Thermodynamic Model for Calorimetric and Phase Coexistence Properties of Coal Derived Fluids

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The work on the thermodynamic model was performed by the principal investigator with some assistance from the graduate student, Mr. Xiaojin Xi. Experimental work on the VLE apparatus and the chromatographic characterizations of coal liquids is being performed by the graduate student Mr. Shaukat Mahmood. All the work is supervised and directed by the principal investigator, V.N. Kabadi. The project has also benefitted from the assistance of two undergraduate students, Ms. Kimberley Rollins and Ms. Angelia Charles.

DISCLAIMER

ABSTRACT

On September 1, 1989 work was initiated on a project to extend the available vapor-liquid equilibrium model for coal fluids to allow satisfactory predictions of excess enthalpies of coal liquids at high pressures. The available vapor liquid equilibrium model was developed with support from previous grant from DOE-PETC (Grant no. DE-FG22-89PC90541). The current project also involves measurement of some model compound VLE data and chromatographic characterization of coal liquids for distribution of heteroatoms. A computational thermodynamic model for VLE, excess enthalpies and heat capacities of coal derived liquids has been developed. The model uses the modified UNIFAC correlation for the liquid phase. Some unavailable UNIFAC interactions parameters have been regressed from experimental VLE and excess enthalpy data. The computations are carried out using the method of continuous thermodynamics. Model is used to derive interesting conclusions on the effect of oxygen, nitrogen, and sulfur heteroatoms on the thermodynamic properties of coal liquids. When compared with limited experimental data available for coal liquids the model shows good agreement. Some progress has been made on binary VLE measurements and size exclusion chromatography of coal liquids.

PROJECT OBJECTIVE AND SCOPE

The objective to this project is to develop a thermodynamic model for phase equilibria and calorimetric properties of coal derived fluids. Through efforts of a previous project (DE-FG22-86PC90541), a model for phase equilibria of coal derived liquids is already available. In this project, this model is to be extended to include calorimetric properties as well. The modification involves the use of the modified UNIFAC correlation with suitably regressed parameters, combined with an appropriate equation of state to represent compressibility of the liquid phase. To accomplish this satisfactorily, the proposed work includes three tasks: (1) Refinement of the characterization procedure to include distribution of sulfur, oxygen, and nitrogen heteroatoms in coal liquids. This is to be accomplished by size exclusion chromatography of coal liquid samples, followed by elemental and FTIR analysis of separated fractions. (2) Measurement of high temperature (up to 400°C) and high pressure (up to 1000 psi) VLE data for binary systems of selected model compounds. The VLE apparatus assembled as a part of the previous project will be used for this purpose, and (3) Development of the thermodynamic model. The final product will include a computer program which with measurable properties of coal liquids as input, will give results for phase coexistence properties and excess enthalpies in the liquid phase.

TECHNICAL HIGHLIGHTS AND MILESTONES

In this report, we present the results of application of our thermodynamic model for VLE and calorimetric properties of coal liquids. The thermodynamic model for defined mixtures was presented in a previous report (October 1, 1990) and includes the following methods:

1. Group characterization of compounds by the method of White and Coworkers [1,2]

2. Modified UNIFAC correlation of Larsen et al [3] for the activity coefficient in the liquid phase

3. Truncated virial equation with Hayden-O'Connell correlation [4] for vapor phase

4. Joback's modification of Lydersen's method [5] for estimation of critical pressure and acentric factors

5. Lee-Kesler correlation [6] for vapor pressures

6. Modified Rackett equation [7] for liquid densities

7. Rowlinson-Bondi [5] corresponding states method for pure liquid heat capacities.

8. Joback's group contributions method [5] for ideal gas heat capacities.

The group characterization of aromatic compounds and the details of the thermodynamic model were described in the previous report. In particular, the model development included generation of UNIFAC group parameters for the modified UNIFAC correlation. The functional groups and their UNIFAC volume and surface area group parameters are given in Table 1 and UNIFAC binary group interactions parameters are presented in Table 2. A number of binary interaction parameters are unavailable because of lack of VLE and enthalpy data.

The main objective of this work is to apply the method of continuous thermodynamics to VLE and calorimetric properties of coal liquids and to determine the best representation of coal fluids by continuous distributions. In particular, we wish to determine the parameters for distribution functions that are most suitable for this purpose. Coal derived fluids consist of mainly polynuclear aromatic compounds

with finite amounts of oxygen, nitrogen and sulfur heteroatoms. Molecular weight would be a good parameter for purely hydrocarbon compounds. Separate distributions may be defined for compounds containing heteroatoms. Or, alternatively a bivariate distribution with molecular weight and a second parameter representative of the composition of the heteroatoms may be used. Here, we have used univariate function with molecular weight as the single parameter. Various distributions are employed, one for hydrocarbons, one for hydrocarbons containing oxygen, one for hydrocarbons containing nitrogen, and one for hydrocarbons containing sulfur.

Thermodynamic Model for Coal Fluids

The thermodynamic model developed in this work is a combination of the continuous thermodynamic method and the thermodynamic model for defined mixtures. As an example, the procedure for the bubble point temperature calculation using our model is outlined below.

For a given coal fluid initially single or multiple continuous distributions with molecular weight as the characterizing parameter, have to be defined. Molecular weight range, MW_i to MW_f, mean molecular weight, $\overline{MW}$ and variance of molecular weight, σ^2_{MW}, must be known to generate a continuous distribution. The mean and variance are first scaled between 0 and 1 by the following equations,

$$\Delta MW = MW_f - MW_i \tag{1}$$

$$\theta_M = \frac{(\overline{MW} - MW_i)}{\Delta MW} \tag{2}$$

$$\sigma^2_M = \frac{\sigma^2_{MW}}{\Delta MW^2} \tag{3}$$

where θ_M and σ^2_M are the mean and the variance scaled between 0 and 1. Distribution parameters α and β are next calculated from,

$$\alpha = \frac{\theta^2_M(1-\theta_M)}{\sigma^2_M} - \theta_M \qquad (4)$$

$$\beta = \alpha\left(\frac{1}{\theta_M} - 1\right) \qquad (5)$$

Equations 4 and 5 are inverted forms of the following equations.

$$\theta = \frac{\alpha}{\alpha+\beta} \qquad (6)$$

$$\sigma^2 = \frac{\alpha\beta}{(\alpha+\beta)^2(\alpha+\beta+1)} \qquad (7)$$

The corresponding univariate distribution function is then given by,

$$F(y) = \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} \, y^{\alpha-1}(1-y)^{\beta-1} \qquad (8)$$

where the distributed variable y is given by

$$y = \frac{MW-MW_l}{MW_f-MW_l} \qquad (9)$$

note that y is bounded between 0 and 1.

For each distribution, the relative compositions of different functional groups are considered independent of molecular weight. The bubble point temperature calculation involves computation of temperature and vapor phase composition from the knowledge of pressure and liquid phase composition. The first step in the calculation involves discretization of the continuous distributions by using the Gaussian quadrature technique. The number of quadrature points are chosen according to the desired accuracy of the calculation. In this work we have used ten quadrature points to represent a distribution. To generate the quadrature points, the continuous distribution F(y) first has to be scaled to the range -1 < x < 1. The transformation for this is simply given by,

$$x = 2y-1 \qquad (10)$$

The weighting functions and the compositions of the quadrature points are then determined using equations 11 through 14.

$$\int_{-1}^{1} F(x)\,dx = \sum_{i}^{n} w_i\, F(x_i) \qquad (11)$$

$$w_i = \frac{\pi}{n}(1 - x_i^2)^{\frac{1}{2}} \qquad (12)$$

$$x_i = -\cos\left[\frac{(2i-1)\pi}{2n}\right] \qquad (13)$$

Mole fraction of each quadrature point is defined by

$$z_i = \eta_j\, F(x_i)\, w_i \qquad (14)$$

where η_j is the mole fraction of the continuous distribution j.

The distributions are thus converted to n discretized quadrature points with known composition. These n quadrature points are now treated as n components of a multicomponent system, and the bubble point temperature, vapor phase compositions are calculated using the thermodynamic model described before. The discrete compositions of the vapor phase are next converted to a continuous distribution as follows. First the mean molecular weight $\overline{MW}$ and the variance σ^2_{MW} corresponding to distribution j in the vapor phase are calculated as

$$\overline{MW} = \frac{\sum_k W_k \, MW_k}{\eta_j} \tag{15}$$

$$\sigma^2_{MW} = \frac{\sum W_k \, MW_k^2}{\eta_j} - \overline{MW}^2 \tag{16}$$

where W_k is the mole fraction of quadrature point k in the vapor phase and η_j is the mole fraction of the continuous distribution j in the vapor phase or

$$\eta_j = \sum_{k=1}^{n} W_k \tag{17}$$

From $\overline{MW}$ and σ^2_{MW}, the continuous distribution F(y) is generated using equations 1 through 9 as described before. A dew point calculation is carried out in a similar way when the vapor phase composition is known instead of the liquid phase.

Furthermore, a procedure is also developed for the computation of heat capacities of coal liquids. The liquid phase distributions representing a coal liquid are initially discretized by the method of quadratures. Each quadrature point is considered a pure liquid. The heat capacity of the coal liquid is then computed as a sum of three terms as follows

$$c_p = c_p^E + \sum_{I=1}^{N} Z_I (c_{pI}^L - c_{pI}^0) + \sum_{I=1}^{N} Z_I c_{pI}^0 \qquad (18)$$

The first term is the excess heat capacity which is obtained from the modified UNIFAC correlation; the second term represents the residual pure liquid heat capacities summed over all the quadrature points. Rowlinson-Bondi [5] corresponding states method was used for this term and is given below:

$$\frac{c_p^L - c_p^0}{R} = 1.45 + 0.45(1-T_r)^{-1} + 0.25\omega[17.11$$
$$+ 25.2(1-T_r)^{\frac{1}{3}} T_r^{-1} + 1.742(1-T_r)^{-1}] \qquad (19)$$

The ideal gas heat capacity required in equations 18 and 19 was calculated using Joback's group contribution method [5]

$$c_p^0 = \left(\sum_j n_j \Delta a - 37.93\right) + \left(\sum_j n_j \Delta b + 0.210\right) T$$
$$+ \left(\sum_j n_j \Delta c - 3.91 \times 10^{-4}\right) T^2 + \left(\sum_j n_j \Delta d + 2.06 \times 10^{-7}\right) T^3 \qquad (20)$$

where c_p^0 is in J/(mol °K) and T is temperature in °K. The group contributions Δa, Δb, Δc and Δd corresponding to the sixteen groups of Table 1 are tabulated in Table 3. Thus a method for computation of heat capacities of coal liquids is available and uses the same functional group characterization of coal liquids as in our VLE model

Definition of Continuous Distributions and Corresponding Average Molecules

Although we have made an assumption that for each continuous distribution,

the relative composition of the functional groups is independent of molecular weight, this functional group composition must be known. Furthermore, for the results to be reflective of thermodynamics of coal fluids, the functional group compositions must correlate with available experimental data for coal liquid distillates. Fortunately, some data of this type appeared in the literature recently [1]. In all the calculations for the parametric study, the compositions of the different groups in the average molecule are chosen such that the composition is close to a representative coal liquid. In particular, we have defined four continuous distributions: 1) hydrocarbon distribution, 2) phenolic distribution, 3) pyridinic distribution, and 4) thiophenic distribution. The individual groups in each of these distributions are:

1)   Hydrocarbon distribution: Benzene, benzo group, naphthenic CH_2 and paraffinic CH_2 family.

2)   Phenolic distribution: This distribution contains all the same groups listed for hydrocarbon distribution in the same ratio. In addition, it includes a hydroxyl group (-OH) with the ratio of hydroxyl to benzene group of 1:1.

3)   Pyridinic distribution: This distribution contains all the same groups listed for hydrocarbon distribution in the same ratio. In addition it includes a pyridinic group with the ratio of pyridinic to benzene group of 1:1.

4)   Thiophenic distribution: This distribution again contains all the same groups listed for hydrocarbon distribution in the same ratio. In addition, it includes a thiophenic group with the ratio of thiophenic to benzene group of 1:1.

Same parameters are used to generate each of these four distributions.

Of all the groups listed in Table 1 and in the original data of White and coworkers [1], only the following groups appear in the average molecules of the four distributions: benzene, benzo group, paraffinic CH_2, naphthenic CH_2, hydroxyl group, pyridine and thiophene. All the hydrocarbon functional groups are thus lumped into the first four groups. Specifically, all paraffinic alkyl groups have been lumped into paraffinic CH_2, all hydroaromatic groups are lumped into a naphthenic CH_2. Furthermore, a multi-ring aromatic is represented by a benzene group and multiple benzo groups. Although more detailed group definitions could have been used, such an exercise would introduce more complications in the calculations without adding

appreciably to the useful information that could be derived from the results.

This study was intended to address the thermodynamics of H-Coal and Wilsonville distillates studied by White and coworkers [1] whose published functional group compositions data show that oxygen, nitrogen, and sulphur heteroatoms are primarily in the phenolic -OH, pyridine and thiophene groups. We have, therefore, included these three additional groups in our study. For coal distillates with non-negligible concentrations of other functional groups, such as, ether linkages, amine, sulfide etc., similar studies as ours could be carried out.

The average molecules for the four distributions were generated in the following manner. Arbitrary, but realistic ratios were chosen for the relative compositions of the four hydrocarbon groups. These ratios were considered the same for all distributions. In addition, for the phenolic, pyridinic and thiophenic distributions, hydroxyl, pyridine and thiophene groups were added to the respective average molecules in amounts equal to the molar compositions of the benzene group. The group compositions of the average molecules of the four distributions, normalized to a molecular weight of 100 g/mol, are listed in Table 4.

An assumption that is made in defining the four distributions is that oxygen, nitrogen and sulfur functionalities each appears on separate molecules, and that the concentrations of compounds containing two or more of oxygen, nitrogen and sulfur functionalities on the same molecule are negligible. This assumption is justifiable for low molecular weight coal liquids (<200). However, to apply these studies to high molecular weight coal liquids additional distributions with average molecules containing two or more of hydroxyl, pyridine and thiophene groups need to be defined. The consequences of our assumptions will be later tested when the model is applied to predict boiling ranges of H-coal and Wilsonville distillates. In the next section we present the results of the calculations using our continuous thermodynamics model with the distributions and the average molecules defined as described above.

Results and Discussion

Here, we report results for thermodynamics of coal liquids obtained from the continuous thermodynamics model presented in the previous sections. All the results presented here are for bubble point, dew point calculations, and liquid heat capacities.

In all our calculations, we used the hydrocarbon, phenolic, pyridinic and thiophenic distributions described before, the distribution parameters and the corresponding average molecules given in Table 4. Initially, results were obtained with the feed composed of the above distributions in various combinations and compositions. The objective was to investigate whether the compounds containing the oxygen, nitrogen and sulfur heteroatoms need to be represented by separate distributions or could be averaged with the hydrocarbons into a single continuous distribution.

These results are organized into three studies. In the first study, we study the effect on the thermodynamic properties, when the feed consists of two separate distributions (hydrocarbon distribution and one of the other three distributions) or a single equivalent distribution with the same composition of the functional groups. The properties compared include bubble point temperature, dew point temperature, group compositions of coexisting phases and liquid heat capacities. It should be noted here that when the feed is represented by a single distribution, the functional group composition of the liquid and vapor phases computed are identical, even though the molecular weight distributions corresponding to the two phases are different. This is because corresponding to each distribution there is an average molecule with fixed relative group compositions. Therefore, the results for two distributions will compare well with those for a single distribution, when the calculated molecular weight distributions corresponding to the two distributions are close to overlapping; or, the average molecules corresponding to the two distributions exhibit similar behavior. Differences in results would be expected if the average molecules corresponding to two distributions represent vastly different types of functional groups.

We have furthered our investigation by comparing the results obtained when the feed consists of three distributions in certain mole fractions or two equivalent distributions obtained by averaging two of the three distributions or a single distribution obtained by averaging all three distributions. Each of these studies is valuable to arrive at final recommendations for the application of the continuous thermodynamics approach to coal fluids. Finally, we show comparisons of our model results with some experimental data available in the literature.

Two Distributions Versus One Equivalent Distribution Case

For this and all the later studies, results are reported for bubble point and dew point temperatures and the functional group compositions in the computed coexisting phases i.e. vapor phase for the bubble point calculation and liquid phase for the dew point calculation. Additionally, heat capacity of the liquid phase is computed as described before. Comparison of heat capacities is not done for calculations involving thiophenic distributions, because UNIFAC binary interaction parameters for thiophenic group were regressed using only VLE data. Excess enthalpy data are not available for mixtures involving thiophenic compounds. The calculated coexisting phases are represented by different molecular weight distributions for different cases; therefore, to better exhibit the differences between different calculations, we compare the group compositions calculated per unit mass instead of per unit mole of the coexisting phases. The procedure used to calculate the composition of a group from the results of a bubble point temperature calculation is outlined below.

In a calculation where the coal liquid is described by two distributions in the liquid phase, the bubble point temperature, the overall distribution composition in the vapor phase, and the function $F(y)$ corresponding to each distribution (equation 8) are computed using the model explained before. The above information is also determined for the equivalent single distribution calculation. For a given range of molecular weights the distributed variable y is related to molecular weights by equation 9. The mass of material (m_{12}) of molecular weight from MW_1 to MW_2 per

one mole of distributions is given by,

$$m_{12} = \int_{y_1}^{y_2} MW F(y) \, dy = \frac{1}{MW_f - MW_i} \int_{MW_1}^{MW_2} MW F(MW) \, d(MW)$$

(21)

where y_1 and y_2 are the values of the distributed variable corresponding to MW_1 and MW_2. Using equation 9, m_{12} may be written as

$$m_{12} = MW_i \int_{y_1}^{y_2} F(y) \, dy + (MW_f - MW_i) \int_{y_1}^{y_2} y F(y) \, dy$$

(22)

The above integral is computed for each distribution.

When the integration is from the initial molecular weight MW_i to the final molecular weight MW_f, the corresponding result from equation 22 gives the mass of the total material (m_j) per unit mole of distribution j. In this calculation, the first integral becomes unity and an analytical expression is available for the second integral and is given below.

$$\int_0^1 y F(y) \, dy = \int_0^1 y^a (1-y)^{\beta-1} \, dy = \frac{\Gamma(a)\Gamma(\beta)}{\Gamma(a+\beta)}$$

(23)

where α and β are the distribution parameters, and a is $\alpha + 1$.
Furthermore, if η_j is the calculated mole fraction of distribution j in the vapor phase, the mass of the material corresponding to distribution j per unit mole of the vapor is simply given by $m_j \eta_j$.

Now, suppose that we wish to calculate the composition of group k in 100g of the vapor. As each distribution is defined by a fixed average molecule, from Table 4, we calculate moles of group k per unit mass for each distribution j. If these are

denoted by μ_{kj}, the required moles of group k (n_k) per 100g of the vapor is calculated from the following equation,

$$n_k = \frac{\sum_j \mu_{kj} m_j \eta_j}{\sum_j m_j \eta_j} \times 100 \qquad (24)$$

In the first study on two distributions versus single distribution calculations, a hydrocarbon and a phenolic distribution corresponding to the mean molecular weight of 176.3 g/mol are considered based on the composition given in Table 4. The results of bubble point and dew point calculations with feeds comprising of 0.05 to 0.95 mole fractions of each of the distributions are shown in Table 5. For the feed comprising of equimolar mixture of the two distributions, the group compositions of the coexiting phases are tabulated in Table 6 and the distributions themselves are plotted in Figures 1 and 2 for the bubble point and dew point calculations respectively. The comparisons of bubble/dew point temperatures and liquid heat capacities calculated using two distributions and an equivalent single distribution show differences between the two sets of values, but these results by themselves are not enough to justify two distribution calculations. It is the differences between the calculated group compositions of coexisting phases that we believe are more significant, and want to draw attention to. The vapor/liquid phase compositions listed in Table 6 show high deviation of as much as 25% for the composition of hydroxyl group in the redistributed vapor/liquid phases.

This study shows that the phenolic distribution has to be considered as a separate distribution to avoid large errors in estimating thermodynamic properties of oxygen containing coal derived fluids. Figures 1 and 2 show the plots of the distributions for the liquid, and the vapor phases for the two and single distribution bubble point and dew point calculations. The separation of the two distributions in the vapor phase in Figure 1 and liquid phase in Figure 2 is responsible for the differences in the computed thermodynamic properties.

In the second part of the study a hydrocarbon and a pyridinic distribution corresponding to the mean molecular weight of 176.3 gms./mol are considered. The temperatures at pressure of 1.013 bars are shown in Table 7. It can be seen that even at significant composition of the pyridinic distribution the deviation in bubble/dew point temperatures and liquid heat capacities are less. The redistributed group compositions of the coexisting phases are tabulated in Table 8. The comparison of pyridinic group composition for the two calculations shows about 18% difference in the composition which cannot be ignored. The liquid, vapor phase distributions for the two, and single distribution calculations are shown in Figures 3 and 4. Separation of pyridinic and hydrocarbon distributions is observed, but the separation is not as large as in the case of phenolic distribution.

In the next calculation hydrocarbon and thiophenic distributions of mean molecular weight of 176.3 gms/mol are considered. The temperatures are tabulated in Table 9. Comparisons of the temperatures show negligible differences between the two and single distribution calculations. The redistributed group compositions in the coexisting phases are listed in Table 10. The thiophenic group composition remains almost the same for the two calculations. This study clearly shows that the thiophenic distribution can be averaged with a hydrocarbon distribution without affecting the phase equilibrium properties of the coal derived fluid. The liquid, vapor phase distributions for the two, single distribution calculations are shown in Figures 5 and 6. The curves corresponding to two distributions practically overlap.

Three, Two Equivalent, One Equivalent Distributions study

In this study three independent distributions, namely, hydrocarbon (I), phenolic (II) and pyridinic (III) with mean molecular weight of 176.3 gms/mol are used to see the effect of phenolic distribution on averaging of the other two distributions, and to further see the differences in the results when all three distributions are averaged into one. Bubble point and dew point calculations are carried out for three sets of distribution compositions $(x_I = 0.1, x_{II} = 0.4)$, $(x_I = 0.3, x_{II} = 0.4)$ and $(x_I = 0.5, x_{II} = 0.4)$.

Significant results from these calculations are shown in Table 11. In general, little differences in results are observed between three and two equivalent distributions calculations, but results for equivalent single distribution calculations vary considerably from the other two sets. This once again shows that the thermodynamic properties of coal liquids are very sensitive to the distribution of phenolic compounds. The distributions of coexisting phases corresponding to $(x_I = 0.3, x_{II} = 0.4)$ calculations are plotted in Figures 7 and 8. Again large separations are observed between phenolic and the other two distributions.

Estimation of boiling ranges for experimental data

In this section bubble point and dew point temperatures are estimated as boiling ranges for the experimental data obtained from the work of White and coworkers [1]. The distillates considered in this study are H-Coal and Wilsonville distillates. Since, the concentrations of nitrogen, sulphur groups were very low, two distributions have been considered as follows,

Distribution 1 : Benzene, Benzo group, Napthenic CH_2, Paraffinic CH_2, Pyridine and Thiophene.

Distribution 2 : Benzene, Benzo group, Napthenic CH_2, Paraffinic CH_2 and Hydroxyl group.

For the first distribution the relative ratios of the different groups are fixed as given in the data. In the second distribution the ratios are the same as in the first distribution apart from having the hydroxyl group to benzene group in the ratio of 1:1. These ratios of the groups of the distributions are then scaled to the mean molecular weight of the distillate. Mean molecular weights of the distillates were obtained from the work of Allen [8]. A mass balance calculation is carried out with the actual number of hydroxyl groups given in the experimental data as the basis. This gives the number of all other groups in the second distribution. Then, a mass balance is carried out for the amount of benzene groups in the first distribution, using the number of groups in the actual data, and the groups in the second distribution. By, this way the overall composition of the first and second distributions can be evaluated. Distribution

parameters were chosen such that variance for each distribution was adjusted to give a well behaved bell-shaped curve. For each distillate the overall composition of the two distributions and the individual group composition of the distributions are tabulated in Tables 12 and 13 for the H-Coal distillates and in Tables 14 and 15 for the Wilsonville distillates.

Bubble point and dew point temperatures calculated for the different distillates are tabulated for single and two distributions calculations in Tables 16 and 17. It can be seen that the temperatures predicted for both the H-Coal and Wilsonville distillates are quite close to the experimental boiling range for low and moderate boiling fractions and the errors increase towards the high boiling fractions. These errors could be due to the following reasons,

1) The temperatures given as boiling range for each of the distillates have only been approximated as bubble point and dew point temperatures.

2) The model uses the UNIFAC model which applies only at moderate temperatures and pressures. We have stretched applicability of this model in these calculations.

3) At high molecular weights, additional distributions with average molecules having mixed oxygen, nitrogen and sulfur functionalities need to be defined.

Comparison with Experimental Heat Capacity Data:

Limited heat capacity data on coal liquid distillates are available in the literature. One such data set is that of Gray and Holder [9,10], who have measured heat capacities of SRC II coal distillates. They have also reported data on elemental analysis and molecular weights of these fractions. For two of these fractions (Fraction 6 and Fraction 8), we have generated distribution parameters for a phenolic distribution and a hydrocarbon distribution with trace amounts of pyridine and thiophenic groups. The distribution parameters, compositions of distributions and group compositions of the average molecules are given in Table 18. These were then used to compute liquid heat capacities at various temperatures. Comparison between calculated and experimental heat capacities are shown in Table 19. Very good

agreements are observed.

Conclusions

A thermodynamic model for coal fluids has been successfully develored. The model uses the continuous thermodynamic framework to approximate the unknown compounds in the respective molecular weight ranges and an average molecule method for defining the group composition for the distribution. The characterization of the fluid is done in terms of functional groups for which the thermodynamic parameters are available from literature. Group contribution techniques have been used to account for liquid and vapor phase non-idealities.

The model developed is capable of doing phase equilibrium calculations for continuous and semi-continuous mixtures using representative one parameter single and multiple distributions, and is capable of calculating calorimetric properties of coal liquids. The detailed parametric study carried out under different conditions of pressure, composition, boiling range has given very valuable information of the effect of averaging different types of distributions. Three major inferences have been derived out of the detailed parametric study.

1) Phenolic distributions have to be treated as separate distributions from other distributions in order to avoid major errors in estimating thermodynamic properties.

2) Pyridinic distribution may be averaged with hydrocarbon distribution without causing serious errors, but for accurate results pyridinic group should be included in separate distribution.

3) Thiophenic distributions can be averaged with hydrocarbon distributions without affecting the thermodynamic properties. Calculations with different combinations of three or more distributions did not give any further useful information.

The boiling ranges of H-Coal and Wilsonville distillates estimated as bubble

point/dew point temperatures are reasonably accurate for low and moderate boiling ranges. The high deviation of temperatures for higher boiling ranges could be because of the following assumptions made in the work,

1) The bubble point and dew point temperatures estimated have been approximated as the boiling range the given distillate.

2) The model uses the UNIFAC model which applies only at moderate temperatures and pressures. We have stretched applicability of this model in these calculations.

3) At high molecular weights, additional distributions with average molecules having mixed oxygen, nitrogen and sulfur functionalities need to be defined.

The thermodynamic model predicted heat capacities of coal liquids in close agreement with available experimental values. A very significant conclusion of this study is that detailed information of distribution of heteroatoms espeicially oxygen in coal liquids is necessary if accurate prediction of thermodynamics is needed. Analytical methods to obtain such information need to be devised.

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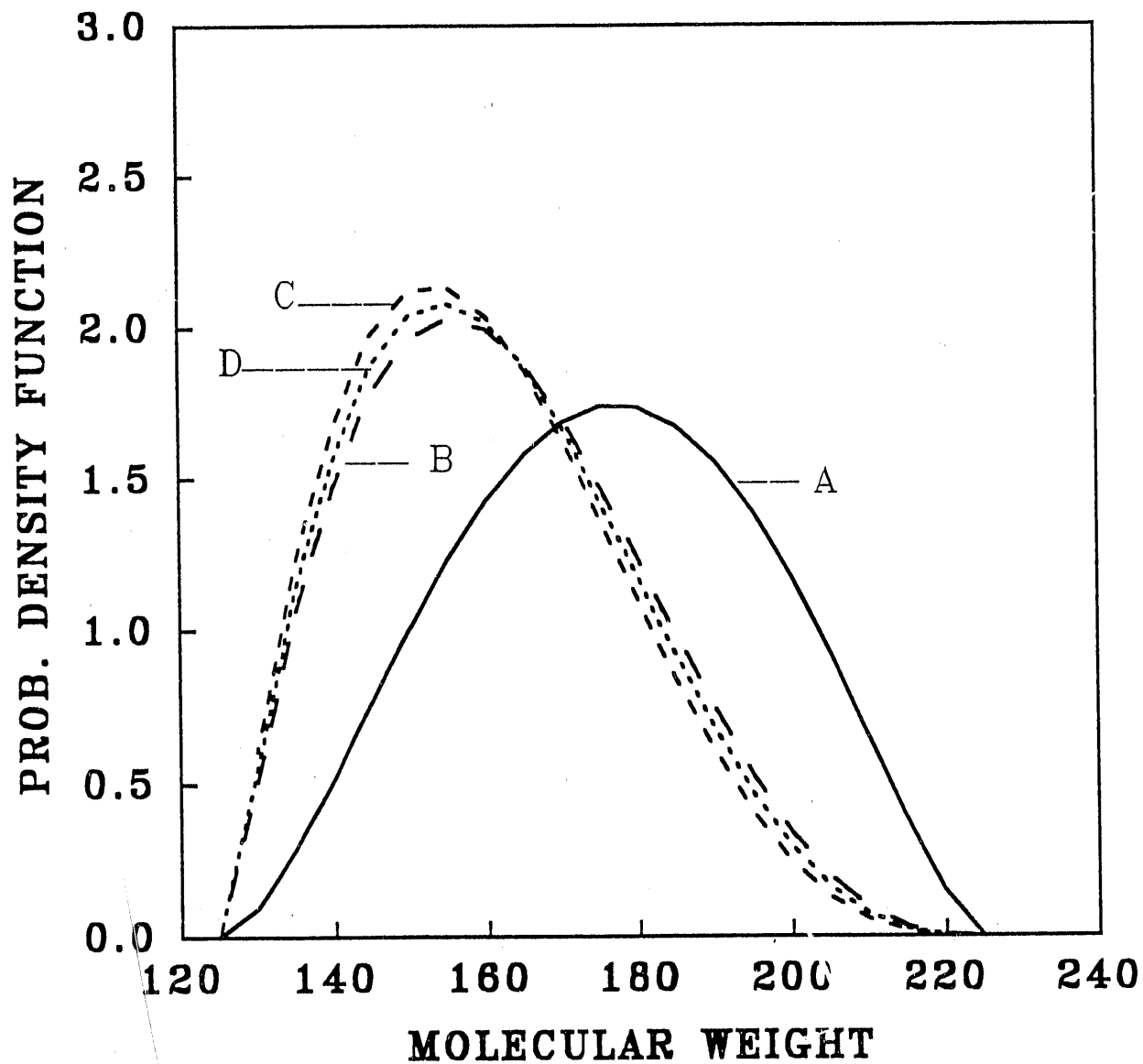
Figure 1: Molecular weight distributions for the Bubble point calculation of Table 5; $X_I = 0.5$, $X_{II} = 0.5$ case. A represents all distributions in the liquid phase. B,C represent hydrocarbon and phenolic distributions in the vapor phase for two distribution calculation and D is the vapor phase distribution for the single distribution calculation.

Figure 2: Same as Figure 1 but for Dew point calculation of Table 5; $X_I = 0.5$, $X_{II} = 0.5$ case. A represents vapor phase and B,C,D are for liquid phases.
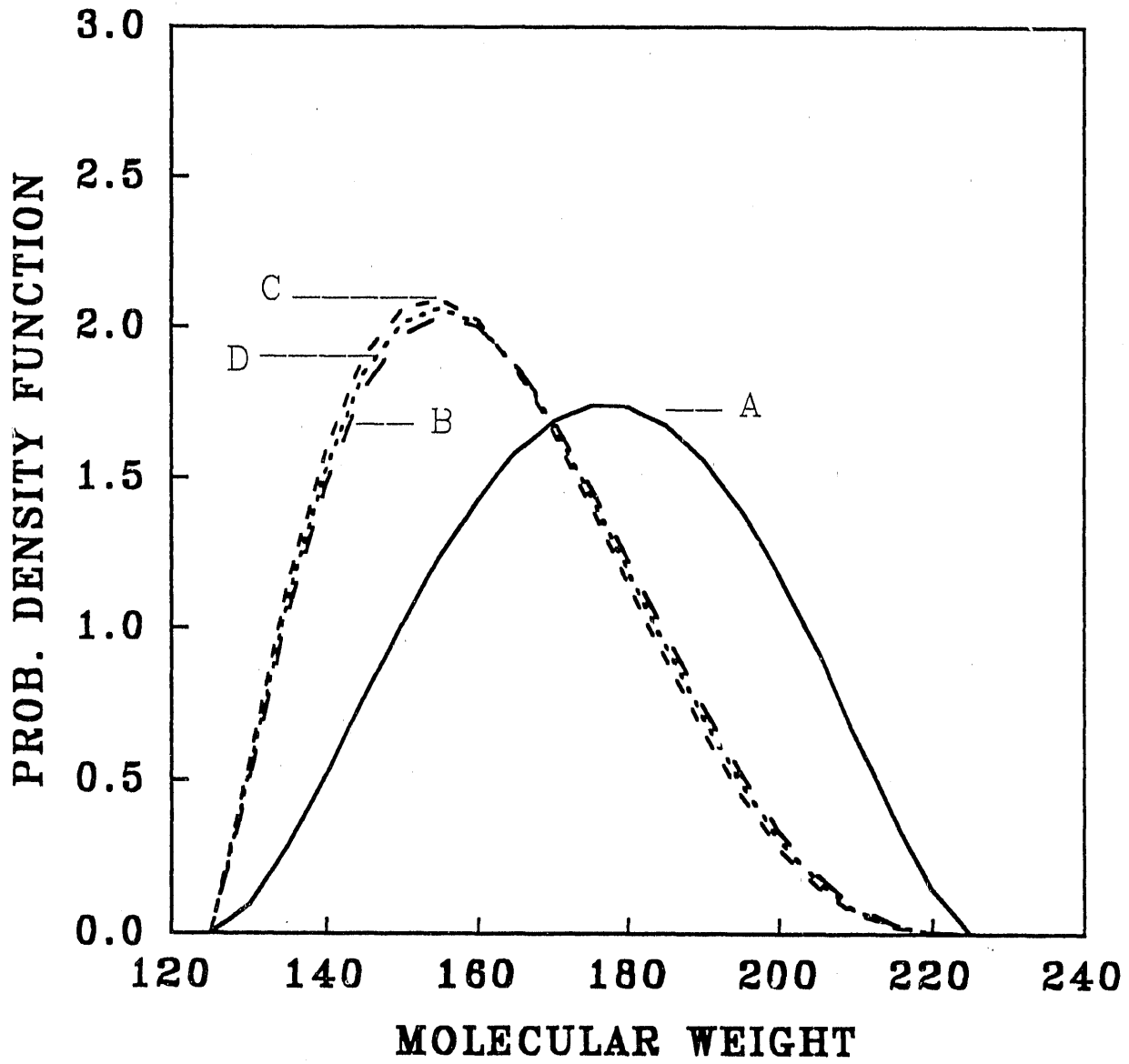
Figure 3: Same as Figure 1, but for the Bubble point calculation of Table 7; $X_I = 0.5$, $X_{II} = 0.5$; and C represents Pyridinic distributions.
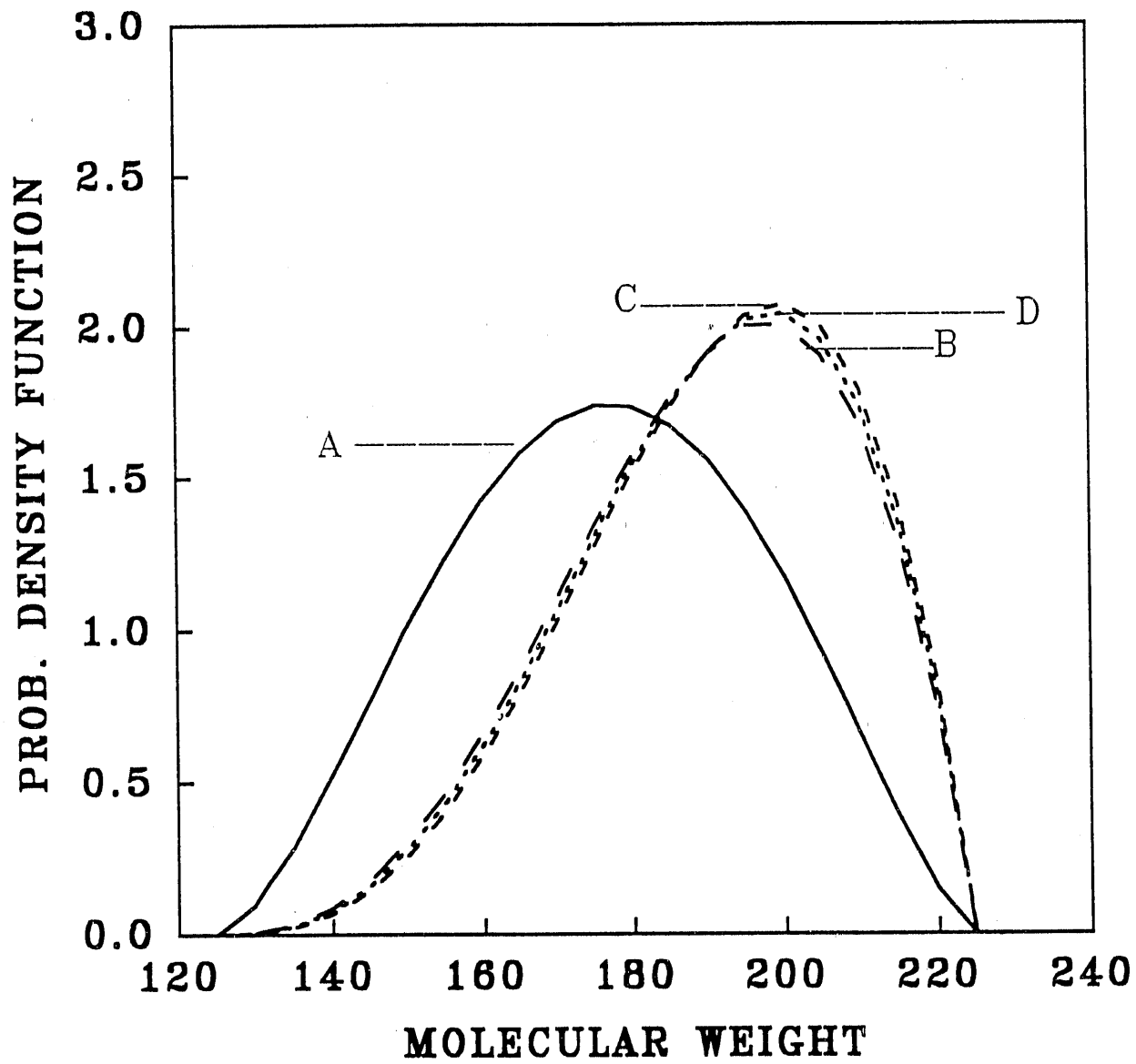
Figure 4: Same as Figure 3, but for Dew point calculations. A represents vapor phase and B,C,D are for liquid phases.
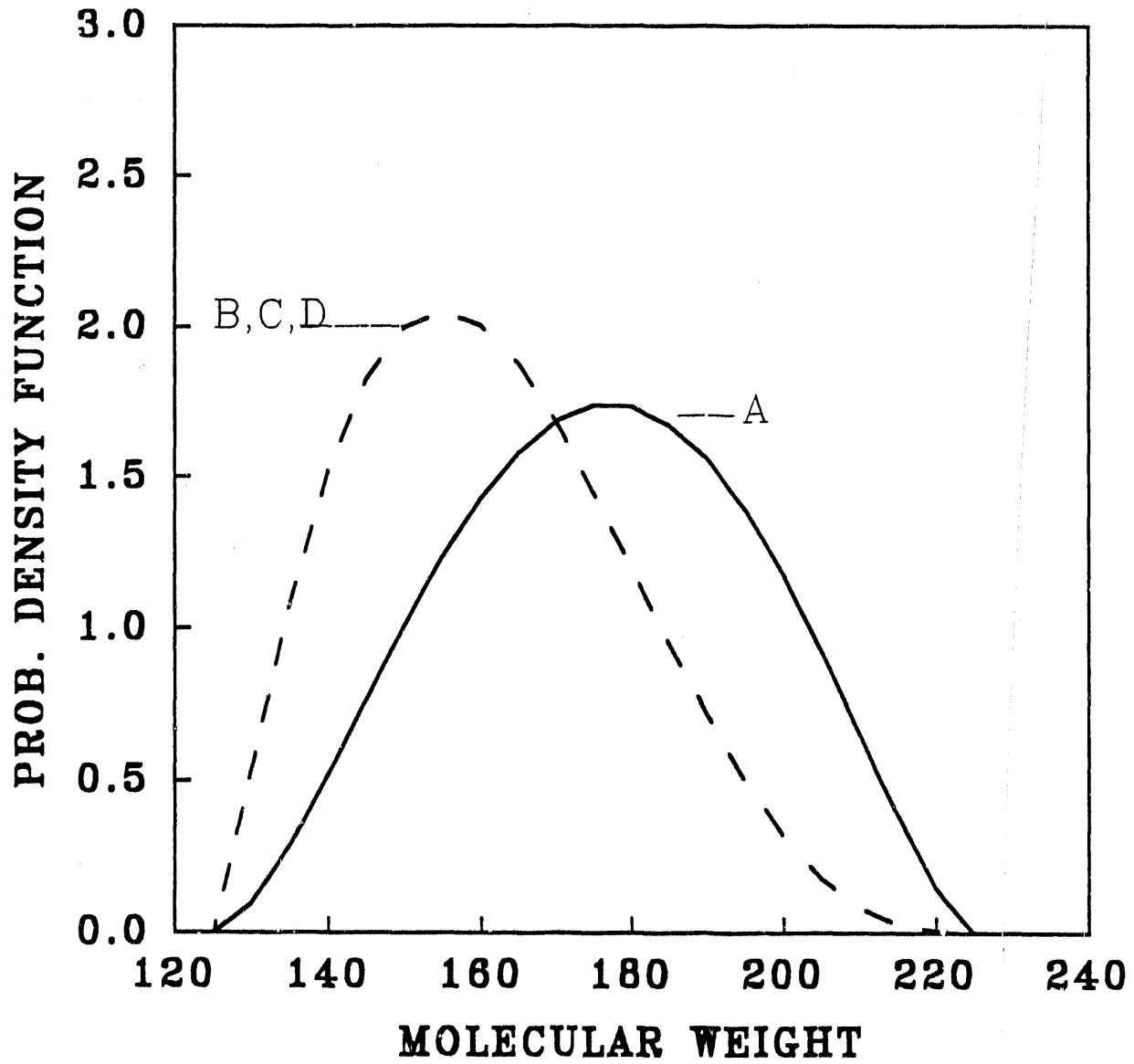
Figure 5: Same as Figure 1, but for the Bubble point calculation of Table 9; $X_I = 0.5$, $X_{II} = 0.5$ case; and C represents Thiophenic distributions.
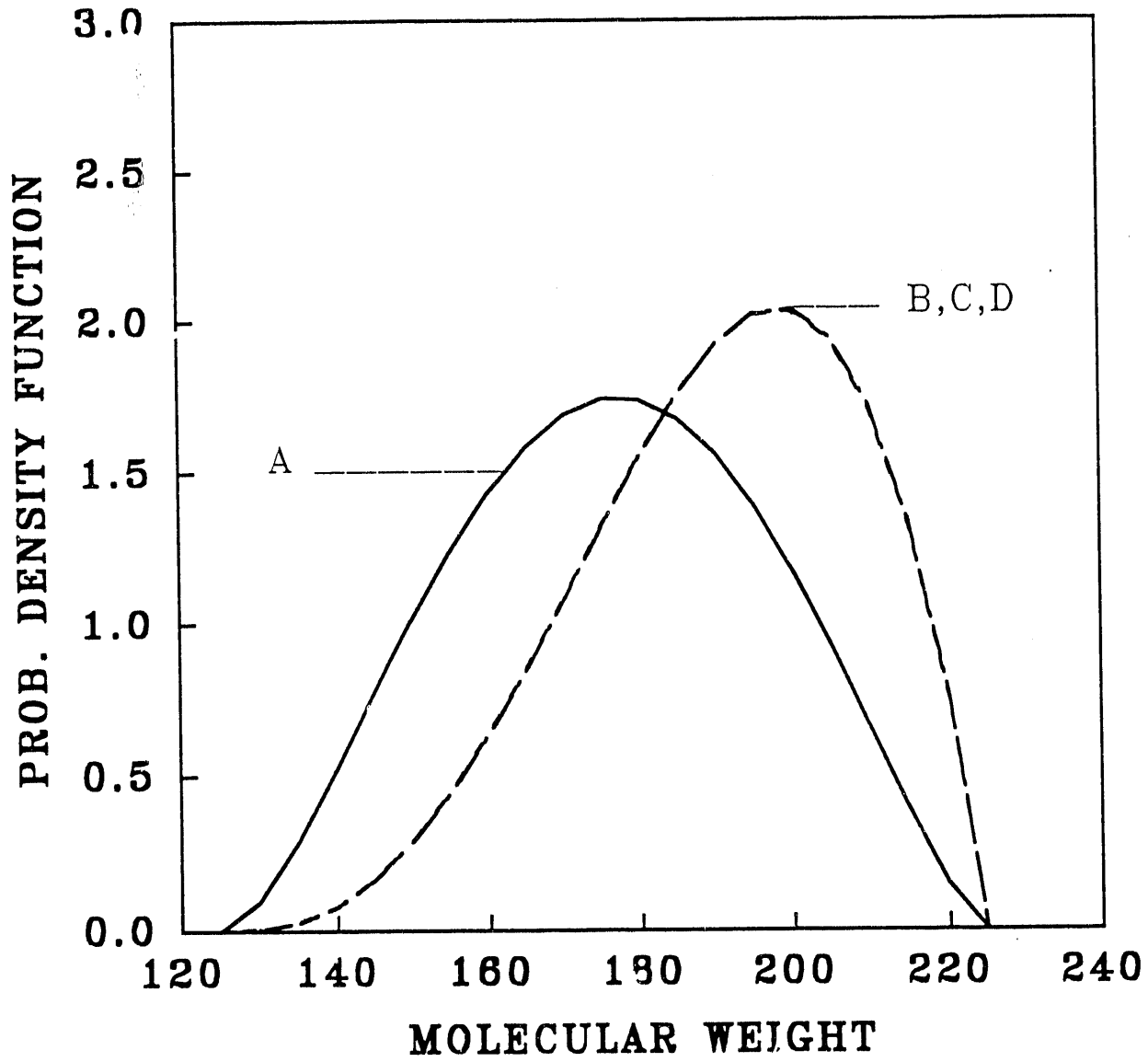
Figure 6: Same as Figure 5, but for Dew point calculation. A represents vapor phase and B,C,D are for liquid phases.
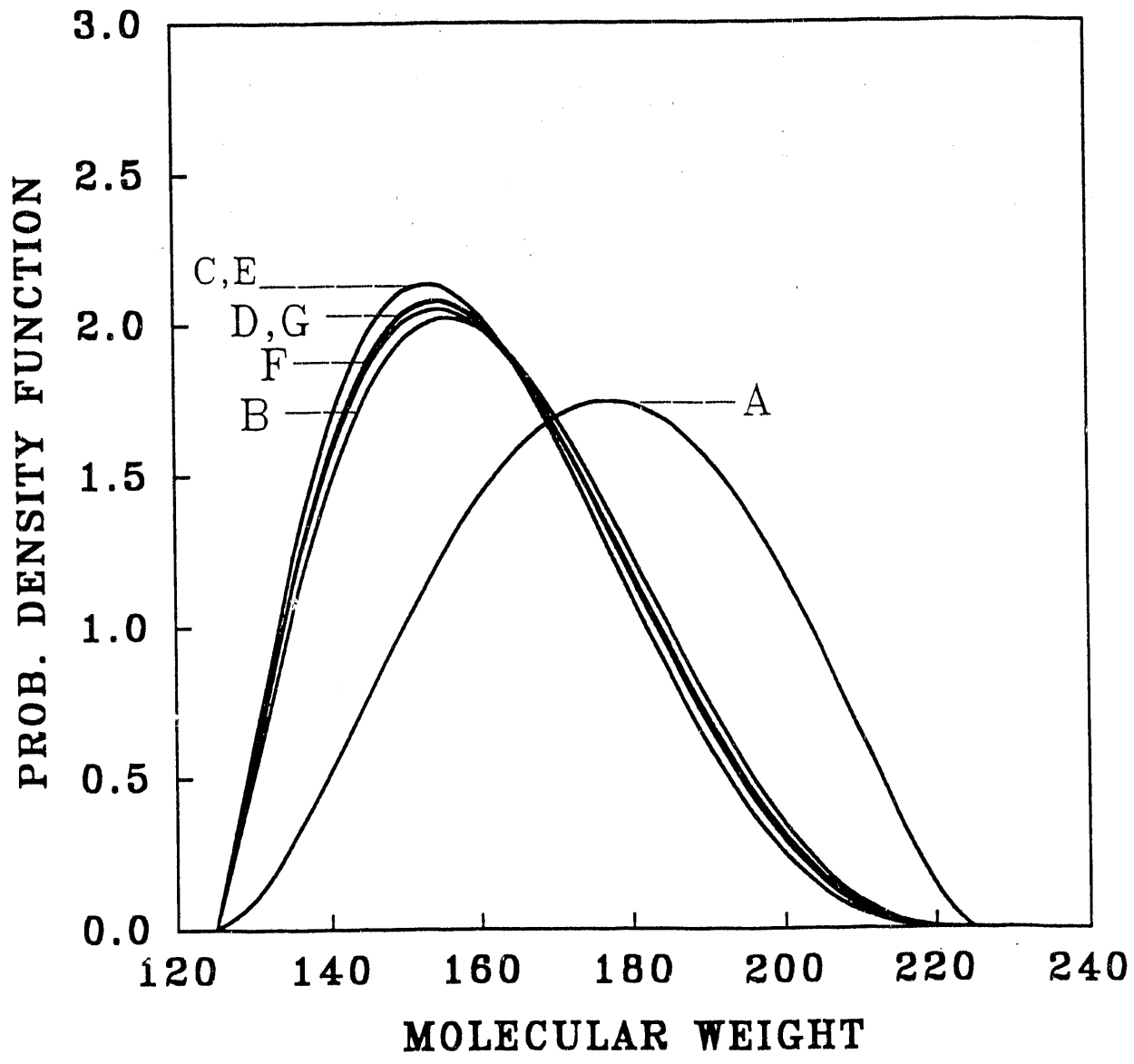
Figure 7: Molecular weight distributions for the Bubble point calculation of Table 11; $X_I = 0.3$, $X_{II} = 0.4$, $X_{III} = 0.3$ case. A represents all distributions in the liquid phase. B,C,D represent distributions in the vapor phase for three distribution calculation. E,F represent vapor phase distributions for the two distribution calculation and G is the vapor phase distribution for single distribution calculation.
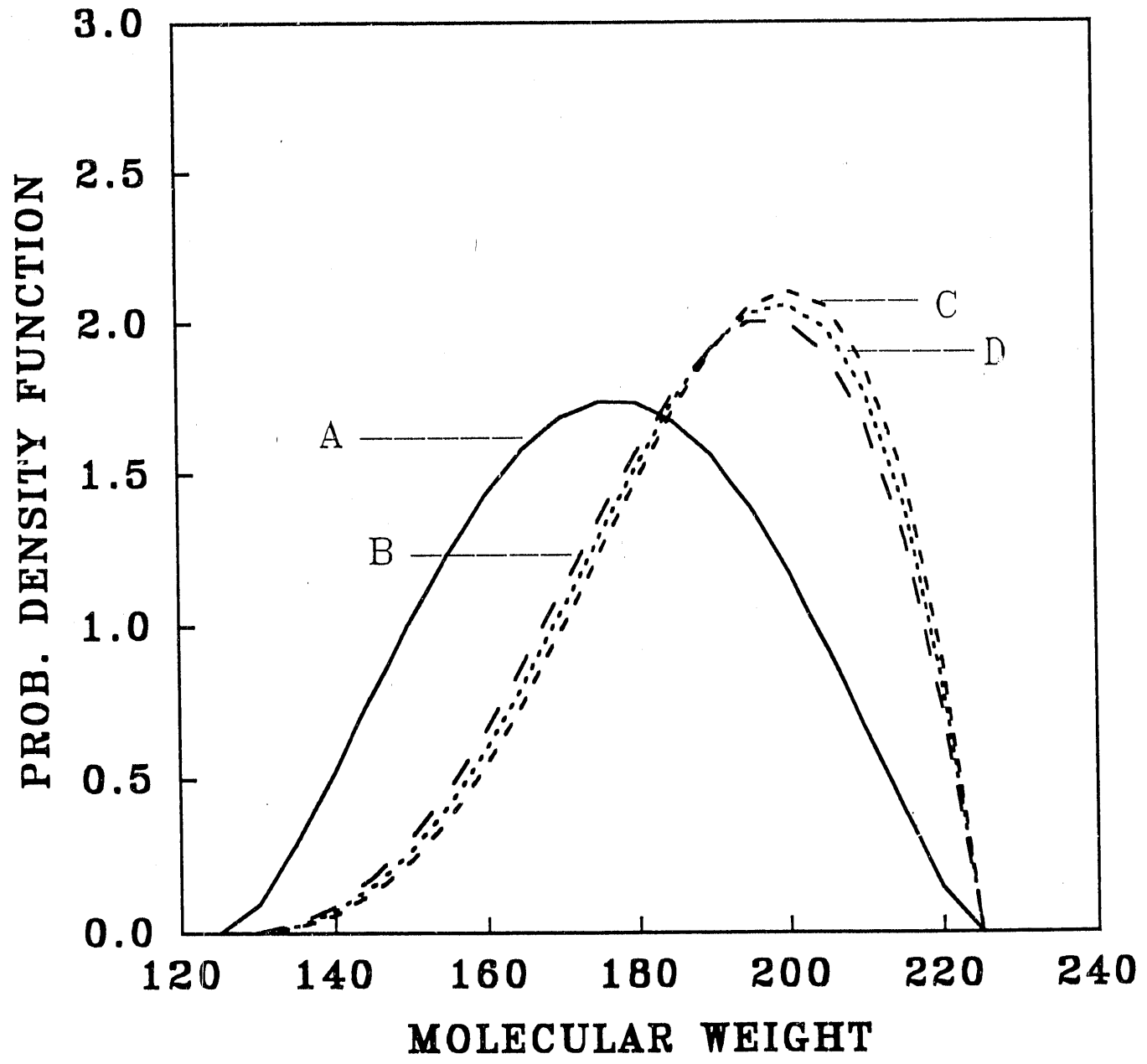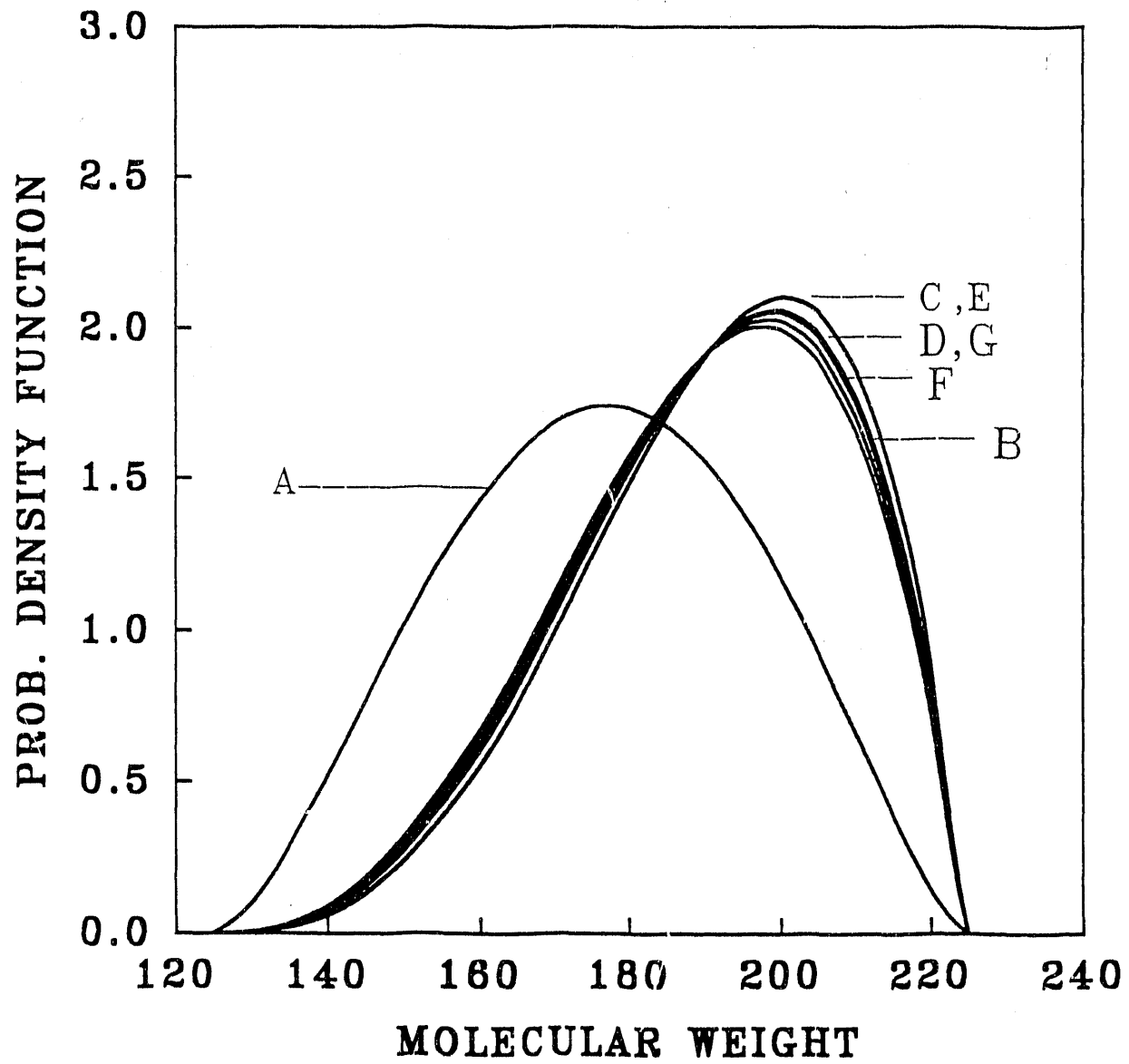
Figure 8: Same as Figure 7 but for Dew point calculation of Table 11; $X_I = 0.3, X_{II} = 0.4, X_{III} = 0.3$ case. A represents vapor phase and B,C,D,E,F, G are for liquid phases.

Table 1

Functional Groups[a] and their UNIFAC Parameters
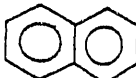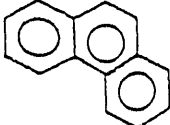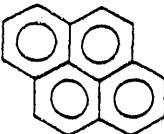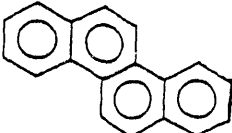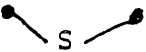
Group ID	Name	Structure	R_k	Q_k	ΔR	ΔQ
1	Monoaromatic (Benzene)		3.1878	2.400	0.1661	0.280
2	Diaromatic (naphthalene)		4.9808	3.440	0.1661	0.280
3	Triaromatics		6.7738	4.480	0.1661	0.280
4	Tetraaromatics (Pyrene)		7.5042	4.720	0.1661	0.280
5	Tetraaromatics (Chrysene)		8.5668	5.520	0.1661	0.280
6	Benzo-Group		1.7930	1.040	0.1661	0.280
7	Hydroxyl	- OH	1.0000	1.200		

Table 1 (cont'd)

Functional Groups[a] and their UNIFAC Parameters

Group ID	Name	Structure	R_k	Q_k	ΔR	ΔQ
8	Pyridine		2.9993	2.113	0.1661	0.280
9	Quinoline Ring		1.7646	1.033	0.1661	0.280
10	Indole Ring		1.3447	0.744	0.1661	0.280
11	Amine	- NH2	0.6948	1.400	0.2047	0.513
12	Thiophene		2.8572	2.140	0.1661	0.280
13	Aryl Thiophene		1.7946	1.340	0.1661	0.280
14	Diarylthiophene		0.7320	0.540		
15	Naphthenic CH2 Group	- CH2 -	0.6744	0.540	0.2274	0.270
16	Paraffinic CH3 Group	- CH3	0.9011	0.848	0.2272	0.282

a   The functional groups are taken from reference 1

●─   Bonded to an aromatic ring

TABLE 2

Modified UNIFAC Interaction Parameters a(ij,n)

ID	1-6	7	8,9	10	11	12,13	14	15,16
1-6		712.6 -1.459 9.000	99.33 0.2329 1.530	NA	72.6 -0.4299 0.0	-4.9129 0.1686 -0.0673	NA	-1.447 -0.5638 -1.612
7	587.3 -0.6787 9.000		311.8 2.405 9.000	NA	-176.5 -0.1073 -1.016	-1027.2 -7.588 -314.6	NA	637.5 -5.832 -0.8703
8 9	-62.93 -0.1398 -0.9703	28.72 -0.2570 9.000		NA	41.4541 0.8617 -29.324	80.77 0.5597 5.410	NA	-52.03 -0.5553 0.0
10	NA	NA	NA		NA	NA	NA	NA
11	902.7 -5.763 0.0	-173.7 1.642 0.0	8.7782 0.8038 12.9992	NA		NA	NA	346.5 1.595 0.0
12 13	0.7595 0.6514 -0.4134	-399.1 7.451 -91.24	84.07 -0.0999 11.62	NA	NA		NA	20.35 0.3211 10.40
14	NA	NA	NA	NA	NA	NA		NA
15 16	62.88 -0.2493 1.103	972.8 0.2687 8.773	273.8 0.1763 0.0	NA	420.7 -2.256 0.0	355.3 0.6484 -2.626	NA	

a(1-6--12,13), a(7--12,13), a(8,9--12,13) are regressed with VLE data.
a(12,13--15,16) is regressed with Enthalpy data.
a(8,9-11) are regressed with both VLE and Enthalpy data.

Table 3

Joback's Group Contributions for Ideal Gas Heat Capacities

Group ID	Δa	Δb	Δc	Δd
1	-12.84	0.3444	-9.840E-6	-9.540E-8
2	-33.62	0.6612	-2.971E-4	8.400E-9
3	-54.40	0.9780	-5.844E-4	1.122E-7
4	-70.90	1.1800	-8.684E-4	2.478E-7
5	-75.18	1.2948	-8.717E-4	2.160E-7
6	- 8.56	0.2296	-6.560E-6	-6.360E-8
7	- 2.81	0.1110	-1.160E-4	4.940E-8
8	- 1.87	0.2832	3.530E-5	-1.010E-7
9	2.41	0.1684	3.858E-5	-7.370E-8
10	7.52	0.0918	1.037E-4	-9.460E-8
11	26.90	-0.0412	1.640E-4	-9.760E-8
12	8.14	0.2344	2.114E-5	-8.470E-8
13	12.42	0.1196	2.442E-5	-5.290E-8
14	19.60	-0.0056	4.020E-5	-2.760E-8
15	- 6.03	0.0854	-8.000E-6	-1.800E-8
16	19.50	-0.0081	1.530E-4	-9.670E-8
Naphthenic CH group	-20.50	0.1620	-1.600E-4	6.240E-8
Naphthenic C group	-90.90	0.5570	-9.000E-4	4.690E-7
Paraffinic CH2 group	-0.909	0.0950	-5.440E-5	1.190E-8
Paraffinic CH group	-23.00	0.2040	-2.650E-4	1.200E-7
Paraffinic C group	-66.20	0.4270	-6.410E-4	3.010E-7
Substituted Amine - NH	- 1.21	0.0762	-4.860E-5	1.050E-8
Substituted Amine - N	-31.10	0.2270	-3.200E-4	1.460E-7

For groups with aromatic rings i.e. groups 1-6, 8-10 and 12-13, following are the increments in contributions for each H substitution:

| | - 6.11 | 0.0436 | -1.404E-4 | 8.370E-8 |

Table 4

Group Composition of Average Molecule of Molecular
Weight 100 gms/mol Corresponding to Hydrocarbon, Phenolic
Pyridinic and Thiophenic Distributions [†]

| | Compositions of Groups, in gmoles of groups/100.0 gms | | | |
Group	Hydrocarbon distribution	Phenolic distribution	Pyridinic distribution	Thiophenic distribution
Benzene	0.3525	0.3326	0.2757	0.2720
Benzo	0.4396	0.4150	0.3439	0.3392
Naphthenic CH_2	0.8963	0.8452	0.7010	0.6915
Paraffinic CH_2	2.6496	2.4995	2.0724	2.0443
-OH	---------	0.3326	----------	----------
Pyridine	---------	----------	0.2757	----------
Thiophene	---------	----------	-----------	0.2720

[†] Following is the list of parameters used for all the distributions:

$MW_i = 125$, $MW_f = 225$, $MW = 176.3$, $\sigma^2_{MW} = 400$, $\theta = 0.513$,

$\sigma^2_M = 0.04$, $\alpha = 2.6911$, $\beta = 2.5547$

Table 5

Bubble Point and Dew Point Temperatures for Two Distributions[*]
and Equivalent Single Distribution, Second Distribution: Phenolic
Distribution, Mean Molecular Weight = 176.3 gms/mol, P = 1.013 bars

Feed Composition[+] in mole fractions of distributions		Two Distribution Case			One Distribution Case	
X_i		Temp (K)	Y_i	Liquid C_p, J/mol°K	Temp (K)	Liquid C_p
0.95	Bubble Point	521.0	0.974	465.0	520.9	457.9
	Dew Point	552.1	0.880	534.7	549.4	509.7
0.80	Bubble Point	525.1	0.881	483.9	524.5	460.6
	Dew Point	560.7	0.659	564.1	553.7	513.2
0.60	Bubble Point	530.9	0.715	498.2	529.3	464.1
	Dew Point	567.9	0.470	571.7	559.4	517.9
0.50	Bubble Point	533.7	0.613	500.9	531.7	465.9
	Dew Point	570.5	0.392	570.4	562.3	520.2
0.40	Bubble Point	536.3	0.500	500.7	534.1	467.6
	Dew Point	572.5	0.317	566.9	565.1	522.5
0.20	Bubble Point	540.7	0.252	492.3	538.8	471.1
	Dew Point	575.2	0.167	553.9	570.9	527.2
0.05	Bubble Point	543.0	0.061	479.7	542.4	473.6
	Dew Point	576.4	0.045	538.4	575.2	530.6

[*] The distribution parameters and average molecules for this Table and Tables 7, 9, and 11 are listed in Table 4.

[+] In this case and all later Tables X, Y correspond to mole fractions of distribution in the liquid and vapor phases for bubble point calculation, and the vapor and liquid phases for dew point calculation.

Table 6

Calculated Functional Group Compositions in the
Coexisting Phases for the Bubble Point/Dew Point
Calculations of Table 5; $X_I = 0.5$, $X_{II} = 0.5$ Case.

Groups	Feed* (liquid/vapor) composition in moles/100gms.	Vapor/liquid phase composition for Bubble Point/Dew Point calculation in moles/100 gms. Two distribution case.	
		Bubble Point	Dew Point
Benzene	0.3425	0.3449	0.3403
Benzo	0.4272	0.4302	0.4246
Napthenic CH_2	0.8709	0.8767	0.8651
Paraffinic CH_2	2.5745	2.5920	2.5579
-OH	0.1663	0.1276	0.2032

* This is also the calculated composition of the coexisting phase in case of Single distribution calculation.

Table 7

Bubble Point and Dew Point Temperatures for Two Distributions and Equivalent
Single Distribution, Second Distribution: Pyridinic Distribution,
Mean Molecular Weight = 176.3 gms/mol, P = 1.013 bars

Feed Composition in mole fractions of distributions		Two Distribution Case			One Distribution Case	
X_i		Temp (K)	Y_i	Liquid C_p, J/mol°K	Temp (K)	Liquid C_p, J/mol°K
0.95	Bubble Point	520.5	0.965	456.8	520.7	456.7
	Dew Point	549.4	0.923	508.3	549.1	508.2
0.80	Bubble Point	523.0	0.854	456.1	523.6	455.7
	Dew Point	553.4	0.716	507.5	552.4	507.4
0.60	Bubble Point	526.5	0.688	455.0	527.4	454.4
	Dew Point	558.2	0.488	506.3	556.8	506.3
0.50	Bubble Point	528.4	0.595	454.3	529.4	453.8
	Dew Point	560.4	0.389	505.7	559.0	505.7
0.40	Bubble Point	530.4	0.494	453.6	531.3	453.1
	Dew Point	562.5	0.299	505.1	559.0	505.2
0.20	Bubble Point	534.5	0.268	452.0	535.2	451.7
	Dew Point	566.4	0.139	503.9	565.6	503.9
0.05	Bubble Point	537.9	0.071	450.7	538.1	450.6
	Dew Point	569.1	0.033	503.0	568.9	503.0

Table 8

Calculated Functional Group Compositions in the
Coexisting Phases for the Bubble Point/Dew Point
Calculations of Table 7; $X_I = 0.5$, $X_{II} = 0.5$ Case.

Groups composition in moles/100gms. case.	Feed* (liquid/vapor) Bubble Point/Dew Point calculation in moles/100 gms. Two distribution	Vapor/liquid phase composition for	
		Bubble Point	Dew Point
Benzene	0.3141	0.3215	0.3055
Benzo	0.3917	0.4010	0.3810
Napthenic CH_2	0.7986	0.8175	0.7767
Paraffinic CH_2	2.3610	2.4168	2.2962
Pyridine	0.1379	0.1112	0.1688

*This is also the calculated composition of the coexisting phase in the case of
Single distribution calculation.

Table 9

Bubble Point and Dew Point Temperatures for Two Distributions and Equivalent Single Distribution, Second Distribution: Thiophenic Distribution

Mean Molecular Weight = 176.3 gms/mol, P = 1.013 bars

Feed Composition in mole fractions of distributions			Two Distribution Case			One Distribution Case
X_I	X_{II}		Temp (K)	Y_I	Y_{II}	Temp (K)
0.95	0.05	Bubble Point	520.4	0.961	0.039	519.7
		Dew Point	549.9	0.918	0.082	548.0
0.80	0.20	Bubble Point	522.0	0.826	0.174	519.8
		Dew Point	553.7	0.750	0.250	548.0
0.60	0.40	Bubble Point	523.3	0.611	0.389	519.8
		Dew Point	555.8	0.585	0.415	548.1
0.50	0.50	Bubble Point	523.4	0.497	0.503	519.9
		Dew Point	555.9	0.509	0.491	548.1
0.40	0.60	Bubble Point	523.1	0.385	0.615	519.9
		Dew Point	555.4	0.431	0.561	548.2
0.20	0.80	Bubble Point	521.9	0.177	0.823	520.0
		Dew Point	552.9	0.252	0.748	548.2
0.05	0.95	Bubble Point	520.5	0.041	0.959	520.0
		Dew Point	549.7	0.075	0.925	548.3

Table 10

Calculated Functional Group Compositions in the
Coexisting Phases for the Bubble Point/Dew Point
Calculations of Table 9; $X_I = 0.5$, $X_{II} = 0.5$ Case.

Groups	Feed* (liquid/vapor) composition in moles/100 gms.	Vapor/liquid phase composition for Bubble Point/Dew Point calculation in moles/100 gms. Two distribution case.	
		Bubble Point	Dew Point
Benzene	0.3122	0.3120	0.3130
Benzo	0.3894	0.3891	0.3903
Napthenic CH_2	0.7939	0.7933	0.7958
Paraffinic CH_2	2.3469	2.3452	2.3525
Thiophene	0.1360	0.1368	0.1335

*This is also the calculated composition of the coexisting phase in the case of
Single distribution calculation.

Table 11

Comparison of Results Using Three, Two Equivalent, and
One Equivalent Distributions

	$X_I=0.1$ $X_{II}=0.4$			$X_I=0.3$ $X_{II}=0.4$			$X_I=0.5$ $X_{II}=0.4$		
	3	2	1	3	2	1	3	2	1
Bubble point temperature	541.3	541.5	539.0	537.0	537.5	535.1	532.9	533.2	531.2
Dew point temperature	575.5	575.2	570.4	572.7	572.2	566.0	569.6	569.3	561.6
Moles of -OH in 100 gms of vapor (BPT Calculation)	0.1164	0.1171	0.1330	0.1063	0.1076	0.1330	0.0977	0.0984	0.1330
Moles of -OH in 100 gms of liquid (DPT Calculation)	0.1518	0.1527	0.1330	0.1609	0.1627	0.1330	0.1713	0.1724	0.1330
Moles of Pyridine 100 gms of vapor (BPT Calculation)	0.1398	0.1488	0.1379	0.0722	0.0933	0.0827	0.0236	0.0324	0.276
Liquid C_p, J/mol°K (BPT Calculation)	483.2	483.1	460.6	489.3	489.1	462.1	495.3	495.2	463.4
Liquid C_p, J/mol°K (DPT Calculation)	553.6	554.3	514.9	560.1	561.5	516.1	567.5	568.4	517.3

* BPT and DPT stand for bubble point temperature and dew point temperature respectively.

Table 12

Feed Group Composition Data for Two Distributions* Calculation for
H-Coal Distillates

Distribution 1

	Boiling Ranges (K)								
	(478-505)	(505-533)	(533-561)	(561-589)	(589-616)	(616-644)	(644-672)	(672-700)	(700-728)
Mean Mol. Wt.	143.8	160.9	176.3	195.6	213.1	233.7	249.6	262.1	295.2
Overall Composition	0.367	0.191	0.151	0.115	0.089	0.134	0.200	0.283	0.357

Group Composition in mol/mean mol. wt.

Benzene	0.726	0.831	0.768	0.850	0.905	1.063	0.954	0.939	0.883
Benzo group	0.0273	0.338	0.453	0.673	0.625	0.768	1.570	1.649	2.157
Naphthenic CH_2	1.643	1.728	1.774	1.613	1.876	1.717	1.310	1.356	1.493
Paraffinic CH_2	3.467	3.752	3.830	4.009	4.810	4.821	4.073	4.739	5.447
Hydroxyl group	0.726	0.831	0.768	0.850	0.905	1.063	0.954	0.939	0.883

* For this and Tables 13 to 15, distribution parameters were chosen such that $(MW_f - MW_i) \cong 80$ gms/mol.

☞ Obtained from (Allen, 1987)

Table 13

Feed Group Composition Data for Two Distributions Calculations for

H-Coal Distillates

Distribution 2

	Boiling Ranges (K)								
	(478-505)	(505-533)	(533-561)	(561-589)	(589-616)	(616-644)	(644-672)	(672-700)	(700-728)
Mean Mol. Wt.	143.8	160.9	176.3	195.6	213.1	233.7	249.6	262.1	295.2
Overall Composition	0.633	0.809	0.849	0.885	0.912	0.866	0.799	0.716	0.643

Group Composition in mol/mean mol. wt.

Benzene	0.701	0.811	0.812	0.905	0.949	01.093	0.976	0.949	0.865
Benzo group	0.263	0.329	0.480	0.717	0.655	0.790	1.605	1.667	2.113
Naphthenic CH_2	1.587	1.686	1.879	1.718	1.967	1.765	1.340	1.371	1.463
Paraffinic CH_2	3.350	3.660	4.057	4.271	5.042	4.957	4.170	4.791	5.334
Pyridine	0.055	0.043	0.039	0.025	0.065	0.149	0.172	0.168	0.262
Thiophene	0.006	0.006	0.003	0.008	0.008	0.002	0.138	0.000	0.000

Table 14

Feed Group Composition Data for Two Distributions Calculation for
Wilsonville Distillates
Distribution 1

	Boiling Ranges (K)						
	533-561	561-589	589-616	616-644	644-672	672-700	700-728
Mean Mol.Wt.	176.3	195.6	213.1	233.7	249.6	262.1	295.2

Overall Composition	0.4035	0.2366	0.1807	0.1340	0.1608	0.2210	0.2421

Group Composition in mol/mean mol. wt.

	533-561	561-589	589-616	616-644	644-672	672-700	700-728
Benzene	0.6588	0.6788	0.7279	0.8652	0.8214	0.2210	0.7599
Benzo group	0.3515	0.4964	0.4968	0.6133	1.0245	1.4913	1.8662
Naphthenic CH_2	2.0443	2.1717	2.4493	2.2583	2.2752	2.1678	2.1511
Paraffinic CH_2	4.6708	5.2384	5.9003	6.1945	6.0834	6.1701	6.0889
Hydroxyl group	0.6588	0.6788	0.7279	0.8652	0.8214	0.7012	0.7599

Table 15

Feed Group Composition Data for Two Distributions Calculation for
Wilsonville Distillates
Distribution 2

	Boiling Ranges (K)						
	533-561	561-589	589-616	616-644	644-672	672-700	700-728
Mean Mol. Wt.	176.3	195.6	213.1	233.7	249.6	262.1	295.2
Overall Composition	0.5965	0.7634	0.8193	0.8660	0.8391	0.7790	0.7579

Group Composition in mol/mean mol. wt.

	533-561	561-589	589-616	616-644	644-672	672-700	700-728
Benzene	0.6847	0.7044	0.7539	0.9038	0.8492	0.7122	0.7729
Benzo group	0.3657	0.5151	0.5140	0.6407	1.0592	1.5146	1.8981
Naphthenic CH_2	2.1248	2.2537	2.5343	2.3589	2.3522	2.2016	2.1880
Paraffinic CH_2	4.8476	5.4364	6.1048	6.4704	6.2894	6.2664	6.8451
Pyridine	0.0370	0.0332	0.0462	0.0481	0.0522	0.0828	0.1023
Thiophene	0.0212	0.0234	0.0210	0.0137	0.0125	0.0175	0.0000

Table 16
Predicted Bubble Point and Dew Point for
H-Coal Distillates

EXPERIMENTAL BOILING RANGE	TWO DISTRIBUTIONS		1 DISTRIBUTION	
	BP (K)	DP (K)	BP (K)	DP (K)
478 - 505	474.26	514.70	476.24	497.54
505 - 583	502.67	537.76	503.95	522.72
533 - 561	530.89	550.63	525.57	544.56
561 - 589	563.84	589.64	565.74	588.63
589 - 616	596.87	620.89	598.52	619.86
616 - 644	652.16	664.02	653.51	662.25
644 - 672	709.74	717.73	692.22	695.05
672 - 700	716.58	728.59	720.00	724.10
700 - 728	787.87	791.87	720.43	724.36

Table 17
Predicted Bubble Point and Dew Point for
Wilsonville Distillates

EXPERIMENTAL BOILING RANGE	TWO DISTRIBUTIONS BP (K)	DP (K)	1 DISTRIBUTION BP (K)	DP (K)
533 - 561	534.05	551.98	526.99	552.75
561 - 589	563.73	583.39	563.242	583.03
589 - 616	595.4	613.92	569.02	612.94
616 - 644	639.35	647.75	637.08	648.85
644 - 672	676.48	678.33	674.09	677.59
672 - 700	701.12	710.18	702.2	707.93
700 - 728	766.61	776.78	762.43	771.82

Table 18

Distribution Parameters and Group Compositions used in
calculation of Liquid Heat Capacities of SRC II
fraction 6 and fraction 8 for comparison with Data of
Gray and Holder (1983)

	Fraction 6		Fraction 8	
	Dist. 1	Dist. 2	Dist. 1	Dist. 2
MW_i	100	100	120	120
MW_f	180	180	200	200
MW	140	140	161	161
σ^2_{MW}	350	350	350	350
X	0.4885	0.5115	0.7490	0.2510
Groups and their Compositions in an Average molecule with Mol. wt. of 100 gms/mol :				
Benzene	0.7640	0.7410	0.8150	0.7840
Benzo	-	-	-	-
Naphthenic CH_2	1.0910	1.0580	0.9470	0.9120
Paraffinic CH_2	1.0910	1.0580	0.9470	0.9120
-OH	-	0.7410	-	0.7840
Pyridine	0.1210	-	0.1120	-
Thiophene	0.0041	-	0.0130	-

Table 19

Model Comparison With Liquid Heat
Capacity Data of Gray & Holder (1983)
SRC II Fractions

Temperature (K)	Liquid Heat Capacity (J/kg°K)			
	Fraction 6 (Avg mol.wt. = 140)		Fraction 8 (Avg mol.wt. = 161)	
	Expt.	Calc.	Expt.	Calc.
298	1980	1890	1910	1835
323	2080	1995	1980	1896
348	2180	2115	2060	1978
373	2280	2219	2150	2110
398	2320	2247	2230	2182
423	2430	2333	2320	2232
448	2530	2435	2420	2337
473	2640	2554	2520	2460
498	-------	-------	2620	2601
525	-------	-------	2750	2761

END

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