. Chem. Thermo., 6, 311 (1974).

Smith, G., Winnick, J., Abrams, D. S., Prausnitz, J. M., Can. J. Chem. Eng., 54, 337 (1976).

Table 1: Vapor Pressures of Four High-Molecular-Weight, Liquid Hydrocarbons

n-Octadecane		n-Eicosane	
t,C	P(sat),Torr*10^3	t,C	P(sat),Torr*10^3
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	Average Error in	
84.10	53.6	P(sat) = 1.6%	
88.10	72.9	A = 26.849	
Average Error in		B = -11230.	
P(sat) = 2.2%			
A = 25.548			
B = -10165.			

Table 1 continued

1-Methyl-Naphthalene

t,C	P(sat),Torr*10^2
5.70	1.32
11.40	2.19
18.10	3.94
22.15	5.35
28.85	9.45
32.25	11.8
34.90	14.2
38.60	17.6

Average Error in P(sat) = 2.0%

A = 20.552

B = -6933.2

2-Ethyl-Naphthalene

t,C	P(sat),Torr*10^2
13.05	1.15
17.90	1.66
22.90	2.55
29.50	4.66
34.85	7.35
39.40	9.87
45.10	15.0

Average Error in P(sat) = 2.7%

A = 21.485

B = -7435.9

Table 2: Vapor Pressures of Three High-Molecular-Weight, Solid Hydrocarbons

Naphthalene

t,C	P(sat),Torr*10^2
7.15	1.32
12.80	2.35
18.40	4.19
18.85	4.45
26.40	9.44
31.85	15.4

Average Error in P(sat) = 1.1%

A = 26.250

B = -8575.

Phenanthrene

t,C	P(sat),Torr*10^3
51.60	3.49
57.00	6.10
61.85	9.91
67.35	15.9
71.80	23.2
78.90	42.4
83.40	66.7
90.30	109.0

Average Error in P(sat) = 2.3%

A = 26.648

B = -10484.

Anthracene

t,C	P(sat),Torr*10^3
85.25	6.69
90.15	10.2
95.65	16.4
100.70	24.9
104.70	34.4
111.90	60.3
116.40	85.2
119.95	110.0

Average Error in P(sat) = 0.8%

A = 26.805

B = -11402.

Figure 1. Gas-Saturation Apparatus for Vapor-Pressure Measurements

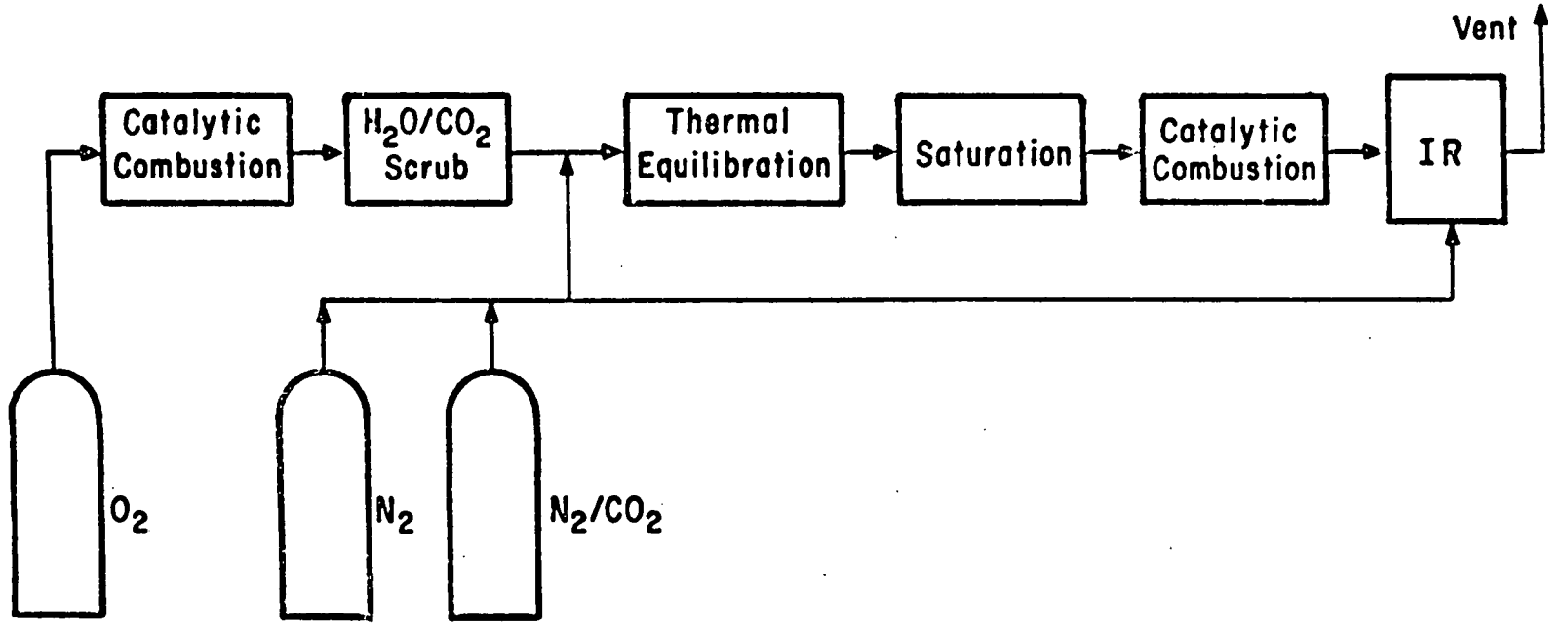


Figure 2. Saturation/Combustion Portion of Gas-Saturation Apparatus

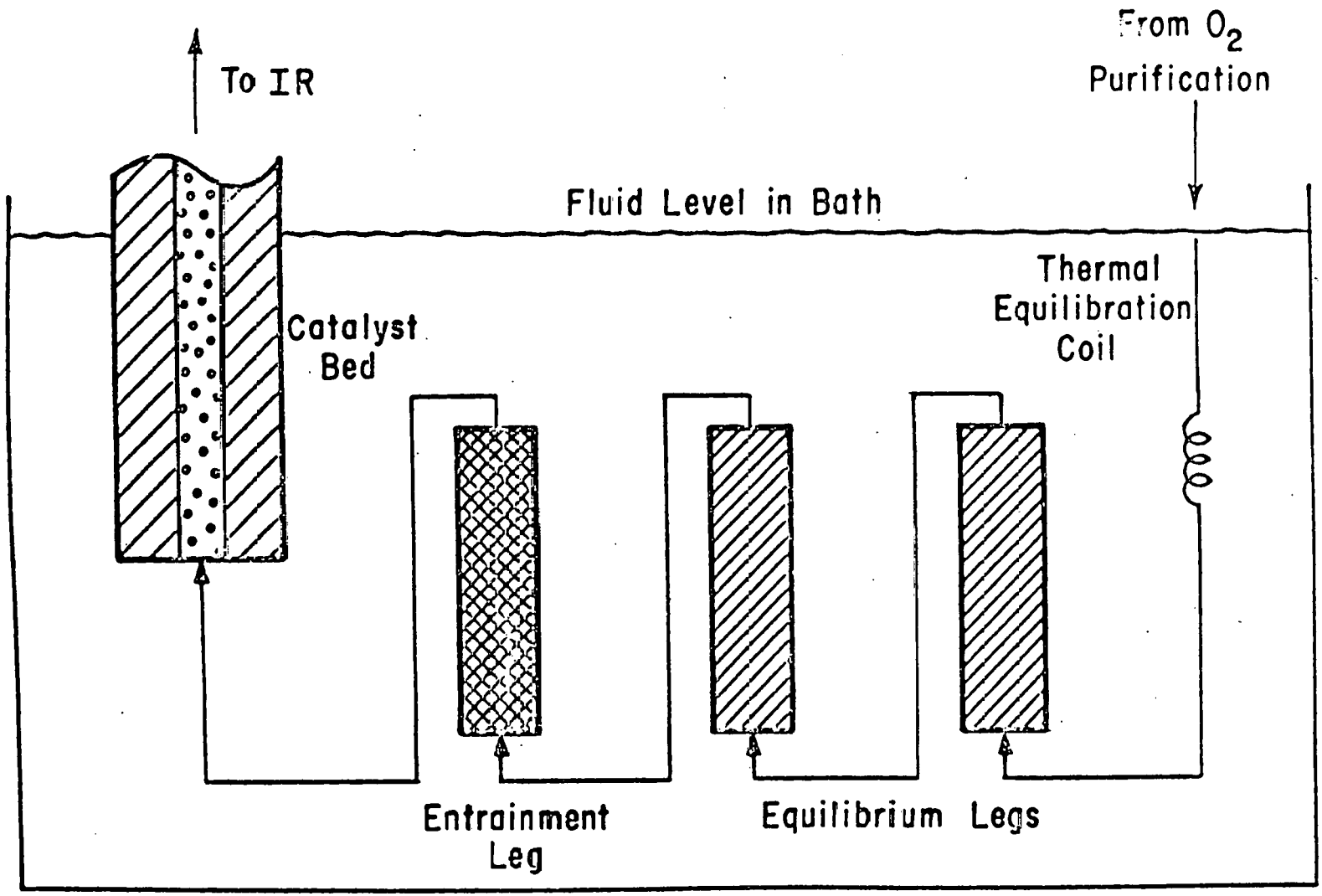


Figure 3. Extrapolation of Vapor-Pressure Data for n-Eicosane at Near-Ambient Temperatures to the Normal Boiling Point, Using SWAP Method ($t_{0.01}$ = 83.85 C; $F_A = F_B = F_N = 0.0$)

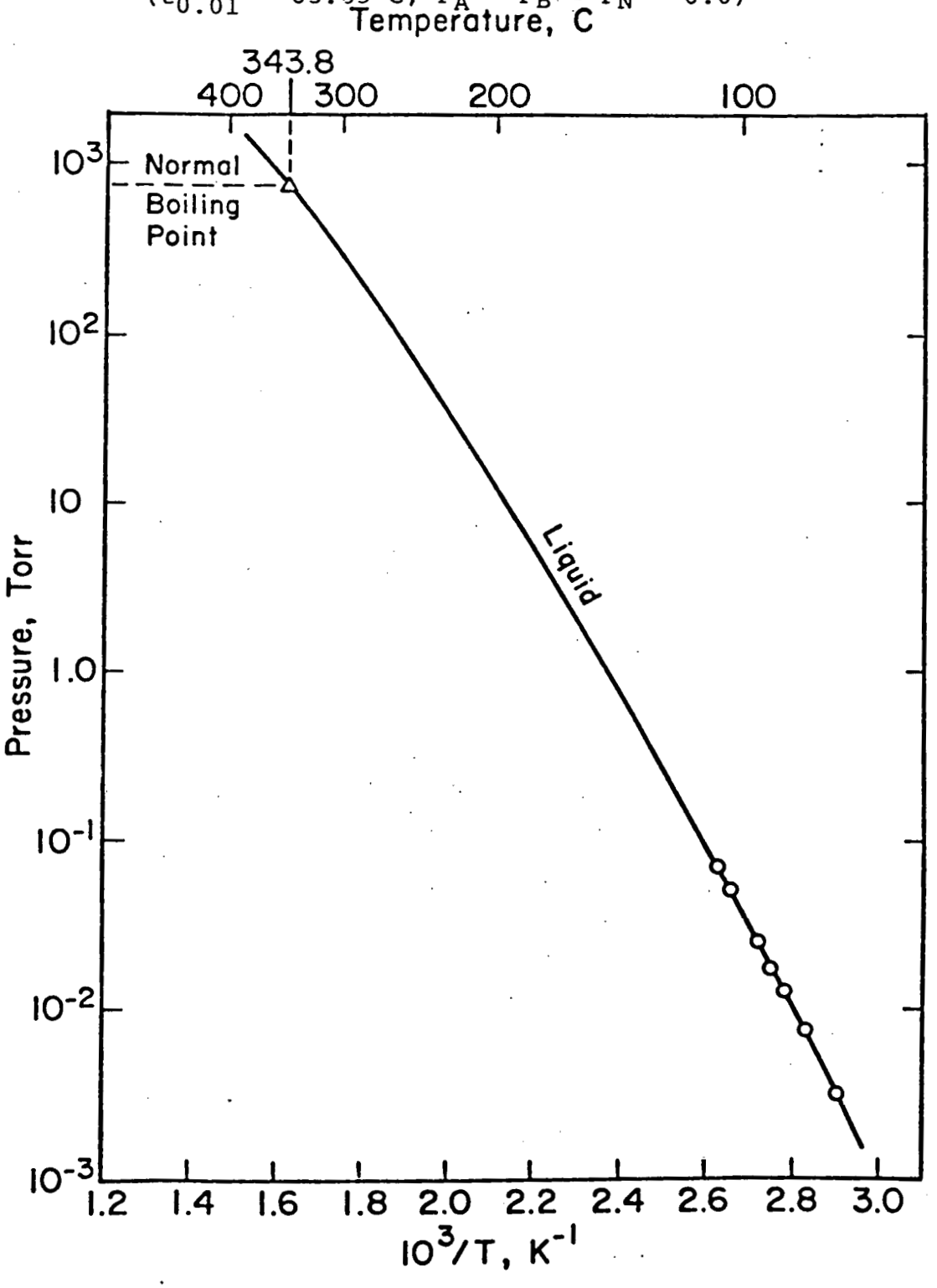
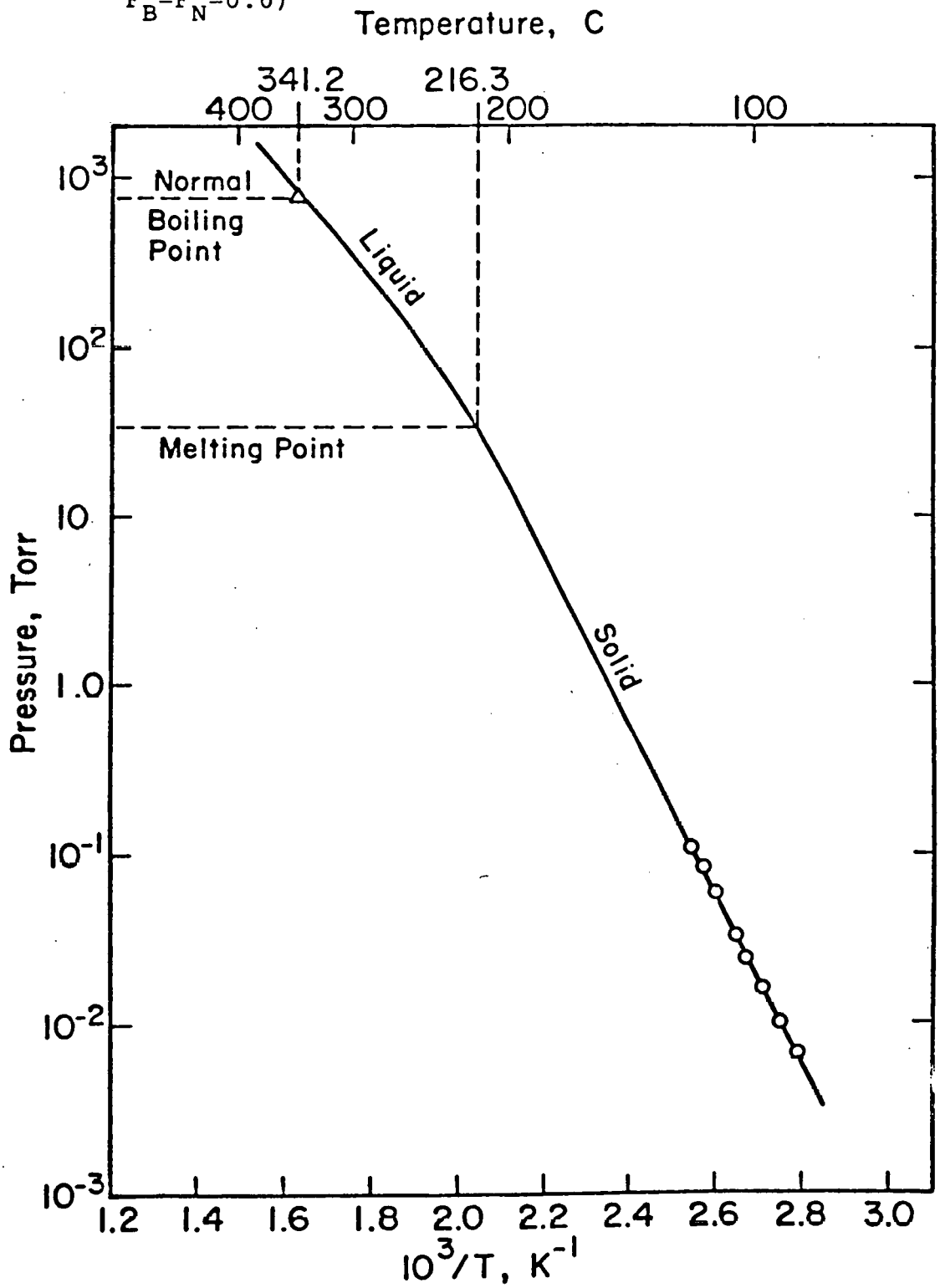


Figure 4. Extrapolation of Vapor-Pressure Data for Anthracene at Near-Ambient Temperatures to the Normal Boiling Point, Using SWAP Method ($t_{m.p.}$ = 216.3 C; $P(sat)_{m.p.}$ = 33.4 Torr; F_A = F_B=F_N=0.0)



APPENDIX IV

ESTIMATION OF VAPOR PRESSURES OF HIGH-BOILING FRACTIONS IN LIQUIFIED FOSSIL FUELS CONTAINING HETEROATOMS NITROGEN OR SULFUR

Heavy hydrocarbons and their derivatives are of increasing interest in fossil-fuel technology, including coal liquefaction and gasification. Following primary liquefaction or gasification, separation operations are required for purifying the product. Design of separation equipment requires quantitative data for physical properties, in particular, vapor pressures. However, little is known about the vapor pressures of heavy hydrocarbons and their derivatives, especially those that are aromatic.

In 1976, Smith et al. (1976) correlated vapor-pressure data for heavy hydrocarbons in the region 10-2,000 torr; the resulting SWAP correlation is reliable to $\pm$10% and can be extrapolated with good results to lower pressures (Macknick, 1978). The SWAP correlation is based on Prigogine's (1957) theory of polysegmented molecules. One of its main advantages is that in characterizing the hydrocarbon, critical properties are not used; fractions of aromaticity, napthenicity, branching and heteroaromaticity are used rather than specific structural information which is required to estimate critical properties. This is important especially for mixtures of complex hydrocarbons where structure is difficult, if not impossible, to determine. Currently available methods for estimating critical properties, based on results for fluids of low and intermediate molecular weight, may not be reliable for high-molecular-weight materials.

In this work we extend SWAP to include hydrocarbon derivatives containing either nitrogen or sulfur as heteroatoms and present evidence showing that the extended correlation is applicable to narrow-boiling petroleum fractions and coal-derived liquids.

SWAP Correlation

For the region 10-2,000 torr, Smith et al (1976) proposed that vapor pressure P is related to absolute temperature T by

$$\ell n \ \tilde{P} = A + B/\tilde{T} + C/\tilde{T}^2 \qquad (1)$$

where reduced pressure $\tilde{P}$ and reduced temperature $\tilde{T}$ are given by

$$\tilde{P} = P/P^*; \ \tilde{T} = T/T^* \qquad (2)$$

Here P* and T* are parameters characterizing the fluid. Coefficients A, B, and C are functions only of molecular flexibility c/n, where n is the number of carbon atoms and 3c is the number of external degrees of freedom (density-dependent rotations and vibrations, in addition to translation) per molecule. These functions are of the form

$$A, \ B \text{ or } C = 1/r \ \ell n\{ (DX^E)^r + (FX^G)^r\} \qquad (3)$$

where $X = (c/n - 0.167)^{-1}$. Parameters D, E, F, G and r are shown in Table 1.

Equation (1) was originally applied to large normal paraffins, where experimental data are relatively plentiful. Vapor pressures of other hydrocarbons are correlated as perturbations about a closely related normal paraffin. We first determine the number of carbon atoms in the normal paraffin which would have a normal boiling point (T_{760}) equal to that of the hydrocarbon in question. This is the effective carbon number of the hydrocarbon,

$$n_{effective} \equiv \left(\frac{3.03191 - \ell n(1078-T_{760})/2.303}{0.04999}\right)^{1.5} \qquad (4)$$

If the normal boiling point is not known, it can be estimated for normal paraffins as shown by Macknick (1978), from another vapor-pressure datum, at a temperature below, possibly far below, the normal boiling point. For compounds other than paraffins, two methods are outlined in Appendix

II to estimate normal boiling point.

For the normal paraffin which has the same T_{760} as that of the compound of interest

$$(c/n)_{\substack{\text{normal}\\\text{paraffin}}} = 0.167 + 1.022/n_{effective} - 0.189/n^2_{effective} \quad (5)$$

To correct for aromaticity, naphthenicity and branching, Smith et al. write

$$c/n = (c/n)_{\substack{\text{normal}\\\text{paraffin}}} + \Delta c/n \quad (6)$$

where

$$\Delta c/n = (0.1319F_A + 0.2429F_N + 0.1992F_B)\exp(-2.532\times10^{-3} T_{760}) \quad (7)$$

where

F_A = fraction of carbon atoms which are part of an aromatic ring

F_N = fraction of carbon atoms which are naphthenic (part of a saturated ring)

F_B = fraction of carbon atoms which are in a terminal branch:

$F_B = (\ell_{CH_3} - 2)/\ell$ where ℓ_{CH_3} is the number of CH_3 groups and ℓ is the total number of carbon atoms, per molecule $(F_B \geq 0)^\dagger$

For parameter P*, a similar procedure is followed

$$P^* = P^*_{\text{normal paraffin}} + \Delta P^* \quad (8)$$

$$P^*_{\text{normal paraffin}} = 5.78 \times 10^5 \exp\{-4.7222/(T_{760} - 100)\} \quad (9)$$

$$\Delta P^* = (0.72F_A + 0.27F_N - 0.65F_B)\ 10^5 \quad (10)$$

where the units of P* are torr.

Parameter T* is evaluated from Equation (1) using one vapor-pressure datum.

† For example for toluene, $\ell_{CH_3} = 1$ and $\ell = 7$. However, we use $F_B = 0$ for toluene.

Extension to Hydrocarbon Derivatives Containing Either Nitrogen or Sulfur

To achieve the desired extension, experimental vapor-pressure data were studied for 21 sulfur-containing and 14 nitrogen-containing fluids (Van de Rostyne, 1978; Edwards, 1980); these fluids are identified in Tables 2 and 3.

The primary effect of introducing a heteroatom like S or N into a hydrocarbon is on the flexibility c/n. Therefore, for each fluid shown in Tables 2 and 3, vapor-pressure data were fit to the SWAP method letting c/n be the adjustable parameter to obtain the best fit. Using Equation (6), values of $\Delta c/n$ were found; these are also shown in Tables 2 and 3.

Since T* is a function of the single vapor pressure datum, for the fluids studied here, we chose the temperature corresponding to 300 torr for determining the best $\Delta c/n$.

To find and subsequently correlate $\Delta c/n$, it was necessary to exercise care in the definitions of parameters T_{760}, F_A, F_N and F_B. We preserve the original SWAP method by perturbing about an effective normal paraffin. However, to obtain good vapor-pressure predictions for heteroatom-containing hydrocarbons, it is necessary further to perturb the model about a structural homomorph of the heteroatom-containing hydrocarbon. This homomorph is obtained by replacing all heteroatoms with equivalent carbon atoms. For example, the homomorph for pyridine is benzene and that for thiophenol is toluene. Then T_{760}, F_A, F_N, and F_B are determined from the homomorph.

Unfortunately, equivalent carbon atoms cannot always be substituted for the heteroatoms, eg. for aromatic five-membered rings containing nitrogen and/or sulfur. It is impossible to obtain an aromatic five-membered ring containing only carbon atoms; hence, a true homomorph does not exist.

In this case we still replace all heteroatoms with carbons even if they are not equivalent carbons. We then determine T_{760} as the normal boiling point of this approximate homomorph. F_A is determined as if all substituted carbon atoms are equivalent whether they are or not. For example, while the homomorph of thiophene contains 1 non-aromatic carbon atom, F_A is set equal to 1.0.

To obtain the best estimate of the effective carbon number, the approximate homomorph should resemble the true homomorph to as great an extent as possible. We encounter another obstacle here, however, if we consider, for instance, thiophene. Our preference, using the rules described above, would be to replace the sulfur atom with carbon and use the normal boiling point of cyclopentadiene to represent T_{760}. However, cyclopentadiene exists only as a dimer and we can not easily obtain a value for T_{760}. Instead we use the next closest approximation to the true homomorph - cyclopentene. Fortunately, normal boiling point is not sensitive to degree of aromaticity. For example, T_{760} for cyclopentane is 322 K and that for cyclopentene is 317 K; also, T_{760} for toluene is 384 K whereas that for methylcyclohexane is 374 K.

Further, the SWAP method is not sensitive to small inaccuracies in T_{760}, as shown by Macknick (1978).

To illustrate the use of the SWAP method for the case of five membered rings, we present an example calculation for thiophene in Appendix I.

Within the scatter of the data, the results shown in Tables 2 and 3 correlate with F_H, the fraction of heteroatomicity. For nitrogen-containing compounds

$$F_H = \frac{\text{no. of nitrogen atoms}}{\text{no. of nitrogen atoms + no. of carbon atoms}} \text{ per molecule} \quad (11$$

A similar definition is used for sulfur-containing compounds.

For both types of compounds, $\Delta c/n$ becomes increasingly negative as F_H rises; molecular flexibility for a nitrogen- or sulfur-containing hydrocarbon derivative is lower than that of a corresponding heteroatom-free hydrocarbon. Introduction of the heteroatom tends to stiffen the molecule.

For nitrogen-containing compounds:

$$\begin{aligned} \Delta c/n &= 0 && 0 \leq F_H < 0.073 \\ \Delta c/n &= 0.9285F_H + 0.6773 && F_H \geq 0.073 \end{aligned} \quad (12)$$

For sulfur-containing compounds:

$$\Delta c/n = 0.7847F_H^3 - 1.635F_H^2 - 0.02029F_H \quad (13)$$

Equations (12) and (13) are used in addition to Equation 7 to determine the total $\Delta c/n$ used in Equation 6.

Appendix I gives illustrative calculations showing how the extended SWAP correlation can be used to calculate vapor pressures of hydrocarbon derivatives containing either nitrogen or sulfur heteroatoms.

Discussion

When Equations (12) and (13) are used, the vapor pressures

of all compounds shown in Tables 2 and 3 are reproduced with an average error of less than 10% over the experimentally-available range. Maximum errors are also less than 10% except for pyrrole (12%) and dimethyl pyrrole (17%).

For fluids whose molecules contain both sulfur and nitrogen, a reasonable approximation may be provided by adding the contributions from Equations (12) and (13) to determine $\Delta c/n$. Experimental data for such fluids are extremely rare. However, data are available for thiazole and methyl 2-thiazole (Boublik et al., 1973) in the range 100-760 torr. When SWAP is used for these fluids, the maximum error in the predicted vapor pressure is 4%.

To gain some perspective on the accuracy of SWAP compared to that of other methods, we have calculated maximum and average errors for two representative compounds, one containing nitrogen (2,4 dimethylquinoline), and one containing sulfur (thiophenol), over the available range of data. In addition, we have calculated maximum and average errors for these compounds supposing that their true structures were not known, to simulate the usefulness of the three methods on mixtures where structure is unlikely to be well defined. These are shown in Table 4.

The nitrogen-containing compound was altered to be 3-methyl 1-naphthalene amine and the sulfur-containing compound was altered to be 1-ethyl thiophene. These perturbations changed primarily the position and character of the heteroatoms and leave fraction aromaticity largely unchanged. Since Macknick (1970) has previously shown that SWAP is a superior method in the face of uncertainties in aromacity, we desire here to show

SWAP's advantages in terms of uncertainties in heteroatomicity character. We assume that fraction heteroatomicity can be determined with good accuracy.

For both compounds the accuracy of the SWAP method either equals or exceeds that of the Riedel-Plank-Miller method and that of the Lee-Kesler method (Reid et al. 1977). More important, when structure is perturbed, the accuracy of the SWAP method is affected to a much lesser extent. Note that the percent error for the SWAP method hardly changes when molecular structure is misrepresented in contrast to that for the methods of Riedel-Plank-Miller or Lee-Kesler.

Each method requires input data to determine applicable constants. The SWAP method needs only approximate structure expressed through fractions of aromaticity, naphthenicity, branching, and heteratomicity, and one vapor-pressure datum. On the other hand, the Lee-Kesler and Riedel-Plank-Miller methods both require critical temperature and critical pressure as well as one vapor-pressure datum. Since critical properties are often not available, they were estimated using Lydersen's group contribution method (Reid et al., 1977) which requires detailed structural information and molecular weight.

Mixtures

Perhaps the major utility of the SWAP correlation lies in it applicability to narrow-boiling mixtures of heavy hydrocarbons (cùts or fractions), where detailed molecular structure is not known. To illustrate, we compare calculations using SWAP to the petroleum-cut data of Myers and Fenski (1955) who studied four sets of narrow-boiling petroleum fractions, designated OLA tar, Sovaloid C, Was I and Wax II. Both OLA tar

and Sovaloid C were characterized as predominantly alkylated anthracenes and phenanthrenes, also possibly containing some four-ring, polynuclear aromatics. The degree of alkylation was small. The two waxes were stated to be typical high-boiling normal paraffins. Based on this information, we set $F_A = 1$ for the OLA tar and for Sovaloid C; we set $F_A=0$ for the waxes. All other characterization factors (F_B, F_N, F_H) were set to zero. T_{760} was estimated from an extrapolation of the experimental data. Table 5 shows maximum and average errors through the range of experimental data, generally 0.2 to 100 torr. Agreement is good, especially considering the rough quality of the characterizations of the compounds and considering that the maximum deviations occur at 0.2 torr where we expect the largest experimental uncertainty.

For comparison, we have also used the Lee-Kesler and Riedel-Plank-Miller methods to estimate the vapor pressures of the petroleum-cut data of Myers and Fenske. These methods require critical constants ;
Lydersen's method (Reid, et al., 1977)
was used to estimate the critical properties. Lydersen's method requires knowledge of exact molecular structure and molecular weight. Since molecular structure was not known, it was estimated as follows: OLA tar and Sovaloid C were assumed to be 1,6 diethyl-4 methyl anthracene; Wax I was assumed to be n-tricosant; Wax II was assumed to be n-octacosane. Table 5 presents maximum and average calculated relative errors.

In all cases the accuracy of the SWAP method either equals or exceeds that of the Riedel-Plank-Miller and Lee-Kesler

methods. This is particularly true for Wax II where the maximum and average errors of the SWAP method are approximately one-tenth those of the other two methods.

The advantage of SWAP results from its use of rough characterizations rather than exact structure to characterize the properties of a given compound or mixture. These characterizations (F_A, F_N, F_H) are often easy to determine experimentally; they tend to give a sufficiently accurate representation of the character of unknown compounds.

Extrapolation of a rough characterization to exact structure can lead to large errors in that structure, especially for mixtures. Translation of the estimated structure to critical properties using a group contribution method magnifies those errors. Finally, use of the incorrect critical properties leads to larger errors in vapor-pressure especially far from the available vapor-pressure datum SWAP avoids these problems by using the rough characterization directly.

Unfortunately, no published data are presently available for narrow-boiling fractions of hydrocarbons containing nitrogen and/or sulfur heteroatoms. However, the evidence presented here suggests that the extended SWAP method, as discussed here, should provide good estimates for the vapor-pressures of such fractions.

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TABLE 1

Parameters in Equation (3)

	D	E	F	G	r
A	5.4224×10^{5}	-3.326×10^{0}	9.0692×10^{0}	6.4197×10^{-2}	-0.53853
B	4.6512×10^{-23}	1.3450×10^{1}	2.0617×10^{-3}	-2.1884×10^{-1}	0.17427
C	2.6646×10^{25}	-1.8775×10^{1}	1.0278×10^{0}	-7.5590×10^{-1}	-0.11956

TABLE 2

Parameter c/n Obtained from Vapor-Pressure Data[a] for Nitrogen-Containing Compounds

Compound	Range of Data (torr)	$-10^3 \Delta c/n$
2,5-Dimethyl pyrrole	70 - 1,700	133
Pyrrole	70 - 2,000	169
2,4-Dimethyl quinoline	90 - 800	8.94
Quinaldine	110 - 760	32.8
Quinoline	110 - 760	-36.3
Isoquinoline	100 - 760	-1.97
2-Methyl 5-Ethyl pyridine	20 - 760	6.74
3-Methyl pyridine	70 - 2,000	57.3
4-Methyl pyridine	70 - 2,000	57.2
2-Methyl pyridine	150 - 2,000	62.1
Pyridine	150 - 2,000	90.9
Diethylamine	300 - 900	115
Dimethylamine	5 - 760	244
Methylamine	4 - 760	375

[a]taken from T. Boublik, V. Fried, E. Hala. The Vapor Pressures of Pure Substances. Elsevier Scientific Publishing Company, Amsterday (1973).

TABLE 3

Parameter Δc/n Obtained from Vapor-Pressure Data for Sulfur-Containing Compounds

Compound	Range of Data (torr)	Data Source	$-10^3 \Delta c/n$
Methanethiol	10 - 1,500	2	294
1-Propanethiol	150 - 2,000	1	97.3
2-Propanethiol	180 - 2,000	1	130
1-Hexanethiol	70 - 2,000	1	27.3
1-Heptanethiol	70 - 1,300	1	19.9
2-Methyl 1-butanethiol	70 - 2,000	1	43.9
2-Methyl 2-butanethiol	150 - 2,000	1	37.6
3-Methyl 2-butanethiol	70 - 2,000	1	47.0
2-Methyl 2-pentanethiol	70 - 2,000	1	29.4
2-Methyl 2-propanethiol	150 - 2,000	1	95.3
Thioanisole	70 - 900	1	52.4
1-Undecanethiol	10 - 1,500	2	12.1
1-Eicosanethiol	10 - 1,500	2	5.31
Thiophenol	10 - 1,500	2	55.1
2-Methylbenzenethiol	10 - 1,500	2	24.6
3-Methylbenzenethiol	10 - 1,500	2	36.3
4-Methylbenzenethiol	10 - 1,500	2	21.6
Ethanethiol	10 - 1,500	2	160
Thiophene	10 - 1,500	2	83.8
2-Methylthiophene	10 - 1,500	2	64.4
3-Methylthiophene	10 - 1,500	2	63.7

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TABLE 4

Accuracies of Three Vapor Pressure Correlations

Used For Estimation For Compounds of Unknown Structure

METHOD	Thiophenol				2,4 Dimethylquinoline			
	Correct Structure		Incorrect Structure		Correct Structure		Incorrect Sturcture	
	MAX	AVE	MAX	AVE	MAX	AVE	MAX	AVE
SWAP	6.9	2.1	7.7	2.4	1.7	0.4	1.8	0.4
Lee-Kesler	6.1	4.8	8.7	1.8	2.5	0.9	10.5	4.7
Reidel-Plank-Miller	7.2	1.1	10.0	2.1	4.5	1.9	10.0	4.5

TABLE 5

Calculated Vapor Pressures Using SWAP, Lee-Kesler, Riedel-Plank-Miller for Petroleum Fractions

(Range 0.2 - 100 torr)

Deviation From Experiment %

	SWAP		Lee-Kesler		Riedel-Plank-Miller	
	maximum	average	maximum	average	maximum	average
OLA tar	18.7	8.0	18.4	10.1	15.4	10.0
Sovaloid C	22.9	7.8	23.7	10.8	20.8	9.1
Wax I	19.5	6.6	24.9	8.2	30.0	8.6
Wax II	6.8	3.3	58.6	21.2	64.0	23.1

APPENDIX - IV-I

Sample Calculations

To illustrate the extended SWAP correlation for predicting vapor pressures of sulfur- and nitrogen-containing hydrocarbons, we present calculations for two representative pure liquids: thiophene and quinoline. Required data for the estimations are approximate mole fractions of n-paraffinic, branched paraffinic, naphthenic, aromatic, sulfur and nitrogen atoms in the sample. Also needed are the normal boiling point of the structural homomorph and a single vapor-pressure datum.

Nitrogen-Containing Hydrocarbon

quinoline: $F_N = 0$ $F_B = 0$ $F_A = 1.0$ $F_H = 0.1$

T,P datum - 471.4 K, 300 torr

homomorph = naphthalene ($T_{760} = 491.1$ K)

1. n_{eff} from Equation (4):

$$n_{eff} = [(3.03191-\{\ln(1078-491.1)\}/2.303)/0.04999]^{1.5}$$
$$= 12.12$$

2. $c/n_{\text{normal paraffin}}$ from Equation (5):

$$c/n_{\text{normal paraffin}} = 0.167+1.022/12.12-0.189/(12.12)^2$$
$$= 0.2500$$

3. $\Delta c/n$ from Equation (7):

$$\Delta c/n = [0.1319(1)+0.2429(0)+0.1992(0)]\exp[-0.002532(491.1)]$$
$$= 0.03804$$

4. $\Delta c/n_H$ from Equation (12):

$$\Delta c/n_H = -0.9285(0.1) + 0.06773$$
$$= -0.0251$$

5. $P^*_{\text{normal paraffin}}$ from Equation (9):

$$P^*_{\text{normal paraffin}} = 5.78\times10^5 \exp[-4.7222/(491.1-100)] = 571063$$

6. ΔP^* from Equation (10)

$$[0.72(1)+0.27(0)-0.65(0)]10^5 = 72000$$

7. Summing the contributions to c/n and P^*:

$$c/n = 0.25+0.03804-0.0251 = 0.2629$$

$$P^* = 571063+72000 = 643063 \text{ torr}$$

8. From c/n = 0.2629,

$$X \equiv (0.2629 - 0.167)^{-1} = 10.43$$

9. We now calculate A, B, and C from Equation (3) using the appropriate constants from Table 1.

$$A = [1/(-0.53853)]\ln\{[(5.4224\times10^5)(10.43)^{-3.326\times10^0}]^{-0.53853} + [(9.0692\times10^0)(10.43)^{6.4197\times10^{-2}}]^{-0.53853}\} = 2.027$$

and similarly:

$$B = -6.149 \text{ and } C = -2.861$$

10. T^* can now be obtained by solving Equation (1) using the vapor pressure datum:

$$0 = 2.027-\ln(300/643043)-6.149T^*/471.4 -2.861T^{*2}/(471.4)^2$$

Only one solution is possible:

$$T^* = 498.3K$$

11. As a test, calculate the vapor pressure at 485.8K

$$\ln(P/643063) = 2.027-6.149/(485.8/498.3) -2.861/(485.8/498.3)^2$$

$$P = 438.6 \text{ torr}$$

The reported vapor pressure at this temperature is 430.6 torr; the error is 1.9%.

Sulfur-Containing Hydrocarbon

The method for sulfur-containing hydrocarbons is to that used for nitrogen-containing hydrocarbons:

thiophene: $F_N = 0$ $F_B = 0$ $F_A = 1.0$ $F_H = 0.2$

T,P datum - 329.8 K, 300 torr

homomorph = cyclopentene (T_{760}= 317.)

1. n_{eff} from Equation (4) :

$$n_{eff}=\left[(3.03191-\{\ln(1078-317.)\}/2.303)/0.4999\right]^{1.5}$$

$$= 5.252$$

2. $c/n_{\text{normal paraffin}}$ from Equation (5):

$$c/n_{\text{normal paraffin}} = 0.167+1.022/5.252-0.189/(5.252)^2$$

$$= 0.3547$$

3. $\Delta c/n$ from Equation (7):

$$\Delta c/n = \left[0.1319\ (1)+0.2429\ (0)+0.1992\ (0)\right]\ \exp\left[-0.002532(317.)\right]$$

$$= 0.0591$$

4. $\Delta c/n_H$ from Equation (13):

$$\Delta c/n_H = 0.7847(0.2)^3-1.635(0.2)^2-0.02029(0.2)$$

$$= 0.0632$$

5. $P^*_{\text{normal paraffin}}$ from Equation (9):

$$P^*_{\text{normal paraffin}} = 5.78\times10^5\ \exp\left[-4.7222/(317.-100)\right]$$

$$= 565558$$

6. ΔP^* from Equation (10):

$$\Delta P^* = \left[0.72(1)+0.27(0)-0.65(0)\right]\ 10^5 = 72000$$

7. Summing the contributions to c/n and P*,

$$c/n = 0.3547+0.0591 - 0.0632=0.3506$$

$$P^* = 565857+72000=637558 \text{ torr}$$

8. From c/n = 0.3506

$$X = (0.3506 - 0.167)^{-1} = 5.447$$

9. Evaluate A, B, and C from Equation (3) using the appropriate constants from Table 1.

$$A = [1/(-0.53853)]\ \ln\{[(5.4224\times10^{5})(5.447)^{-3.326\times10^{0}}]^{-0.538} + [(9.0692\times10^{0})(5.447)^{6.4197\times10^{-2}}]^{0.53853}\}$$

$$= 2.207$$

and similarly:

$$B = -6.434 \text{ and } C = -1.544$$

10. T^* is obtained by solving Equation (1) using the single vapor pressure datum:

$$0 = 2.207\ \ln(300/637558) - 6.434T^*/329.8 - 1.544T^{*2}/(329.8)^2$$

Only one solution is possible:

$$T^* = 393.3 \text{ K}$$

11. Finally, as a test, calculate the vapor pressure at 337. 8K

$$\ln(P/637558) = 2.207 - 6.434/(337.8/393.3) - 1.544/(337.8/393.3)^2$$

$$P = 398.7 \text{ torr}$$

The reported vapor pressure at this temperature is 400 torr; the error is 0.3%.

APPENDIX IV-II - 1

Estimation of T_{760} For Determination of SWAP Parameters

We realize that in most cases T_{760}, the normal boiling point, will not be available for calculating $P^*_{\text{normal paraffin}}$, $n_{\text{effective}}$, or $\Delta c/n$. Fortunately, since the SWAP method is relatively insensitive to the value of T_{760} used, we can estimate it with little loss in accuracy. We suggest one of the following two methods:

I. Molecular weight (M) and fraction aromaticity (F_A) are known.

$$T_{760} = (1-F_A)PAR + F_A AR \qquad \text{(II-1)}$$

$$PAR = 65.09M^{0.417} - 139.5M^{-0.139} \qquad \text{(II-2)}$$

$$AR = 41.87M^{0.564} - 28.25M^{0.370} \qquad \text{(II-3)}$$

If sulfur is present:

$$M_{\text{homomorph}} = \frac{M_{\text{measured}}}{(1-F_H)+F_H(32/12)} \qquad \text{(II-4)}$$

T_{760} is in degrees Kelvin. No correction is needed for nitroger

II. One vapor pressure datum (T_d, P_d), fraction aromaticity (F_A) and fraction heteroatomicity (F_H) are known.

$$T_{760} = (1-F_A)(A+BT_d+CT_d^2)+F_A(D+ET_d+FT_d^2) + GF_H+HF_H^2 \qquad \text{(II-5)}$$

$$A = 28.4 - 5.22\ \ell nP \qquad \text{(II-6)}$$

$$B = 1.51 - 0.0709\ \ell nP \qquad \text{(II-7)}$$

$$C = -1.92 \times 10^{-4} + 2.38 \times 10^{-5} \ln P \quad \text{(II-8)}$$

$$D = -142 + 22.2 \ln P \quad \text{(II-9)}$$

$$E = 2.39 - 0.210 \ln P \quad \text{(II-10)}$$

$$F = -1.15 \times 10^{-3} + 1.71 \times 10^{-4} \ln P \quad \text{(II-11)}$$

G and H depend on whether the heteroatom is N or S.

For nitrogen:

$$G = 52.1 \ln P - 558 \quad \text{(II-12)}$$

$$H = -99.7 \ln P + 749 \quad \text{(II-13)}$$

For sulfur:

$$G = -2.10 \ln P - 386 \quad \text{(II-14)}$$

$$H = 8.48 \ln P + 394 \quad \text{(II-15)}$$

T_{760} is in degrees Kelvin and P is in torr.

Method I has been derived (Macknick, 1978) for pure hydrocarbons with no heteroatomicity and is preferred for these compounds because of its better accuracy. Method I also estimates quite well the homomorph T_{760} of compounds containing the heteroatom S provided the measured molecular weight is corrected for sulfur content using equation (II-4). Since nitrogen and carbon have almost the same molecular weights, there is no correction for nitrogen containing compounds when using Method I. Figure 1 can be used for quick hand calculations.

Oftentimes it is difficult or inconvenient to determine the molecular weight of an unknown compound. In this case, method II is recommended. When the compound is a pure hydrocarbon and a vapor pressure datum above 10 torr is available, T_{760} can be estimated within 10 K (Gonzalez, 1979). The homomorph normal boiling point for compounds containing nitrogen or sulfur can be estimated within 40 K when the vapor pressure datum is above 10 torr.

The combined results of equations (II-11) through (II-14) were used to estimate the homomorph normal boiling point from the data of two compounds containing both nitrogen and sulfur (thiazole and methyl-2-thiazole). Simple addition of the two contributions yielded results of accuracy comparable to that obtained for compounds containing only one heteroatom. This suggests that Method II can be used to estimate the homomorph normal boiling point of compounds containing both nitrogen and sulfur.

To illustrate the use of Methods I and II for estimating T_{760}, we present calculations for OLA tar. Since molecular weight is not known for this petroleum fraction, we assume that its molecular weight can be represented by that of 1,6 diethyl-4 methyl anthracene (224.3). A convenient vapor pressure datum is 474.3 K at 5 torr.

Method I

From equation (II-2):

$$PAR = 65.09(224.3)^{0.417} - 139.5(224.3)^{-0.139}$$
$$= 556.3$$

From equation (II-3):

$$AR = 41.87(224.3)^{0.564} - 28.25(224.3)^{0.370}$$
$$= 677.4$$
$$F_A = 14/19 = 0.74$$

From equation (II-1):

$$T_{760} = (1-0.74)(556.3) + (0.74)(677.4)$$
$$= 645.9 \text{ K}$$

Method II

From equations (II-6 through II-11):

$$A = 28.4 - 5.22\ \ell n(5) = 20.00$$

$$B = 1.51 - 0.0709\ \ell n(5) = 1.40$$

$$C = -1.92 \times 10^{-4} + 2.38 \times 10^{-5}\ \ell n(5) = -2.30 \times 10^{-4}$$

$$D = -142 + 22.2\ \ell n(5) = -106$$

$$E = 2.39 - 0.210\ \ell n(5) = 2.05$$

$$F = -1.15 \times 10^{-3} + 1.71 \times 10^{-4}\ \ell n(5) = -8.75 \times 10^{-4}$$

Since the cut exhibits no heteroatomicity, it is not necessary to calculate G or H.

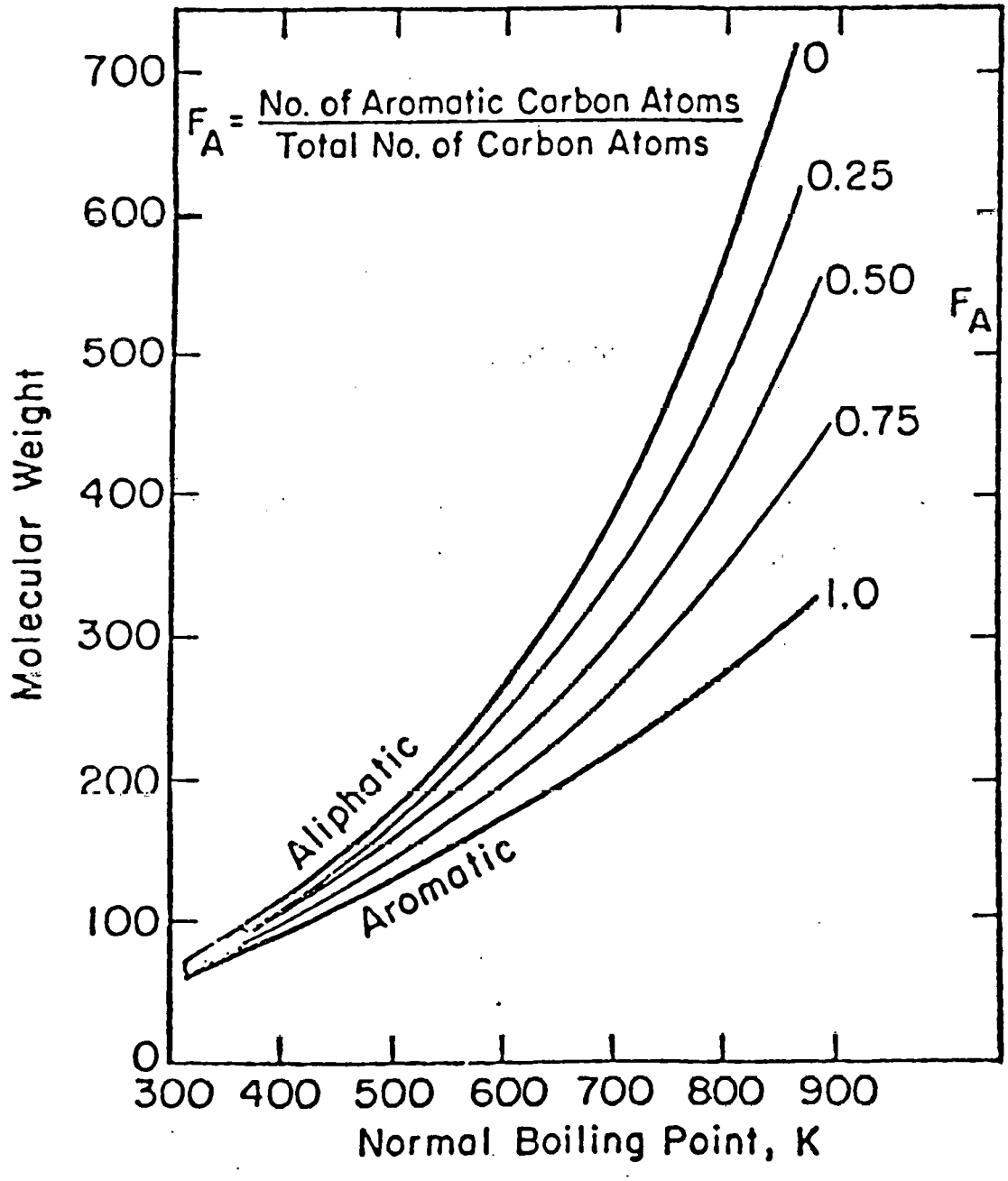
From Equation (II-5):

$$T_{760} = [1-0.74][20+1.40(474.3)-2.3\times10^{-4}(474.3)^2] + [0.74][-106+2.05(474.3)-8.75\times10^{-4}(474.3)^2]$$

$$= 659.8\ K$$

The extrapolated value of T_{760} used in the calculations for Table 5 was 652 K.

Figure 1 Molecular Weight Estimation as a Function of Normal Boiling Point and Approximate Chemical Structure[a]



[a]from Macknick (1975)

APPENDIX V

VAPOR PRESSURES OF HEAVY LIQUID HYDROCARBONS BY A GROUP-CONTRIBUTION METHOD

APPENDIX V

VAPOR PRESSURES OF HEAVY LIQUID HYDROCARBONS BY A GROUP-CONTRIBUTION METHOD

Abstract

The group-contribution method gives parameters for a vapor-pressure equation based on a kinetic theory of fluids. All parameters are obtained from molecular structure only. Good representation is obtained for vapor-pressure data for 67 hydrocarbon liquids in the region 10-1500 mm Hg. This group-contribution method is useful for estimation of vapor pressures and enthalpies of vaporization for those heavy hydrocarbons where no experimental data are available.

An abundance of experimental vapor-pressure data is in the literature for low-molecular-weight hydrocarbons. However, with the exception of normal paraffins, reliable vapor pressures are scarce for compounds which have normal boiling points over 200 C. For rational process design, especially for alternative energy processes, it is important to have good estimates for thermodynamic properties of heavy hydrocarbons. Since it is rarely feasible economically to determine experimentally all necessary data, correlations are often used to extend limited experimental information. However, for many high-molecular-weight hydrocarbons, no experimental data at all are available. Therefore it is desirable, when possible, to estimate physical properties from theoretically based correlations. This work presents a group-contribution method for determining parameters in a vapor-pressure equation.

Many vapor-pressure equations have been proposed. Most are either empirical or integrations of the Clapeyron equation coupled with simplifying assumptions. In almost all cases these equations take a form where the pressure is an exponential function of the temperature and of the adjustable parameters; this exponential dependence requires accurate prediction of parameter values. Since common vapor-pressure equations contain at least three, and often more, adjustable parameters with no clear physical significance, it is not possible to determine unambiguous values of these parameters

by group contribution.

Many equations use critical data to develop a corresponding-states relation. Such relations are suitable for most light compounds, but not for heavy hydrocrabons which are thermally unstable in the critical region. Critical data for heavy hydrocarbons are usually not known.

Several authors have correlated vapor pressures for homologous series, but such correlations are limited to specific compounds. While such correlations are sometimes more accurate, a group-contribution method, based on carbon-types, is more general because it can be used for a wide variety of hydrocarbons. Not only can one estimate the vapor pressure of a homologous series, but in addition, it is possible to estimate the effect of substituting various branches and side chains onto an unbranched parent molecule.

The AMP Equation

Extending a suggestion by Moelwyn-Hughes (1961), Abrams, Massaldi, and Prausnitz (1974) presented an equation relating pressure P to absolute temperature T:

$$\ln P = A + B/T + C \ln T + DT + ET^2 \qquad (1)$$

where

$$A = \ln \left(\frac{R}{V_2}\right) + \left(s - \frac{1}{2}\right) \ln \left(\frac{E_0}{R}\right) - \ln [(s-1)!] + \ln \alpha \qquad (2)$$

$$B = -E_0/R \qquad (3)$$

$$C = \frac{3}{2} - s \tag{4}$$

$$D = \frac{(s-1)}{(E_0/R)} \tag{5}$$

$$E = \frac{(s-3)(s-1)}{2(E_0/R)^2} \tag{6}$$

Here V_w is the (hard-core) van der Waals volume; E_0 is the enthalpy of vaporization of the hypothetical liquid at T = 0; s is the number of equivalent oscillators per molecule, and R is the gas constant (82.06 cm^3-atm/gmole-K); E_0/R is in kelvins and the universal constant α is equal to 0.0966 when P is in atm and T is in kelvins.

Abrams (1974) and Macknick (1977) have shown that this equation gives reliable results for large molecules and that it is suitable for representing vapor-pressure data in the range 10^{-6} to 2 atm. While Equation (1) has only three fundamental parameters (V_w, s, and E_0/R), the equation has a form similar to that of popular empirical equations with five adjustable parameters. The three fundamental parameters have physical significance; they reflect the size and shape, flexibility, and intermolecular forces of the molecules. The small number of parameters and their physical significance facilitates correlation by a group-contribution method.

AMP Parameters from Group Contribution

As shown by Abrams (1974) and by Macknick (1977), parameters s, E_0/R, and V_w can be calculated from a non-linear

fit of experimental vapor pressure data. In this work, when experimental data are not available, the parameters can be found from a group-contribution method:

$$s = \sum_i \nu_i s_i \tag{7}$$

$$E_0/R = \sum_i \nu_i (\varepsilon_{0i}/R) \tag{8}$$

$$V_w = \sum_i \nu_i v_{wi} \tag{9}$$

where s_i, ε_{0i}, and v_{wi} are contributions from a group containing carbon-type (i); ν_i is the number of carbon atoms of type (i) in a molecule. Table 1 gives contributions to s and E_0/R by carbon type. The (hard-core) van der Waals volume V_w is found from Bondi's (1968) group-contribution correlation.

Group parameters s_i and ε_{0i} were determined from experimental vapor-pressure data for 67 liquid hydrocarbons: 20 normal paraffins, 21 branched paraffins, 19 aromatics, and 7 naphthenics. The data were obtained from American Petroleum Institute Projects 42 and 44 [1966, Zwolinski (1971)]. The Simplex [Nelder (1965)] regression routine was used to correlate the data. Table 1 gives the hydrocarbons used for evaluation of different group contributions. Whenever possible, the experimental data for data reduction were in the range 10-1500 mm Hg. However, accurate experimental data

for heavy hydrocarbons are sparse; for some compounds the only reliable experimental datum is the normal boiling point. Therefore, the group-contribution method given here is likely to be more accurate near normal-boiling-point temperatures.

Carbon-type analysis does not take into account differences in molecular fine structure. For example, the method given here does not distinguish between 1-methyl-naphthalene and 2-methyl-naphthalene. However, the method does account for differences in gross molecular structure; a distinction is made, for example, between 1,2-dimethyl-naphthalene and 1-ethyl-naphthalene. Inability to account for fine structure usually produces an error of less than ±7 C at the normal boiling point. Predictions for highly branched compounds are less reliable than those for compounds whose molecules contain only simple substitutions on a non-branched parent molecule.

Results

Tables 2 and 3 compare predicted and experimental boiling points and enthalpies of vaporization. In Table 2, T_{10} and T_{760} are respectively, the temperatures where the vapor pressures equal 10 and 760 mm Hg; ΔT is the difference between calculated and experimental values.

Experimental enthalpies were obtained by differentiating the experimental vapor-pressure data using a form of the Clausius-Clapeyron equation valid at low pressures:

$$\frac{d(\ell n\ P)}{dT} = \frac{\Delta H^V}{RT^2} \qquad (10)$$

Calculated enthalpies of vaporization were determined using Equations (1) and (10) to give,

$$\Delta H^V_{calc} = R[-B + CT + DT^2 + 2ET^3] \qquad (11)$$

For 67 liquids, the average error in T_{760} is ±2.1 C, and that for ΔH^V at the normal boiling point is ±5.4%.

Equation (1) holds for a large range of pressures; gross errors are not expected even for temperatures well below the normal boiling point. For example, for eicosane ($n\text{-}C_{20}H_{42}$), Macknick (1978) reports that $T_{0.01}$ = 83.85 C; $T_{0.01}$ is the temperature where the vapor pressure is 10^{-2} mm Hg. Using the group contributions given here, and recalling that they were determined from data in the range 10-1500 mm Hg, the calculated $T_{0.01}$ is 79.60 C; this error of 4.25 C is remarkably low, considering an extrapolation in pressure of a little more than three orders of magnitude.

Since the derivation of Equation (1) assumes ideal-gas behavior, it is not applicable at temperatures near the critical region. For eicosane, Reid et al. (1977) report T_c = 494 C and P_c = 11.0 atm. At the critical pressure, the group-contribution method estimates T = 514 C, giving an error of 20 C.

Tables 4 and 5 give sample group-contribution calculations for compounds which were not used in obtaining the

group parameters. Figure 1 compares experimental and predicted vapor pressures. Agreement is about the same as that indicated in Table 2.

Conclusions

The semi-theoretical correlation presented here can supply reliable estimates for vapor pressures and enthalpies of vaporization for heavy hydrocarbons. This correlation is especially useful for preliminary design considerations where it is not economically feasible to make experimental measurements.

Nomenclature

A, B, C, D, E	AMP equation parameters, functions of E_0/R, V_w, and s
E_0	AMP equation parameter: energy of vaporization of hypothetical liquid at T = 0.
ΔH^V	Enthalpy of vaporization, Kcal/gmole
P	Vapor pressure, atm
R	Gas constant, 82.06 cm^3-atm/gmole-K
s	AMP equation parameter: number of equivalent harmonic oscillators per molecule
s_i	Contribution by group (i) to parameter s
t	Temperature, C
T	Temperature, K
v_{wi}	Contribution by group (i) to parameter V_w
V_w	AMP equation parameter: (hard-core) van der Waals volume, cm^3/gmole

Greek Letters

α	AMP equation universal constant equal to 0.0966 when P is in atm and T is in kelvins
ε_{0i}	Contribution by group (i) to parameter E_0
ν_i	Number of (i) groups per molecule

Subscripts

0.01,10,760	At pressures of 10^{-2}, 10, and 760 mm Hg, respectively
c	At critical point

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Table 1. Group Contributions to Vapor-Pressure Parameters s and E_0/R

Carbon-Type		s_i	$_i/R,K$	Vapor-Pressure Data Used to Obtain Group Parameters
Aliphatic	$-CH_3$	2.359	1162.7	Normal paraffins C_5-C_{40}
Aliphatic	$-CH_2-$	0.479	674.0	Normal paraffins C_5-C_{40}
Aliphatic	$-\overset{|}{C}-H$	-2.189	-372.9	Branched paraffins $\sim C_{10}$
Aliphatic	$-\overset{|}{C}-$	-4.318	-1127.1	Branched paraffins $\sim C_{10}$
Aromatic	Ar_2C-H	1.175	939.5	Benzene
Aromatic	Ar_2C-R	-0.520	583.0	Substituted aromatics
Condensed Aromatic	$Ar_2C(Cond)$	-0.774	432.5	Naphahalene, Anthracene, Chrysene
Condensed Aromatic	$Ar(Cond)_2C$	0.321	632.5	Pyrene
Naphthalene	CH_2	1.188	928.0	Cyclohexane
Haphthenic	$C(H)R$	-1.936	-431.0	Substituted cyclohexane

Table 2. Comparison of Experimental and Predicted Vapor Pressures for Representative Liquids.

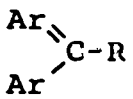
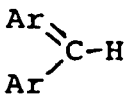
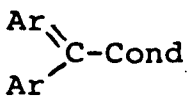
Compound	T_{760}, C		ΔT_{760}	T_{10}, C		ΔT_{10}
	Experimental	Calculated	C	Experimental	Calculated	C
n-$C_{10}H_{22}$	174.2	173.9	-0.3	57.6	52.9	-4.7
n-$C_{20}H_{42}$	343.8	344.0	0.2	198.3	195.8	-2.5
n-$C_{40}H_{82}$	525.0	524.6	-0.4	353.0	360.6	7.6
3-Ethyl-octane	122.3	130.7	8.4	12.5	8.1	-4.4
3,3-Dimethyl-octane	161.2	156.4	5.2	45.0	42.1	2.9
2,3,-Dimethyl-3-ethyl-hexane	163.7	154.7	1.0	45.0	36.3	-8.7
Naphthalene	217.9	218.5	0.6	86.6	88.0	1.4
Anthracene	341.2	340.2	-1.0	176.2	181.4	5.2
Chrysene	448.0	448.5	0.5	--	--	--
2,6-Dimethyl-anthracene	370.0	369.3	-0.8	--	--	--
n-Hexadecyl-benzene	378.0	372.5	-5.5	227.0	224.0	-3.0
2-Methyl-3-ethyl-naphthalene	277.0	378.9	1.9	132.0	138.7	6.7
n-Octyl-cyclohexane	263.6	262.7	-0.9	126.0	122.6	-3.4
n-Hexadecyl-cyclohexane	379.0	379.7	0.7	224.0	223.7	-0.3

Table 3. Comparison of Experimental and Predicted Enthalpies of Vaporization at the Normal Boiling Point for Representative Liquids

Compound	ΔH^v, Kcal/gmole Experimental	Calculated	% Error
$n\text{-}C_{10}H_{22}$	10.12	9.59	-5.3
$n\text{-}C_{20}H_{42}$	15.28	15.14	-0.9
$n\text{-}C_{40}H_{82}$	25.00[a]	23.10	7.6
3-Ethyl-octane	10.11	9.22	-8.7
3,3-Dimethyl-octane	9.87	8.96	-9.2
2,3-Dimethyl-3-ethyl-hexane	9.98	8.49	-15.0
Naphthalene	10.85	10.96	1.0
Anthracene	14.10	14.05	-0.4
n-Hexadecyl-benzene	17.01	16.60	-2.4
2-Methyl-3-ethyl-naphthalene	13.23[a]	12.93	-2.2
n-Octyl-cyclohexane	12.56	11.96	-4.8
n-Hexadecyl-cyclohexane	16.55	16.14	-2.5

[a]Because of a lack of experimental data, ΔH^v_{exp} was calculated from the slope of the vapor-pressure curve between T_{10} and T_{760}.

Table 4. Sample Calculation for Parameters in Equation (1): 1,2-dimethyl-naphthalene

Carbon-type	ν_i	s_i	ε_{0i}/R, K	v_{wi}, $cm^3/gmole$[†]
Aliphatic - CH_3	2	2.359	1162.7	13.67
Aromatic 	2	0.520	583.0	5.54
Aromatic 	6	1.175	939.5	8.06
Condensed Aromatic 	2	-0.774	432.5	4.74

$s = \sum_i \nu_i s_i = 9.18$

$E_0/R = \sum_i \nu_i (\varepsilon_{0i}/R) = 9993.4$ K

$V_w = \sum_i \nu_i v_{wi} = 96.26$ $cm^3/gmole$

[†]Source: Bondi (1968).

Table 5. Sample Calculation for Parameters in Equation (1): 2-methyl-5-ethyl-heptane

Carbon-type	ν_i	s_i	ε_{0i}/R, K	v_{wi}, $cm^3/gmole$[†]
Aliphatic - CH_3	4	2.359	1162.7	13.67
Aliphatic $-CH_2-$	4	0.479	674.0	10.23
Aliphatic $-\overset{|}{\underset{|}{C}}H$	2	-2.189	-372.9	6.78

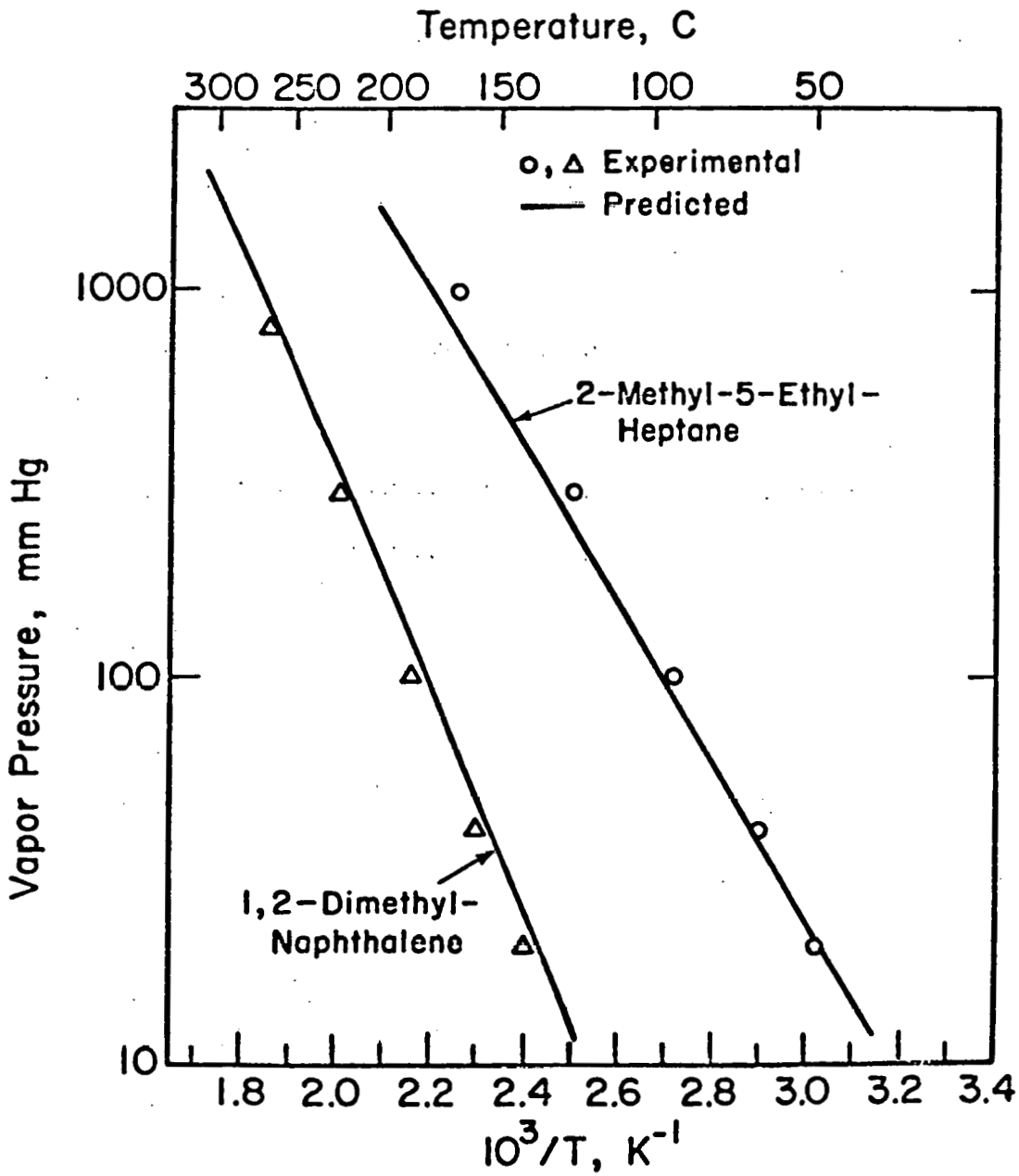
$s = \Sigma \nu_i s_i = 6.974$

$E_0/R = \sum_i \nu_i (\varepsilon_{0i}/R) = 6601.0$ K

$V_w = \sum_i \nu_i v_{wi} = 109.16$ $cm^3/gmole$

[†]Source: Bondi (1968).

Figure 1. Comparison of Experimental and Predicted Vapor Pressures



APPENDIX VI

VAPOR PRESSURES OF SOME NITROGEN-CONTAINING COAL-DERIVED LIQUIDS

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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. Using knowledge of the molecular structure and low-temperature vapor-pressure data, the vapor pressure at high temperatures can be predicted using a semi-empirical 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-inch ID 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 (i.e. Teflon tpe, 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 (TM) and Drierite (TM) 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 percent palladium on 1/8-inch alumina pellets. Catalyst temperature is 600 to 650°C. With the large excess of oxygen, every organic molecule is combusted completely to CO_2, NO_2 and H_2O:

$$C_nH_m N_y + (n + y + m/4) O_2 \rightarrow nCO_2 + (m/2)H_2O + yNO_2 \quad (1)$$

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 to 2500 ppm of CO_2. Neither water nor NO_2 interfere 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:

$$P(sat) = \frac{(\text{ppm } CO_2)P(atmo)}{n}\left[\frac{P(sample)}{P(atmo)}\right] \quad (2)$$

where P(sat) is the vapor pressure of the sample; 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(atmo) 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(atmo)], 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 percent 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 percent of full scale. The temperature is gradually lowered and data collection begins when the system has re-equilibrated.

Saturation of the oxygen stream with the sample can be checked by varying the flow rate; the vapor-pressure readings should remain unchanged. To 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 the bath for each temperature range; below 10°C, a mixture of 50 percent ethylene glycol and 50 percent water; water for 10 to 35°C, and for high temperatures (35 to 150°C), Dow silicon oil.

All organic chemicals are from Aldrich Chemical Company 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 percent purity and distilled in a Perkin-Elmer spinning-band column at 5 mm Hg. The top cut (5 percent by volume) was discarded, as were the bottoms (15 percent by volume). Quinoline (96 percent initial purity) was purified by boiling under vacuum until 5 percent by weight of the sample was boiled off. A vacuum oven was used to purify N-ethyl carbazol (98.5 percent) which is solid at room temperature (m.p. 60°C). The sample was baked at about 125°C for several days. 5-ethyl 2-methyl pyridine required no further purification at 99+ percent purity.

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

Results and Discussion

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

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

where P is in mm Hg, and T is in kelvins. The assumption of a straight line fit is valid due to the short temperature range used here.

Table 1 summarizes the data. Temperature and pressure ranges and average percent deviation are also presented. The percent deviation is defined by

$$\text{Percent deviation} = ([P_{(exp)} - P_{(calc)}]/P_{(exp)})100$$

where $P_{(exp)}$ is the experimentally determined value and $P_{(calc)}$ is from the straight-line fit.

Also,

$$\text{Average percent deviation} = \sum_i |\text{percent deviation}|/i$$

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 1 are shown in Tables 2 through 5. Each of these presents temperature, experimental vapor pressure, calculated vapor pressure and percent deviation.

Although the exact freezing point of 5-ethyl 2-methyl pyridine is not known, a small sample (∿ 2 mℓ) immersed for 5 minutes in a -25°C bath did not freeze, assuring that the reading at -20.39°C is still well within the liquid range.

Acknowledgment

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TABLE 1: SUMMARY OF EXPERIMENTAL RESULTS

Compound	a	b	Temperature Range °C	Pressure Range mm Hg	Average % Deviation
Quinaldine	21.55	-7365.2	8.75-39.49	1.07×10^{-2}-1.35×10^{-1}	1.91
5-Ethyl 2-Methyl Pyridine	20.94	-6204.4	-20.39- +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-Ethyl Carbazol	21.92	-9010.4	74.66-100.65	$1.85\ 10^{-2}$-$1.10\ 10^{-1}$	2.17

TABLE 2: QUINALDINE VAPOR PRESSURES

t,°C	$P_{(exp)}$ mm Hg	$P_{(calc)}$ mm Hg	% Deviation
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 3: 5-ETHYL 2-METHYL PYRIDINE VAPOR PRESSURES

t, °C	$P_{(exp)}$ mm Hg	$P_{(calc)}$ mm Hg	% Deviation
-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 4: QUINOLINE VAPOR PRESSURES

t, °C	$P_{(exp)}$ mm Hg	$P_{(calc)}$ mm Hg	% Deviation
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 5: N-ETHYL CARBAZOL VAPOR PRESSURES

t, °C	$P_{(exp)}$ mm Hg	$P_{(calc)}$ mm Hg	% Deviation
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

Figure Captions

MS JE 9-80

Figure	Caption
1	Schematic Diagram of Gas-Saturation Apparatus
2	Oxygen Saturated with Organic Vapor is Combusted to Carbon Dioxide, Water and Nitrogen Dioxide.

Figure 1: Schematic Diagram of Gas-Saturation Apparatus

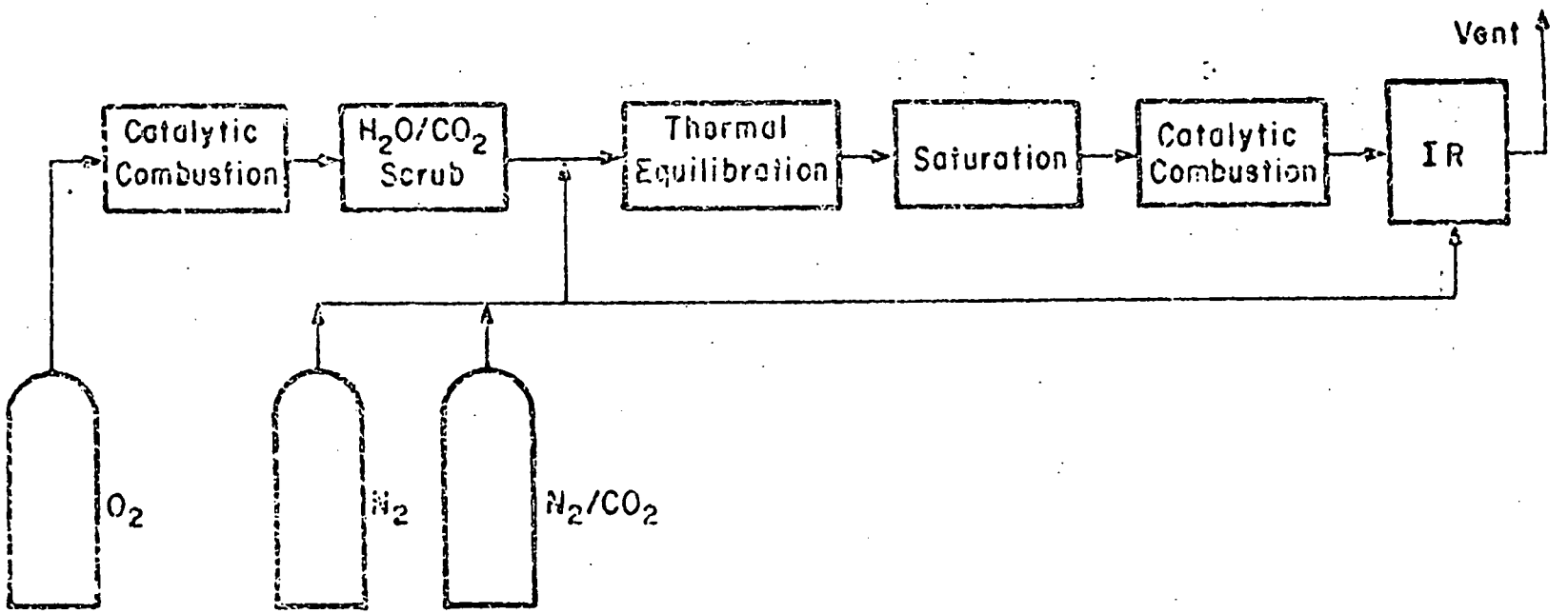
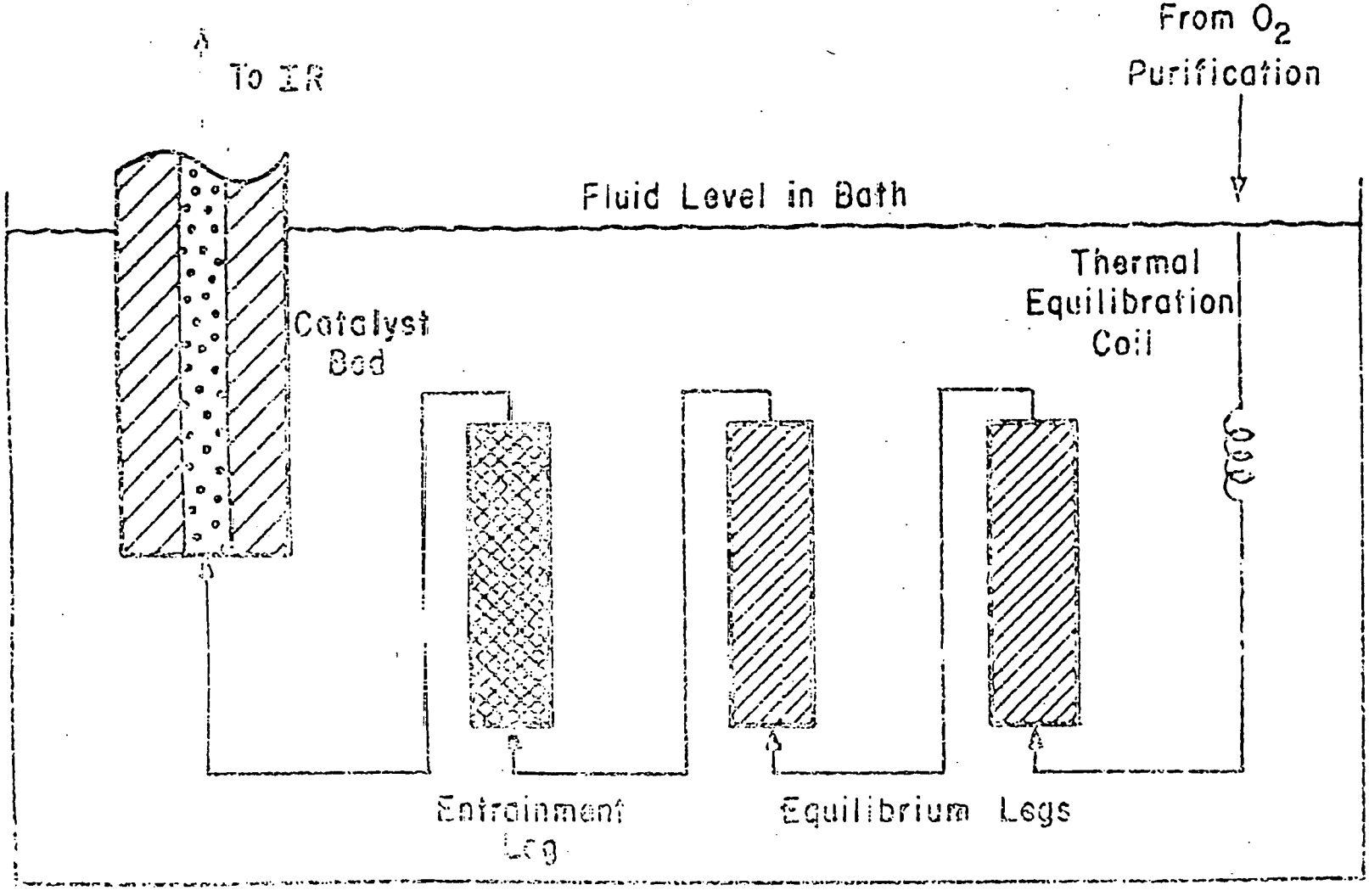


Figure 2: Oxygen Saturated with Organic Vapor is Combusted to Carbon Dioxide, Water and Nitrogen Dioxide



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