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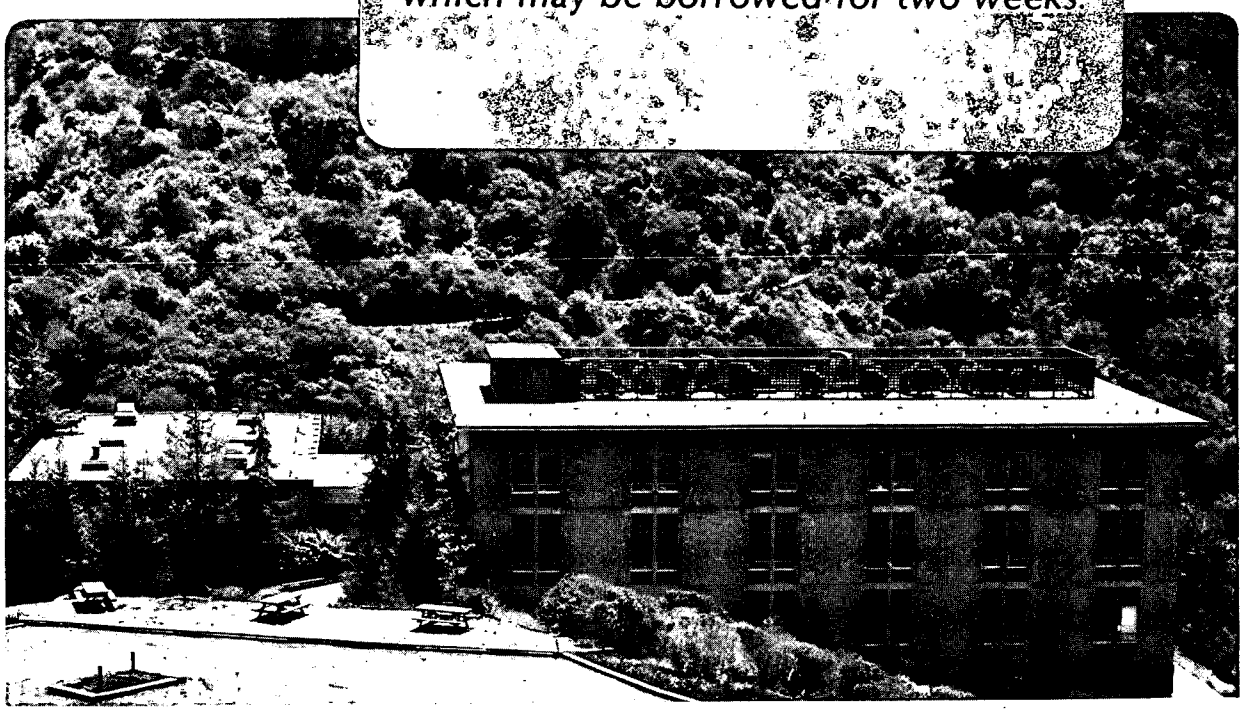

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A CORRELATION FOR THERMODYNAMIC PROPERTIES OF HEAVY FOSSIL-FUEL FRACTIONS

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ABSTRACT

A correlation is developed for calculation of thermodynamic properties of heavy fossil fuels, based on a recent version of the perturbed-hard-chain equation of state. Since the correlation does not require experimental vapor pressures or densities as input data, it is useful for heavy fossil fuels where vapor pressures and densities are difficult or impossible to measure. For fossil-fuel fractions, equation-of-state parameters are found from approximate molecular-structure (characterization) data coupled with a calibration based on pure-component (model compound) data. Interaction parameters are given for mixtures of fossil fuels with methane, ethane, carbon dioxide, hydrogen and hydrogen sulfide. While the correlation presented here is useful for calculating vapor-liquid equilibria, it is not intended for conventional fossil fuels, where other correlations are satisfactory. Instead, it is intended for heavy fossil fuels, where conventional correlations are often not reliable and where the usual input data are often unavailable.

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Supplementary material is available through the corresponding author.

INTRODUCTION

As the world continues to deplete its petroleum reserves, high-quality crude oil can remain neither plentiful nor inexpensive. When reserves of light crude oil run low, heavy crude oil, coal liquids and other heavy fossil fuels may be required to meet the world's energy needs. Heavy fossil fuels contain molecules that are larger and more aromatic and that contain more heteroatoms (nitrogen, oxygen and sulfur) than those found in light crudes. To process heavy fossil fuels, their thermodynamic properties must be known.

Most current correlations for thermodynamic properties of fossil fuels use normal boiling point and liquid density at 60°F as input parameters [American Petroleum Institute (1983), Tsonopoulos et al. (1986), Twu (1984), Lin and Chao (1984), Watanasiri et al. (1985)]. While these correlations are useful in many cases, they have some serious disadvantages.

Many of the boiling-point and density-based correlations are not applicable to fuels containing a significant number of heteroatoms. Further, for heavy fossil fuels, the needed liquid densities and boiling points may be experimentally inaccessible. In some cases, accuracy may be lost upon using a correlation to extrapolate available densities and vapor pressures to 60°F and the normal boiling point. For very heavy fossil fuels, reliable vapor pressures and liquid densities may be unavailable, thereby preventing use of the common correlations.

Several attempts have been made to construct correlations based on group-contribution methods or on molecular-structure data [e. g. Allen (1986), Smith et al. (1976), Edwards and Prausnitz (1981a), Edwards et al. (1981b), Macknick and Prausnitz (1979), Ruzicka (1983a), Ruzicka et al. (1983b), Jensen et al. (1981), Gang et al. (1986)]. Correlations based on molecular structure can easily be applied to heteroatomic compounds and often do not require vapor-pressure data. However, to predict properties of heavy fossil fuels, some of these correlations require elaborate chemical analyses to determine the number of functional groups in a sample [Allen et al. (1984)]. Therefore, group-contribution correlations are often not useful for process-engineering calculations.

The correlation proposed here uses approximate but easily accessible structural data to determine equation-of-state parameters, in a manner similar to that indicated by Alexander et al. (1985b)

for the Redlich-Kwong-Soave equation of state and also by Wilhelm and Prausnitz (1985). The approximate structural data follow from experimental characterization measurements using standard analytical instruments.

The correlation presented here does not require boiling-point and density data. Instead, it uses characterization data that reflect molecular structure. The correlation presented here provides estimates of any configurational thermodynamic property, i.e. any property that can be obtained from an equation of state, including vapor pressure, density, fugacity, configurational entropy and enthalpy; it is useful for VLE calculations for mixtures which may also include light gases.

This work does not replace previously established successful correlations; instead, it augments our ability to estimate thermodynamic properties, especially for those fuels where the ordinary input data (density and boiling point) are inaccurate and inaccessible.

CHARACTERIZATION DATA

Experimental characterization data are needed as input for the correlation. These data can be obtained using standard experimental methods as described, for example, by Alexander et al. (1985a) and by Rodgers et al. (1987) These methods first separate a fossil fuel into fractions containing molecules of similar size or boiling point. Elemental analysis, molecular-weight measurements, NMR and IR spectroscopy are then performed for each fraction. Similar procedures have been reported by others [Schwager and Yen (1979), Bartle et al. (1979), Zygmunt and Bartle (1983)].

Elemental analysis gives the relative abundance of C, H, N, O, and S atoms. The NMR spectrum is used to distinguish amongst four classes of carbon-bonded hydrogen: hydrogen bonded to an aromatic carbon (H_{aro}); hydrogen bonded one carbon away from an aromatic carbon (H_α); hydrogen bonded to a nonterminal carbon further than one carbon away from an aromatic ring (H_β); and hydrogen bonded to a methyl group that is not bonded to an aromatic ring (H_γ). IR spectroscopy is used to distinguish between ether and hydroxy oxygen and to distinguish among primary amines, secondary amines and other nitrogen groups.

For each fraction, the characterization data are reduced to provide the average number of the

following atoms or groups per molecule; carbon atoms (C); different kinds of hydrogen (H_{aro}, H_α, H_β, H_γ); all nitrogen atoms (N_t); secondary amine groups (NH); primary amine groups (NH_2); all oxygen atoms (O_t); hydroxyl groups (OH); all sulfur atoms (S). There are a total of ten groups identified in the characterization. Molecules containing no heteroatoms are characterized by five atoms (C, H_a, H_α, H_β, H_γ). Five other groups refer to heteroatomic structures. For a mixture, characterization parameters need not have integer values.

Characterization data are needed to determine constants in a suitable equation of state. In this correlation we use a new version of the perturbed-hard-chain equation of state.

EQUATION-OF-STATE CONSTANTS

A modified perturbed-hard-chain equation of state, recently developed by Cotterman et al. [Cotterman et al. (1986a), Cotterman and Prausnitz (1986b)], is used as the basis of the correlation. For a nonpolar pure fluid, this equation of state has three constants: an attractive energy parameter (T^*), a molecular-size parameter (v^*), and a parameter that indicates molecular flexibility (c). T^* and v^* have units of Kelvin, and $cm^3/mole$ respectively. Parameter c is dimensionless. Following Prigogine (1957), parameter T^* is defined by

$$T^* = \frac{\varepsilon_{ii} q}{ck} \tag{1}$$

The product, cT^*, is equal to $\varepsilon_{ii} q/k$, where ε_{ii} is a characteristic potential energy between two representative segments of two molecules of type i, q is the molecular area of interaction and k is Boltzmann's constant.

As discussed later, for calculating mixture properties, T^* and v^* are factored into products of other parameters. In addition to Equation 1 we write

$$v^* = r v^*_{seg} \tag{2}$$

Where r is the number of segments per molecule.

As suggested by theory and as observed by data reduction, [Cotterman et al. (1986a), Cotterman and Prausnitz (1986b)], for carbon numbers greater than five or six, $\varepsilon_{ii} q/k$, v^*, and c are nearly

linear functions of carbon number for homologous series. Using the equation of state, all configurational thermodynamic properties of a pure fluid can be calculated when T^*, v^* and c are known.

CALIBRATION: CORRELATING METHOD FOR PURE COMPONENTS

The perturbed-hard-chain equation of state was initially developed for pure fluids and for well-defined mixtures. To extend the perturbed-hard-chain equation of state to fossil-fuel fractions, it is first necessary to establish a calibration i.e. to correlate known equation-of-state parameters with known characterization parameters. To establish this correlation, a data bank is used. This bank contains vapor-pressure and density data for 233 model compounds containing five or more atoms other than hydrogen. In this data bank, vapor-pressure data range from 6.67×10^{-4} bar to a pressure corresponding to eight tenths of the critical temperature; liquid densities are at temperatures between the melting point and eight tenths of the critical temperature. Characterization parameters of the compounds in the data bank are obtained by inspection of the known structures. Table I shows the distribution of model compounds. (A complete list of model compounds, data sources and data ranges is given in the supplemental material.) These compounds were chosen to represent typical oils and coal liquids. Olefins and acetylenes were not included in the data bank.

Because of the large number of hydrocarbons in the data bank, no single hydrocarbon can have a very large effect on the correlation. Unfortunately, the number of heteroatomic compounds in the data bank is severely limited by the scarcity of thermodynamic data, especially liquid densities.

Because our correlation is based on fits to data for pure components of known structure, the correlations are established independently of errors or biases in any characterization method. Therefore, in principle, the correlation can be used with experimental results from any chemical-analytical techniques for measuring the required structural parameters.

Three equation-of-state parameters ($\varepsilon_{ii}q/k$, v^* and c) are correlated with structural data. (Polar moments of the model compounds were not considered here.) The values of $\varepsilon_{ii}q/k$ and c are strongly linked; they are weakly correlated with v^*. The combination of c and $\varepsilon_{ii}q/k$ strongly

influences calculated vapor pressures while v^* has a major effect on calculated densities.

Because the values of the equation-of-state parameters are not orthogonal, it was not possible to correlate all of the pure-component parameters to characterization data at once. To establish the correlation, all three equation-of-state parameters were first fit to vapor-pressure and density data using methods described by Cotterman et al. (1986a). Next, parameter v^* was correlated to structural data using the results of the three-parameter fit and correlating methods described below. The other two parameters, $\varepsilon_{ii}q/k$ and c, were then refit to vapor-pressure and density data with v^* calculated using the correlation. Then, $\varepsilon_{ii}q/k$ was correlated to molecular structure. Next, c was fit to thermodynamic data while v^* and $\varepsilon_{ii}q/k$ were calculated using the previously established correlations. The results of this fit were used to correlate c to molecular-structural data. After c was correlated, $\varepsilon_{ii}q/k$ and c were refit and correlated alternately with the other two parameters held at their correlated values until the correlations no longer improved. This procedure converged in one or two iterations.

To correlate equation-of-state parameters with structural data for pure compounds, we used the "ACE" subroutine [Breiman and Friedman (1983)]. Equation-of-state parameters were fit to functions of the form

$$P_i = \sum_{j=1}^{n} \Phi_{ij}(x_j) \tag{3}$$

where P_i is an equation-of-state parameter and Φ_{ij} is an optimum function of characterization variable x_j. For the independent variables (x_j) in Equation 3, tests were made using various combinations of characterization variables or functions of multiple characterization variables. None of the forms tested is significantly better than a simple linear form:

$$P_i = A_{i0} + \sum_{j=1}^{10} A_{ij} x_j \tag{4}$$

Where A_{ij}'s are universal coefficients found from data regression. To illustrate, suppose parameter P_i is v^*. In that case, Equation 4 is

$$\begin{aligned} v^* = {} & A_{i0} + A_{i1}C + A_{i2}H_{aro} + A_{i3}H_\alpha + A_{i4}H_\beta + A_{i5}H_\gamma + \\ & A_{i6}O_t + A_{i7}OH + A_{i8}N_t + A_{i9}NH + A_{i10}NH_2 \end{aligned} \tag{5}$$

The coefficients in Equation 4 were determined by linear regression with the error in P_i weighted by $1/P_i^{1/2}$. This weighting provides a compromise between a fit based on minimizing relative errors, which favors small molecules, and a fit based on linear errors, which favors large molecules. In Equation 4, coefficients which correspond to hydrocarbon structures (A_{ij} for j running from 0 to 5), were determined using only data for compounds that do not include heteroatoms. The coefficients corresponding to heteroatomic groups were then determined from data for heteroatomic hydrocarbon derivatives.

RESULTS FOR MODEL COMPOUNDS

Tables II and III show coefficients of Equation 4 determined from thermodynamic properties and characterization parameters of the model compounds. Due to insufficient density data, the value of the sulfur (S) coefficient in the v^* correlation is entirely determined by fitting the properties of thiophene. The sulfur terms for $\varepsilon_{ii}q/k$ and c were determined from fitting the vapor-pressure and density data for thiophene and vapor-pressure data for other thiophenic compounds. It is not possible to gauge the errors in the correlation as deviations from optimal equation-of-state parameters, because the parameters are closely linked through the correlation method.

For homologous series, the correlations behave as expected from previous work [Cotterman et al. (1986a)]. Figure 1 shows a plot of calculated parameters T^*, v^*, and c as a function of carbon number for n-alkanes. The shapes of the curves are similar to those shown by Cotterman et al. (1986a). As expected, most of the coefficients shown in Tables II and III are positive. There are two exceptions to this generalization: the carbon (C) coefficient for c, and the hydroxyl (OH) coefficient for v^*. The effect of (OH) on v^* is most likely due to hydrogen bonding causing closer packing of the molecules. The effect of (C) on c follows upon noting that, since most carbons are accompanied by hydrogen, the net effect of a carbon and its associated hydrogen is to increase c. However, if a carbon is not bonded to hydrogen, it most likely indicates a condensed-ring structure with lower flexibility, decreasing c.

Figures 2 and 3 show calculated vapor pressures for three types of molecules: an alkane ($H_{aro}/C = H_\alpha/C = 0$, $H_\beta/C = 1.775$, $H_\gamma/C = 0.225$), a naphthene ($H_{aro}/C = H_\alpha/C = 0$, $H_\beta/C = 1.5$, $H_\gamma/C = 0.15$), and an aromatic ($H_{aro}/C = 0.5$, $H_\alpha/C = 0.25$, $H_\beta/C = H_\gamma/C = 0$). Vapor pressures calculated for a carbon number of forty are shown in Figure 2. Figure 3 shows similar results for a carbon number of 50. Figure 4 shows enthalpies of vaporization for fluids with a carbon number of forty. The correlation correctly predicts lower vapor pressures and higher enthalpies of vaporization as the molecule becomes more condensed.

Tables IV and V show errors in calculated thermodynamic properties of the model compounds using the parameters from Equation 4. The average percent deviation in vapor pressure is between 20 and 50 percent for all categories. These errors indicate that the calculated vapor pressures are very sensitive to equation-of-state parameters. Small deviations in the parameters produce large errors in vapor pressures. Liquid densities are less sensitive to equation of state parameters. Errors for the two extreme homologous series (n-alkanes, condensed structures), tend to be higher than the average for two reasons: these series lie on the edges of the correlated space, and the thermodynamic properties as a function of the characterization parameters change abruptly near values associated with these series.

Deviations between experimental and calculated thermodynamic properties are larger than those obtained with conventional correlations because those correlations use some thermodynamic-property data as input. By contrast, the correlation presented here uses only structural characterization data.

To check the ability of the correlations to predict thermodynamic properties, calculations were made for ten pure fluids not included in the data base used to construct the correlations. The errors in these calculations were similar to those shown in Tables IV and V, indicating that the correlation can be used with confidence to estimate properties of pure components. Detailed results are given in the supplementary material.

It has often been observed that it is very difficult to calculate vapor pressures accurately without using at least one vapor-pressure datum as input (Reid et al. (1987). If one vapor pressure datum where used to determine either $\varepsilon_{ii}q/k$ or c, accuracy would improve dramatically.

RESULTS FOR FOSSIL-FUEL FRACTIONS

The correlations given by Equation 4 (and by tables II and III) were used to provide parameters for the perturbed-hard-chain equation of state. That equation was then used to predict thermodynamic properties of petroleum fractions and coal-liquid fractions characterized by Rodgers et al. (1987) Vapor pressures and densities for these samples (except for the SRC samples) have been reported elsewhere [Schwarz et al. (1987a)]. Table VII gives a list of these samples, their boiling ranges, boiling point and liquid density at 60°F. The boiling points and liquid-density values in Table VI are extrapolated from measured vapor pressures and densities [Schwarz et al. (1987a)]. The characterization data reported by Rodgers et al. (1987) include results of elemental analysis, NMR and IR spectroscopy, and two independent molecular-weight measurements. One molecular-weight measurement was made using gel-permeation chromatography as described by Rodgers et al. (1987) The other molecular-weight measurement was made using mass spectroscopy. Additional characterization data for the SRC samples are given by Harrison et al. (1985). Appendix A shows a sample calculation for converting raw characterization data from Rodgers et al. (1987) to the characterization parameters needed in Equation 4.

Since calculated vapor pressures are highly sensitive to molecular weight, special care must be taken to obtain the best possible measurement of molecular weight.

For the mass-spectral measurements reported by Rodgers et al. (1987), the sample was vaporized at approximately 10^{-7} *torr* over a temperature range from ambient to 280°C. While the sample was vaporizing, 30 scans were made at 26-second intervals. The sample was ionized by electron impact with an ionization voltage of 10 eV. A 5 kV accelerating voltage was used.

For some samples, molecular weights were measured by vapor-pressure osmometry (ASTM method D2503) in benzene or chloroform or by cryoscopy in benzene. The measurements made in chloroform were performed by Heppner (1985). The other osmometry and cryoscopy measurements were made by Chevron Research Corporation.

As shown in Appendix A, all characterization parameters are the products of molecular weight and a number dependent only on elemental analysis and spectroscopic data.

Molecular weight is the most important characterization datum. Additional molecular-weight estimates were made by fitting molecular weight to measured vapor pressures and densities as follows: Assuming the elemental analysis and spectroscopic data reported by Rodgers et al. (1987) to be correct, characterization parameters were then calculated as a function of molecular weight, as shown in Appendix A. These functions were inserted into Equation 4. The molecular weight was adjusted to produce agreement between experimental data and thermodynamic properties calculated using the parameters obtained from Equation 4. This adjustment of molecular weight has almost no effect on calculated mass densities, but small adjustments have a strong effect on vapor pressures. Table VII shows various estimates of molecular weight.

Calculations were first performed using the elemental-analysis and spectroscopic data reported by Rodgers et al. (1987) coupled with various molecular-weight measurements. These calculations often give poor predictions of vapor pressure. Calculated vapor pressures are both too high and too low depending on which molecular-weight measurement is used. Poor vapor-pressure predictions result from sensitivity to equation-of-state parameters $\varepsilon_{ii}q/k$ and c which are linear functions of molecular weight.

Because of inconsistencies in the molecular-weight measurements, some molecular-weight measurements were empirically corrected for suspected systematic errors. Measured molecular weights were correlated to the optimal molecular weights as determined by fitting molecular weight to vapor-pressure and density data. It was found that the molecular weights measured by mass spectroscopy or vapor-pressure osmometry can be corrected to obtain optimized molecular weights; the correction factor is a function of characterization parameters. For molecular weights measured by vapor-pressure osmometry in benzene,

$$MW_{opt} = MW_{meas}^{vpo}(1.158-0.8764H_{\gamma}/H_{hc}) \tag{6}$$

For measurements using mass spectroscopy,

$$MW_{opt} = MW_{meas}^{ms}(1.757-1.750H_{\alpha}/H_{hc}-1.319H_{\gamma}/H_{hc}) \tag{7}$$

The corrections for vapor-pressure-osmometry measurements are between plus and minus four percent. For the mass-spectroscopy measurements, the corrections range from twelve to forty percent.

The hydrogen fractions appearing in Equations 6 and 7 can be obtained directly from integration of an NMR spectrum. Equations 6 and 7 are based on NMR-peak assignments used by Alexander et al. (1985a) and Rodgers et al. (1987). These equations should not be used if calculations are based on different peak assignments used by other workers. Appendix B shows a sample calculation using the molecular-weight corrections to calculate equation-of-state parameters.

Equations 6 and 7 were tested for stability by refitting the coefficients in the equations with one of the fossil-fuel fractions deleted from the correlated data set. For the mass-spectroscopy correlation, the data base contained ten fractions. In this case, ten stability tests were performed using data sets of nine fractions. The worst deviation between the correlations shown above and a correlation based on a partial data set was 2%.

Vapor pressures and liquid densities of the fossil fuel fractions were calculated using molecular weights corrected using Equations 7 and, when molecular weights from vapor pressure osmometry were available, Equation 6. For comparison, vapor pressures were predicted using a modified version of the Maxwell-Bonnell correlation [Tsonopoulos et al. (1986)] and the SWAP correlation [Smith et al. (1976), Edwards et al. (1981b)]. The required input information for the SWAP method was estimated from the data of Rodgers et al. (1987). Liquid densities were also calculated using the Rackett equation with standard correlations for molecular weights and critical properties [American Petroleum Institute (1983)]. For the correlations which require normal boling points, they were estimated from measured vapor pressures and from normal boiling points given by the midpoint of the boiling range obtained from distillation data. Results of these calculations are summarized in Table VIII. The supplemental material contains results for each individual fraction.

Table VIII shows that predictions of vapor pressures made with the correlations presented here are in general superior to those made using a normal boiling point derived from distillation data. However, results obtained using the new correlation are not as good as those obtained with the modified Maxwell-Bonnell correlation provided that the input boiling point datum is from extrapolated vapor-pressure data. These results suggest that boiling points obtained from distillation data may not be reliable for correlations using normal boiling point as a primary input parameter.

The SWAP method suffers from difficulties in estimating the naphthenicity of the samples. This often results in poor predictions.

Fractions WCLP cuts 4 and 5 contain a large amount of oxygen. The high oxygen content has little effect on the accuracy of the correlation presented here but it appears to affect results obtained using the Maxwell-Bonnell method.

Vapor pressures and densities were also calculated as follows; the structural correlations were used to obtain $\varepsilon_{ii}q/k$ and v^* but c was adjusted to match the extrapolated normal boiling point. For this calculation, average absolute deviations in calculated vapor pressures were 11% using corrected molecular weights from mass spectroscopy and 9% using corrected molecular weights from vapor-pressure osmometry. The errors resulting from these calculations are slightly smaller than those, shown in Table VIII, obtained from the modified Maxwell-Bonnell correlation. When c was adjusted to fit the the normal boiling point, results for calculated liquid densities were slightly better than those shown in Table VIII.

Increasing the correlated value of $\varepsilon_{ii}q/k$ by 9%, reduces average errors in predicted liquid densities to a few tenths of a percent and eliminates the consistent positive bias in the predictions. While such adjustment tends to improve calculated liquid densities considerably, it causes larger errors in calculated vapor pressures.

These comparisons show once again that it is difficult to predict vapor pressure without at least *one* reliable vapor-pressure datum [Smith et al. (1976), Alexander et al. (1985b)]. If one accurate vapor-pressure datum is available, it is preferable to use a version of the Maxwell-Bonnell [American Petroleum Institute (1983), Tsonopoulos et al. (1986)] correlation for vapor pressures. However, in some cases, the only available boiling-point datum may not be reliable, (e.g. boiling points obtained from distillation data) and, for very heavy substances, no boiling data at all may be available. In this work, no boiling-point data are used as input parameters. Only characterization data are used. It appears that these data can provide a reasonable (but not very accurate) vapor pressure.

Density results presented in Table VIII show that, if at least one liquid-density datum is available, standard methods are superior to predictions from the equation of state. Results for the Rackett

equation are not strongly affected by poor boiling-point estimations. Using the correlations given here, the poor and biased estimates of liquid densities are not consistent with results obtained for model compounds. It is likely that for fractions, the bias is the result of the pseudocomponent approximation which is unable to compensate for the fact that a fraction is a mixture and not simply a hypothetical pure compound with the average molecular structure.

The correlation presented here is not intended for predictions of thermodynamic properties of *light* or *medium* fractions. For densities and vapor pressures of such fractions, other well-established methods are as good and in some cases better. However, for very heavy substances, there are few options. For such substances, a semi-theoretical equation of state provides the only reliable basis for correlating thermodynamic properties. Further, equations of state are useful for process calculations because they are easily adapted for mixtures containing fractions and volatile components (e.g. methane or hydrogen) at high pressures.

MIXTURES OF FRACTIONS AND VOLATILE COMPONENTS

Using the mixing rules presented by Cotterman and Prausnitz (1986b), the equation of state used in this work can be extended to mixtures. To use these mixing rules, the three pure-component equation-of-state parameters are defined in terms of the five parameters shown in Equations 1 and 2. Binary interaction parameters (k_{ij}, k_{ji}, and k_B) are also needed to calculate mixture properties. The parameter k_{ij} is used to calculate an average attractive interaction energy (ε_{ij}) between molecules i and j when i is in excess at high density:

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2}(1-k_{ij}) \tag{8}$$

The parameter k_{ji} serves a purpose similar to that for k_{ij} except it applies to a molecule of i dissolved in an excess of j. The third interaction parameter, k_B, applies to the interaction energy in the virial limit. In this work k_B, the interaction parameter for the low density limit is taken to be zero. The high-density mixture parameters (k_{ij} and k_{ji}) are assumed equal.

For a fossil-fuel fraction, ε/k (per segment) was taken to be 100 K, similar to that for pure hydrocarbons. The parameter q is determined from the correlated value of $\varepsilon q/k$. The volume of a

molecular segment (v^*_{seg}) is set at 10 $cm^3/mole$. To determine r for a fraction, the correlated value of v^* is divided by v^*_{seg}. For pure well-defined components including light gases, we use previously published values [Cotterman et al. (1986a), Cotterman and Prausnitz (1986b)] of equation-of-state parameters.

Previous work shows that for interactions of a light gas and a homologous series of hydrocarbons, as molecular size rises, k_{ij} tends to increase to an asymptote. The asymptote height and the rate of increase in k_{ij} depend on structural details of the homologous series. The exact relationship between k_{ij} and molecular size is not always clear because of scatter in k_{ij}'s determined from experimental VLE measurements. Values of k_{ij} are strongly influenced by the type, the domain and by any bias of the experimental data used to determine the parameter. Since k_{ij} is usually a small correction to the interaction energy, under most conditions a large relative error in k_{ij} does not strongly affect calculated phase equilibria. Therefore, k_{ij} cannot be correlated with high accuracy. However, a function correlating scattered values of k_{ij} can yield good estimates of thermodynamic properties.

To determine a correlation for k_{ij} for light-gas/heavy-fraction equilibria, interaction parameters, we used experimental VLE data for binaries containing H_2, CH_4, CO_2, C_2H_6, and H_2S with model compounds and fossil-fuel fractions. The data were fit using the methods described by Cotterman and Prausnitz (1986b). Table IX shows a summary of the model-compound data used. Included in the data bank were Henry's constants, P-T-x-y, P-T-x, and light-gas-partial-pressure-T-x data. A listing of data types, sources and ranges is in the supplemental material.

In general, the model compounds were either saturated hydrocarbons or highly aromatic. Few data are available for model compounds with mixed aromatic and saturated structures (H/C near 1.5). Mixtures of CO_2, CH_4, and H_2 with quinoline and mixtures of H_2 with thianaphthene were included. Interaction parameters for these mixtures were similar to those for mixtures of light gases with pure hydrocarbons. Because of the scarcity of equilibrium data for heteroatomic substances, corrections for some heteroatomic structures could not be included in the correlations. Unusually high values of k_{ij} were calculated for binaries including m-cresol. These data were not included in

the correlation because of the difficulty in ascertaining the effect of the OH group from the limited data available.

Equilibrium data for mixtures of the SRC fractions and hydrogen are given by Harrison et al. (1985). Data for mixtures of H_2S and H_2 with some of the WCLP fractions are given by Tewari (1985). Solubility data for CO_2, CH_4 and C_2H_6 in the Exxon and WCLP fractions are given by Schwarz and Prausnitz (1987b). For the calculations in this work, all reported mole fractions were adjusted for differences between corrected molecular weights calculated from Equations 6 and 7 and molecular weights reported with the mixtures phase-equilibrium data. In developing the correlations for k_{ij}, corrected molecular weights from mass spectroscopy were used.

Values of k_{ij} calculated from experimental data were smoothed according to

$$k_{ij} = M_{i0} + M_{i1}H/C - (M_{i2} - M_{i4}H/C)\exp(-M_{i5}C) \tag{9}$$

where M_{ik} are coefficients that depend on the gas. Table X shows M_{ik} values for various gases interacting with fossil-fuel fractions and average errors in calculated k_{ij}.

When correlating parameters, it is desirable to avoid using gas-solubility for fractions to avoid effects of errors in characterization. However, because gas solubility data are rare for mixtures containing large unsaturated hydrocarbons, for all gases except hydrogen, gas solubility data for the fractions were included in obtaining the correlations for k_{ij}. Appendix C shows a sample calculation of k_{ij} and predicted Henry's constants.

The exponential decay term was not needed to fit the hydrogen data. Because of the small size of hydrogen molecules, all of the hydrocarbon molecules considered here are large relative to hydrogen. As a result, k_{ij} for hydrogen reaches the large-molecular-weight asymptote rapidly.

For fraction-fraction interactions, k_{ij} is set to zero.

To illustrate the use of these correlations, Figure 5 shows K values calculated for a mixture of light gases the aromatic compound whose vapor-pressure curve is shown in Figure 2. Figure 6 shows calculated Henry's constants for methane in the forty and fifty-carbon atom compounds whose vapor pressures are shown in Figures 2 and 3. Henry's constant for methane in the heavier solvent is

roughly four fifths of that in the lighter similar solvent. The Henry's constants vary in this way because a small gas molecule (methane) only interacts with a small number of molecular segments, regardless of solvent size. As a result, the ratio of methane to solvent segments is nearly constant for solvents that have similar molecular structures and that are much larger than methane. Figure 6 also indicates the dependence of Henry's constants on structure. Aromatic molecules are nearly an order of magnitude worse solvents than the alkanes.

Tables XI shows errors for gas solubilities in fossil-fuel fractions calculated using k_{ij} from Equation 9. Because the molecular weights of some fractions were not measured using vapor pressure osmometry, calculations could not be completed for all fractions using both methods of measuring molecular weight. Using the two different methods of obtaining molecular weight, The large apparent differences in predictions for solubilities of hydrogen sulfide and hydrogen are due to the smaller amount of data available for comparison with the vapor-pressure-osmometry method. For CH_4, C_2H_6 and CO_2, as temperature falls, positive errors in calculated pressures tend to decrease and the magnitude of negative errors tend to increase. Predicted pressures for hydrogen follow the opposite trend with temperature. The available data do not indicate any significant effect of temperature on the accuracy of the H_2S-solubility calculations. The solubility data for the fractions tend to be for small amounts of gas in the heavy liquid. The negative bias in calculated pressures is probably due to the tendency of the equation of state to underestimate pressures for dilute mixtures when mixture parameters are fit over a wide range of composition.

CONCLUSIONS

A new correlation has been developed for thermodynamic properties of heavy fossil fuels. It uses the perturbed-hard-chain equation of state with parameters obtained from approximate molecular-structure (characterization) data. This correlation provides thermodynamic properties of heavy fossil-fuels without using conventional input parameters (boiling point and density at 60 °F) which may not be available or accessible for heavy fractions.

Because the correlations is based on an equation of state, it is easily extended to mixtures

using conventional procedures.

When approximate structural parameters are used to correlate thermodynamic properties, calculated results are not as accurate as those obtained with standard methods. In conventional methods, experimental boiling points and densities are used as input data. The method presented here does not have the advantage of using known thermodynamic data to predict other thermodynamic data.

In principle, group-contribution methods may provide accuracy because more structural detail is used in the correlation. However, detailed analytical data or thermodynamic data are rarely available for a heavy fossil-fuel fraction. The present work is useful whenever direct thermodynamic data or detailed structural data cannot be obtained.

In any effort to correlate thermodynamic properties using approximate structural parameters, the most pressing difficulty is to obtain accurate estimates of molecular weights. Therefore, much care must be exercised in measuring the molecular weight or, if that cannot be done, in empirically correcting inaccurate molecular weights. Improvements in the correlation method presented here (or in any other correlation based on molecular structure), are likely to be strongly linked to advances in experimental methods for chemical analysis of complex mixtures.

NOMENCLATURE

A_{ij} = correlation parameter

C = average number of carbon atoms per molecule

c = molecular flexibility parameter for equation of state

H = average number of hydrogen atoms per molecule

H_{aro} = average number of hydrogen atoms bonded to aromatic carbons per molecule

H_{hc} = average number of hydrogen atoms bonded to carbon per molecule

H_{alpah} = average number of hydrogen atoms bonded to alpha carbons per molecule

H_{β} = average number of carbon bonded hydrogen atoms which are not bonded to aromatic, terminal or alpha carbons per molecule

H_{γ} = average number of hydrogen atoms to non-alpha methyl groups per molecule

k = Boltzmann's constant, $1.381\times10^{-23} JK^{-1}$

k_B = low density interaction parameter for equation of state

k_{ij}, k_{ji} = high density interaction parameters for equation of state

M_{ij} = correlation parameter

MW = molecular weight

N_t = average number of nitrogen atoms per molecule

NH = average number of secondary amines per molecule

NH_2 = average number of primary amines per molecule

O_t = average number of oxygen atoms per molecule

OH = average number of hydroxy groups per molecule

P_i = equation-of-state parameter (v^*, $\varepsilon_{ii}q/k$ or c)

q = dimensionless molecular surface area parameter for equation of state

r = number of segments per molecule

S = average number of sulfur atoms per molecule

T^* = interaction energy parameter for equation of state, K

v^* = molecular volume parameter for equation of state, $cm^3/mole$

v^*_{seg} = molecular volume per segment, $cm^3/mole$

x_j = characterization parameter

Greek Symbols

ε_{ij} = interaction energy parameter between molecules of type i and j for equation of state, J

Φ_{ij} = optimum function

Subscripts and Superscripts

meas = measured

ms = from mass spectroscopy

opt = optimal value

vpo = from vapor pressure osmometry

LITERATURE CITED

Alexander, G. L.; Creagh, A. L.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* 1985a, 24, 301.

Alexander, G. L.; Schwarz, B. J.; Prausnitz J. M. *Ind. Eng. Chem. Fundam.* 1985b, 24, 311.

Allen, D. T.. *Fluid Phase Equilib.* 1986, 30, 353.

Allen, D. T.; Petrakis, L.; Grandy, D. W.; Gavalas, G. R.; Gates, B. C. *Fuel* 1984, 63, 803.

American Petroleum Institute, *Technical Data Book-Petroleum Refining,* 4th ed.; American Petroleum Institute: Washington D.C., 1983.

Bartle, K. D.; Ladner, W. R.; Martin, T. G.; Snape, C. E.; Williams, D. F. *Fuel* 1979, 58, 413.

Breiman, L.; Friedman, J. "Estimating Optimal Transformations for Multiple Regression and Correlation" Technical Report No. 9; Department of Statistics, University of California, Berkeley: Berkeley, CA, 1983.

Cotterman, R. l.; Schwarz, B. J.; Prausnitz, J. M. *AIChE J.* 1986a, 32, 1787

Cotterman, R. L.; Prausnitz, J. M. *AIChE J.* 1986b, 32, 1799

Edwards, D. R.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* 1981a, 20, 280.

Edwards, D.; Van de Rostyne, C. G.; Winnick, J.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* 1981b, 20, 138.

Gang, J.; Walsh, J. M.; Donohue, M. D. *Fluid Phase Equilib.* 1986, 31, 123.

Harrison, R. H.; Scheppele, S. E.; Sturm, G. P. Jr.; Grizzle, P. L. *J. Chem. Eng. Data* 1985, 30, 183

Heppner, R. A. "Analysis of Fossil Fuel Fractions"; Final Report Contract TDC 5.9/1034; Western Research Institute: Laramie, Wyoming, 1985.

Jensen, T.; Fredenslund, A.; Rasmussen, P. *Ind. Eng. Chem. Fundam.* 1981, 20, 239.

Lin, H.-M.; Chao, K.-C. *AIChE J.* 1984, 30, 981.

Macknick, A. B.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* 1979, 18, 348.

Prigogine I. *The Molecular Theory of Solutions;* Interscience: New York, 1957.

Reid, C. R.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids,* 4th ed.; McGraw-Hill: New York, 1987.

Rodgers, P. A.; Creagh, A. L.; Prange, M. M.; Prausnitz, J. M. submitted to *Ind. Eng. Chem. Res.* 1987.

Ruzicka, V. Jr. *Ind. Eng. Chem. Fundam.* 1983a, 22, 266.

Ruzicka, V. Jr.; Fredenslund, A.; Rasmussen, P. *Ind. Eng. Chem. Process Des. Dev.* 1983b, 22, 49.

Schwager, I.; Yen, T. F. *Anal. Chem.* 1979, 51, 569.

Schwarz, B. J.; Wilhelm, J. A.; Prausnitz, J. M. submitted to *Ind. Eng. Chem. Res.* 1987a

Schwarz, B. J.; Prausnitz, J. M. submitted to *Ind. Eng. Chem. Res.* 1987b

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

Tewari, K. C. "Correlation of Thermodynamic Properties of Coal Liquids"; Final Technical Report NSF/CPE-8317270; Air Products and Chemicals, Inc.: Allentown, PA, 1985.

Tsonopoulos, C.; Heidman, J. L.; Hwang, S.-C. *Thermodynamics and Transport Properties of Coal Liquids;* Wiley: New York, 1986.

Twu, H. C. *Fluid Phase Equilib.* 1984, 16, 137.

Watanasiri, S.; Owens, V. H.; Starling, K. E. *Ind. Eng. Chem. Process Des. Dev.* 1985, 24, 294.

Wilhelm, A.; Prausnitz, J. M. *Fuel* 1985, 64, 501.

Zygmunt, J. S.; Bartle, K. D. *Fuel* 1983, 62, 900.

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APPENDIX A: SAMPLE CALCULATION TO OBTAIN EQUATION-OF-STATE PARAMETERS FOR A FOSSIL FRACTION FROM CHARACTERIZATION DATA. PART I

For fraction WCLP 5, the characterization data provided by Rodgers et al (18) are:

$$weight\ \%\ C = 85.15$$
$$weight\ \%\ H = 10.25$$
$$weight\ \%\ N = 0.33$$
$$weight\ \%\ S = 0.20$$
$$weight\ \%\ O = 4.07$$

From NMR spectroscopy,

$$H_\alpha/H_{hc} = 0.213$$
$$H_\beta/H_{hc} = 0.398$$
$$H_\gamma/H_{hc} = 0.183$$
$$H_{aro}/H_{hc} = 1.0-H_\alpha/H_{hc}-H_\beta/H_{hc}-H_\gamma/H_{hc}$$
$$= 1.0-0.213-0.398-0.183 = 0.206$$

From IR spectroscopy, the abundance of OH is 1.9×10^{-2} $moles/100\ grams$. There are no detectable NH or NH_2 groups.

The number of carbon atoms for each 100 grams of sample can be calculated as

$$C/100\ grams = weight\ \%\ C/\ atomic\ weight\ of\ carbon \tag{1-A}$$
$$= 85.15/12.01115 = 7.089$$

Similar calculations can be performed for the other elements yielding

$$H/100\ grams = 10.16$$
$$N/100\ grams = N_t/100\ grams = 0.023$$
$$S/100\ grams = 0.0062$$
$$O/100\ grams = O_t/100\ grams = 0.254$$

$H_{hc}/100\ grams$ can be calculated from

$$H_{hc}/100\ grams = \tag{2-A}$$
$$H/100\ grams-OH/100\ grams-NH/100\ grams-2\times NH_2/100\ grams$$
$$= 10.16-1.9\times10^{-2}-0.0-2\times0.0 = 10.14$$

The hydrogen type distribution is obtained from

$$H_\alpha/100\ grams = H_{hc}/100\ grams \times H_\alpha/H_{hc} = 10.14 \times 0.213 = 2.16 \qquad (3\text{-A})$$

Similarly,

$$H_\beta/100\ grams = 4.04$$

$$H_\gamma/100\ grams = 1.86$$

$$H_{aro}/100\ grams = 2.09$$

For a given molecular weight, MW, the average number of carbon atoms per molecule (C) can be calculated from

$$C = (MW/100) \times (C/100\ grams) = (MW/100) \times 7.089 = 0.07089MW \qquad (4\text{-A})$$

Equations similar to Equations 4-A can be used to yield

$$H_\alpha = 0.0216MW$$

$$H_\beta = 0.0404MW$$

$$H_\gamma = 0.0186MW$$

$$H_{aro} = 0.0209MW$$

$$N_t = 0.00023MW$$

$$O_t = 0.00254MW$$

$$OH = 1.9 \times 10^{-4}MW$$

$$S = 6.2 \times 10^{-5}MW$$

There are no detectable NH or NH_2 groups.

Appendix B shows the final calculation of characterization parameters and equation-of-state parameters. The calculation yielding the final characterization parameters is not completed in this appendix, because, as discussed in this work, additional corrections to MW are needed.

APPENDIX B: SAMPLE CALCULATION TO OBTAIN EQUATION-OF-STATE PARAMETERS FOR A FOSSIL FRACTION FROM CHARACTERIZATION DATA. PART II

From Rodgers et al (18), the molecular weight of fraction WCLP 5 measured by mass spectroscopy is 140. From Equation 7 and from characterization data shown in Appendix A,

$$MW = 140(1.757 - 1.750 \times 0.213 - 1.319 \times 0.183) = 160 \qquad (1\text{-B})$$

From Equation 4-A,

$$C = 0.07089MW = 0.07089 \times 160 = 11.34$$

and

$$H_\alpha = 3.46$$

$$H_\beta = 6.46$$

$$H_\gamma = 2.98$$

$$H_{aro} = 3.34$$

$$N_t = 0.037$$

$$O_t = 0.406$$

$$OH = 0.030$$

$$S = 0.010$$

Using Equation 4 and the coefficients appearing in Tables II and III, we obtain

$$\varepsilon q/k = 106.11 + 48.281C + 36.856H_{aro} + 26.517H_\alpha + 15.810H_\beta + 11.152H_\gamma +$$
$$171.12N_t + 186.31NH + 177.23NH_2 + 52.928O_t + 364.10OH + 176.51S =$$
$$106.11 + 48.281\times11.34 + 36.856\times3.34 + 26.517\times3.46 + 15.81\times6.46 + 11.152\times2.98 +$$
$$171.12\times0.037 + 186.31\times0.0 + 177.23\times0.0 + 52.928\times0.406 + 364.10\times0.030 + 176.51\times0.010 = 1044K$$

Similarly, calculating v^* and c yields

$$v^* = 104.0cm^3/mole$$

$$c = 2.506$$

$$T^* = \varepsilon q/ck = 1044/2.506 = 416.6K$$

Using the calculated parameters, at $500K$ the predicted vapor pressure is $1.06bar$ and the saturated liquid density is $0.737g/cm^3$.

APPENDIX C: SAMPLE CALCULATION TO OBTAIN EQUATION-OF-STATE PARAMETERS FOR A MIXTURE CONTAINING FOSSIL-FUEL FRACTIONS

Using Equation 8 with the M_{ij} values in Table XV, for methane

$$k_{ij} = 0..2235 - 0.0774H/C - (0.5724 - 0.2173H/C)exp(-0.16C)$$

From the parameters in Appendix B H/C is 1.435 and C is 11.34

$$k_{ij} = 0..2235 - 0.0774\times1.435 - (0.5724 - 0.2173\times1.435)exp(-0.16\times11.34) = 0.0700$$

Using the equation of state parameters for methane given previously (22,23), the calculated Henry's constant for methane in WCLP cut 5 at 500 K is 438 bar.

Table I. Summary of Compounds In The Correlation Data Bank

class	carbon No. range	No. of compounds
n-alkanes	5-44	20
branched alkanes	5-42	41
naphthenes	5-21	13
other saturated hydrocarbons	6-31	60
condensed aromatics	6-14	4
other condensed hydrocarbons	9-18	7
other hydrocarbons	7-31	55
all hydrocarbons	5-44	200
pyridines	5-9	6
pyrroles	4-12	2
anilines	6-7	4
furans	4-12	3
phenols	6-9	11
thiophenes	4-12	7

Table II. Coefficients in Equation 4 for Hydrocarbons

cquation-of-state	coefficients (A_{ij})					
parameter (P_i)	intercept	C	H_{aro}	H_α	H_β	H_γ
$\varepsilon q/k$ (K)	106.11	48.281	36.856	26.517	15.810	11.152
v^* ($cm^3/mole$)	3.6449	1.9856	6.7651	4.4846	4.0046	3.9211
c	0.42933	-0.056347	0.24716	0.18034	0.12088	0.11828

Table III. Coefficients in Equation 4 for Heteroatomic Groups

equation-of-state parameter (P_i)	coefficients (A_{ij})					
	N_t	NH	NH_2	O_t	OH	S
$\varepsilon q/k$ (K)	171.12	186.31	177.23	52.928	364.10	176.51
v^* ($cm^3/mole$)	2.3937	2.0478	3.5319	5.0676	-1.9784	7.1123
c	0.36350	0.41090	0.49684	0.21380	0.95826	0.38986

Table IV. Summary of Errors in Vapor-Pressure Calculated for the Correlated Data Base

class	*A%AAD*	*W%AAD*	*A%Bias*	*W%Bias*
n-alkanes	36	62	36	62
branched alkanes	20	81	5.1	81
naphthenes	22	53	-11	53
other saturated hydrocarbons	20	69	-3.7	69
condensed aromatics	44	68	27	68
other condensed hydrocarbons	47	122	45	122
other hydrocarbons	27	80	-6.7	-80
all hydrocarbons	25	122	3.1	122
pyridines	20	36	1.5	36
pyrroles	24	28	3.2	28
anilines	7.2	9.2	0.0	8.4
furans	18	24	2.1	24
phenols	19	35	1.3	35
thiophenes	26	74	3.5	74

For a property z, and a data set of n points on a single substance,

$$\%AAD = 100\left(\sum_{i=1}^{n}\frac{|z_i^{calc.}-z_i^{meas.}|}{z_i^{meas.}}\right)/n$$

$$\%Bias = 100\left(\sum_{i=1}^{n}\frac{(z_i^{calc.}-z_i^{meas.})}{z_i^{meas.}}\right)/n$$

For a class containing m substances,

$$A\%AAD = \sum_{j=1}^{m}\%AAD_j/m$$

$$A\%Bias = \sum_{j=1}^{m}\%Bias_j/m$$

W%AAD and *W%Bias* are worst *%AAD* and worst *%Bias* for any substance in a class.

Table V. Summary of Errors in Liquid-Density Calculated for the Correlated Data Base

class	*A%AAD*	*W%AAD*	*A%Bias*	*W%Bias*
n-alkanes	1.4	2.4	0.6	2.4
branched alkanes	1.7	7.7	0.6	7.7
naphthenes	2.0	6.9	-1.7	-6.9
other saturated hydrocarbons	1.3	5.3	0.2	5.3
condensed aromatics	2.9	6.1	-1.2	-6.1
other condensed hydrocarbons	2.8	6.2	1.4	6.2
other hydrocarbons	1.5	4.5	0.0	-4.5
all hydrocarbons	1.6	7.7	0.2	7.7
pyridines	1.9	3.9	-0.2	-3.9
pyrroles	4.1	4.3	-0.1	-4.3
anilines	2.2	3.3	0.2	3.3
furans	5.6	8.6	1.4	8.6
phenols	1.5	2.4	0.2	2.4
thiophenes†	1.7	1.7	1.7	1.7

† Volume results refer only to data for thiophene

Table VI. Standard Characterization Data for Fossil-Fuel Samples

fraction		source	boiling range[a] (K)	boiling point[b] (K)	density at 60°F[c] g/cm^3
Exxon A	cut 1	crude oil	644 - 658	647	0.903
	cut 3		672 - 686	667	0.922
	cut 5		700 - 714	697	0.930
Exxon B	cut 1	crude oil	616 - 644	587	0.917
	cut 3		672 - 700	639	0.943
	cut 4		700 - 728	667	0.960
WCLP	cut 4	coal liquid	492 - 505	473	0.942
	cut 5		505 - 533	499	0.936
	cut 7		589 - 617	605	0.961
	cut 8		617 - 644	631	0.984
SRC	middle	coal liquid	473 - 598		
	heavy		598 - 698		

a Estimated from distillation. Data for SRC samples are given by Harrison et al. (1985).

b Estimated from subatmospheric vapor pressures.

c Estimated from densities at temperatures above 60°F.

Table VII. Molecular Weights of Fossil-Fuel Fractions as Measured by Several Methods

fraction		molecular weight measured by				
		gel permeation[a] chromatography	mass spectroscopy[a]	ASTM D2305 in benzene	ASTM D2305 in chloroform[b]	optimal fit to thermodynamic properties
Exxon A	cut 1	224	228	307	323	307
	cut 3	257	265	344	355	330
	cut 5	248	274	386	390	390
Exxon B	cut 1	199	201	256	262	233
	cut 3	221	248	307	360	282
	cut 4	232	269	334	363	315
WCLP	cut 4	153	122	135*	-	148
	cut 5	159	140	157*	-	164
	cut 7	163	209	240	-	240
	cut 8	185	215	243	-	256
SRC	middle	148	153	154*	-	-
	heavy	210	202	222	-	-

a Measured by Rodgers et al. (1987)

b Measured by Heppner (1985).

* Measured by freezing-point depression in benzene.

Table VIII. Summary of Errors in Predictions of Vapor Pressures and Liquid Densities of Fossil-Fuel Fractions

method	*A%AAD*	*A%Bias*	*W%AAD*	*W%Bias*
		vapor pressure		
1	17	1.9	25	-25
2	20	2.4	28	-28
3	14	7.8	25	25
4	45	-26	78	-78
5	21	19	48	48
6	35	-24	76	-76
		liquid density		
1	5.0	5.0	11.5	-11.5
2	4.6	4.6	11.5	-11.5
7	0.4	0.1	1.3	1.3
8	0.5	0.4	1.5	1.5

METHODS

1 present work, molecular weight from Equation 6

2 present work, molecular weight from Equation 7

3 modified Maxwell-Bonnell correlation, normal boiling point from measured vapor pressures [Tsonopoulos et al. (1986)]

4 modified Maxwell-Bonnell correlation, normal boiling point from distillation midpoint [Tsonopoulos et al. (1986)]

5 SWAP correlation, normal boiling point from measured vapor pressures [Smith et al. (1976) and Edwards et al. (1981b)]

6 SWAP correlation, normal boiling point from distillation midpoint [Smith et al. (1976) and Edwards et al. (1981b)]

7 Rackett equation, normal boiling point from measured vapor pressures [American Petroleum Institute (1983)]

8 Rackett Equation, normal boiling point from distillation midpoint [American Petroleum Institute (1983)]

Table IX. Summary of Model Compound Data Used for Correlation of k_{ij}

gas	carbon no. range	no. of model substances	temperature range (K)	maximum pressure (bar)
H_2	5-30	22	248-730	689
CH_4	5-44	27	176-704	303
C_2H_6	6-30	21	233-517	130
CO_2	5-44	35	273-704	176
H_2S	6-16	18	278-478	130

Table X. Parameters for Correlation of k_{ij}

gas	M_{i0}	M_{i1}	M_{i2}	M_{i3}	M_{i4}	avg. abs. error in k_{ij}
H_2	0.1579	–0.0698	0.0	0.0	0.0	0.03
CH_4	0.2235	–0.0774	0.5724	0.2173	0.16	0.01
C_2H_6	0.1109	–0.0241	0.1409	0.0320	0.06	0.008
CO_2	0.0742	0.0207	0.1894	0.0149	0.14	0.02
H_2S	0.0290	0.0150	0.6166	0.2235	0.32	0.008

Table XI. Summary of Errors in Predictions of Pressure for Solubilities of Gases in Fossil-Fuel Fractions

	corrected molecular weight from							
	VPO				MS			
gas	*A%AAD*	*A%Bias*	*W%AAD*	*W%Bias*	*A%AAD*	*A%Bias*	*W%AAD*	*W%Bias*
H_2	16	12	26	22	15	4.3	26	22
CH_4	8.3	-6.1	20	-20	7	1	-7.1	25
C_2H_6	7.4	-5.0	15	-15	7.6	-4.9	11	-11
CO_2	10	-9.7	23	-23	10	9.7	23	-23
H_2S	12	8.1	12	8.1	13	12	15	12

CAPTIONS

Figure 1. Correlated Equation-of-State Parameters for N-Alkanes

Figure 2. Calculated Vapor Pressures for Three Fluids Whose Molecules Contain Forty Carbon Atoms

Figure 2. Calculated Vapor Pressures for Three Fluids Whose Molecules Contain Fifty Carbon Atoms

Figure 4. Calculated Heats of Vaporization for Three Fluids Whose Molecules Contain Forty Carbon Atoms. Temperature Range is for Boiling Points Between 0.0005 and 1.0 Bar

Figure 5. K-Factors for a Mixture of a Heavy Aromatic Hydrocarbon With Five Gases at 650 K

Figure 6. Henry's Constants of Methane in Solvents of Varying Size and Structure

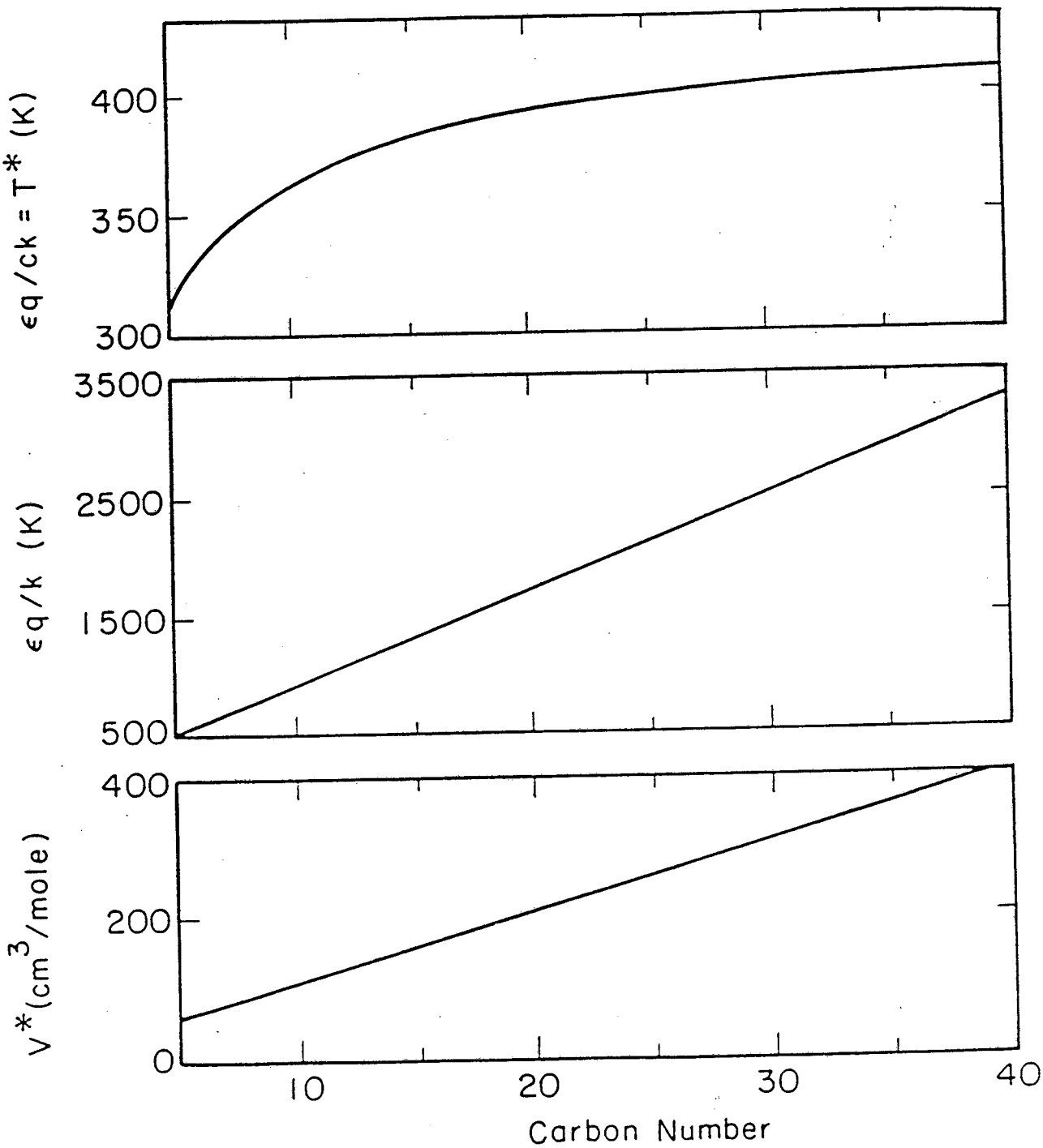
400
350
300
εq/ck = T* (K)
3500
2500
1500
500
εq/k (K)
400
200
0
V*(cm3/mole)
10
20
30
40
Carbon Number

Figure 1.

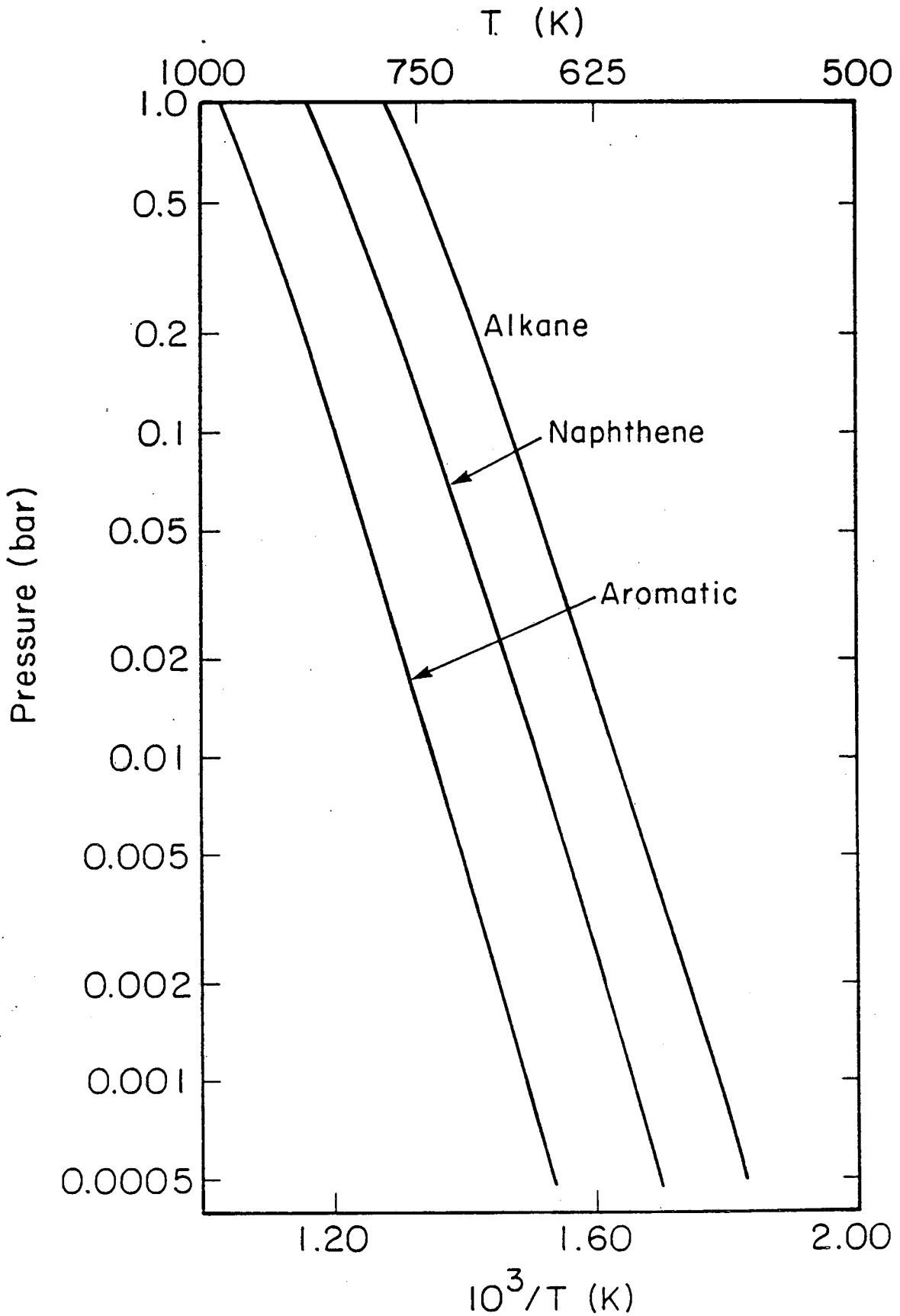
T (K)
1000
750
625
500
1.0
0.5
0.2
0.1
0.05
0.02
0.01
0.005
0.002
0.001
0.0005
Pressure (bar)
Alkane
Naphthene
Aromatic
1.20
1.60
2.00
$10^3/T$ (K)

Figure 2.

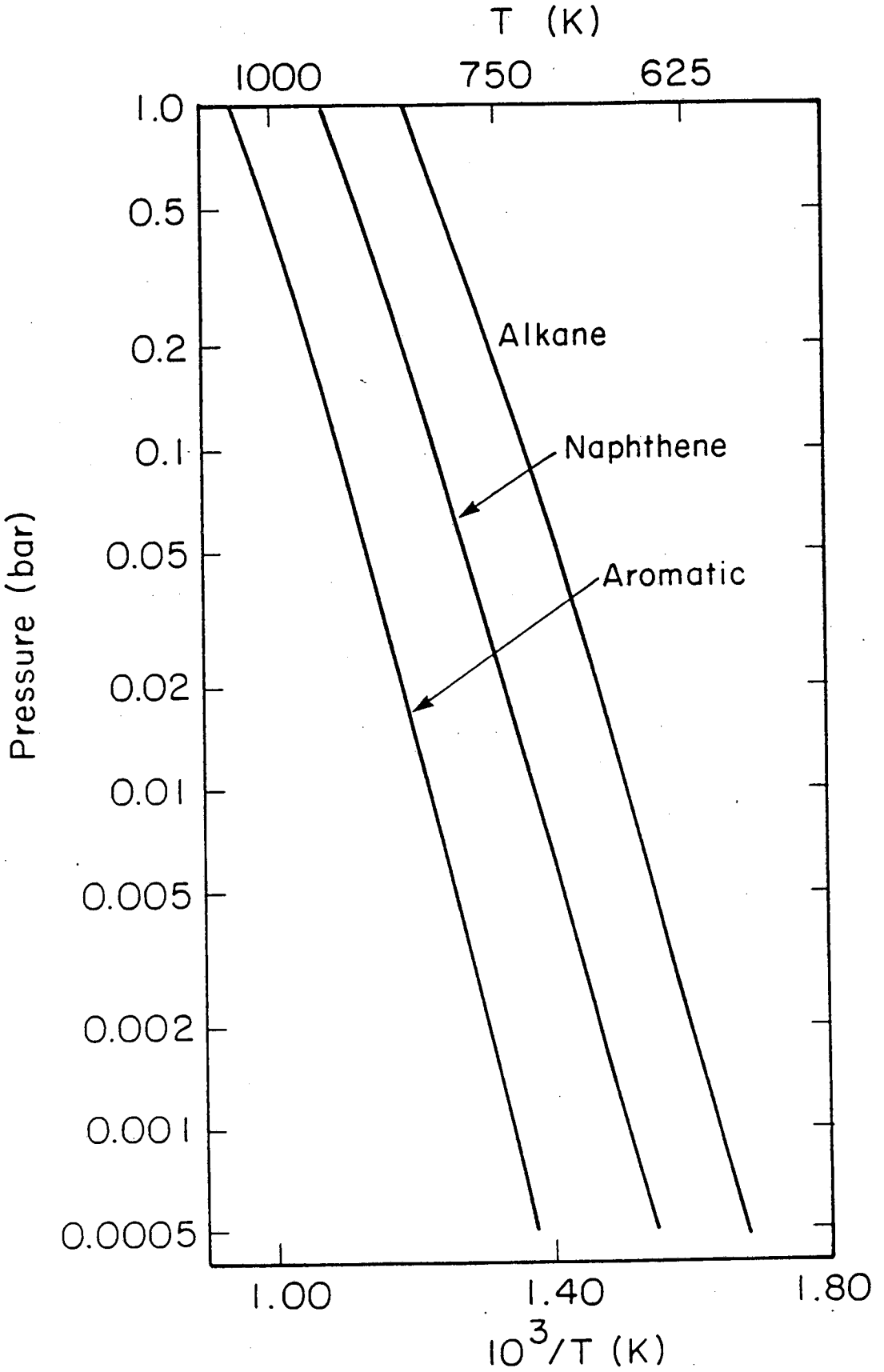
T (K)
1000
750
625
1.0
0.5
0.2
0.1
0.05
0.02
0.01
0.005
0.002
0.001
0.0005
Pressure (bar)
Alkane
Naphthene
Aromatic
1.00
1.40
1.80
10^3/T (K)

Figure 3.

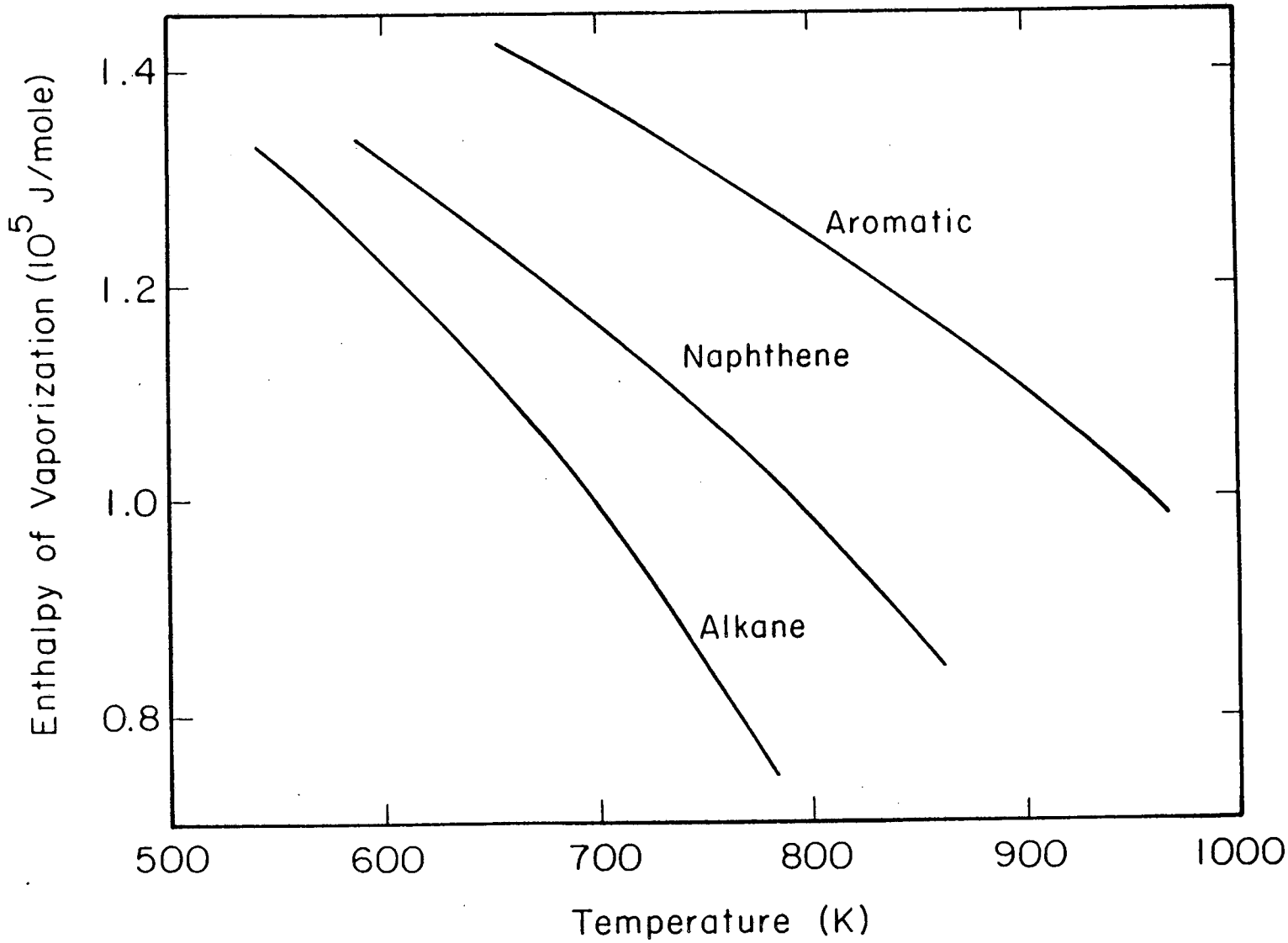
Enthalpy of Vaporization (10^5 J/mole)
1.4
1.2
1.0
0.8
500
600
700
800
900
1000
Temperature (K)
Aromatic
Naphthene
Alkane

Figure 4.

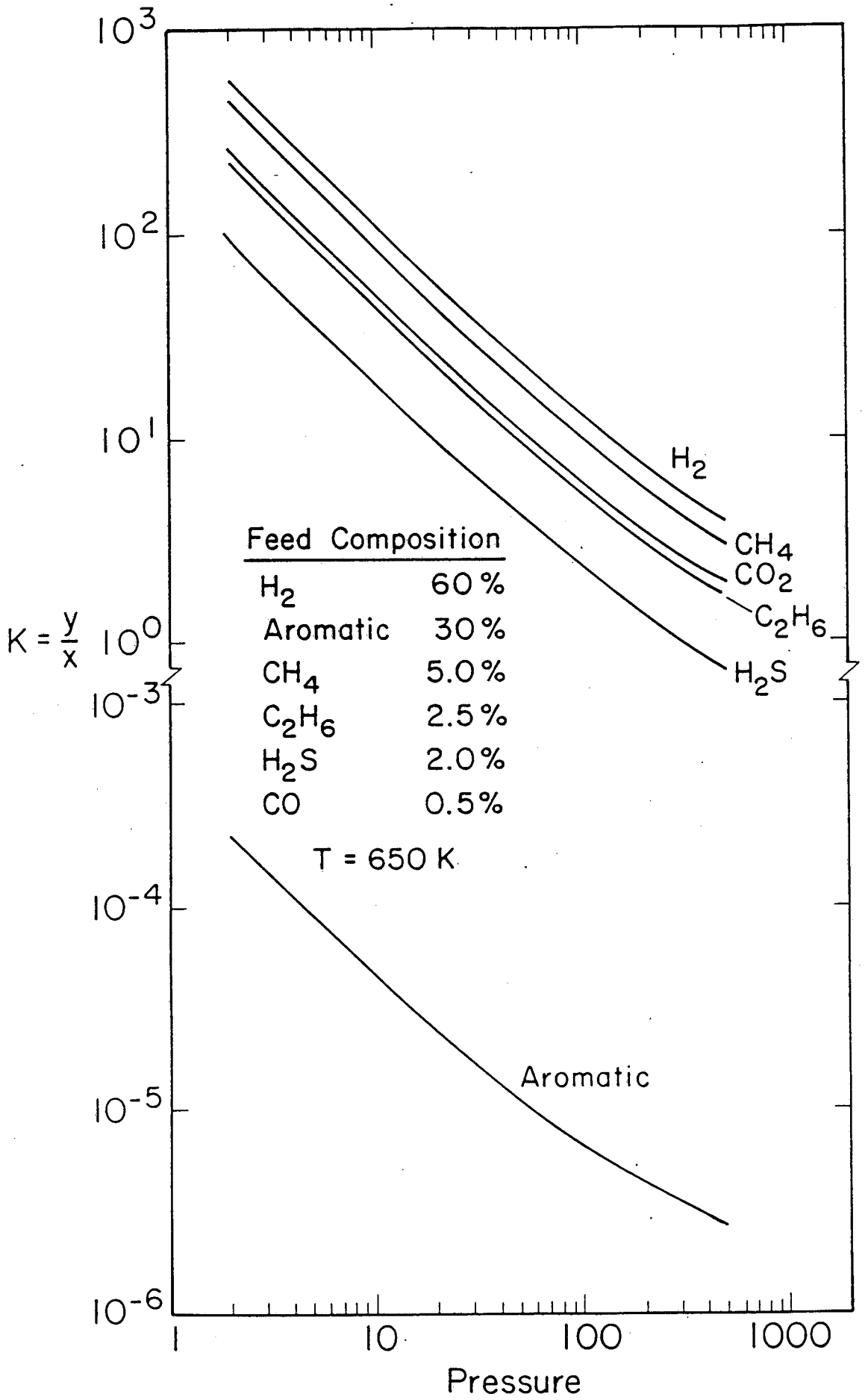
10^3
10^2
10^1
10^0
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$K = \frac{y}{x}$
H_2
CH_4
CO_2
C_2H_6
H_2S
Feed Composition
H_2 60 %
Aromatic 30 %
CH_4 5.0 %
C_2H_6 2.5 %
H_2S 2.0 %
CO 0.5 %
T = 650 K
Aromatic
1
10
100
1000
Pressure

Figure 5.

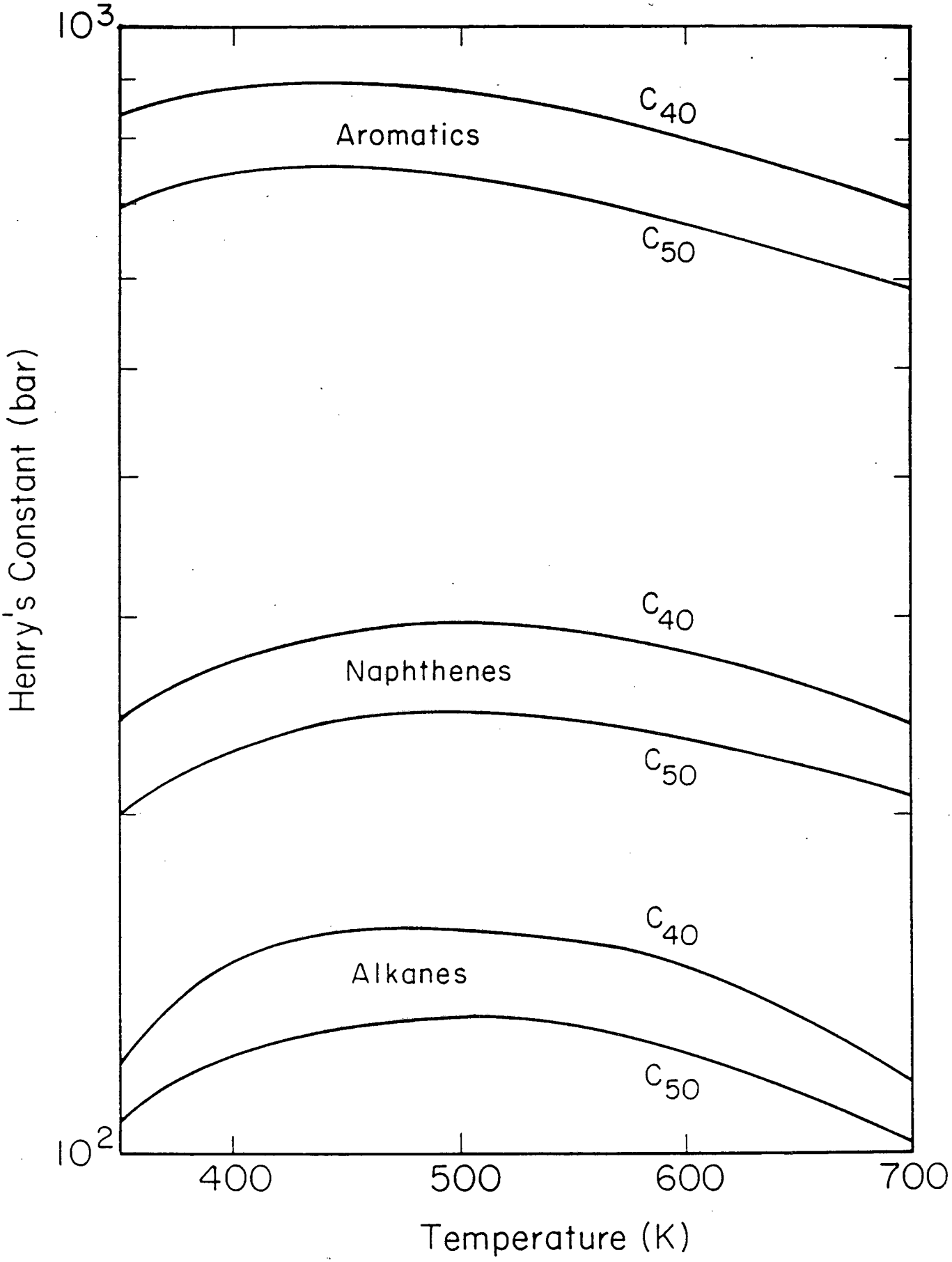
10^3
10^2
Henry's Constant (bar)
Aromatics
C_{40}
C_{50}
Naphthenes
C_{40}
C_{50}
Alkanes
C_{40}
C_{50}
400
500
600
700
Temperature (K)

Figure 6.

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