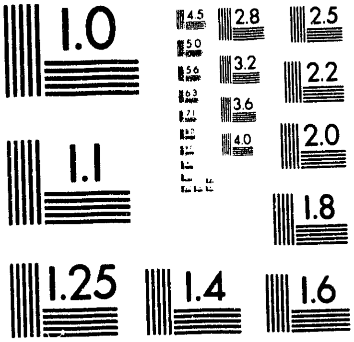
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Thermodynamic Model for Calorimetric and Phase Coexistence Properties of Coal Derived Fluids

Final Technical Report

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ABSTRACT

The work on this project was initiated on September 1, 1989. The project consisted of three different tasks. 1. A thermodynamic model to predict VLE and calorimetric properties of coal liquids. 2. VLE measurements at high temperature and high pressure for coal model compounds and 3. Chromatographic characterization of coal liquids for distribution of heteroatoms. The thermodynamic model developed is an extension of the previous model developed for VLE of coal derived fluids (DOE Grant no. DE-FG22-86PC90541). 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 model is successful in predicting binary VLE and excess enthalpy data. Further refinements of the model are suggested.

An apparatus for the high pressure high temperature VLE data measurements has been built and tested. Tetralin-Quinoline is the first binary system selected for data measurements. The equipment was tested by measuring 325°C isotherm for this system and comparing it with literature data. Additional isotherms at 350°C and 370°C have been measured.

The framework for a characterization procedure for coal derived liquids has been developed. A coal liquid is defined by a true molecular weight distribution and distribution of heteroatoms as a function of molecular weights. Size exclusions liquid chromatography, elemental analysis and FTIR spectroscopy methods are used to obtain the molecular weight and hetroatom distributions. Further work in this area should include refinements of the characterization procedure, high temperature high pressure VLE data measurements for selective model compound binary systems, and improvement of the thermodynamic model using the new measured data and consistent with the developments in the characterization procedure.

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

A thermodynamic model for vapor liquid equilibrium and calorimetric properties of coal derived fluids has been developed. The model is based on the UNIFAC activity coefficient correlation and the method of continuous thermodynamics. A coal derived liquid is defined as a mixture of a few distributions of molecular weight, each distributions containing a molecular species with fixed relative compostions of various functional groups. In addition to aromatic rings, particular attention is paid to phenolic, pyridinic and thiophenic functionalities in coal liquids. characterization procedure to include distribution of sulfur, oxygen and nitrogen heteroatoms in coal liquids.

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 especially oxygen in coal liquids is necessary if accurate prediction of thermodynamics is needed. Analytical methods to obtain such information need to be devised. Also, more high temperature, high pressure VLE and liquid enthalpy data for coal model compounds are necessary to extend the UNIFAC correlation to apply at higher temperatures.

A flow apparatus has been built for high temperature (<500°) and high pressure (<200 psi) vapor liquid equilibria measurements. The apparatus has been tested by reproducing and isotherm for the tetralin-quinoline system. Two higher temperature isotherms have been measured for the same system. For refinement of the thermodynamic model described above, binary systems for future VLE data measurements have been identified. They are (1) benzene-ethyl benzene, (2) m-cresol-benzene and (3) m-cresol ethyl benzene. These data should allow regression of high temperature parameters for UNIFAC such that the model should give more accurate predictions for higher boiling coal liquid fractions.

The framework for a characterization procedure for coal derived liquids has been developed. A coal liquid is defined by a true molecular weight distruibution and distribution of heteroatoms as a function of molecular weight. This definition is consistent with the treatement of coal fluids in our thermodynamic model and the results of the characterization measurements could be directly incorporated in the thermodynamic model for prediction of VLE and enthalpies. Size exclusions liquid chromatography, elemental analysis and FTIR spectroscopy methods are used to obtain the molecular weight and heteroatom distributions. The characterization procedure is demonstrated by generating molecular weight distributions and distributions of phenols, pyridines and hydrocarbons for four coal derived liquid samples.

In what follows, the details of the three areas of effort, namely, thermodynamic mode, VLE measurements and characterization procedure are presented. A short section on further work necessary in these areas is also provided.

PART I

THERMODYNAMIC MODEL FOR VLE AND LIQUID ENTHALPY

MODEL FOR DEFINED POLYNUCLEAR AROMATIC COMPOUNDS

Through a previous project funded by DOE-PETC (DE-FG22-86PC90541), a thermodynamic model was developed for VLE calculations with coal fluids [1,2]. This model involved the UNIFAC correlation [3] for the liquid phase and the Hayden - O'Connell correlation [4] for the vapor phase. Coal fluids were characterized by molecular weight distributions and functional group compositions. The same functional groups were used as in the work of White and coworkers [5,6]. The functional groups are listed in Table 1.

VLE calculations for coal fluids were carried out by the method of continuous thermodynamics [7,8]. Coal fluids were defined by molecular weight distributions each with an average molecule of fixed relative compositions of functional groups. Separate distributions were defined for nitrogen and oxygen containing compounds. Two parameter beta density functions were used, with the parameters defined in terms of the mean and the variance of the distribution. Known distributions corresponding to a phase were discretized to a finite number of points by the method of Gaussian Quadratures. Generally, ten quadrature points were used to represent each distribution. Phase equilibria calculations were then carried out for the multi-component system made up of the discrete components each with known composition of functional groups. The process was reversed to convert the computed compositions of discrete components in a coexisting phase to continuous distributions of molecular weight.

In the current work, our objective is to modify the thermodynamic model to allow computation of excess enthalpies in the liquid phase in addition to the VLE properties. For application of the model to coal fluids, we plan to use the same continuous thermodynamics procedure as outlined above. We devoted the first year of the project to the development of a thermodynamic model for VLE and excess enthalpies of mixtures of aromatic compounds such as the ones that exist in coal liquids. This required a databank of VLE data and excess enthalpy data for binary and ternary systems of such compounds. A VLE databank was already available from our work on the previous project. During the first few months of this project an excess enthalpy databank was compiled. The systems, number of data points and literature references for the databank were listed in a previous technical report.

The original UNIFAC correlation used in our initial VLE model was not designed to predict enthalpies. However, a later modification of the UNIFAC model [9], which has a more extensive temperature functionality for the binary group interaction parameters, was developed to correlate both VLE data and liquid enthalpies simultaneously. The interaction parameters in this model, were in fact, regressed from both VLE and enthalpy data. In this work, we have developed the modified UNIFAC model for the functional groups given in Table 1. Table 2 gives the UNIFAC group volume parameter R and group surface area parameter Q for all the sixteen groups. R and Q represent reduction in R and Q for each hydrogen substituted by another group. Most of the binary interaction parameters for these groups were already available [9], but a few had to be regressed from VLE and enthalpy data. Benzene-thiophene, OH-thiophene and pyridine-thiophene interaction parameters were regressed from only VLE data, thiophene-paraffinic CH_2 parameters were regressed from only enthalpy data, whereas pyridine-amine parameters were regressed from both VLE and enthalpy data. No interaction parameters could be obtained for groups 10 and 14, namely indole ring and diarylthiophene linkage, because of lack of experimental VLE and enthalpy data for systems containing these functional groups. Such data are, therefore, very much needed.

Excepting for the group interaction parameters for indole ring and diaryl-thiophenic linkage, the new thermodynamic model for multi-component aromatic compounds has been developed. The model uses the modified UNIFAC correlation for the liquid phase and the Hayden-O'Connell correlation for the vapor phase. The model also uses the Joback's modification of Lydersen's method [10] for estimation of critical properties and acentric factors, Lee-Kesler correlation [11] for vapor pressures and modified Rackett equation [12] for liquid densities. Thus, the model is the same as our previous VLE model [1,2] with modified UNIFAC correlation replacing the original UNIFAC method. The modified UNIFAC equations for activity coefficients and excess enthalpies are given in the Appendix.

The thermodynamic model was tested with experimental VLE and excess enthalpy data for binary systems. For VLE data comparisons, bubble point temperature calculations were carried out, and computed temperatures and vapor compositions were compared with the experimental data. Average absolute percent errors for these quantities are listed in Table 4. In all 52 binary systems were evaluated for a total of 1720 temperature points and 1103 vapor composition points. Average percent errors of 1.8% for the temperature and 8% for vapor mole fractions of component 1 reflects a good agreement with experimental data. These results are equivalent to the results obtained using the original UNIFAC correlation.

Results are also given for excess enthalpies of 88 binary systems in Table 5. Errors are presented in two forms. In addition to average absolute percent errors we also give average absolute deviation in excess enthalpy in Joules/mole. The reason for doing this is that for some systems where excess enthalpies are very small, average percent errors do not qualify the results properly; for example; see the results for the systems benzene - 2 methyl pyridine and benzene - 3 methyl pyridine. An average absolute error of 63 J/mol for 2855 data points shows a reasonable accuracy for a correlation of this type. One point to note here is that a group contribution correlation like UNIFAC is not sensitive to the structure of a molecule and cannot differentiate between isomers with same organic formula. In a number of cases, excess enthalpies for different isomers vary appreciably. Although this is a weakness of the model, we believe that this model is quite appropriate for applications to coal liquids which contain a maze of compounds and exact identification of individual compounds is impossible.

In what follows we show the extension of the above model to compute VLE and excess enthalpies of coal derived liquids. Some limited comparisons of the model with experimental data are also shown.

APPLICATION TO COAL DERIVED FLUIDS

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 [1,6]
2. Modified UNIFAC correlation of Larsen et al [9] 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 [10] for estimation of critical pressure and acentric factors
5. Lee-Kesler correlation [11] for vapor pressures
6. Modified Rackett equation [12] for liquid densities
7. Rowlinson-Bondi [10] corresponding states method for pure liquid heat capacities.
8. Joback's group contributions method [10] for ideal gas heat capacities.

The group characterization of aromatic compounds and the details of the thermodynamic model were described in the previous section. 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 2 and UNIFAC binary group interactions parameters are presented in Table 3. 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, 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,

$$\alpha = \frac{\theta_M^2(1-\theta_M)}{\sigma_M^2} - \theta_M \tag{4}$$

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

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

$$\theta = \frac{\alpha}{\alpha+\beta} \tag{6}$$

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

The corresponding univariate distribution function is then given by,

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

where the distributed variable y is given by

$$y = \frac{MW-MW_i}{MW_f-MW_i} \tag{9}$$

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,

$$x = 2y - 1 \tag{10}$$

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

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

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

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

Mole fraction of each quadrature point is defined by

$$z_i = \eta_j F(x_i)\, w_i \tag{14}$$

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 MW and the variance σ^2_{MW} corresponding to distribution j in the vapor phase are calculated as

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

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

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 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

$$c_p = c_p^E + \sum_{i=1}^{N} Z_i \left(c_{pi}^L - c_{pi}^o\right) + \sum_{i=1}^{N} Z_i c_{pi}^o \tag{18}$$

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 [10] corresponding states method was used for this term and is given below:

$$\begin{aligned}\frac{c_p^L - c_p^o}{R} &= 1.45 + 0.45(1-T_r)^{-1} + 0.25\omega[17.11 \\ &\quad + 25.2(1-T_r)^{\frac{1}{3}} T_r^{-1} + 1.742(1-T_r)^{-1}]\end{aligned} \tag{19}$$

The ideal gas heat capacity required in equations 18 and 19 was calculated using Joback's group contribution method [10]

$$\begin{aligned}c_p^o &= \left(\sum\nolimits_j n_j \Delta a - 37.93\right) + \left(\sum\nolimits_j n_j \Delta b + 0.210\right) T \\ &\quad + \left(\sum\nolimits_j n_j \Delta c - 3.91x10^{-4}\right) T^2 + \left(\sum\nolimits_j n_j \Delta d + 2.06x10^{-7}\right) T^3\end{aligned} \tag{20}$$

where c_p^o 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 6. 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 [6]. 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 [6], 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 [6] 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 7.

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 7. 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,

$$m_{12}=\int_{y_1}^{y_2} MW F(y)\, dy=\frac{1}{MW_f-MW_i}\int_{MW_1}^{MW_2} MW F(MW)\, d(MW) \tag{21}$$

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

$$m_{12}=MW_i\int_{y_1}^{y_2} F(y)\, dy+(MW_f-MW_i)\int_{y_1}^{y_2} yF(y)\, dy \tag{22}$$

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.

$$\int_0^1 yF(y)\, dy=\int_0^1 y^{a}(1-y)^{\beta-1} dy=\frac{\Gamma(a)\Gamma(\beta)}{\Gamma(a+\beta)} \tag{23}$$

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 7, 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,

$$n_k = \frac{\sum_j \mu_{kj} m_j \eta_j}{\sum_j m_j \eta_j} x100 \tag{24}$$

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 7. 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 8. For the feed comprising of equimolar mixture of the two distributions, the group compositions of the coexiting phases are tabulated in Table 9 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 9 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 10. 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 11. 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 12. 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 13. 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 14. 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 [13]. 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 15 and 16 for the H-Coal distillates and in Tables 17 and 18 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 19 and 20. 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 [14,15], 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 21. These were then used to compute liquid heat capacities at various temperatures. Comparison between calculated and experimental heat capacities are shown in Table 22. Very good agreements are observed.

Conclusions

A thermodynamic model for coal fluids has been successfully developed. 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 especially oxygen in coal liquids is necessary if accurate prediction of thermodynamics is needed. Analytical methods to obtain such information need to be devised. Also, more high temperature, high pressure VLE data on model coal compounds are necessary so that UNIFAC model may be extended for accurate predictions at high temperatures.

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APPENDIX

Modified UNIFAC Correlation

Activity coefficient of component i in a mixture:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \qquad \text{— (1)}$$

$\ln \gamma_i^c$ - combinational part
$\ln \gamma_i^r$ - residual part

$$\ln \gamma_i^c = \ln\left(\frac{\omega_i}{x_i}\right) + 1 - \left(\frac{\omega_i}{x_i}\right) \qquad \text{---- (2)}$$

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad \text{— (3)}$$

$$r_i = \sum_k \nu_{ki} R_k \qquad \text{— (4)}$$

x_i - mole fraction of component i
ν_{ki} - number of groups k in molecule i
R_k - volume group parameter for group k

$$\ln \gamma_i^r = \sum_k \nu_{ki} \left(\ln \Gamma_k - \ln \Gamma_k^i\right) \qquad \text{— (5)}$$

$$\ln \Gamma_k = \frac{z}{2} Q_k \left[- \ln\left(\sum_m \theta_m \tau_{mk}\right) + 1 - \sum_i \frac{\theta_i \tau_{ki}}{\sum_j \theta_j \tau_{ji}} \right] \qquad \text{— (6)}$$

Γ_k - activity coefficient of group k at mixture composition
Γ_k^i - activity coefficient of group k at a group composition

corresponding to pure component i

$\frac{z}{2} Q_k$ - surface area parameter for group k

$$\Theta_k = \frac{n_k \frac{z}{2} Q_k}{\sum_m n_m \frac{z}{2} Q_m} \qquad \text{---- (7)}$$

n_k - total number of groups k in the mixture

$$T_{mk} = \exp\left(-a_{mk}/T\right) \qquad \text{---- (8)}$$

$$a_{mk} = a_{mk,1} + a_{mk,2}\left(T - 298.15\right) + a_{mk,3}\left(T \ln \frac{298.15}{T} + T - 298.15\right) \qquad \text{--- (9)}$$

$a_{mk,n}$ - binary group interaction parameters

Excess Enthalpy of Mixture:

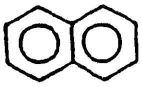
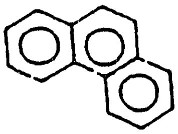
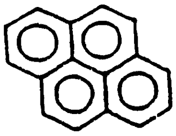
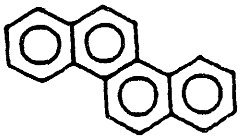
$$\left[\frac{\partial\left(g^E/T\right)}{\partial T}\right]_{P,x} = -\frac{h^E}{T^2} \qquad \text{— (10)}$$

$$\frac{g^E}{RT} = \sum_i x_i \left(\ln \gamma_i^c + \ln \gamma_i^r\right) \qquad \text{— (11)}$$

$$h^E = -RT \sum_i \sum_k x_i \nu_{ki} \left[T\left(\frac{\partial \ln \Gamma_k}{\partial T}\right)_{P,x} - T\left(\frac{\partial \ln \Gamma_k^i}{\partial T}\right)_{P,x}\right] \qquad \text{— (12)}$$

Table 1

Functional Groups[a] used in the Characterization Procedure

Group ID	Name	Structure
1	Monoaromatic (Benzene)	
2	Diaromatic (Naphthalene)	
3	Triaromatics	
4	Tetraaromatics (Pyrene)	
5	Tetraaromatics (Chrysene)	
6	Benzo-Group	
7	Hydroxyl	— OH
8	Pyridene	
9	Quinoline Ring	
10	Indole Ring	
11	Amine	— NH_2
12	Thiophene	
13	Aryl Thiophene	
14	Diarylthiophene	
15	Naphthenic CH2 Group	— CH_2 —
16	Paraffinic CH3 Group	— CH_3

[a] The functional groups are taken from the work of White and Coworkers [3,4]

•— bonded to an aromatic ring

TABLE 2

Functional Groups and Their Modified UNIFAC Parameters

Group ID	Name	R_K	Q_K	ΔR	ΔQ
1	Monoaromatic (Benzene)	3.1878	2.4000	0.1661	0.2800
2	Diaromatics (naphthalene)	4.9808	3.4400	0.1661	0.2800
3	Triaromatics	6.7738	4.4800	0.1661	0.2800
4	Tetraaromatics (Pyrene)	7.5042	4.7200	0.1661	0.2800
5	Tetraaromatics (Chryene)	8.5668	5.5200	0.1661	0.2800
6	Benzo-Group	1.7930	1.0400	0.1661	0.2800
7	-OH	1.0000	1.2000		
8	Pyridine	2.9993	2.1130	0.1661	0.2800
9	Quinoline Ring	1.7646	1.0330	0.1661	0.2800
10	Indole Ring	1.3447	0.7440	0.1661	0.2800
11	$-NH_2$	0.6948	1.4000	0.2047	0.5128
12	Thiophene	2.8572	2.1400	0.1661	0.2800
13	Aryl Thiophene	1.7946	1.3400	0.1661	0.2800
14	Diarylthiophene	0.7320	0.5400		
15	Naphthenic $-CH_2-$ Group	0.6744	0.5400	0.2274	0.2700
16	Paraffinic $-CH_3$ Group	0.9011	0.8480	0.2272	0.2816

TABLE 3

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 4

Results for Bubble Point Temperature and Vapor Composition Calculations Using Modified UNIFAC Model

Binary System	No. of Data Points	Average % Error in T	Average % Error in Y
Benzene Thiophene #	31(T) 10(Y)	0.8570	9.1722
Benzene Pyridine	69(T) 25(Y)	1.9131	5.1940
Benzene Aniline	169(T) 90(Y)	2.9616	6.9052
Benzene Toluene	216(T) 109(Y)	1.8884	2.9112
Benzene Ethylbenzene	11(T) 11(Y)	1.3443	2.3540
Benzene M-Xylene	34(T) 34(Y)	1.7707	2.4029
Benzene P-Xylene	26(T) 26(Y)	1.5540	0.9851
Benzene N,N-Dimethyl Aniline	8(T) 8(Y)	1.6202	0.1038
Benzene Isopropylbenzene	9(T) 9(Y)	2.0461	3.1094
Benzene Propylbenzene	10(T) 10(Y)	1.2542	2.2070
Benzene Biphenyl	46(T) 46(Y)	2.4850	0.2605
Benzene M-Terphenyl	24(T) 0(Y)	2.1194	
Toluene Pyridine	72(T) 6(Y)	1.4465	2.4394
Toluene Aniline	84(T) 73(Y)	2.0256	10.8208

Toluene 2-Methyl Pyridine	11(T) 0(Y)	2.7777	
Toluene 3-Methyl Pyridine	11(T) 0(Y)	1.4562	
Toluene Ethylbenzene	4(T) 0(Y)	1.8225	
Ethylbenzene Aniline	62(T) 62(Y)	1.0552	2.1602
Ethylbenzene Isopropylbenzene	18(T) 18(Y)	1.1385	7.9160
Ethylene Butylbenzene	17(T) 17(Y)	0.4289	2.5260
Pyridine M-Xylene	8(T) 8(Y)	0.7835	2.7865
M-xylene Aniline	6(T) 6(Y)	1.2567	8.0557
P-Xylene M-Xylene	18(T) 9(Y)	1.0674	0.9739
P-Xykene Aniline	6(T) 6(Y)	1.2025	8.4868
1,2,4-Trimethyl Benzene 1,2,3-Trimethyl Benzene	51(T) 0(Y)	0.3489	
1,3,5-Trimethyl Benzene 1,2,3-Trimethyl Benzene	50(T) 0(Y)	0.5668	
1,3,5-Trimethyl Benzene 1,2,4-Trimethyl Benzene	32(T) 0(Y)	1.0189	
2-Methyl Napthalene 1-Methyl Napthalene	58(T) 58(Y)	1.4186	5.4723
Phenanthrene Anthracene	3(T) 0(Y)	2.1987	
Pyridine 2-Methyl Pyridine	11(T) 11(Y)	2.2266	17.0578
Pyridine 3-Methyl Pyridine	11(T) 0(Y)	0.9493	

Aniline N-Methyl Aniline	30(T) 30(Y)	0.7103	1.4953
Aniline N-n-Dimethyl Aniline	27(T) 27(Y)	0.5045	2.1073
2-Methyl Pyridine 2,6-Dimethyl Pyridine	10(T) 10(Y)	6.1544	18.0343
2,6-Methyl Pyridine 3-Methyl Pyridine	11(T) 11(Y)	3.9893	29.6194
N,n-Dimethyl Aniline N-Methyl Aniline	27(T) 27(Y)	0.7138	1.0883
Quinoline Isoquinoline	12(T) 12(Y)	1.1660	4.3191
Isoquinoline Quinaldine	12(T) 12(Y)	0.8264	27.6807
7-Methyl Quinoline Lepidene	10(T) 10(Y)	0.3954	7.1141
M-cresol Quinoline *	66(T) 66(Y)	1.5502	6.3089
Benzene Phenol	28(T) 28(Y)	1.7562	3.8859
Toluene Phenol	9(T) 0(Y)	0.6996	
Pyridine Phenol	12(T) 11(Y)	3.1919	74.3372
Thiophene Phenol #	10(T) 10(Y)	0.2512	5.5832
M-Cresol Tetralin *	69(T) 69(Y)	2.3860	31.1774
Tetralin Quinoline *	37(T) 37(Y)	0.6623	5.1041
Thiophene Toluene	14(T) 7(Y)	0.2526	13.1334
Thiophene Pyridine #	14(T) 14(Y)	0.7841	2.2036

Piperidene Pyridine	66(T) 0(Y)	5.5489	
Pyridine Aniline #	9(T) 9(Y)	0.7649	4.3009
Benzene Quinoline *	34(T) 34(Y)	1.3744	12.5415
Benzene Tetralin *	27(T) 27(Y)	0.8564	10.9231
<u>Overall</u>	1720(T) 1103(Y)	1.8062	8.0090

(T) — The number of temperature data points
(Y) — The number of vapor composition data points
* — High pressure data
\# — Using newly regressed binary interaction parameters

TABLE 5

Results for Excess Enthalpy by Using Modified UNIFAC Model

Binary System	No. of Data Points	Absoulte Deviations in Excess Enthalpy, J/mol	Average % Error in Excess Enthalpy
Cyclohexane Thiophene #	8	4.4513	0.5233
Benzene Pyridine	59	2.2492	58.2891
Pyridine Aniline #	11	26.8556	2.1952
Cyclohexane Pyridine	93	57.7333	7.2725
Toluene Pyridine	43	19.8477	16.2037
Pyridine,2-Ethyl Pyridine	9	54.1300	77.5984
Cyclohexane,Methyl Pyridine	10	56.9289	6.1590
Pyridine Benzene,1,2-Dimethyl	15	38.0833	9.9522
Pyridine Benzene,1,4-Dimethyl	28	39.3582	14.0854
Pyridine Ethylbenzene	12	73.8650	38.8631
Pyridine Cyclohexane,Ethyl	12	52.5098	4.8154
Benzene Phenol	8	47.0442	6.1324
Benzene Aniline	43	350.9881	71.0156
Benzene Pyridine,2-Methyl	40	75.5735	190.3318

Benzene Pyridine,3-Methyl	22	28.5969	1161.5625
Benzene Pyridine,4-Methyl	3	37.5455	292.8181
Benzene Cyclohexane	832	10.1069	2.1524
Benzene Cyclohexanol	10	89.6113	30.9559
Benzene Toluene	112	10.5422	20.5445
Benzene Pyridine,2,6-Dimethyl	33	28.6231	63.9526
Benzene Pyridine,3,5-Dimethyl	17	5.7439	35.1822
Benzene Pyridine,2-Ethyl	12	16.9049	148.9306
Benzene Cycloheptane	11	84.5816	14.3806
Benzene Cyclohexane,Methyl	55	49.6259	8.9338
Benzene Benzene,1,2-Dimethyl	57	36.5643	34.9124
Benzene Benzene,1,3-Dimethyl	59	49.8355	34.1748
Benzene Benzene,1,4-Dimethyl	302	6.2461	7.3904
Benzene Benzene,Ethyl	29	12.1703	32.4906
Benzene Aniline,N-Ethyl	11	131.8362	53.9280
Benzene Cyclohexane,Ethyl	9	113.9381	19.7111
Benzene Cyclooctane	10	98.9285	15.7436

Benzene Isopropylbenzene	7	58.1111	67.9549
Benzene Propylbenzene	11	25.7376	26.2918
Benzene Benzene,1,2,4-Trimethyl	13	52.4021	19.6778
Benzene Benzene,1,3,5-Trimethyl	22	88.7598	28.6476
Benzene Butylbenzene	10	35.3474	25.1707
Benzene Aniline,N,n-Dimethyl	10	31.0849	336.4721
Benzene,Pentyl Benzene	10	47.4181	23.8510
Benzene Benzene,Hexyl	10	47.2223	19.2350
Benzene Methane,diphenyl	12	2.1713	65.2720
Benzene Biphenyl,2,2-Dimethyl	7	54.2927	44.2034
Cyclohexane Phenol	12	643.6700	67.4826
Cyclohexane Aniline	40	378.4697	42.0273
Aniline Toluene,3-Hydroxy	7	407.0656	22.2282
Aniline Aniline,N-Methyl	7	119.6497	74.1871
Benzene,1,2-Dimethyl Aniline	11	393.8580	46.3470
Benzene,1,3-Dimethyl Aniline	12	526.0680	53.8331
Benzene,1,4-Dimethyl Aniline	12	430.6073	48.7207

Aniline Aniline,N-n-Dimethyl	6	195.2658	49.0029
Cyclohexane Pyridine,2-Methyl	16	273.8348	29.2520
Pyridine,2-Ethyl Pyridine,2-Methyl	8	7.6963	155.1522
Cyclohexane,Methyl Pyridine,2-Methyl	9	146.3841	15.2152
Pyridine,2-Methyl Benzene,1,2-Dimethyl	15	24.0724	13.8001
Pyridine,2-Methyl Ethylbenzene	12	12.3583	14.7703
Cyclohexane Pyridine,3-Methyl	8	341.1441	32.3450
Cyclohexane Pyridine,4-Methyl	4	411.1825	38.3736
Cyclohexane Toluene	58	104.6445	25.3411
Toluene Pyridine,2-Ethyl	12	9.6997	194.5425
Toluene Benzene,1,2-Dimethyl	36	11.1498	30.1182
Toluene Benzene,1,3-Dimethyl	17	7.8555	24.0693
Toluene Benzene,1,4-Dimethyl	41	10.5744	74.5894
Toluene Ethylbenzene	42	15.1196	207.3125
Toluene Cyclohexabe	13	33.7337	6.6094
Toluene Propylbenzene	9	23.3137	1336.0083
Toluene Benzene,1,2,4-Trimethyl	10	8.7413	8.9046

Toluene Benzene,1,3,5-Trimethyl	13	31.2283	29.5875
Toluene Butylbenzene	31	448.4926	88.7460
Benzene,Pentyl Toluene	10	53.2507	197.5197
Toluene Benzene,Hexyl	12	58.4376	142.5095
Cyclohexane Toluene,Alpha-Hydroxy	16	87.9217	26.0513
Ethylbenzene Toluene,Alpha-Hydroxy	15	61.5304	17.9306
Pyridine Toluene,3-Hydroxy	9	3604.3687	86.8568
Benzene,1,3-Dimethyl Toluene,3-Hydroxy	16	41.4094	8.1421
Aniline,N,n-Dimethyl Toluene,3-Hydroxy	7	459.3392	46.7522
Pyridine,2-Ethyl Ethylbenzene	12	15.9191	39.0544
Ethylbenzene Benzene,1,2-Dimethyl	78	20.6167	83.2954
Benzene,1,4-Dimethyl Benzene,1,2,4-Trimethyl	10	13.7734	43.8987
Benzene,1,4-Dimethyl Benzene,1,3,5-Trimethyl	13	3.7571	18.8022
Ethylbenzene Propylbenzene	10	2.5633	109.2237
Ethylbenzene Butylbenzene	22	2.8324	16.1456
Benzene,Pentyl Ethylbenzene	9	3.5389	12.4581
Ethylbenzene Benzene,Hexyl	10	2.7466	7.0679

Propylbenzene Butylbenzene	10	1.2272	182.4438
Benzene,Pentyl Propylbenzene	10	3.3086	39.9310
Propylbenzene Benzene,Hexyl	10	2.2893	9.6166
Benzene,Pentyl Butylbenzene	11	0.9336	20.7365
Butylbenzene Benzene,Hexyl	8	1.1900	14.5547
Benzene,Pentyl Benzene,Hexyl	9	1.0942	59.8774
Overall	2855	63.3098	44.7794

--- Using newly regressed binary interaction parameters

Table 6

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 7

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 8

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_1		Temp (K)	Y_1	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 9

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 10

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 11

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	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	0.3141	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 12

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 13

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 14

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

	$X_l = 0.1$ $X_u = 0.4$			$X_l = 0.3$ $X_u = 0.4$			$X_l = 0.5$ $X_u = 0.4$		
	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 15

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 16

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	1.586	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 17

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.

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 18

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.

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 19

Predicted Bubble Point and Dew Point for H-Coal Distillates

EXPERIMENTAL BOILING RANGE	TWO DISTRIBUTIONS BP (K)	DP (K)	1 DISTRIBUTION 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 20

Predicted Bubble Point and Dew Point for Wilsonville Distillates

EXPERIMENTAL BOILING RANGE	TWO DISTRIBUTIONS		1 DISTRIBUTION	
	BP (K)	DP (K)	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 21

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 22

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

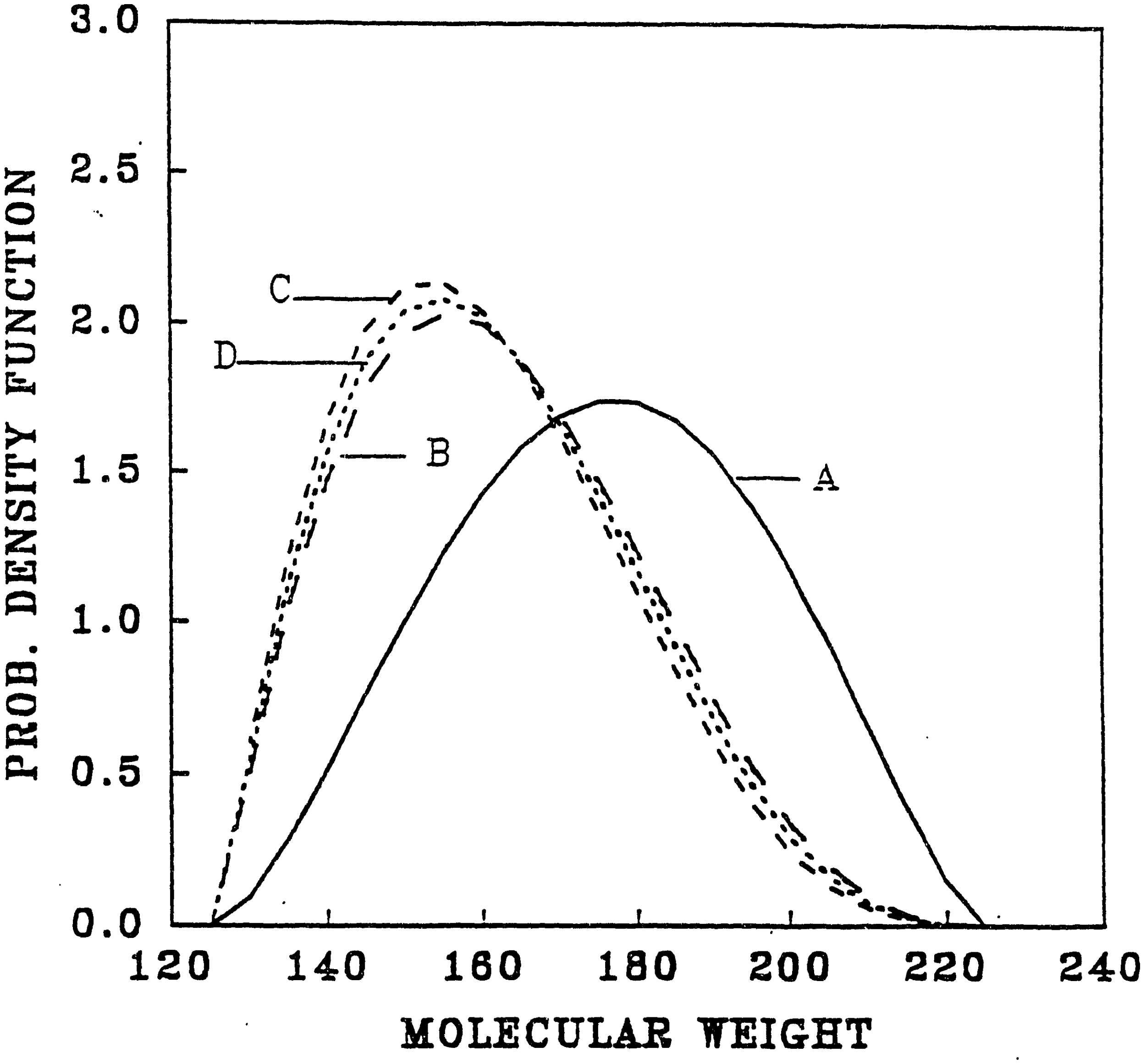


Figure 1: Molecular weight distributions for the Bubble point calculation of Table 5; $X_I=0.5$, $X_{II}=0.5$ case. A represents all distributions in the liquid phase. B,C represent hydrocarbon and phenolic distributions in the vapor phase for two distribution calculation and D is the vapor phase distribution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

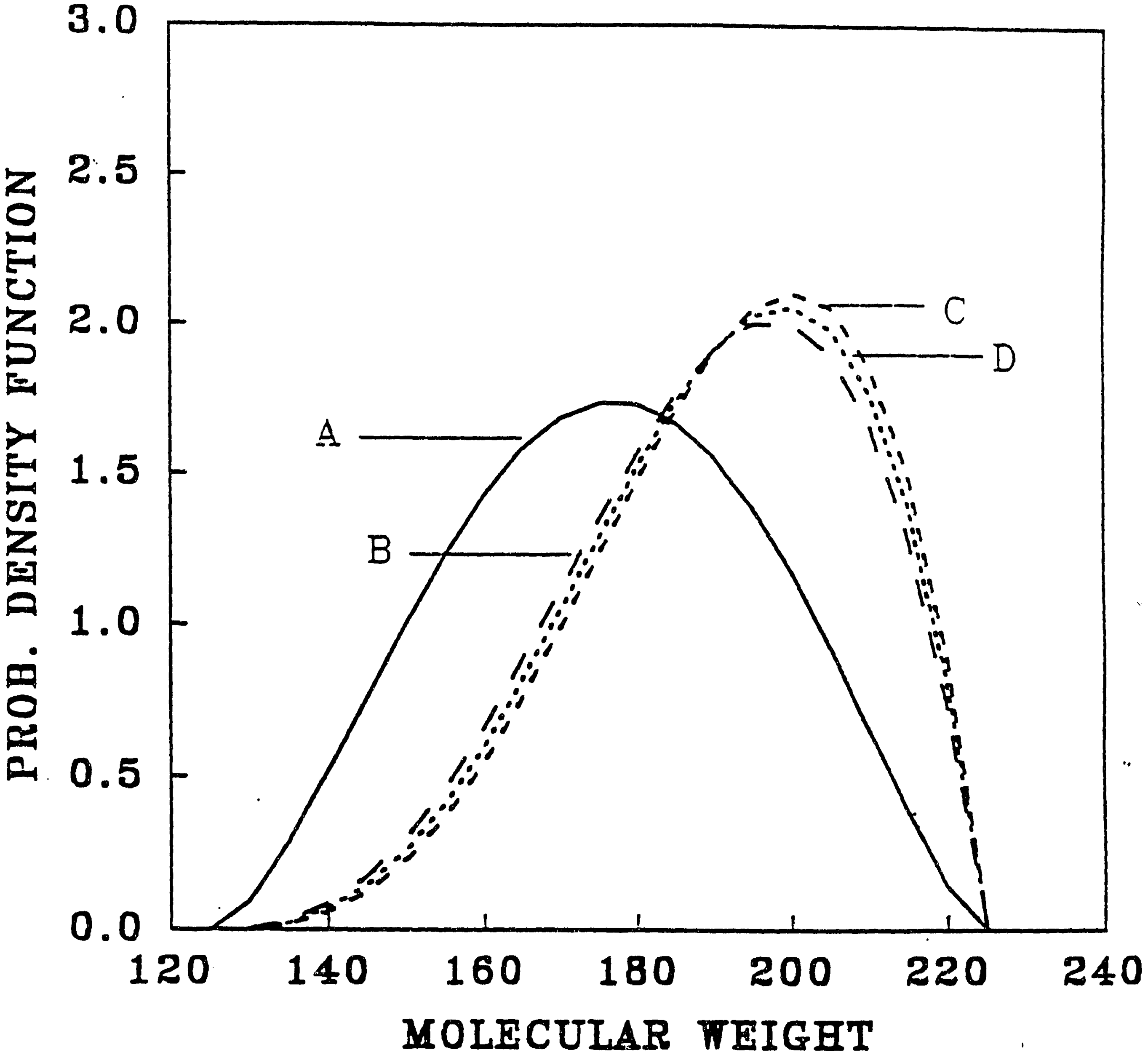


Figure 2: Same as Figure 1 but for Dew point calculation of Table 5; $X_I=0.5$, $X_{II}=0.5$ case. A represents vapor phase and B,C,D are for liquid phases.

Pyridinic

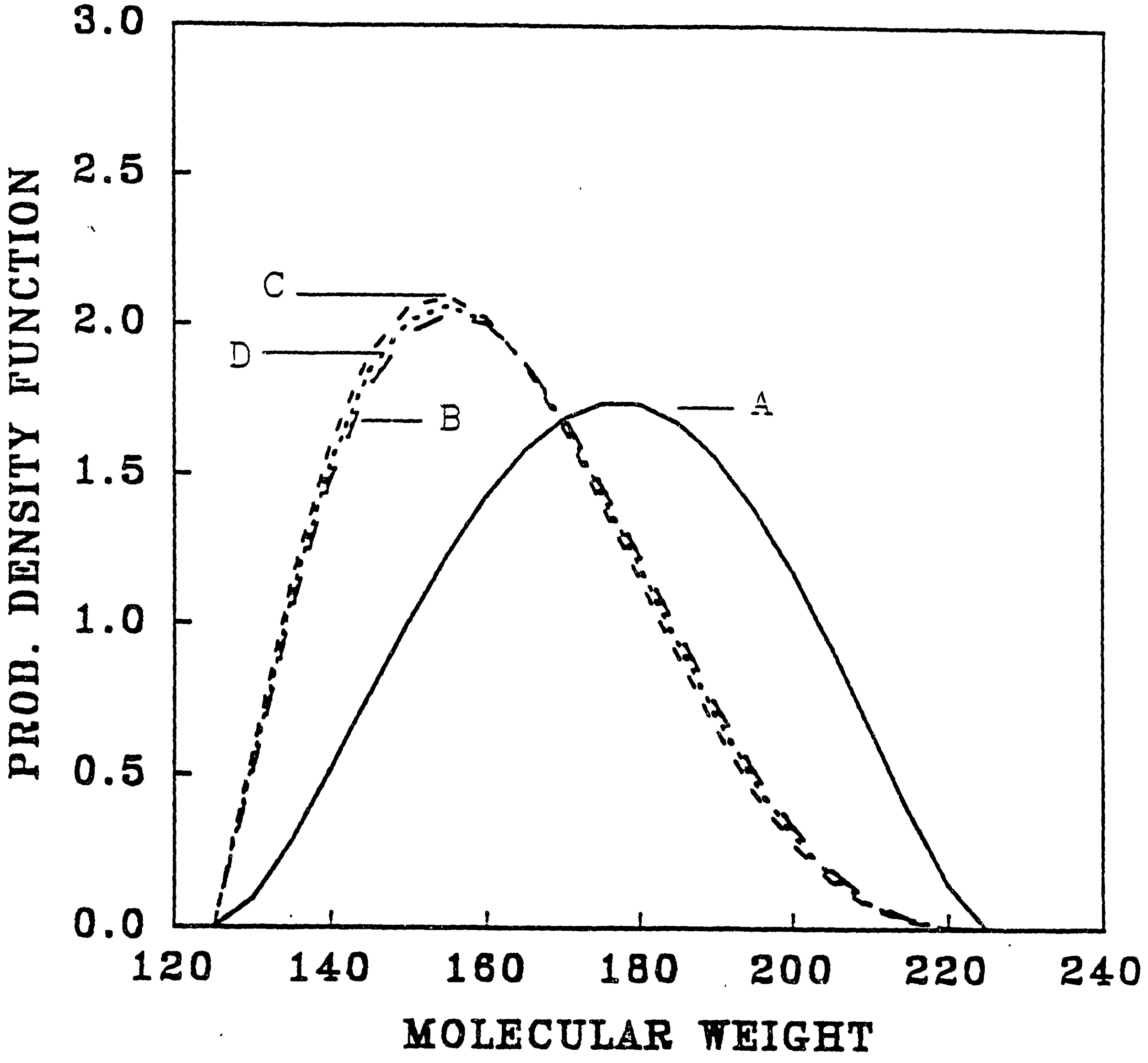


Figure 3: Same as Figure 1, but for the Bubble point calculation of Table 7; $X_I=0.5$, $X_{II}=0.5$; and C represents Pyridinic distributions.

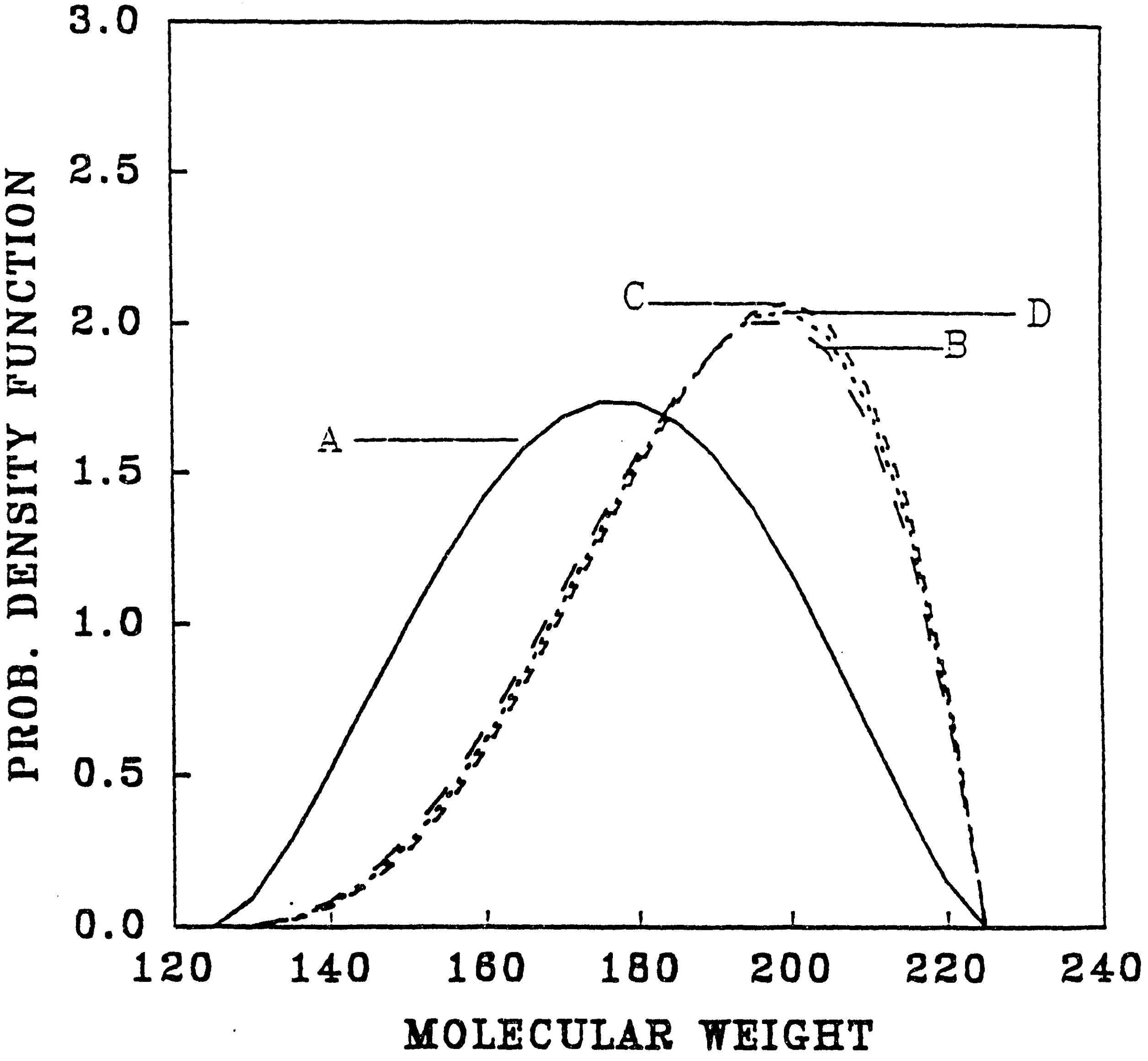


Figure 4: Same as Figure 3, but for Dew point calculations. A represents vapor phase and B,C,D are for liquid phases.

thiophenic

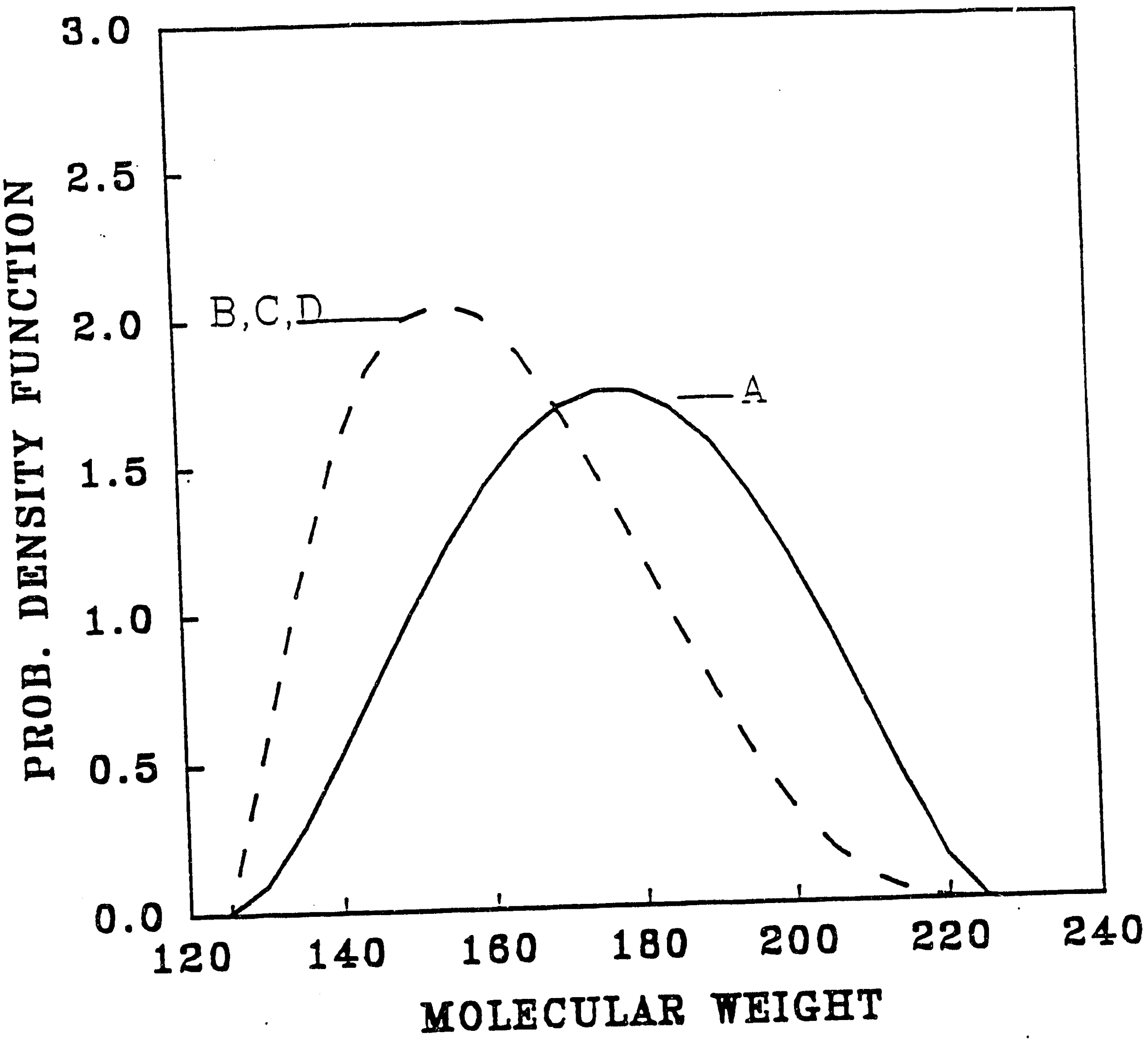


Figure 5: Same as Figure 1, but for the Bubble point calculation of Table 9; $X_I = 0.5$, $X_{II} = 0.5$ case; and C represents Thiophenic distributions.

thiophenic

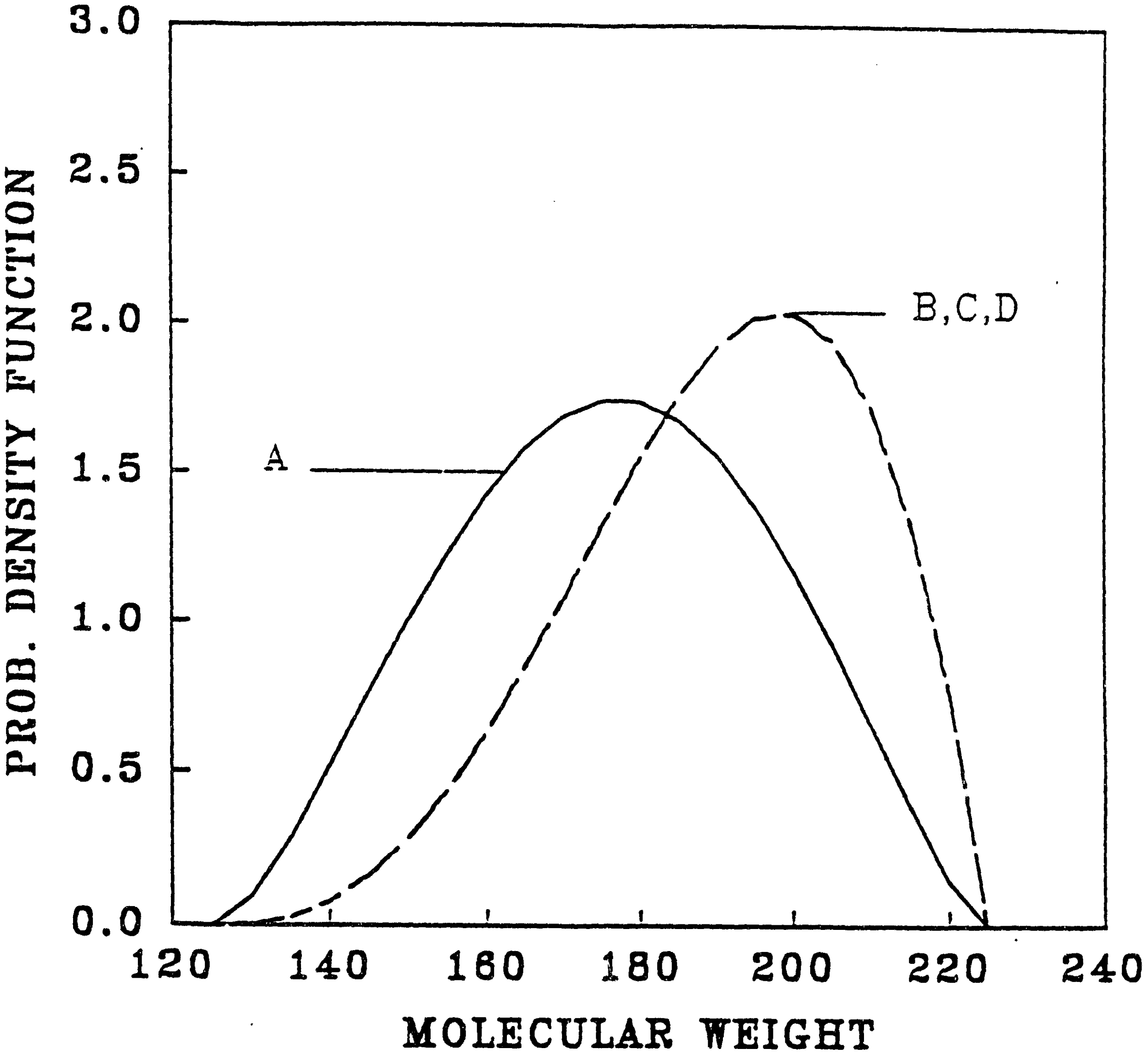


Figure 6: Same as Figure 5, but for Dew point calculation. A represents vapor phase and B,C,D are for liquid phases.

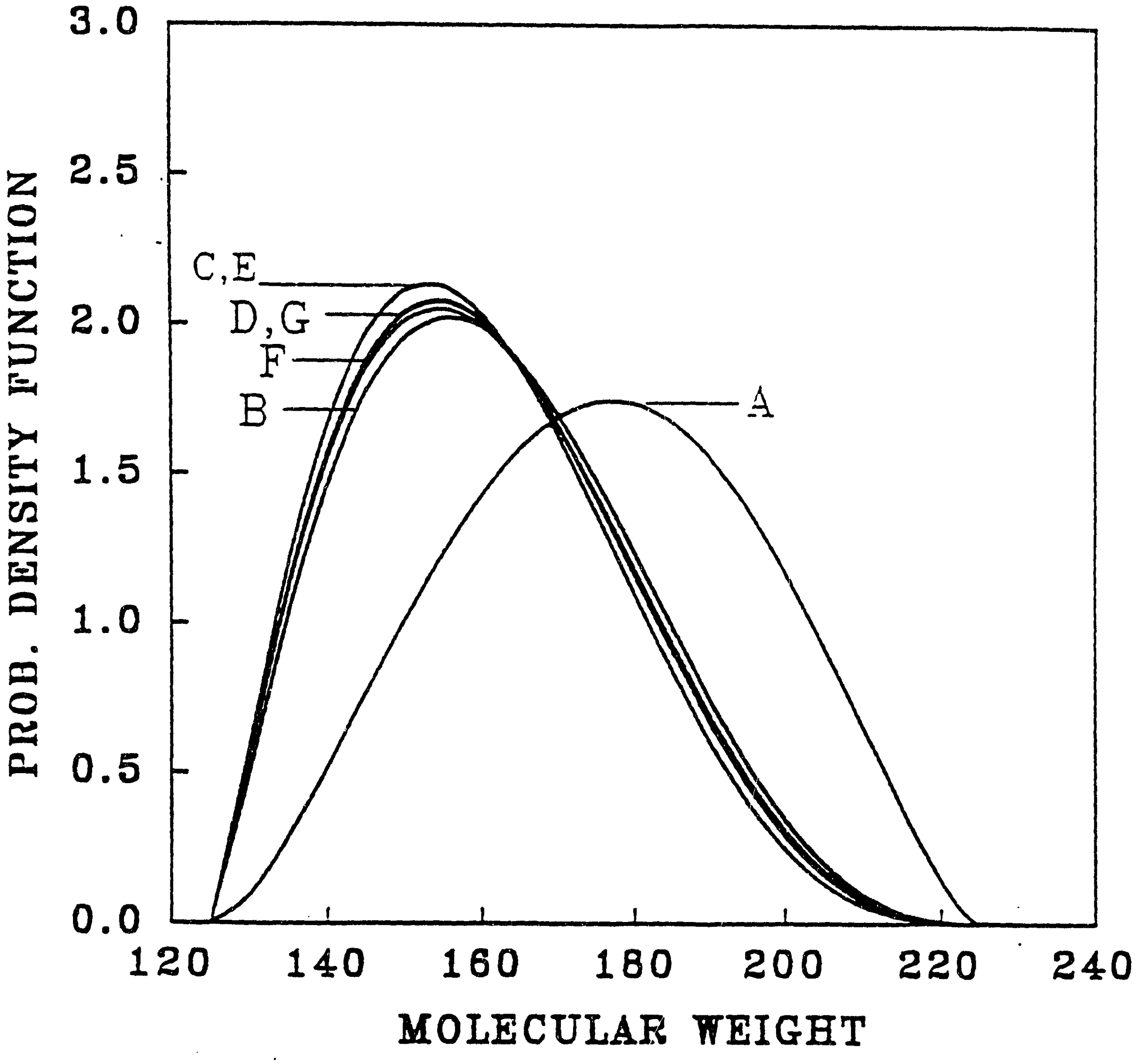


Figure 7: Molecular weight distributions for the Bubble point calculation of Table 11; $X_I = 0.3$, $X_{II} = 0.4$, $X_{III} = 0.3$ case. A represents all distributions in the liquid phase. B,C,D represent distributions in the vapor phase for three distribution calculation. E,F represent vapor phase distributions for the two distribution calculation and G is the vapor phase distribution for single distribution calculation.

DPT. GUA

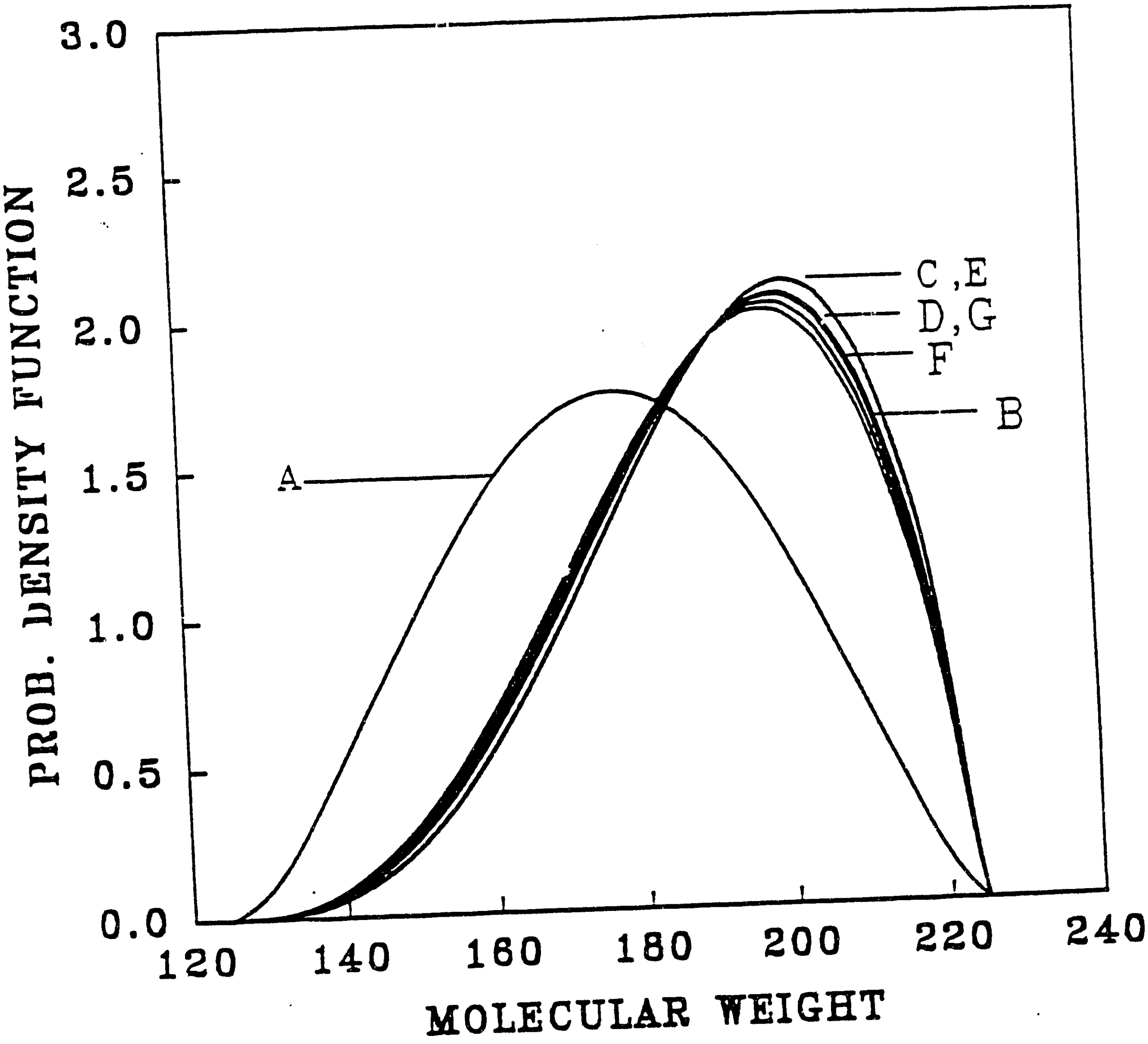


Figure 8: Same as Figure 7 but for Dew point calculation of Table 11; $X_I=0.3, X_{II}=0.4, X_{III}=0.3$ case. A represents vapor phase and B,C,D,E,F, G are for liquid phases.

PART II

HIGH TEMPERATURE HIGH PRESSURE VLE MEASUREMENTS

INTRODUCTION.

Coal derived liquids consist of a very large number of heavy poly-nuclear aromatics and substituted aromatic compounds. For the purpose of design and development of facilities to convert coal as a efficient fuel in the future, it is necessary to characterize the thermodynamic properties, especially the phase equilibrium of different fractions of the coal derived liquids over a wide range of molecular weights. A lot of work has been done to develop the thermodynamic model for prediction of the data required to do necessary calculations. For this purpose, measurement of the Vapor-Liquid Equilibrium data at the elevated temperatures and pressures are important.

A static method has been commonly used for the measurement of the Vapor-Liquid Equilibrium at high pressures and has allowed the collection of accurate data in the relatively low temperature ranges. However, since long residence time is required to attain the equilibrium state, the static method has a disadvantage for measurements at very high temperatures, where thermal decomposition of the components may occur. Another big disadvantage of this system is that the state of equilibrium is difficult to maintained during the process of sampling. Hence to overcome these problems, a flow type high temperature high pressure apparatus was designed and fabricated for the VLE measurements of multicomponent system and coal liquids, with the provision of sampling facilities during the normal operation without disturbing the equilibrium of the system at elevated temperatures and pressures.

Vapor- Liquid Equilibrium data will be measured with this apparatus for the systems of Quinoline, Tetralin, Cresol, Pyridine, Thiophene etc. Initially the effort is to reproduce the data which is already present in the literature. Once this is accomplished, final data for the unknown test mixtures of coal liquids, at extreme conditions of temperatures and pressures, will be measured.

EXPERIMENTAL APPARATUS

The construction of high temperature high pressure apparatus to measure VLE data for both known mixtures of aromatic compounds and heavy polynuclear coal liquids has been completed. Calibrations and checks on the various equipments of the apparatus have been carried out. A Quinoline-tetralin binary mixture was the first system chosen for data measurements. The apparatus was first tested by reproducing a VLE isotherm already available in the literature. Additionally, two higher temperature VLE isotherms have been measured.

The apparatus can be divided into four sections, i.e., Feed section, Equilibration section, Sampling section, and lastly the Control-Panel section. The maximum designed temperature and pressures for this system are 500°C and 2000 psi, respectively. All parts and tubing, including the ones exposed to the high temperature zones, are made of stainless steel (type 316). The tubing used in the fabrication is mostly of 1/4 inch diameter and at some places of 3/8 inch diameter. The fittings used are swagelok compression type, made of the same material SS-316.

This VLE apparatus consists of the equipment/components namely, Feed Tank, Positive displacement Metering Pump, Pre-Heater Oven, Main Heater Oven, Vapor-Liquid Equilibrium Cell with a circular coil of tubing around it in which the liquid gets heated before entering the cell, two Heat-Exchangers, two Control Valves, one Safety Valve, one Pulsation Dampening Bottle and eighteen Plug Valves (most of the fittings are of 1/4" diameter), and two strainers. Details and specifications of the equipment and components used are listed in the Appendix 1.

The purpose of designing and fabrication of this type of apparatus is to provide a steady supply of test liquid mixture, into the vapor-liquid equilibrium cell, at a very small flow rate and under controlled pressures. The liquid is heated, gradually to the equilibrium temperature in two ovens, before it is introduced into the VLE cell to achieve the equilibrium between the liquid and the vapors. Once we have reached this stage, vapor and the liquid will continuously be separated and sent to their respective coolers, through the respective openings out of the VLE cell. The vapors and the liquid streams are cooled and sent to the sample bottles through metering valves, for the collection of the samples. The amount of the sample taken can be controlled by opening of the metering (needle) valves for the desired time period. The excess amount of vapor and liquid streams are sent back to the main feed tank.

The main advantage of this type of flow apparatus is that a steady state continuous system is established, as the amount of vapor and liquid being taken out of the system at equilibrium is continuously compensated by the fresh liquid-mixture stream coming in at the equilibrium temperatures. This way, the system equilibrate after some time of its start-up, by manipulating pressure and level control loops.

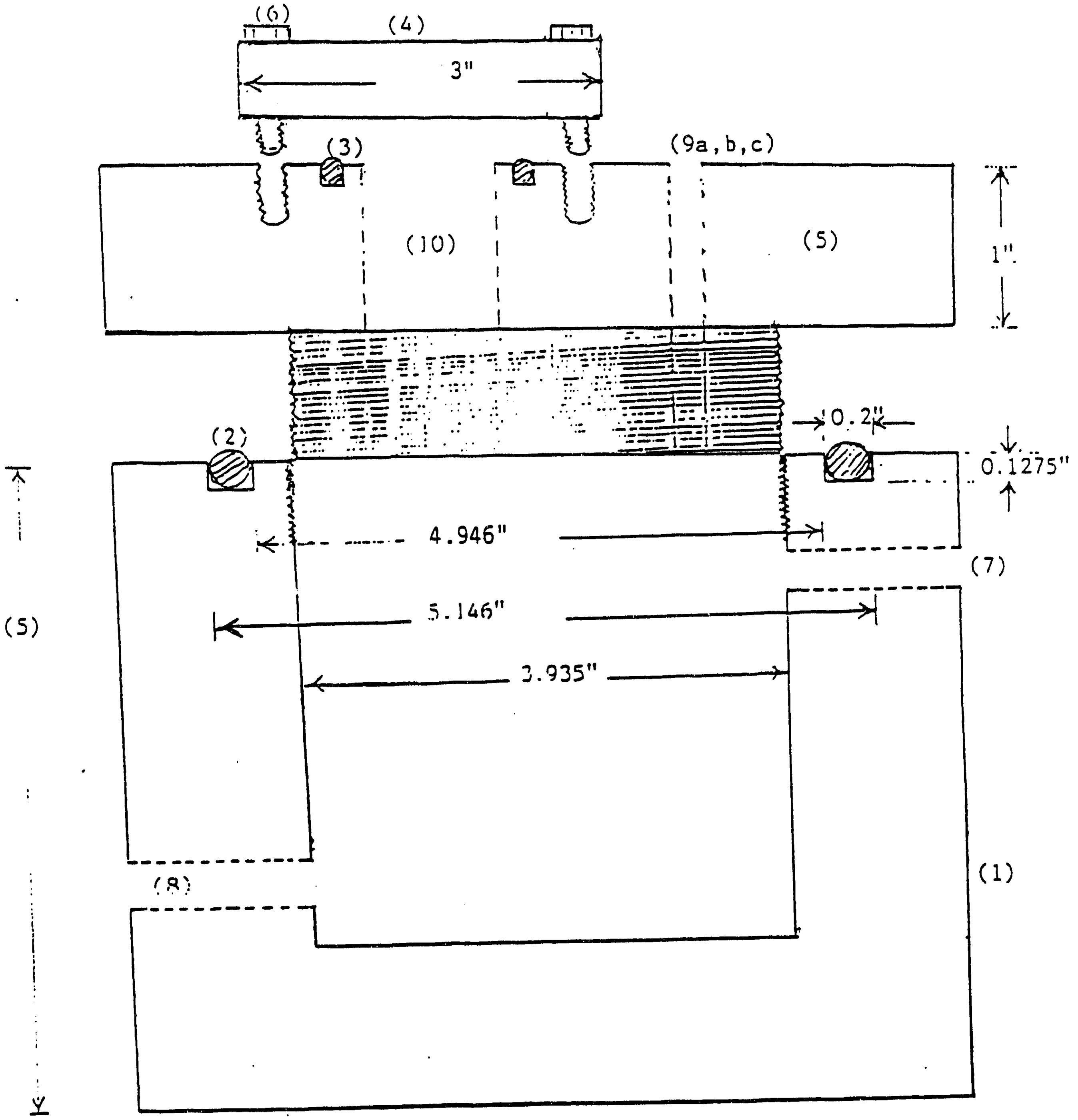
The Control Panel consists of one Pre-Heater controller, one Main Heater control Panel, one Level and Pressure Chart Recorder, two Controllers for the pressure and level control valves, one Thermocouple Key and a Temperature Digital Display and two Pressure Gauges. All these components of the apparatus are very carefully placed on a frame, built from channels, fittings and wood panels.

During the assembling and fabrication of the apparatus, a number of problems regarding the performance of the equipment, were faced. These are mentioned briefly in the following lines:

After closing the cap of the VLE Cell, it was subjected to high pressure test for the detection of leaks from the two O-Rings, placed in the main lid and small flange of the cell. It was found that at pressures of 600 - 800 psi, these two O-rings gave very small/tiny (microscopic size) bubbles in the leak detection media, which looked like foam. Only, after a number of efforts and attempts to get required polish, this problem was solved. The details of the Vapor Liquid Equilibrium Cell is attached in Fig. 1 and 2. It is the most vital part of the VLE apparatus. As it was mentioned before, the feed coming in this cell is heated upstream the cell in two coils, first in the pre-heater and then in the main oven, so that when the liquid enters the VLE cell, it reaches to vapor-liquid equilibrium. As shown in the diagram, there are two O-rings used in the VLE cell assembly to seal it and keep the hot vapors from coming out of the main lid and also through the flange of the cell. The severe conditions of high temperature and pressures, mentioned above require O-ring made of extraordinary type of material, which can resist these conditions, plus a very fine finish/polish is required (16 rms circular-lay finish) at the inner surfaces of the flange, main lid and within the groove of the VLE cell, in which the O-ring sits. Special custom made ventilated silver coated Inconel X-759 O-rings have been used. The advantage of the silver coating and the circular lay finish is that when the temperature of the cell increases, silver softens up and fills the microscopic gaps left in the polish and thus prohibits the leakage of the vapors.

Level detection within the Vapor-Liquid Equilibrium cell was a difficult job. In the models designed for the lesser severe conditions, the level can be monitored by visual contact through the Sapphire Glass windows. But it is not recommended for the high temperature and pressure designed equipments. So, other options were explored and it was found that the level in the cell could be read by the difference in pressures measured from

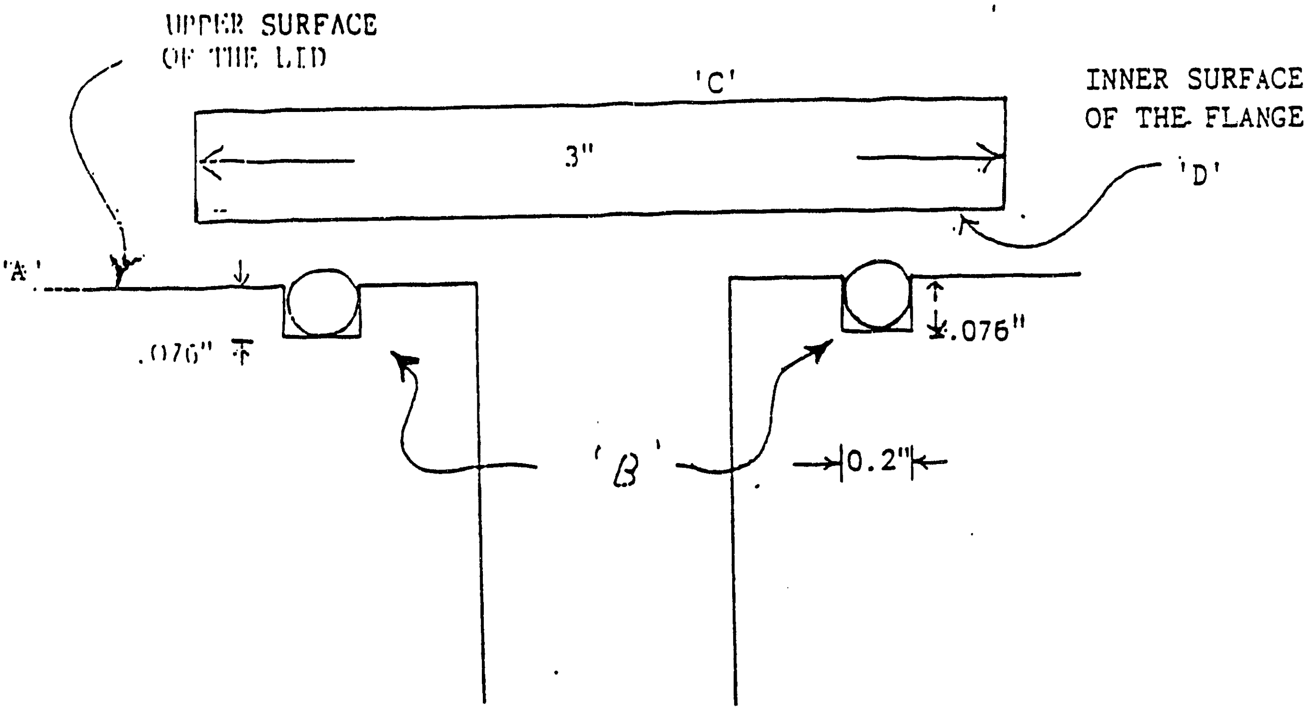
VAPOR LIQUID EQUILIBRIUM CELL



LEGEND:

1- VLE CELL WALL(THICKNESS 1")
2- MAIN CELL BODY O-RING
3- FLANG O-RING
4- FLANG SS316
5- LID OF THE CELL
6- FLANG BOLTS 3/16"
7- LIQUID STREAM INLET
8- LIQUID STREAM OUTLET
9- VAPOR OUTLET
9b-THERMOCOUPLE POINT
9c-PRESSURE SENSING POINT

VLE CELL LID AND FLANGE SURFACES WITH O-RING GROOVE



A- VLE CELL LID SURFACE, WHICH COMES IN CONTACT WITH THE POLISHED SURFACE OF THE FLANGE.

B- GROOVES FOR THE O-RING WITH VERY FINE POLISH OF 16-rms.

C- FLANGE OF 3" DIAMETER.

D- INNER SURFACE OF THE FLANGE. WITH VERY FINE POLISH, i.e., 16-rms OR CLOSE, SO THAT THERE IS A TIGHT SURFACE MATCH WITH THE NICKLE COATED O-RING, ESPECIALLY AT HIGH TEMPERATURE.

E- METAL O-RING (Ventilated with NICKLE coating) the vapor and liquid lines, coming out of the cell. The second option which was available is the measurement of the level by introducing a conductivity probe into the cell. Both of these systems send 4-20·mA response to the PID controller to regulate the liquid flow rate going out of the cell through a control valve , placed in the liquid line downstream the cell.

The fluctuation in the pressure caused by the operation of the positive displacement metering pump was also a big problem, as it would had disturbed the equilibrium continuously. A pulsation dampening bottle has been built, endogenously and installed downstream the pump, which has reduced the fluctuation from 50-80 lbs/stroke to almost 2-5 lbs/stroke. Which is again a good accomplishment, as no such bottle can eradicate the fluctuations completely. It is hopped that this very small fluctuation left will not effect the equilibrium conditions inside the cell as the flow rate of the incoming liquid is very small.

Originally when the system was designed, it was unfortunate that not much of the effort was made to check the compatibility of the VITON O-rings originally present in the plug valves, ordered for the apparatus at that time. So when the system was pressurized for the leak test, these O-rings did not work. They swell and deform on exposure to the liquid mixture of Quinoline and Tetralin, and cause leakages ultimately when subjected to high pressures, even at ambient temperatures. The manufacturer of these valves, i.e., NUPRO Precision Valves And Filters, did not have any kind of O-ring material which was compatible with the liquid being used. It was a difficult job, at the first place, to find the material which was compatible to polynuclear aromatics and secondly to get the O-rings of this material in the same size to replace the original VITON O-rings from the valves mounted on the system. One such effort was a success and a material called KALREZ, made by DUPONT was compatible and luckily all the required O-ring sizes were also available. Now these O-rings are working with no problem.

LEVEL PROBE AND CALIBRATION

The VLE apparatus uses an opaque stainless steel cell unlike the see-through glass window cells used in various other studies in the literature. As a result , reliable level sensing is very crucial in our measurements. Two different sensing methods were tested with the plan to use the one that performed more reliably at the advanced temperatures and pressures of operation of the VLE cell. The first method used a differential pressure (DP) cell and the second one utilized electrical conductance sensors.

DP cell sensor

In this method the liquid level in the cell is measured by a differential pressure (DP) transmitter. A Rosemont DP cell with a full range of 0-6" of water was purchased. The DP cell was connected between the two legs, one coming off the liquid outlet from the cell and the other coming off the vapor line from the top of the cell (see figure 3). The later line is filled with the process liquid up to a certain level which is maintained constant. This level is in general higher than the liquid level in the cell. The DP cell, in effect, gives a reading proportional to the difference between the two levels. The DP cell was calibrated to measure liquid levels from 1/2" to 3" in the VLE cell. The system was installed and tested extensively, and the conclusion was that it did not perform satisfactorily at high temperature and/or high pressures. As a result it was abandoned in favor of the electrical conductivity probe.

Electrical conductivity sensor

This probe was purchased from Delta M corporation who modified their existing LC-2300 conductivity probe to operate at higher temperatures (<500°C) and higher pressures (<1500 psi) according to our specifications. The Delta M LC2000 series of instruments employ thermal based sensors. Power is supplied to the sensors, and the returning sensor signal is converted to a standard 4-20 mA signal by solid state electronics. Figure 4 shows a block diagram of the instrument circuitry. Figure 5 shows the VLE cell fitted with the instrument.

The sensing element in the LC2000 Series level probes is a wire with a linear resistance versus temperature coefficient R(T). The temperature, and therefore the resistance, of this wire at any point along its length is determined by the amount of heater power to the probe and the thermal heat transfer from the probe surface to the surrounding media. The heat transfer properties (thermal conductivity and diffusivity), of the liquid whose level is to be measured is generally significantly greater (as much as 100 times) than the air or vapor phase above it. Therefore an increment of resistance (delta R) in

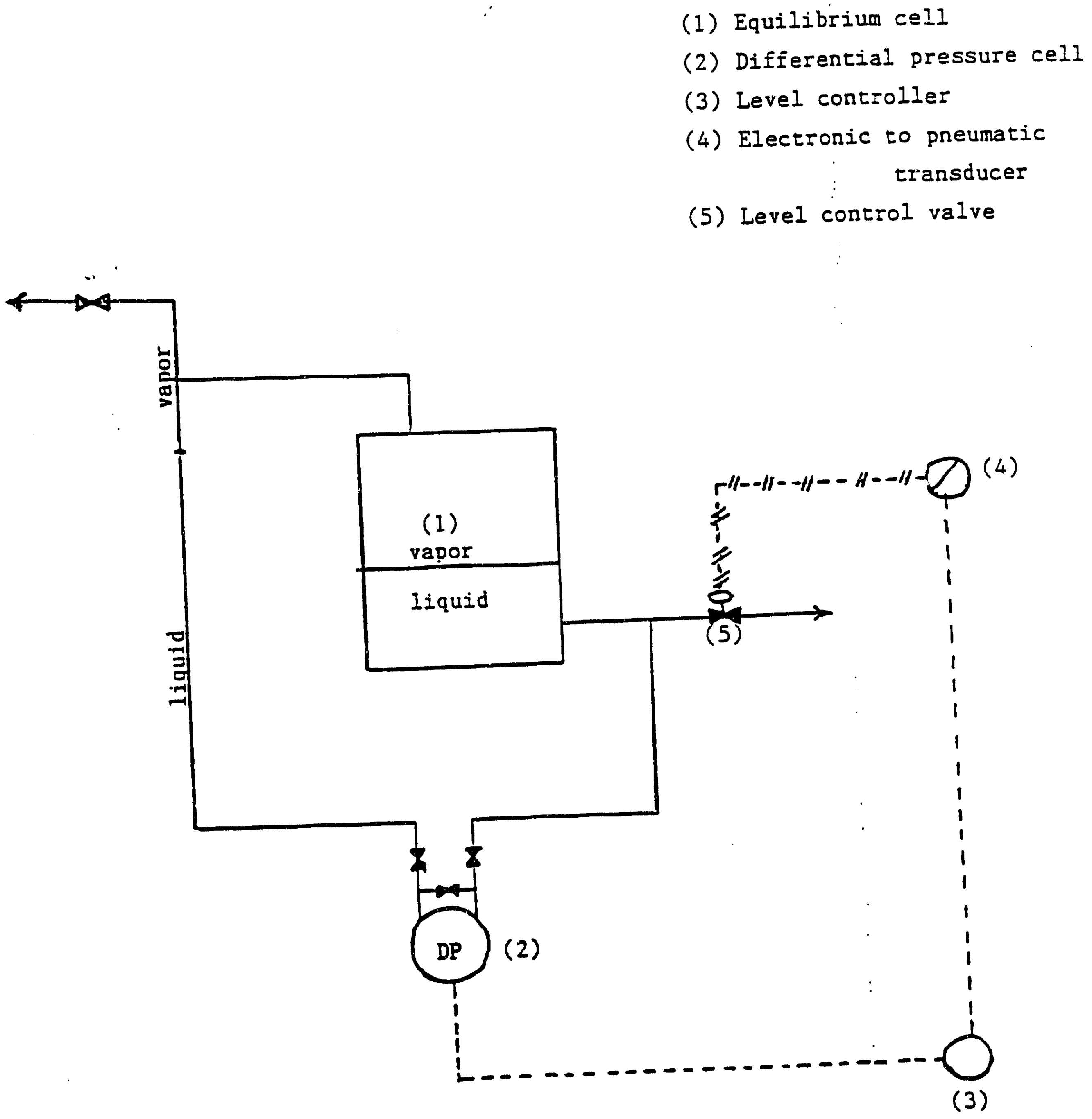


Figure 3: Liquid level control system for the Equilibrium cell in the VLE apparatus

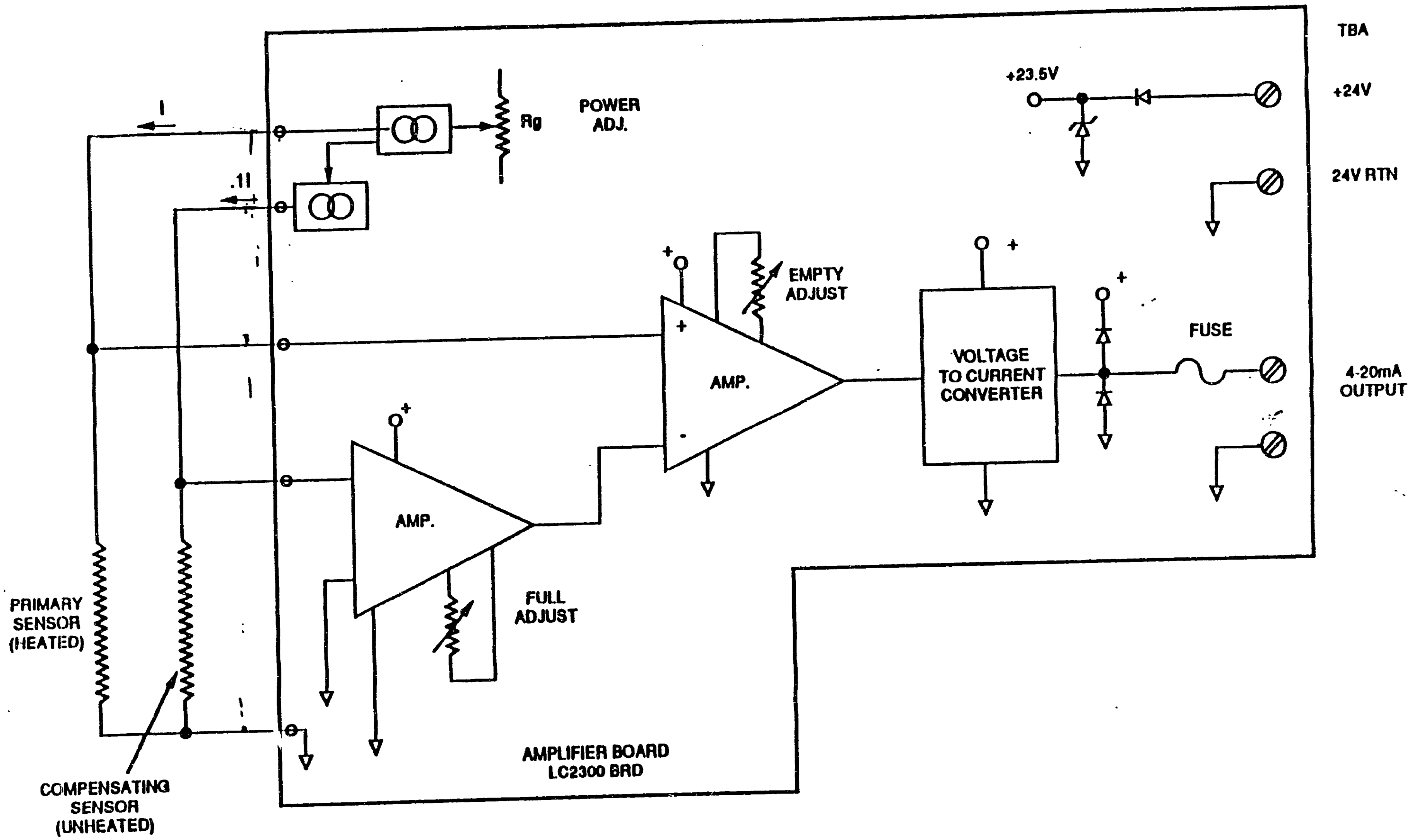


Figure 4: LC2000 Continuous Level Monitoring Instrument Block Diagram

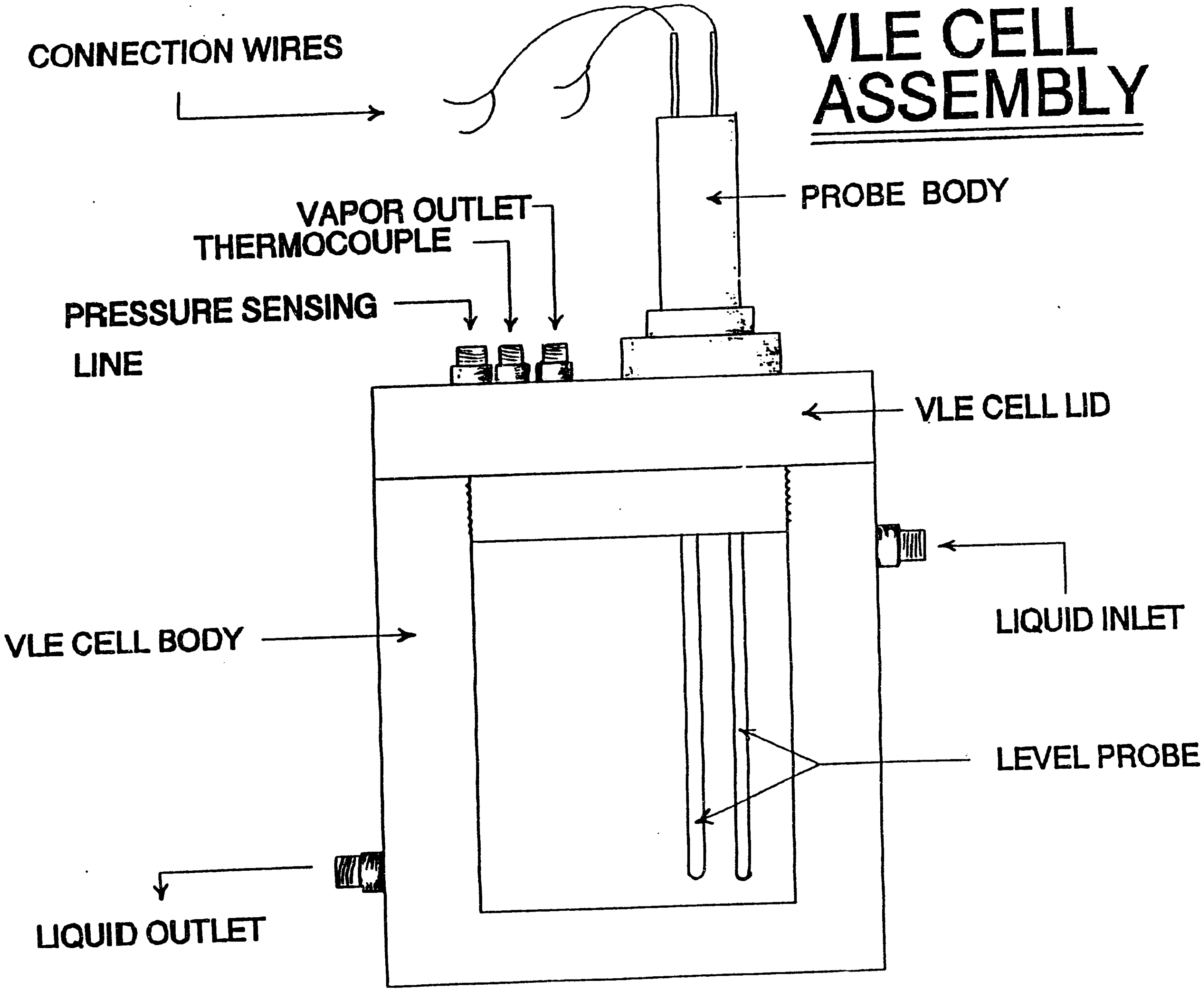

VLE CELL
ASSEMBLY
CONNECTION WIRES
PROBE BODY
VAPOR OUTLET
THERMOCOUPLE
PRESSURE SENSING
LINE
VLE CELL LID
LIQUID INLET
VLE CELL BODY
LEVEL PROBE
LIQUID OUTLET

Figure 5

the sensor wire is directly proportional to the length not submerged in the liquid. With many level sensing techniques, a change in the process temperature will alter the operation of the device, yielding false readings. The Microtuf LC2000 Series design includes a compensation feature which avoids this problem. The heated sensor has a temperature profile which is the sum of the temperature of the media with which it is in contact plus an incremental temperature determined by the amount of self heating and the thermal properties of the two media. The second (unheated) sensor, located adjacent to and parallel with the heated sensor, has a temperature profile which exactly matches the media temperature near the heated sensor. The unheated sensor signal is electronically subtracted from that of the heated sensor, leaving only the thermal based level signal which is now totally independent of the temperature of the media.

The electronics package powers the heated sensor probe with a regulated current and supplies a sense current to the compensating sensor. The voltage output from the analog level sensing circuit is amplified, offset to create zero Volts at the top level, and inverted to make zero Volts correspond the the bottom level. The output driver circuits then convert it into a 4-20 mA signal. Factor which limit the resolution of the LC2000 series of instrument in a installation ore: unstable thermal conditions in the vessel such as unbaffled convection currents, wave action, probe or vessel vibration, inadequate settling time, and the ratio of thermal conductivities between the the two media being monitored. The user must ensure that these factors are held within acceptable limits for the application.

There is a fundamental difference in the response of the heated level probe to rising and falling levels. When liquid rises on the probe, the response is nearly immediate (<0.1 seconds), because the previously warm length of the probe is easily chilled to equilibrium with the liquid. When the liquid level falls, however, it takes a few seconds to warm the freshly-exposed probe length to its equilibrium temperature with the gaseous medium. The falling level response time is a multiple of the rising level response time, typically about 60x.

The Delta M LC2000 Series level of probes provide a reliable measure of level in most every condition with no regular attention. The application will determine the degree of attention necessary to assure the proper operation through calibration and cleaning of the probe sensor elements. When the tank level is unchanging, turning off the power and then restoring it after a period of at least 5 minutes cooling will allow the response time of the falling level to be established. The response to the rising level is immediate be comparison. Interpretation of the indicated level must always be done in consideration of the response time, so this procedure should be familiar to the operator. Once established, the response time should not change unless the probe is replaced, or sludge accumulates on it.

Calibration:

The setup/electronics of the level probe assembly was initially not capable of detecting true level, inside the VLE cell with the change in temperature above the ambient. As the temperature was increased, the level indication also increased. To counter this change a number of modifications were done to the electronics like changing fixed resistors and adjustable pots by ones with larger span/gain to compensate the resistance change in level probe with the change in the temperature. Details of electronics and field wiring of the level probe assembly are given in Appendix3.

The level probe calibration included four steps which allowed zero and gain adjustments using the actual probe response.

Step #1: Full level adjustment. i.e., adjusting entire span.

- The VLE cell was filled to the maximum

-Power to the level assembly was switched on and at least 1/2 hour response time was allowed for the system to stabilize.

-R-16 located on the LC2300 board was adjusted to produce and output of 20 mA on a voltmeter connected in parallel to the R-15. Power was switched off.

Step #2: Empty level adjustment i.e., adjusting the entire span.

-The VLE cell was emptied out fully so that the level probe does not remain in contact or dipped in the liquid.

-The system was powered and was allowed to stabilize for at least 1/2 hour.

-Then the R-18 located on the LC2300 board was turned/adjusted for 4 mA.

-After this the system was fine tuned adjusting R-16 and 18 respectively at the slightly different conditions as needed.

Step #3: High level adjustment by adjusting partial span.

-The level in the VLE cell was again raised to the highest level possible and close to the step 1 level.

-The liquid level was measured independently by the help of a dipstick.

-The current (mA) was determined so as to correspond to the correct level in the VLE cell on the basis of 20 mA = 100% full level and 4 mA = 100% empty level.

-The system was powered and again 1/2 hour response time was allowed for the system to stabilize.

-R-16 was adjusted to bring the mA output to the above mentioned required value of mA.

-Power was switched off.

Step #4: Low level adjustment by adjusting partial span (fine tuning).

-Level in the VLE cell was lowered to the lowest possible.

-Level in the cell was measured by a dipstick.

-The mA output was again determined to correspond to the correct level on the basis of 20 mA = 100% full and 4 mA = 100% empty.

-The system was again powered and was given 1/2 hour to stabilize.

-R-18 was adjusted to bring the mA output to the required value as mentioned above.

All of these steps were repeated at 325°C and 350°C under nitrogen blanket pressure of 100-200 psi.

Unfortunately, despite spending so much time and effort on this level probe, the response and the calibration curve was found linear only at ambient temperature and pressure. As shown in figure 6 (calibration curve), the probe was calibrated at 325°C and 350°C.

During the calibration, the following observations were made about the probe output as a function of temperature and pressure. It was observed that pressure affected the level reading significantly only at low pressures. For pressures from atmospheric to 120 psi, 0.11% level decrease was observed per 1 psi rise in pressure; whereas at higher pressures the output response of the probe was not a much affected by pressure variation with an estimated 0.035% decrease per 1 psi rise in pressure. Variation of the level reading with pressure at 325°C is shown in figure 7. The temperature effect on the probe output was estimated to be about 0.32% rise in reading per degree C rise in temperature. This in effect quantifies the calibrations shown at 325°C and 350°C in figure 6.

Even though the conductivity probe needed to be calibrated at desired temperature, we decided to use it for our measurements because once calibrated it gives reliable and reproducible output. The non-linear calibration curves generally posed difficulties when measuring levels around 0% (empty) and 100% (full). However, all our experiments were conducted with liquid levels between 20% and 40%. From figure 6, it is easily observed that the probe output range corresponding to this range of actual liquid level is 40% to 80% with temperatures ranging from 325°C to 350°C. In general, attempts were made to maintain the probe output reading around 50%.

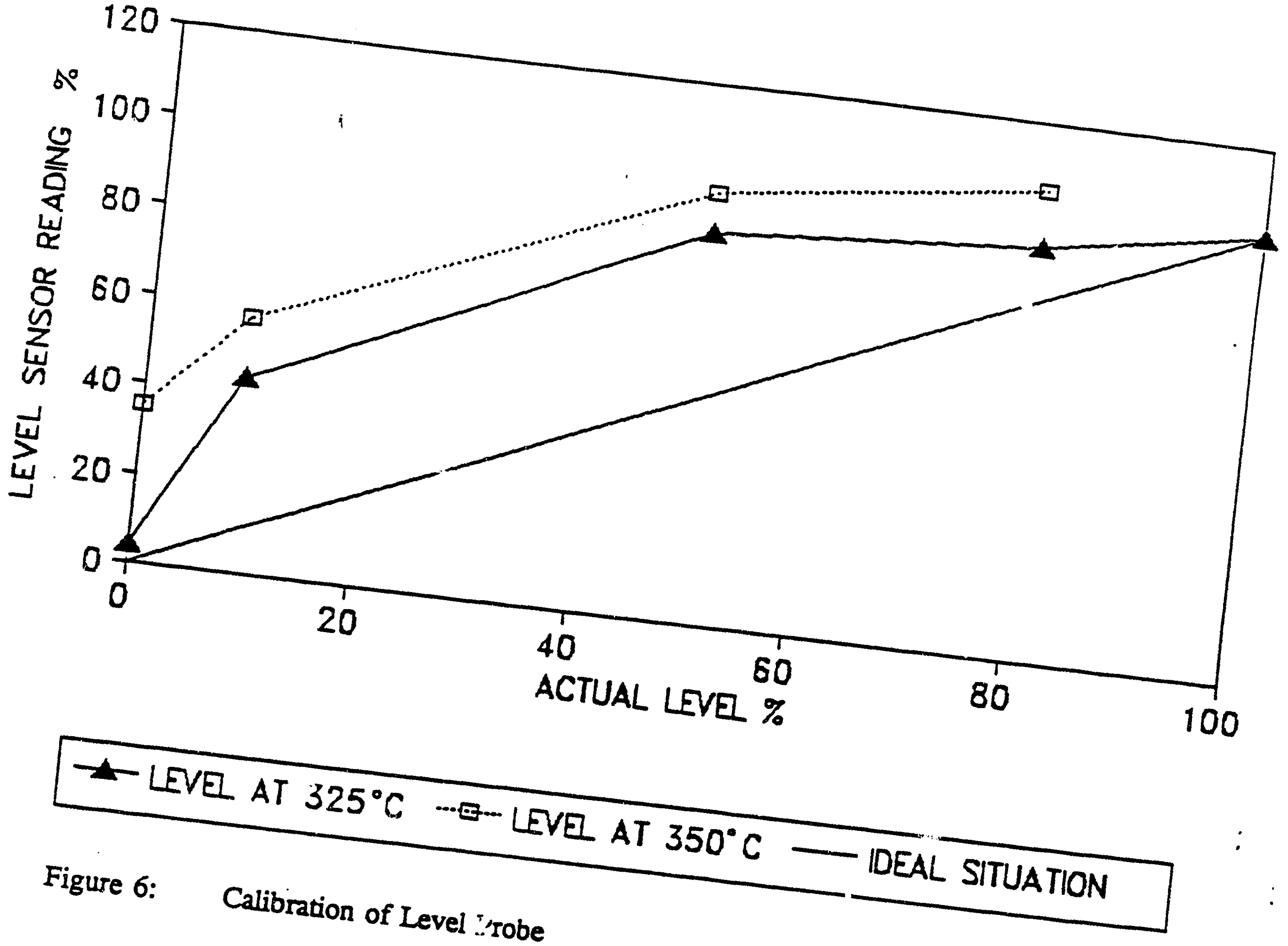


Figure 6: Calibration of Level Probe

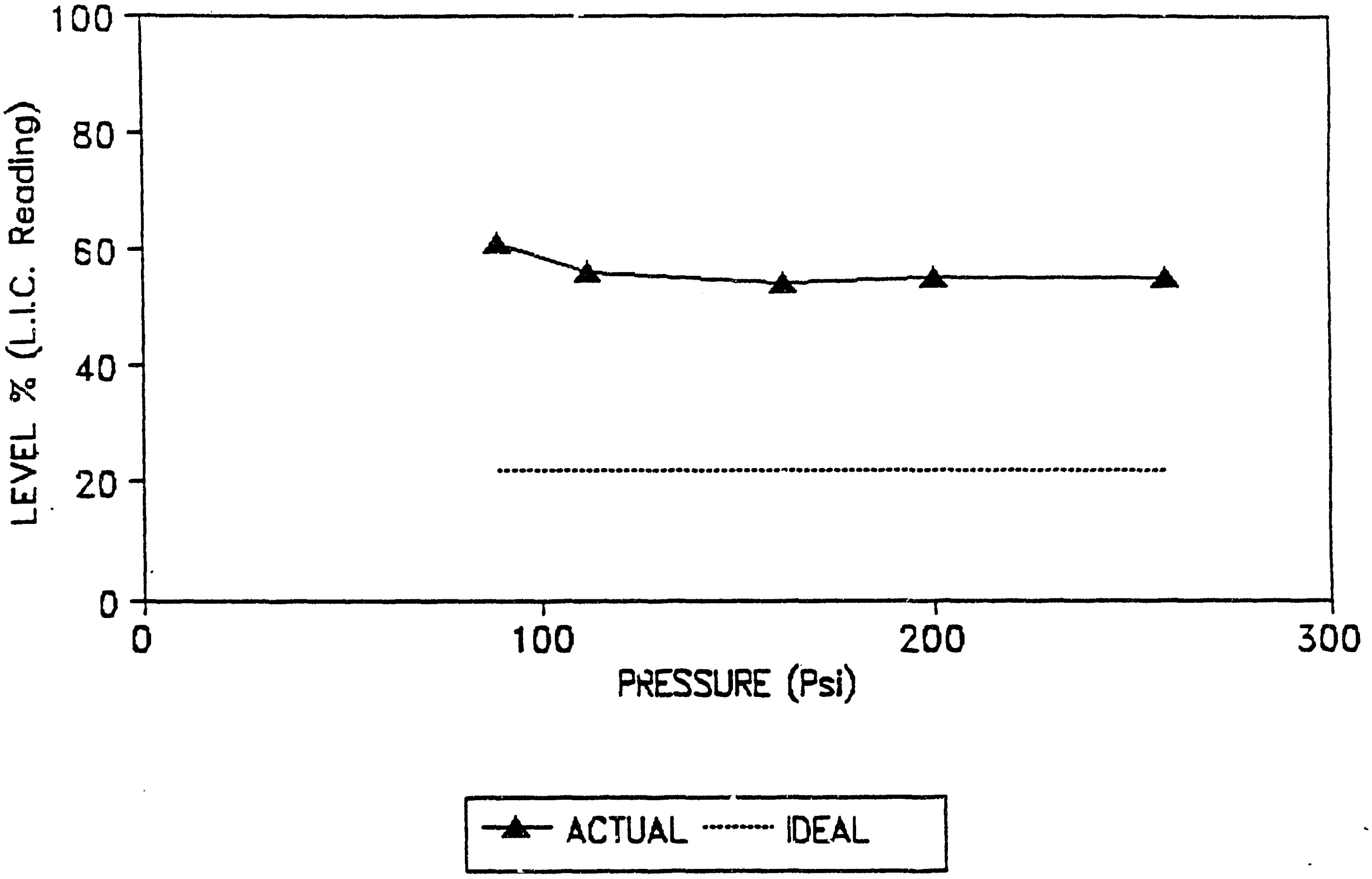


Figure 7: Pressure Dependence of Level Output (325°C)

PROCEDURE

A schematic flow diagram of the flow-type apparatus designed and made for this work is shown in figure 8. Feed from the feed tank (9) is filtered through two strainers (19 & 29) of 60 and 230 microns respectively and is pumped, by a positive displacement metering pump (23), to the pre-heater oven. The liquid stream is heated while it passes through a coil shaped tubing in the pre-heater (24). The coiled tubing provides the maximum surface area for the heat transfer to the liquid flowing through it. Here the temperature of the liquid is raised to the difference of 10 - 20 °C to that of the main heater (25). The feed then enters the second coil placed inside the main heater where the temperature of the liquid stream is again raised so as to bring it close enough, i.e., ± 1 °C to the desired temperature within the vapor-liquid equilibrium cell (10). As the liquid stream is already, or very close to the equilibrium temperature, there establishes equilibrium in the cell. The vapor and liquid flow rates out of the VLE cell is controlled by two control valves (19 & 20), placed at the respective lines. Manipulation of the output of these valves to increase or decrease the flow rates of the vapors and liquid from the cell, help to maintain the pressure and the required level in order to achieve the equilibrium. The vapors and liquid from the cell are carried by two separate lines to the two respective shell and tube heat exchangers (8a & b), where they are cooled down to 35 - 50 °C. Streams from these two heat exchangers are then combined and sent back to the feed tank. Before the point where these streams are combined, there are two sample point extensions (4 & 5) on each line. The third sample point extension (3) is present on the feed line which also becomes the inlet pump. The samples of the feed, vapors, and the liquid streams can be taken once the equilibrium conditions have been established. The quantity of the samples to be taken, can be easily controlled with the help of the metering valves (26) (Needle Valve), placed in the sample extension lines. Once the samples are collected, they are tested and analyzed by the liquid chromatographic methods.

Both the pre-heater and the main oven are provided with independent controllers, which control the set points in the range of ± 1 °C temperature difference. The main heater controller works on the weighted average of the two inputs, one from the interior of the oven and the other from the inside of the vapor-liquid equilibrium cell. Both of these along with the other thermocouples, placed at various locations, are of J type Iron/Constantan. These thermocouples were calibrated against two reference points of water, i.e., freezing and boiling points.

(*) - * is the number of the respective equipment in figure 8.

HIGH TEMPERATURE - HIGH PRESSURE VLE FLOW APPARATUS.

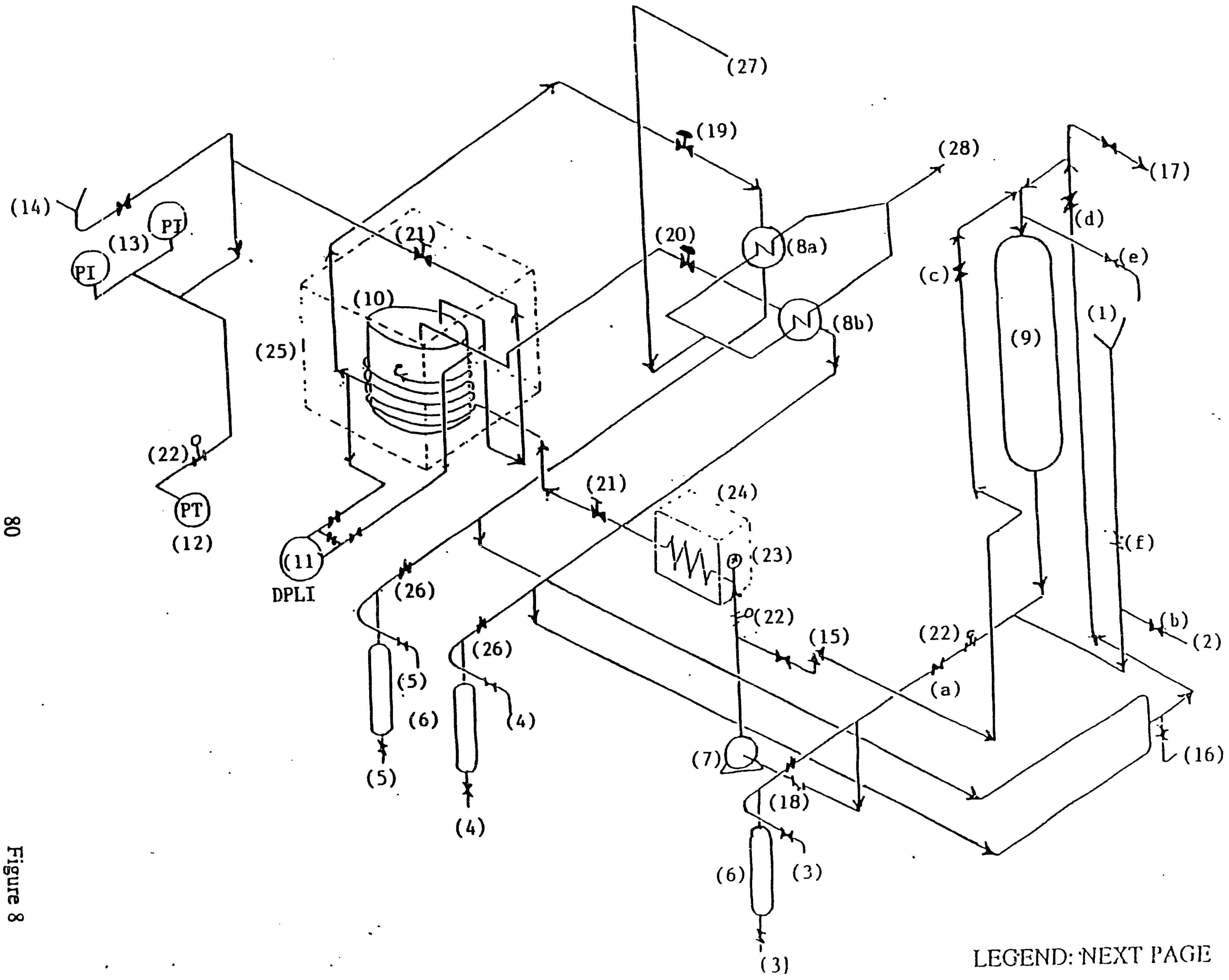


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Figure 8

LEGEND FOR THE PROCESS FLOW DIAGRAM (VLE SYSTEM):

The following numbers of this legend represent different equipment of the vapor-liquid equilibrium system, as marked on the schematic flow diagram, respectively.

1- Feed inlet
2- System purging/pressure test gas inlet point
3- Feed sample points
4- Vapors sample points
5- Liquid sample points
6- Sample collectors:
    a: For Feed
    b: For Vapors
    c: For Liquid
7- Feed Pump (Positive Displacement Pump)
8- Heat-Exchangers:
    a: Liquid Cooler
        Shell-Side Hot Liquid
        Tube-Side Cooling Water
    b: Vapors Cooler
        Shell-Side Hot Vapors
        Tube-Side Cooling Water
9- Feed Tank
10- Vapor-Liquid Equilibrium Cell
11- Differential Pressure Level Indicator
12- Pressure Transmitter
13- Pressure Gauges
14- Pressure Transmitter line filling point
15- Pressure Relief/Safety Valve
16- Drain Point
17- Vent Point
18- Strainer
19- Level Control Valve (Pneumatic)
20- Pressure Control Valve (Pneumatic)
21- High Temperature Hand Control Valve
22- Thermocouples
23- Pump Discharge Pressure Gauge
24- Pre-Heater
25- Main Oven
26- Needle Valve
27- Cooling Water
28- Hot Water to sewer

The pressure and liquid levels are controlled by two feedback control loops. The pressure of the VLE cell is measured by the Rosemount pressure transmitter, which sends a 4-20 mA signal to the controller which then manipulates the flow rate of the vapor out of the VLE cell through a control valve placed in the vapor line.

The liquid level inside the VLE cell is measured by the Delta-M LC2300 Level Sensor. The probe, after sensing the level, sends the signal to the LIC (level indicator and controller). The controller then sends a signal to the control valve through the current to the pneumatic transducer, for the manipulation of the flow rate in order to keep the level constant.

METHOD OF ANALYSIS

The analysis of the sample obtained from the Vapor-Liquid apparatus is carried out by the Liquid Chromatographic methods, as mentioned earlier in this report. The components of the samples being tested will be separate by distribution between two phases. One of these phases constitutes is a stationary bed of large surface area (Column) and the other is a fluid (Mobile phase), that percolates through or along the stationary bed. Different test methods for the analysis of Polynuclear Aromatics have been used in the past. A couple used in developing our method is given below:

Michael W. Dong (Perkin-Elmer notes) performed the analysis of the polynuclear aromatics (PAHs) by coupled column chromatography. The conditions were:

Instruments:	Perkin-Elmer Series 3B
Detector:	Perkin-Elmer Model LS-4 fluorescence detector in programmed wavelength mode
Column:	Perkin-Elmer HS-3 C-18
Mobile Phase :	60% Acetonitrile to 100% Acetonitrile in 5.0 minutes
Flow Rate:	3.0 mL/min
Pressure:	4300 psi
Ini. Vol.:	10 microliters

J.L. DiCesare, M.W. Dong, and L.S. Ettre (Chromatographia Vol. 14, May 5, 1981) used a different method:

Instrument:	UV Detector at 254 nm
Column:	125 x 4.6 mm i.d. C-18 bonded phase packing 5 micrometer particles packing
Mobile Phase:	Acetonitrile - Water Linear Grad. from 60-100% Acetonitrile in 5.0 minutes
Flow Rate:	4.0 mL/min
Pressure:	2200 psi

Using the above methods for guidelines, and with limited experimentation, we have designed a method for the LC analysis of tetralin-quinoline samples.

Instrument:	Perkin-Elmer LC410 pump

Detector:	Perkin-Elmer UV Spectrophotometric detector kept at 254 nm.
Column:	Perkin-Elmer 3 cm x 3 mm C-18 column
Mobile Phase:	65% Acetonitrile, 35% Water
Flow Rate:	1.8 mL/min
Sample Concentration:	One part sample to 2 parts solvent by volume
Sample Size:	6 microliters
Column Pressure:	1700 psi
Data Analysis:	Waters Maxima Software

With this method we were able to reproduce measurements on test samples to within 1% at all times.

Results and Discussion

To test the newly designed and built flow VLE apparatus, we chose the tetralin-quinoline binary system and decided to reproduce one of the isotherms (325°C) already available in the literature (V. G. Niesen and V. F. Yesavage, J. Chem. Eng. Data, 33, 253, 1988). Additionally we measured two new isotherms at 350°C and 370°C. The choice of this system was to provide data for extension of thermodynamic models for coal liquids to apply at higher temperatures and pressures.

The new measured data are listed in Table 1. Our data for isotherms 325°C, 350° and 350°C and the data of Niesen and Yesavage are plotted in Figures 9-13. Figure 9 is a p-x diagram for all the data. Additionally, each isotherm from 300°C to 370°C is plotted on y-x diagram in Figures 10-13. Comparison of our 325°C isotherm with that of Niesen and Yesavage generally shows good agreements. However, some discrepancies are observed especially with respect to vapor phase compositions for tetralin-rich mixtures. Furthermore, our vapor phase compositions show somewhat of a scatter also for 350°C and 370°C isotherms. Even so, the data could be easily smoothed out and used as a reliable data set.

As a result of this observation and upon further testing of the VLE apparatus we conclude that our data for pressures and liquid phase compositions are very accurate and easily reproducible. However the vapor mole fractions are accurate only to within ±10%. The main reason for this inaccuracy is seen as resulting from a very low flow rate of the vapor combined with a relatively large volume of separation between the VLE cell and the vapor sampling point. As an improvement for VLE measurements on other systems, the design is being improved by bringing the vapor sampling point much closer to the VLE cell and by replacing the currently used large heat exchanger with a simple double pipe heat exchanger. Tests are currently under way to determine whether this improves the reproducibility of the vapor phase composition data.

TABLE 1: VLE data Tetralin-Quinoline binary system

Temperature, ºC	Pressure, bar	X	Y
325	4.925	0.000	0.000
	5.690	0.059	0.116
	5.792	0.140	0.215
	6.136	0.242	0.352
	6.750	0.384	0.502
	7.230	0.520	0.590
	7.930	0.730	0.780
	8.579	1.000	1.000
350	6.774	0.000	0.000
	7.300	0.057	0.120
	7.600	0.140	0.255
	7.850	0.243	0.430
	8.410	0.400	0.535
	8.750	0.525	0.600
	9.250	0.700	0.770
	11.85	1.000	1.000
370	8.785	0.000	0.000
	9.000	0.057	0.990
	9.500	0.135	0.195
	10.25	0.245	0.400
	10.80	0.435	0.495
	11.30	0.530	0.592
	11.95	0.685	0.762
	15.46	1.000	1.000

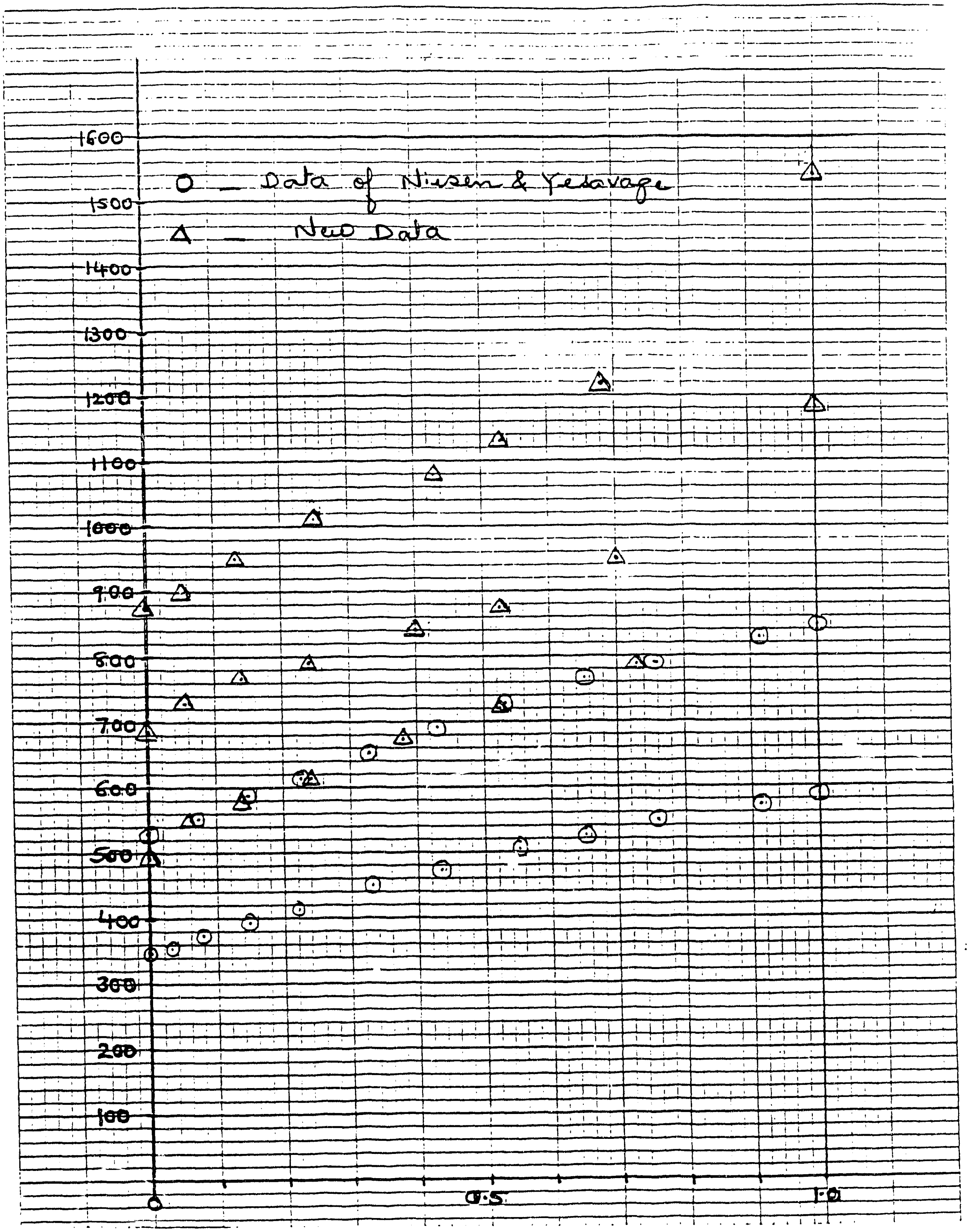


Figure 9: P-x Diagrams for 300, 325, 350 and 370°C isotherms

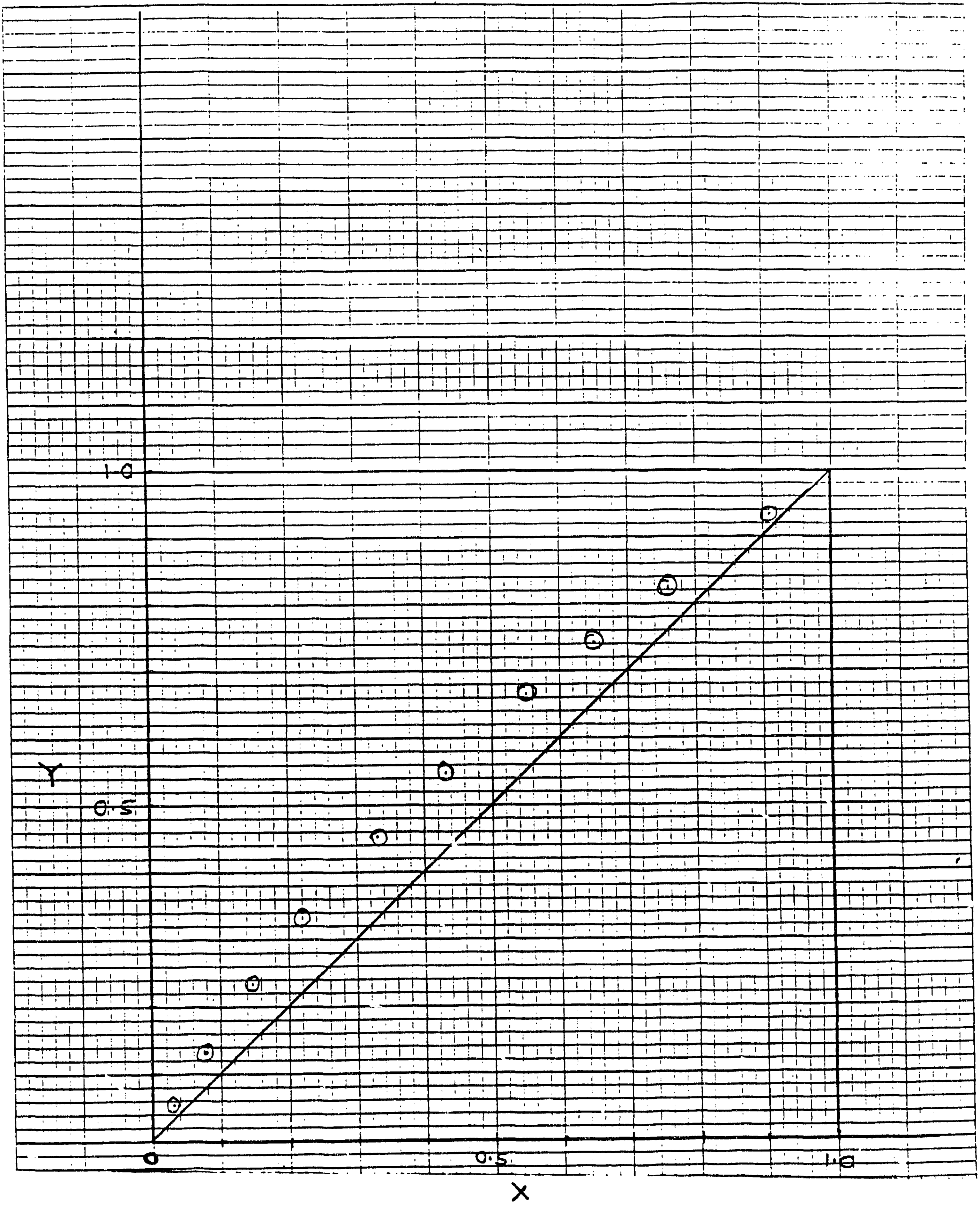


Figure 10: y-x Diagram for 300°C isotherm (data of Niesen and Yesavage)

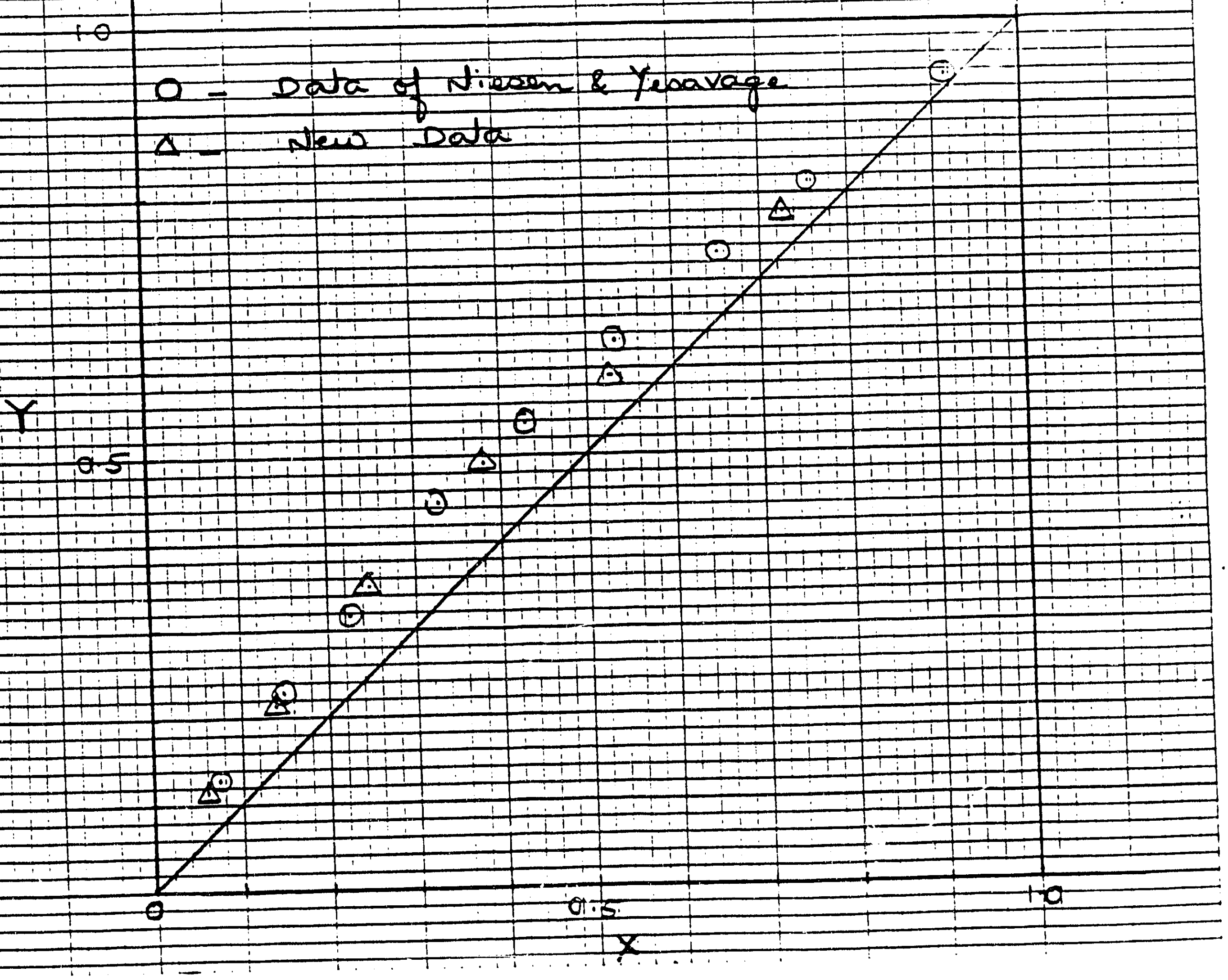


Figure 11: y-x Diagram for 325°C isotherm

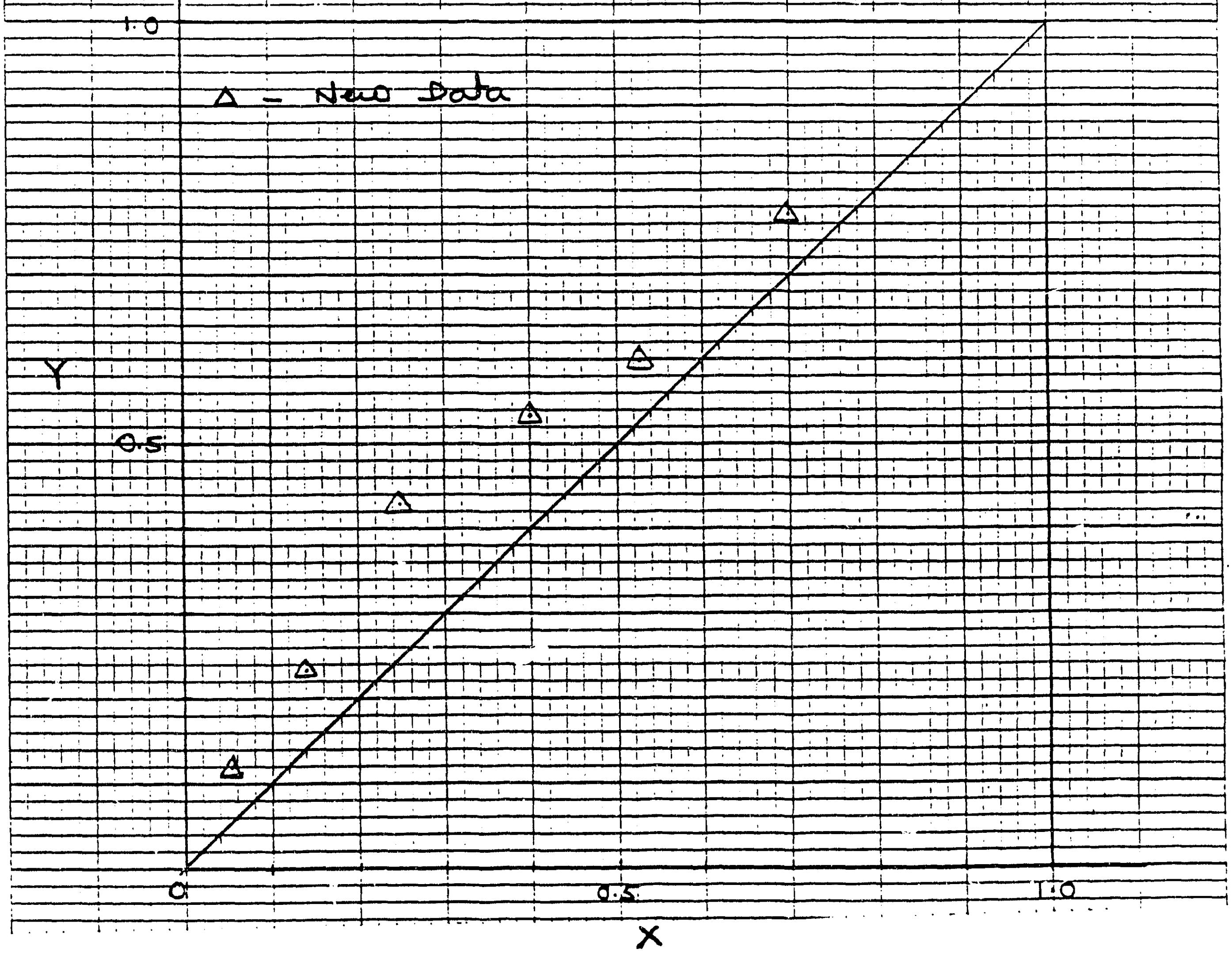
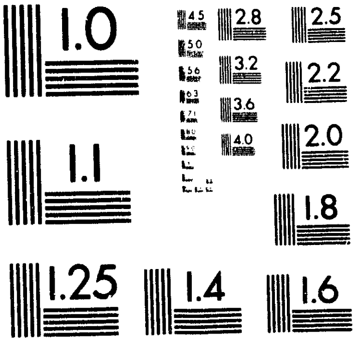


Figure 12: y-x Diagram for 350°C isotherm


1.0
4.5
5.0
5.6
6.3
7.1
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.1
1.8
1.25
1.4
1.6

2 of 2

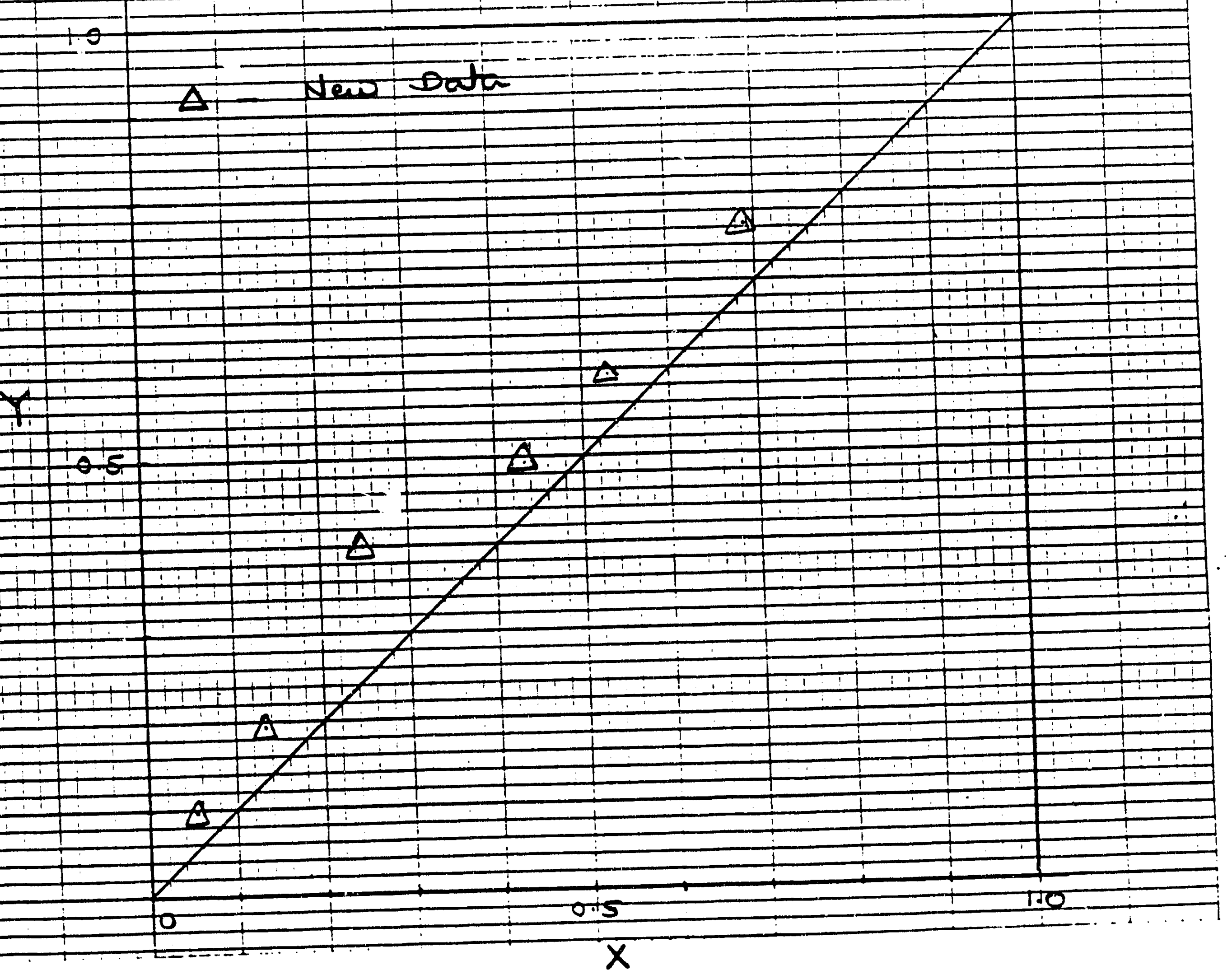


Figure 13: y-x Diagram for 370°C isotherm

APPENDIX #1: Specifications of Equipment in Flow VLE Apparatus

1- **Feed Tank:**
- Material of construction - SS-316
- Capacity - 1 Gallon
- Two threaded connection points of 1/4 inch diameter, used as: Stream inlet - at the top
  Stream outlet- at the bottom
- Capable of handling high pressure and high temperatures.

2- **Diaphragm Metering Pump:**
- Type: Positive Displacement Pump.
- Capacity: 2.4 Gallons per Minutes.
- Pressure Rating: 3000 psi.
- Diaphragm Material: SS-316.
- Adjustable stroke length.
- Driven by 1/2 HP electric motor.

3- **Pre-Heater Oven:**
- Type: Box Type, with recirculating fan and plenum system. It has hard-faced rigid fire clay insulating interior, rugged welded stainless-steel shell and quick acting latch on the hinged door with resilient seal.
- Material of construction: SS-316
- Maximum attainable temperature: 500 C
- Temperature controlled by a time proportionality controller with a dual scale meter and a mirror scale.

4- **Main Oven & Temperature Controller:**
- Type: Box Type, with recirculating fan and plenum system.
- It has stainless-steel lined interior with two step quick acting latch closure and resilient seal.
- Material of construction: SS-316
- Maximum attainable temperature: 800 C

Controller: Honeywell's UDC 5000 digital controller:
- Type: Programmable microprocessor single-zone control system.
- Dual output capacity which allows the controller to go above and below the ambient temperatures. The temperature range is -25 to +500 C.

5- Vapor-Liquid Equilibrium Cell:
- Designed by Chemical Engineering Department at A&T.
- Machined by SAC Die & Tool Shop, Inc.
  P.O.Box 5777, Greensboro, NC. 27403.
- Material of construction: SS-316
- Outer Diameter: 6 inches.
- Height: 6 inches.
- Wall Thickness: 1 inch.
- Inside Diameter: 4 inches.
- Inside Height: 3 inches.
- Volume capacity: 617 cc.
- It was made in two parts, the body and the cap that screws to the body, as shown in the fig. # 1. Four openings are provided on the cap of the cell. The three 1/4 inch openings are for the vapor outlet, Thermocouple and the third is connected to the pressure transmitter for the measurement of the pressure. The fourth large opening (1.25") on the cap of the cell was primarily provided for the insertion of the level measuring probe, Fig 5. But unfortunately the probe developed some error in it and was sent back to the manufacturers for the necessary repairs. The hole, therefore was closed by a flange of exactly the same size, as that of the level sensing probe. The details are shown in the figures 1 and 2.

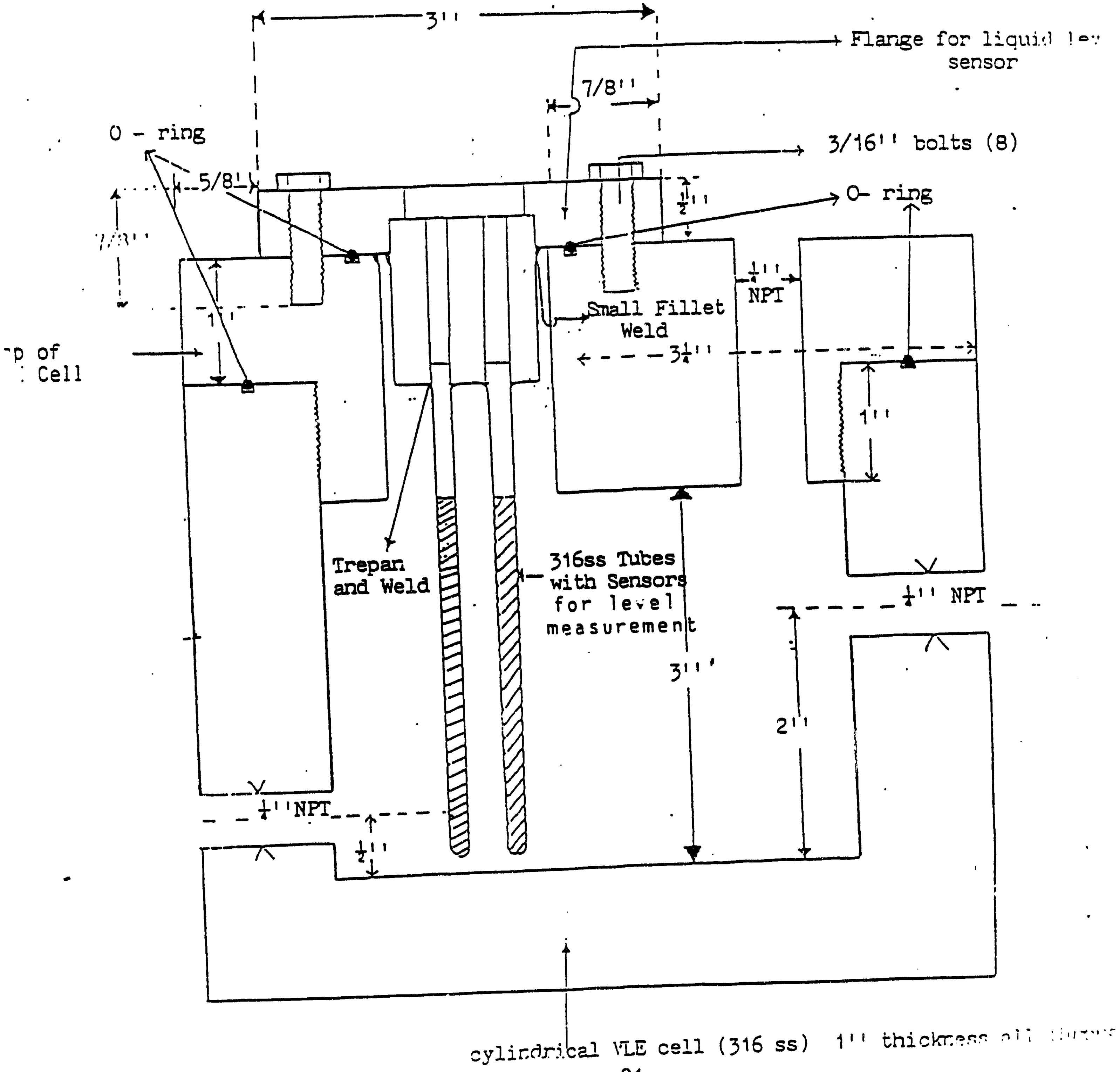
  Two 1/4 inch NPT openings are provided in the side of the cell wall, one for the feed inlet and other for the liquid outlet. The VLE cell is sealed by two metal O-ring. The rings are vented and made of Inconel X-750 material with silver coating, and are designed for the temperatures in excess to 600 C.

6- Metal O-Rings: (Two in number)
- Manufacturer: Advanced Products Company
- Diameter O-Ring # 1 = 1.625"
- Diameter O-Ring # 2 = 5.133"
- Ventilated O-Rings made for two temperature ranges, i.e.,
  - * for low temperatures stainless steel O-Ring coated with silver
  - * for high temperatures Inconel X-750 coated with silver

Fig.5

EQUILIBRIUM CELL FOR THE VLE APPARATUS

(With Conductivity Probe Setting Option)



7- Liquid level sensors:

Two level sensing devices are at option to be used:
1- Conductivity probe
2- Differential pressure transmitter level sensing device

CONDUCTIVITY PROBE LIQUID LEVEL SENSOR

-Manufacturer: Delta M. Corporation
Model LC 2300

- It consists of a probe designed for immersion in the liquid within the VLE cell, whose level is to be measured. An electronic package is in the probe head, which powers the probe and receives its output. This electronic package provides an output representing the fraction of the probe's length immersed in the liquid with 4-20 mA signal.
- The instrument is designed for temperatures up to 550 C and pressures up to 2000 psi.

DIFFERENTIAL PRESSURE LEVEL SENSING SYSTEM

- Manufacturer: Rosemount
Model: 1151 DP
- Material of construction:
  Isolating diaphragm = SS 316
  Drain vent valves = SS 316
  Process flange & adapter = Carbon steel (Cadmium/ Nickel coated)
- It takes pressure sensing from two points, i.e, one from the vapor line and second from the liquid line coming out of the VLE cell. It is equipped with δ-cell of variable capacitance sensing module. Differential capacitance between the sensing diaphragm and the capacitor plates is electronically converted to two wire, 4-20 mA or 10-50 mA dc signal

8- **Pressure Transmitter:**

- Manufacturer: Rosemount
Model: 1151 GP
-It has a variable capacitance sensing diaphragm, which gives an output of 4-20 mA signal to the process controller.

9- **Research Control Valves:** (2 in number)

- Type: Pneumatic pressure control valves.
- Signal Response: 4-20 mA.
- Material of construction:
  Body - Cast iron.
  Stem - SS 316.
- Pressure rating: 5000 psi.

10- Heat Exchangers: (2 in number)

- Manufacturer: ITT Corporation
  Model: 5-115-02-018-001
- Type: Shell and Tube Heat Exchanger
- Material of construction: Mild steel exterior and Stainless steel interior.
- With fixed tube sheet, non removable bundle
- With single pass only
- Shell side = Hot fluid
- Tube side = Cooling water

11- Electric to pneumatic Transducers: (2 in numbers)

- The transducers accept signal in the range of 4-20 mA and 1-5 volts and convert these signals to 3 to 15 psi pneumatic output

12- Process Controllers: (2 in numbers)

- These are powerful microprocess based controllers with digital display. Easily intractable through the push-button keys and displays to manipulate the process variables.
- It has a dual alarm system and pneumatic output via an integral current to a pneumatic transducer.
- Tow such transducers are used, one for the pressure and other for the level feed back control loop.

13- Three Pen Electronic Chart Recorder:

- This is an electronic strip chart recorder with fully isolated inputs. It is set up for two pens with the capability of four pen installation.
- Power requirements are 120 vac, 60 HZ.

14- Thermocouple Assembly consisting of:

Rotary Selector Switch
Digital Temperature Indicator
Thermocouple Rods

- Rotary Selector Switch:

  The three pole rotary selector switch is used for temperature measurements. The isothermal design minimizes temperature gradient between the input and output thermocouple wiring. Thirty channels in addition to OFF are available for the temperature measurement.

- Digital Temperature Indicator:

  It is a single range indicator with single input. It can accommodate 10 ranges of temperatures which are selectable with a row of push buttons below the display. This has a 0.1 degree resolution and can be switched to celsius or fahrenheit scales.

- Thermocouples: (9 in number)
  - J type Iron/Constantan thermocouples are used to measure temperature at different places, as mentioned in appendix 3.
  - Temperature sensing element length: 6 inch.

15- **Pressure Gauges:** (4 in number)

- Two of them are 6"dial, one with 0-200 psi (dub-division= 1 psi) and other is for 0-2000 psi (sub-division = 10 psi) for measuring low and high pressures respectively. They are connected to a same line through a direction-optional plug valve.
- The other two are 4.5" dial pressure gauges with range of 0 to 3000 psi (sub-division =20 psi). They are placed up and down stream of the pump.

16- **Sample Tanks:** (3 in numbers)

- Material of construction: SS-316
- Volume capacity: 300 cc.
- Three of these are used as sample bottles, for the collection of vapor, liquid and feed samples.

17- **Tubing and Valve fittings:**

- 1/4" and 3/8" SS-316 tubing with 0.035 wall thickness.
- Swagelok compression fittings for the 1/4" and 3/8" tubing, in the form of elbows, tees, unions, plugs, male and female connectors, reducer unions, Nupro plug valves, micro-metering valves, line filters and safety valve.

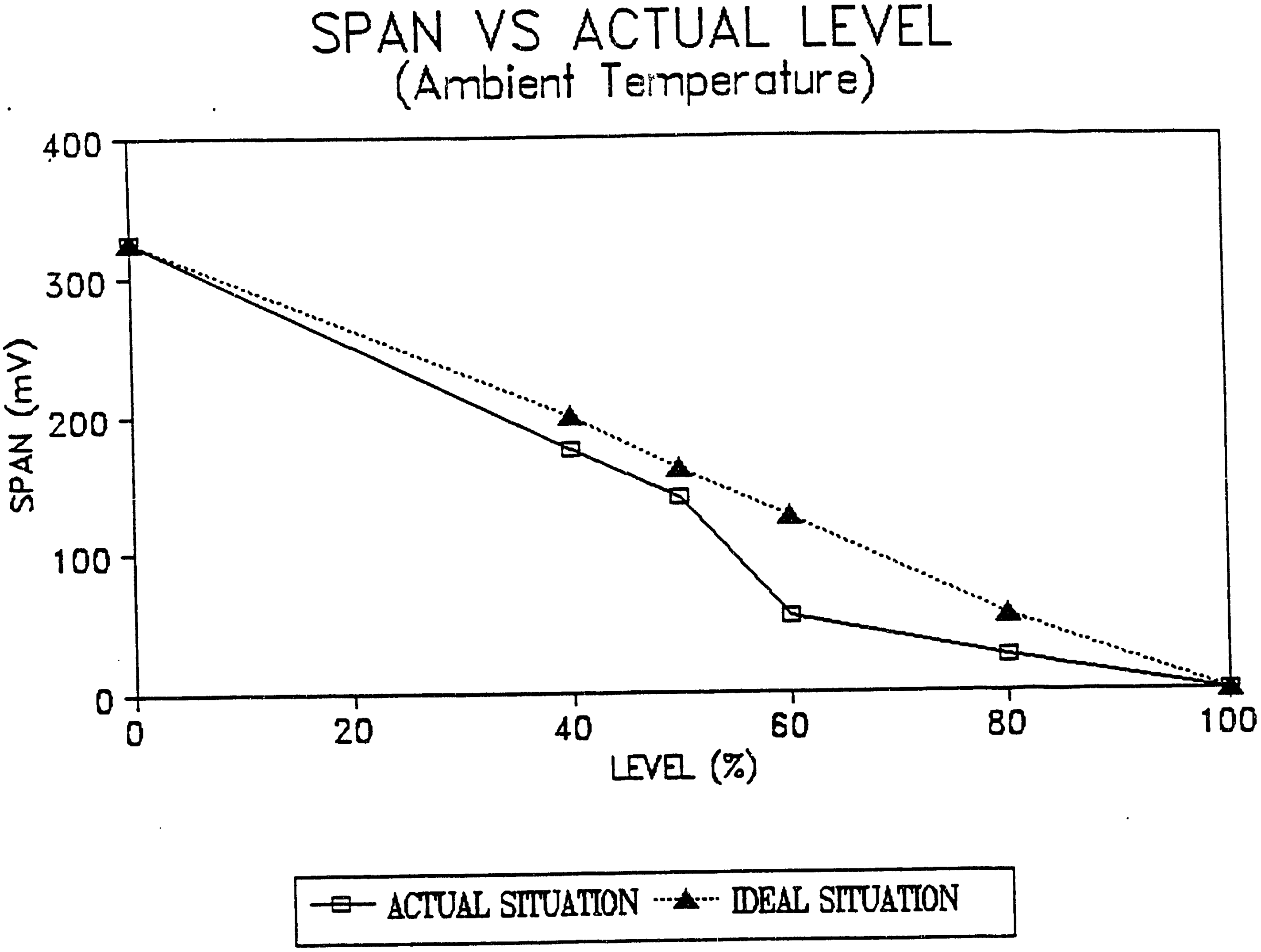
18- **Unistrut Frame & Wood Paneling:**

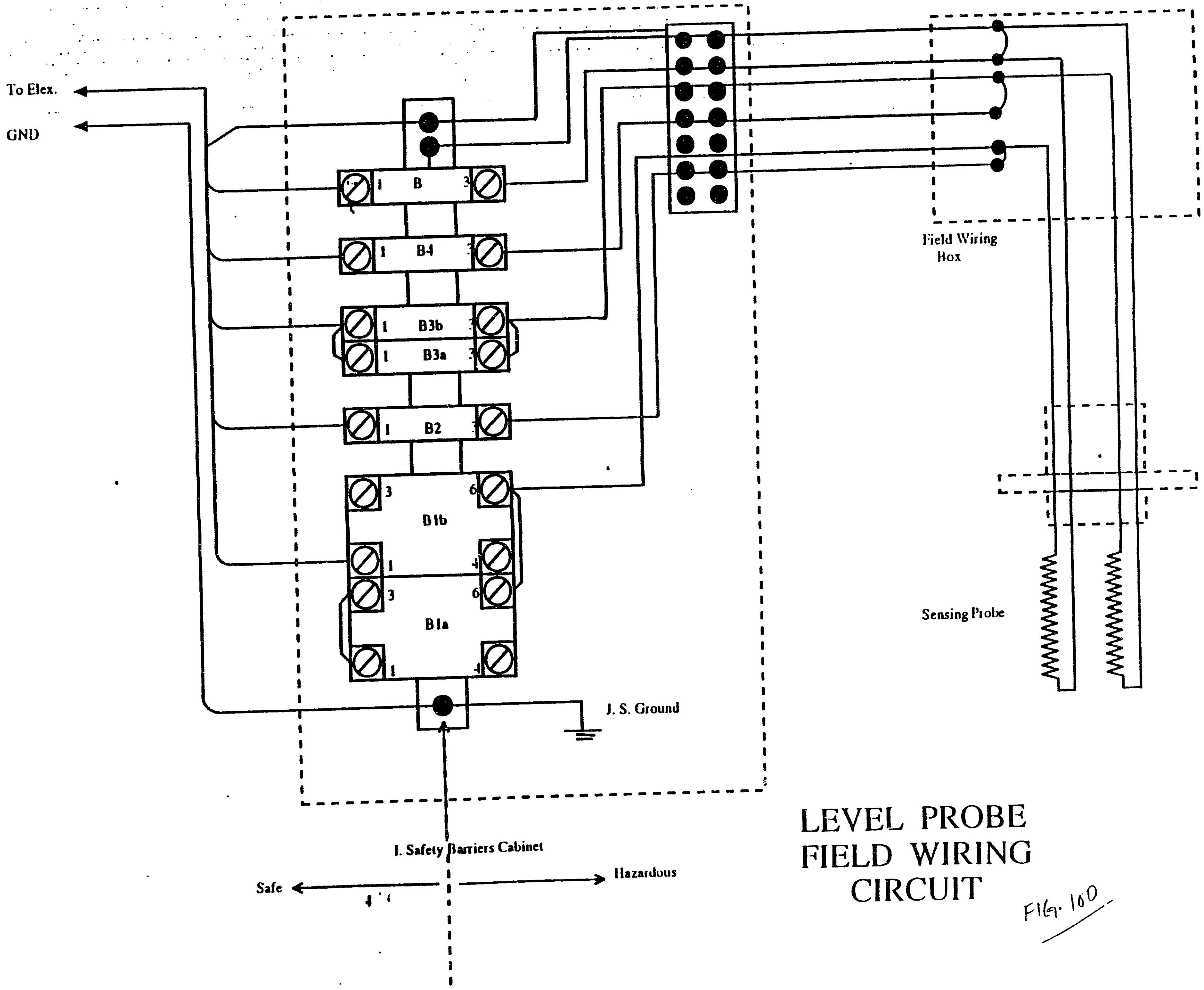
- Unistrut channels and fittings were used to build the frame for the apparatus.
- Wooden panels were fixed to the unistrut frame for the mounting of the displays, pressure gauges, controllers and the three pen recorder. Wooden boards are also provided to support the ovens and their controllers and the pump.

APPENDIX #2: Location of Thermocouples in VLE Apparatus

Thermocouple No.	Location.
1	At Liquid Sample line
2	At Pressure Transmitter line
3	Before Pre-Heater
4	At Pressure Transmitter
5	At Feed line
6	At Vapor Sample line
7	After the Pre-Heater
8	At Vapor line (after oven exit and before the control valve)
9	At Liquid line (just after the main oven)

APPENDIX #3: Electronics and Calibration of Conductivity Level Sensor


SPAN VS ACTUAL LEVEL
(Ambient Temperature)
SPAN (mV)
400
300
200
100
0
0
20
40
60
80
100
LEVEL (%)
ACTUAL SITUATION
IDEAL SITUATION



LEVEL PROBE FIELD WIRING CIRCUIT

FIG. 10D

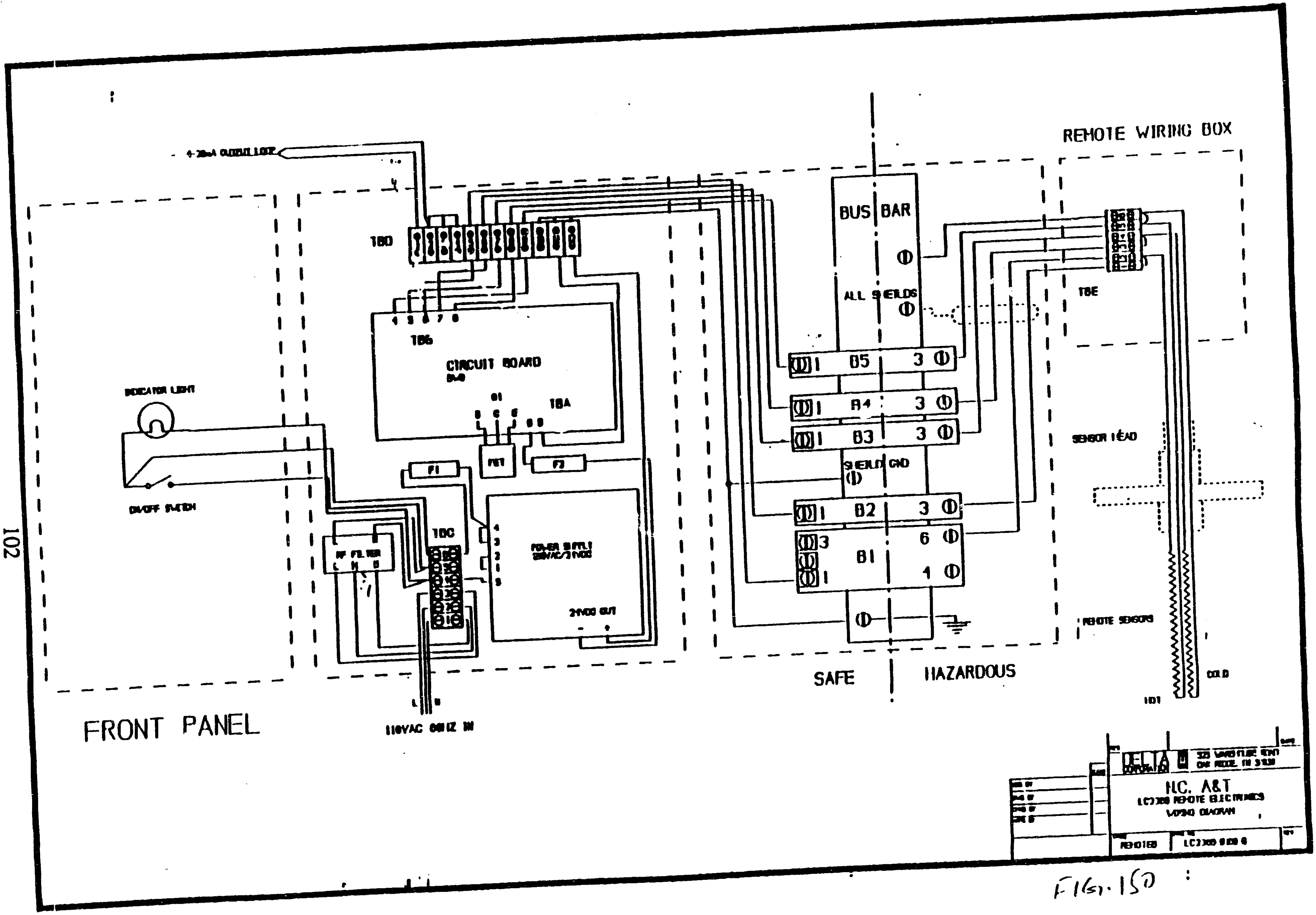

REMOTE WIRING BOX
4-20mA OUTPUT LOOP
TBD
TBE
TB6
CIRCUIT BOARD
TBA
FET
F1
F2
TBC
POWER SUPPLY
24VDC OUT
RF FILTER
INDICATOR LIGHT
ON/OFF SWITCH
110VAC 60HZ IN
FRONT PANEL
BUS BAR
ALL SHIELDS
B5
B4
B3
SHIELD GND
B2
B1
SENSOR HEAD
REMOTE SENSORS
COLD
HOT
SAFE
HAZARDOUS
DELTA CORPORATION
N.C. A&T
LC2000 REMOTE ELECTRONICS
WIRING DIAGRAM

FIG. 15a

DELTA m
RPORATION
5 WAREHOUSE ROAD
OAK RIDGE, TENNESSEE 37830

CALIBRATION DATA SHEET

LEVEL PROBE AND TRANSMITTER

CUSTOMER NC A&T
P.O. NO. NO24484
DM REF. 87LP2057
ITEMS 1
MODEL LC-2300
SERIAL 2057-1

DESCRIPTION REMOTE 2300, 24V, INTRENSIC SAFETY

CALIBRATED FOR: AIR/TIN

TEMPERATURE: 500 deg. C
PRESSURE AMB

OUTPUT AT EMPTY = 4 MA.

OUTPUT AT full 20 MA
HEIGHT = 3 in.

DATE: 4/14/89
BY: BCR

RAH - 39.5K
RAC - 4.22K
RBH - 4.22K
RBC - 39.5K
R17 - 1.33K

57Ω Load w/o Barriers

DELTA m
CORPORATION

CALIBRATION DATA SHEET
LEVEL PROBE AND TRANSMITTER

DELTA M REFERENCE NO.: RANLC1035

CUSTOMER: N.C. A&T

P.O. NUMBER: VERBAL

SERIAL #: LC2057-1

MODEL #: LC2300

DESCRIPTION: LC2000 PROBE WITH REMOTE ELECTRONICS AND INTRINSIC SAFETY .

CALIBRATED FOR: AIR/WATER

TEMPERATURE:

PRESSURE: AMBIENT

OUTPUT AT EMPTY: 4 mA

OUTPUT AT FULL: 20 mA

HEIGHT: 3" ACTIVE

TECHNICIAN: R. MONROE

DATE: 2/28/91

V SET = .64 V
FULL GAIN RESISTOR = 3.9K Ω
EMPTY GAIN RESISTOR = 8.140K Ω

APPENDIX #4: Operating Procedures for Flow VLE Apparatus

PRE-START UP CHECKS

Before the initial start-up of this pilot plant the following precautionary measures must be taken, in order to get the plant running safe and smoothly.

1. Before the initial or any start-up of the plant, make sure that the utilities, like cooling water, air and electricity are available.
2. Check all the instrumentation for their proper working order, i.e.,
    a) Check the opening and closing of the PCV-01 (Pressure Control Valve on the vapor line) for the 0,25,50,75 & 100% open positions and tele them with the readings on the panel board. Remove the errors, if there are any.

    b) Repeat the same procedure for the other control valve (LCV-02), liquid control valve, on the liquid line to the heat exchanger.

    c) Check the setting of the pressure relief valve (PSV-01), at the discharge of the positive displacement pump.

    d) The recorder should be in a proper working order. It should have respective colors of inks for respective parameters to be recorded on the chart, i.e., red for level and blue for the pressure.

    e) Check if the pre-heater and the oven are working properly for the proper set points of the temperatures given by their controllers respectively.
3. Check the oil level in the pump.

4. Make sure that all the drains, vents and sample point valves are closed.
5. Perform the pressure check of the entire system with nitrogen gas and make sure that there are no leaks in the system (fittings and connections).
6. Purge the whole system with nitrogen gas.
7. Wash the system with acetone, if necessary, and drain it in a closed container from the liquid sample points and the lowest drain point. After draining, purge the system again with nitrogen gas into the fumes hood for five minutes and then purge each and every drain point, vent and sample points for at least 30 seconds.
8. Open the cooling water and see that there are no leaks at the heat exchanger connections (tube-side) and the water is properly drained into the sewer line.
9. Make sure that there is no flammable material, cloth, paper, plastic-tape or instrumentation or electrical wires exposed to the process piping.

START-UP PROCEDURE

After completing all the steps indicating in the pre-start-up procedure, proceed as follows:

1. Close all the drain, sample points and the vent valves except the vent valve # 17, which should be partially open.
2. Purge the system with nitrogen or any other inert gas. Every drain and vent valve should be open once or twice for at least thirty seconds, so that all the oxygen present in the system is purged out.
3. Isolate the nitrogen purging by closing the two valves, i.e., the nitrogen cylinder valve and the valve at point 'b', as shown in the flow diagram.
4. Also close the valves labeled on the flow diagram as a,b,c and d, isolating the feed tank from the rest of the system.
5. Leave the highest vent valve # 17 cracked open and valve 'e' full open.
6. Open the feed inlet valve 'f' and fill the system with the test run liquid-mixtures until it comes to desired level seen in the flexible transparent tube, i.e., 70-80% level of the feed tank.
7. Close the valve at 'e' and 'f'.
8. Pressurize the nitrogen purging line again and sightly crack open the valve 'b' keeping the valve # 17 in partial open position.
9. Let the system loop purge for at least five minutes at very slow rate, so that the liquid may not go into the vent line and hence in the fume hood

sewer.

10. Close the two valves, i.e., 'b' and # 17 simultaneously.

11. Open, on manual, the LCV-19 and PCV-20, 100% and 0% respectively.

12. Check the lubricating oil in the gear box of the pump. The oil should be up to the level marked on the dip stick of the pump.

13. Prime the pumphead of the metering pump, following the step mentioned below:

    - Start the pump.
    - Adjust the stroke length to the maximum, i.e., 400.
    - Disconnect the power source to the drive motor.
    - Remove the front reservoir cover assembly.
    - Manually rotate the motor coupling until the pump piston is withdrawn to full suction stroke towards the drive motor end.
    - Unscrew the tube fitting nut at the top of the automatic bleed valve and remove the plastic tube.
    - Remove the bleed valve body from the pumphead.
    - Fill the pumphead with the Pulsa Lube oil, through the automatic bleed valve opening.
    - Rotate the pump coupling manually to move the pump piston forward. Also watch for the oil to appear in the bleed valve port. When it does, reinstall the automatic bleed valve assembly into the pumphead.
    - Keep on rotating the coupling by hand until the piston reaches the

maximum stroke. During this procedure, if at any point the coupling becomes hard to rotate by hand, press the hydraulic make up valve and keep it pressed until the coupling has been rotated completely to the maximum stroke length. The difficulty in rotating the coupling is an indication of the pump getting over-primed and pressing of the hydraulic bleed valve releases the excess oil back to the gear box.

Now the pump is primed hydraulically and ready to operate. The reagent head gets primed automatically once the feed tank discharge valve is opened. The positive displacement pumps prime automatically after they are switched on.

14. Switch on the pump. Adjust the stroke of the pump at minimum by keeping the hand wheel for the stroke adjustment, at the minimum setting. Once the pump has been started the strokes should be gradually increased to about 300 stroke length or the desired stroke length. 400 is the maximum strokes equivalent to 2.6 gallons per hour.
15. Switch on the level sensing probe's electronics box.
16. Switch on the pre-heater and adjust the temperature set point to the desired value on manual control. (50°C above the VLE temperature).

17. Commission the cooling water to the heat exchangers. Make sure that the sewer is clean and the water is drained fluently in order to avoid overflow or spillage of hot/spent water.

18. Switch on the main oven and gradually increase the temperature on the manual control.

19. When the temperature reaches the required set point, put the controller of oven on auto mode.

SHUT-DOWN PROCEDURE

1. Put the system on manual control.
2. Open the control valves slowly to the maximum allowing the main flow of liquid through the system.
3. Slowly decrease the temperature of the main oven, and pre-heater, approximately 5-7°C per minute.
4. When temperature reaches 6°C, open the door of pre-heater and switch off the pre-heater, after 5-10 minutes of operation.
5. When the temperature of the main heater, shown on the thermocouple display, comes to around 80°C, turn off the main oven from the main panel. Open its door for at least 10 minutes before turning the oven off.
6. Keep the system on circulation, till the temperature of the system comes down to the room temperature.
7. Close the cooling water valve to the heat exchangers.
8. If the system is to be run on the same test liquid, then stop the pump, and disconnect all the electrical connections, and also cut the air supply to all the pneumatic controlled systems.
9. If the system is to be prepared for the new test run liquid then:
    - Take a closed container and drain all the liquid within the system into it, from the lowest possible drain point, i.e., from point NUMBER 16.
    - Shut-off the pump immediately after this step.
    - Drain all the individual sample points.

- Keep the system as it is for some time, so that the liquid settles down due to gravity, and then again drain all the lowest points for the possible accumulation of the liquid. Applying some inert pressure will help the drainage of the same.
- Once the system is expected to be drained fully, it should be flushed with acetone, twice or thrice with fresh acetone or until no traces of the system liquids be there.

PART III

A CHARACTERIZATION PROCEDURE FOR COAL DERIVED LIQUIDS

INTRODUCTION

To develop a predictive model for any property of a complex mixture such as coal derived liquids, a procedure to characterize the mixture is necessary. For our thermodynamic model discussed in Part I, we defined coal derived liquids as mixtures of hydrocarbons, pyridines, phenols, and thiophenes, with each molecular type defined by a molecular weight distribution and an average representative molecule. Because of lack of data, molecular weight distributions were defined as beta distribution functions with assumed parameters. The average molecules were defined by functional groups according to the characterization procedure of Allen, White, and coworkers (White et al, Fuel, 67, 119, 1988) who have developed an extensive experimental and computational procedure to determine the detailed functional group composition of a narrow boiling coal derived liquid. For wider boiling coal liquids, a characterization procedure to determine the true molecular weight distributions and distributions of the heteroatoms is very much needed. This is the objective of the current work.

Our initial strategy was to use size exclusion chromatography and separate the coal derived liquid by molecular weights thus obtaining the true molecular weight distribution and to further characterize materials of various molecular weights by functional groups using the procedure of Allen, White, and coworkers. Although, in principle we did not change our strategy, the final characterization procedure is somewhat more complicated because size exclusion chromatography does not work well with coal liquids. The column has different interactions with different molecular types and is not able to separate all materials strictly according to molecular weights. In what follows we discuss the experimental techniques, give a history of our efforts, and finally formulate our characterization procedure.

SIZE EXCLUSION CHROMATOGRAPHY/GEL PERMEATION CHROMATOGRAPHY (OR SEC/GPC)

In size exclusion chromatography, the components of a sample are separated according to the size of their molecules. The packing used in this technique is gel with an inert porous surface. The GPC/size exclusion column packing behaves, in some ways like a sieve. The molecules of sample components can only enter those pores of packing where the diameter is larger than that of the molecules. Thus the smallest molecules spend the longest time in the particles since they can enter all the pores while the molecules having a cross-section larger than the diameter of the largest pores will pass without entering any pore. Thus the larger molecules will pass quickly through the column, while the small molecules emerge later because they also have to diffuse in and out of the pores.

As a result of this process, the chromatograph obtained shows the larger molecules forming the early part of the peaks and the smallest molecules, the later part of the peaks. Since the size of the molecule is related to its molecular weight, the elution time or volume of a given peak can give a fairly good approximation of the component's molecular weight. The shape of the molecules and the functional groups on the molecule are two of the many important factors in the elution time of a particular compound.

SEC/GPC is an excellent tool for molecular weight distribution determination of a homologous series of molecules, like polymers. The molecules are simply collections of similar atoms of the same compound. They just add together to form bigger chains that have higher molecular weights.

EQUIPMENT

The chromatographic equipment used includes Perkin-Elmer LC 410 pump, PL-GEL 5 micron GPC column, and Varex ELSD-II light scattering detector. We used the Varex evaporative light scattering detector (ELSD) because the response time of this detector is mostly sensitive to the mass of the sample and not to molecular types. It has been shown before that the ELSD detector is more suitable than the UV detector for SEC/GPC work (Coulombe, J. Chrom. Science, 26, 1, 1988).

In this detector the eluent is nebulized at the entrance of a heated funnel, thus leaving solute particles in the gas stream. A light source is directed at a right angle to this stream, and a portion of the light scattered by the nongaseous particles is detected and measured by a photomultimeter. This photomultimeter measures a signal proportional to the concentration of the particles, or in other words, the response of this detector "ELSD" is a function of the mass of solute passing through the detector.

The proper settings of temperatures and gas flow rate are extremely important, especially for long term analysis and repetitive work. For the gas flow rate, a scale in millimeters on the rotameter is better to use for the setup than a pressure setting in psi. However, both gas pressure and flow rate were noted in order to check for any malfunction. Any discrepancy between the two is an indication of some blockage; a blocked gas line to the nebulizer can cause very high pressure but low flow.

The precise temperature adjustment of ELSD-II is extremely important in order to get the correct detector response. As it is evident by the name of the detector, the mobile phase is evaporated before the eluent stream. Very fine solute droplets come in contact with the the detector light. Different solvents evaporate at different temperatures. The temperature needs to be higher than the solvent boiling point.

EXPERIMENTAL PROCEDURE AND RESULTS

The objective of this project is the characterization and analysis of different coal derived liquids by molecular weight distribution and quantitative determination of different elements and constituents of these liquids, namely nitrogen, sulfur, and oxygen heteroatoms, which is proposed to be done by FTIR and elemental analysis of the different molecular weight fractions of the coal liquids separated and obtained using the fraction collector.

Four coal derived liquids were used in this study. These were obtained form the Consolidated Coal Company and are listed below.

1. Wilsonville SRC-1
2. Lummus ITSL LC-Finer Product distillate
3. H-Coal pilot plant Run #8
4. H-Coal pilot plant Run #10

The SEC/GPC method had to be initially calibrated using standards. Various hydrocarbons, pyridines, and phenols were used as standards. In what follows we present the work on standards followed by the analysis of coal liquids and finally present the detailed characterization procedure.

STANDARDS CALIBRATION

In the early stages of this project six compounds were used as narrow standards. They are listed below in order of decreasing molecular weights.

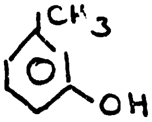
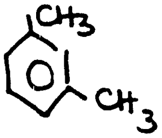
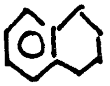
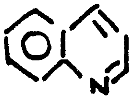
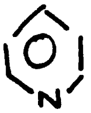
Name	Molecular Weight
Tetralin	132
Quinoline	129
Cresol	108
Xylene	106
Pyridine	79
Benzene	78

After running the trial sample, of minimum concentration, to set up the chromatograph baseline and peak integration parameters in Waters GPC/SEC Maxima software, the above mentioned samples were injected and run in the very same order one by one in the amount of 100 microliters each.

The mobile phase was 100% THF at a flow rate of 1 mL/min, and for all the standards a concentration of 0.5 weight/volume percent was used, i.e. 0.5 grams of standard was dissolved in 100 milliliters of THF. The Varex detector was used. The chromatograms obtained showed that these compounds did not elute in the order of their molecular weights. The elution order of the standards is given in Table 1. No systematic trends with molecular weight are observed.

Table 1

Elution order of low molecular weight standards

Compound	Retention Time (min)	Molecular Weight	Structural Formula
1. Cresol	9.52	108	
2. Xylene	10.39	106	
3. Benzene	10.61	78	
4. Tetralin	10.65	132	
5. Quinoline	10.82	129	
6. Pyridine	11.05	79	

Based on these results it was concluded that the column being used, i.e PL-GEL (Polystyrene Divinyl Benzene) is not able to analyze these materials by the conventional GPC/SEC principle.

As a result, it was decided to divide the standards into different homologous series, namely, aromatic hydrocarbons, phenols, and pyridines. This choice of series was dictated by the most abundant and significant functionalities in the coal derived liquids to be analyzed. A more detailed characterization procedure, in fact, should include homologous series of compounds containing other functionalities such as thiophenes, furans, amines, indoles, carbazoles, etc. as well. The standards divided into homologous series are listed in Table 2.

Table 2
Homologous series of GPC/SEC standards

Compound	Molecular Weight	Formula
1. Hydrocarbons		
Napthalene	128.17	$C_{10}H_8$
Phenanthrene	178.23	$C_{14}H_{10}$
1,2-Bezanthracene	228.00	$C_{18}H_{12}$
2. Phenols		
m-Cresol	108.14	C_7H_8O
1-Napthol	144.17	$C_{10}H_8O$
9-Phenanthrol	194.23	$C_{14}H_{10}O$
4,5-Dihydroxy Phenanthrene	210.00	$C_{14}H_{10}O_2$
Anthrasobin	226.23	$C_{14}H_9O_3$
3. Pyridines		
Quinoline	129.16	C_9H_7N
Acridine	179.00	$C_{13}H_5N$
1,10-Phenanthroline	180.21	$C_{12}H_8N_2$

It was important to use the same method for standards calibration and for coal liquid analysis. After a number of trials involving various studies, following are the details of the method utilized:

Solvent:	Tetrahydrofuran (THF) 100%
Flow rate:	3 mL/min
Pressure:	1860 psi
Detector:	Varex ELSD-II (Evaporative Light Scattering Detector)
Exhaust temp:	61.2 °C
Heater temp:	97.3 °C
Adjust temp:	99.6 °C
Gas:	nitrogen
Gas flow rate:	55 min/15 psi
Column:	PL-GEL
Size:	5 microns
Length:	300 mm
Diameter:	7.5 mm
Packing:	Polystyrene Divinyl Benzene
Nominal pore size:	100 Angstrom
Sample:	Standards and coal liquids
Sample volume:	100 microliters

GPC/SEC analysis was performed on a two column train of a guard column and the PL-GEL GPC column. HPLC grade THF (100%) was continuously pumped through the Perkin-Elmer LC 410 pump at a rate of 3 mL/min. All the data analysis was performed using Waters Maxima Chromatographic software.

Each standard was run at 4-5 different concentrations in THF. This was done to determine the variation of the peak response of the material as a function of its concentration. For liquid standards, mixtures were prepared by adding known volumes of the solute and the solvent; whereas for solids a known mass of the standard was dissolved in a known volume of THF. In all cases the concentrations were converted to mole fractions or mole percents and all the results presented are in these units.

Different concentrations of the standards and the elution times are given in Table 3. The average elution times for the standards are plotted as functions of molecular weight in Figure 1. It is easily observed that the elution times for phenols are significantly lower than those for hydrocarbons and pyridines for equivalent molecular weight. The elution times for hydrocarbons and pyridines are very close, with pyridines showing slightly higher elution times. Figure 1 indicates that a linear relation between elution time and molecular weights may be assumed for each homologous series of standards. The only compound that showed drastic deviation from this behavior is 1,10-phenanthroline which contains two pyridine groups. Such compounds need to be further studied. The equations corresponding to the three straight lines of Figure 1 are

Hydrocarbons

$$t = -0.0021W + 3.92 \qquad (1)$$

Pyridines

$$t = -0.0032W + 4.11 \qquad (2)$$

Phenols

$$t = -0.00206W + 3.59 \qquad (3)$$

Where t is the elution time in minutes and W is the molecular weight.

Peak response gives a measure of the area under the peak and is a function of concentration of the standard in the injected sample. In ideal chromatographic analysis peak response should vary linearly with standard concentration; however, in real life liquid chromatography, nonlinear relations are very commonly encountered. The Maxima software was used to obtain cubic relationships between concentration (C) in mole percent and peak response (R) in millivolts-sec of the form

$$C = aR + bR^2 + cR^3 \qquad (4)$$

Table 4 gives the concentration ranges and the coefficients a, b, and c for all the standards. For the characterization procedure described later, the inverted form of equation 4 is more useful. The following form of equation was found to give a good fit:

$$\log(R) = a_1 + a_2C + a_3C^2 + a_4C^3 \qquad (5)$$

Table 3: Elution times for standards at various concentrations in THF

	Molecular weight	Concentration mole fraction		Retention time (min)
Hydrocarbons				
Naphthalene	128.17	.2006		3.72
		.1569		3.69
		.1121		3.68
		.0594		3.63
		.0306		3.55
			Average:	3.65
Phenanthrene	178.23	.043		3.56
		.022		3.51
		.011		3.50
		.005		3.51
		.0028		3.53
		.0014		3.53
			Average:	3.52
1,2Benzanthracene	228	.0105		3.45
		.0071		3.43
		.0053		3.43
		.0026		3.44
		.0013		3.47
			Average:	3.44
Pyridines				
Quinoline	129.16	1.00		3.75
		0.6143		3.67
		0.4036		3.63
		0.2269		3.70
		0.1462		3.71
		0.0707		3.74
		0.0068		3.64
			Average:	3.69
Acridine	179	.0432		3.57
		.0220		3.53

	Molecular weight	Concentration mole fraction		Retention time (min)
		.0124		3.51
		.0111		3.53
		.0028		3.53
			Average:	3.53
1,10-Phenanthroline	180.21	0.0236		4.02
		0.0115		4.11
		0.0058		4.20
		0.0073		4.29
		0.0005		4.42
			Average:	4.20
Phenols				
m-Cresol	108.14	1.00		3.48
		0.6990		3.40
		0.4363		3.38
		0.2051		3.28
		0.0792		3.41
		0.0391		3.34
		0.0077		3.28
			Average:	3.367
1-Naphthol	144.17	0.1836		3.29
		0.1010		3.39
		0.0532		3.38
		0.0272		3.26
		0.0139		3.21
		0.0069		3.23
			Average:	3.29
9-Phenanthrol	194.23	0.0303		3.22
		0.0153		3.18
		0.0077		3.20
		0.0039		3.19
		0.0019		3.18
		0.0123		3.18
			Average:	3.19

	Molecular weight	Concentration mole fraction		Retention time (min)
4,5-Dihydroxy-phenanthrene	210	0.0215		3.22
		0.118		3.18
		0.0076		3.19
		0.0018		3.20
			Average:	3.19
Anthrarobin	226.23	.0088		3.04
		.0044		3.03
		.0022		3.02
			Average:	3.03

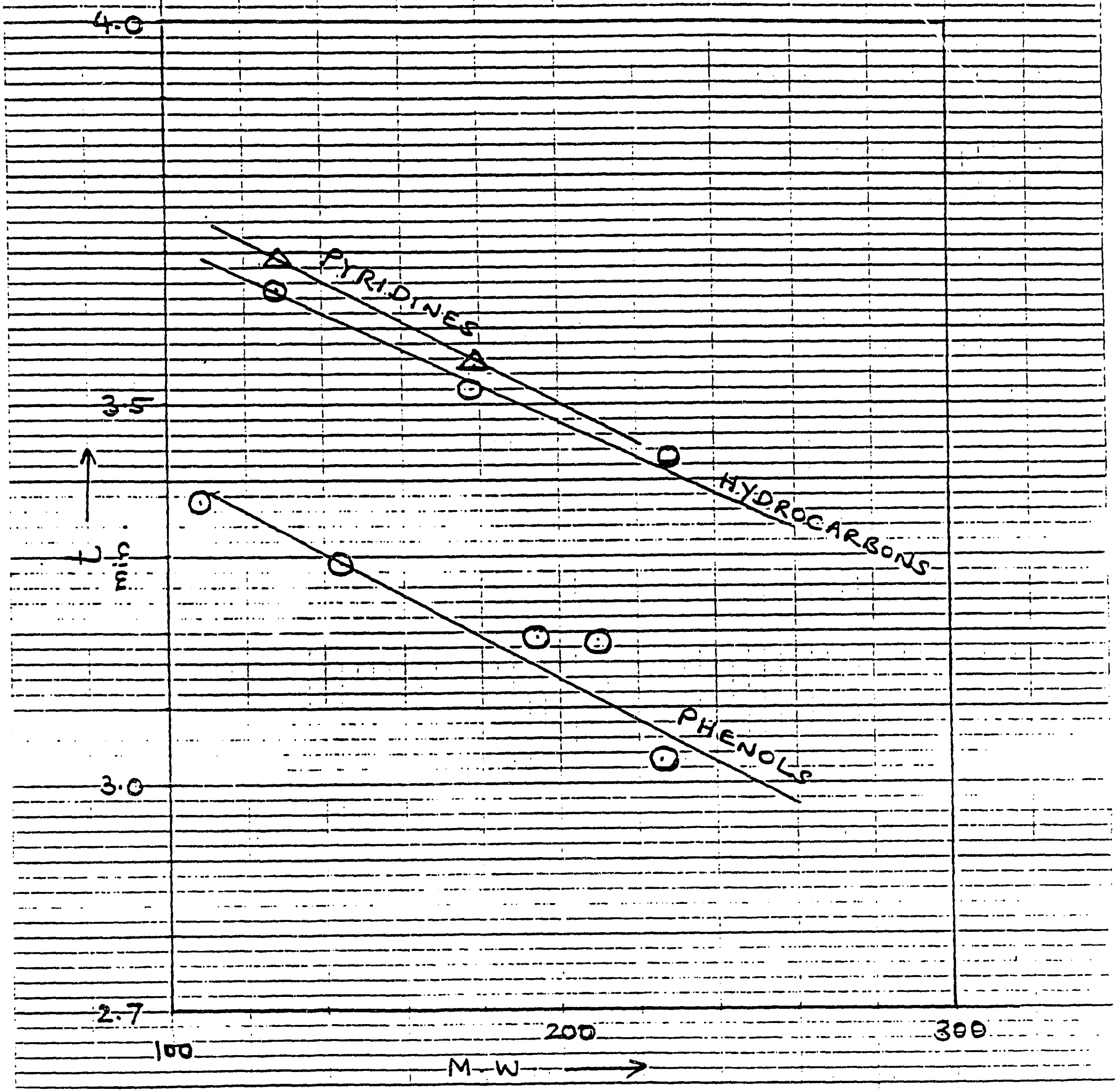


FIGURE 1: ELUTION TIMES VERSUS MOLECULAR WEIGHT

TABLE 4: Coefficients for polynomial fit of concentration versus peak response for the standards

COMPOUND	CONCN. RANGE mole %	a x 10^{7}	b x 10^{14}	c x 10^{22}
Napthalene	3 - 20	4.62 x 10^{3}	-4.32 x 10^{5}	1.071 x 10^{8}
Phenanthrene	0.14 - 4.3	3.2	-1.72	4.61
1,2 - Benzanthracene	0.13 - 1.05	4.64 x 10^{-1}	-8.1 x 10^{-2}	1.01 x 10^{-1}
Quinoline	0.68 - 10	0.11 x 10^{5}	-0.671 x 10^{6}	0.639 x 10^{8}
Acridine	0.28 - 4.32	2.75	-1.1801	2.0552
m - Cresol	0.77 - 10	0.568 x 10^{4}	-0.968 x 10^{6}	0.272 x 10^{5}
1 - Napthol	0.69 - 18.36	3.983	-9.207 x 10^{1}	1.2504
9 - Phenanthrol	0.19 - 3.03	5.455 x 10^{-1}	-7.612 x 10^{-2}	1.589 x 10^{-1}
4,5 - Dihydroxy Phenanthrene	0.18 - 2.15	2.122 x 10^{-1}	1.021 x 10^{-1}	-1.1511 x 10^{-1}
Anthrarobin	0.22 - 0.88	2.200 x 10^{-1}	-3.449 x 10^{-2}	1.308 x 10^{-1}

Furthermore, it was important to have constant coefficients or coefficients functions of molecular weights for the standards within each homologous series. Using equation 4 and coefficients from Table 4, values of logR and C were tabulated and plotted in the concentration range of about 0-10 mole percent. For all the standards the curves were very similar in shape and ran parallel with shifts along the ordinate. This prompted us to keep a_2, a_3, and a_4 constants for all standards and regress a_1 for each standard. a_1 values thus regressed again showed definite trends with molecular weights, and it was easily possible to obtain good polynomial fits. The regression equations for the three homologous series are listed below.

Hydrocarbons:

$$\log(R) = a_o + 0.80C - 0.19C^2 + 0.0175C^3 \tag{6}$$

$$\log(a_o) = -1.817 + 0.025W - 6 \times 10^{-5}W^2 \tag{7}$$

Pyridines:

$$\log(R) = a_o + 1.022C - 0.195C^2 + 0.012C^3 \tag{8}$$

$$\log(a_o) = -0.92 + 0.0094W \tag{9}$$

Phenols:

$$\log(R) = a_o + 0.80C - 0.162C^2 + 0.012C^3 \tag{10}$$

$$\log(a_o) = -1.34 + 0.0226W - 6 \times 10^{-5}W^2 \tag{11}$$

Where W is the molecular weight. Excellent regression fits were obtained with correlation coefficients in excess of 0.98.

It was further observed that it might be possible to consider all standards and obtain a single set of equations without differentiating between different homologous series. This is not surprising because the Varex detector response is sensitive to the mass of the sample and not to the molecular functionalities. The regression equations considering all standards together are given below.

$$\log(R) = a_o + 0.80C - 0.19C^2 + 0.0175C^3 \tag{12}$$

$$\log(a_o) = -1.205 + 0.0188W - 4 \times 10^{-5}W^2 \tag{13}$$

A correlation coefficient of 95% was obtained for the regression fit represented by equation 13. Thus we have developed generalized peak response curves that give peak response as a function of molecular weight and concentration of the sample.

ANALYSIS OF COAL DERIVED LIQUIDS

The four coal derived liquids, Wilsonville SRC-1, Lummus ITSL distillate, H-Coal Run #8, and H-Coal Run #10, were analyzed by the same chromatographic method as employed for the standards. The liquids were initially filtered twice through 0.45 and 0.2 micron filters with vacuum filtration equipment to remove any solid particulates.

For each coal liquid, chromatographic runs were carried out with two objectives: 1. to obtain a chromatogram for elution time and peak response analysis, and 2. to collect fractions of separated materials at known time intervals.

CHROMATOGRAPHIC ANALYSIS

All coal liquids at 100% concentrations overloaded the Varex detector thereby showing a plateau in the chromatogram. Such a chromatogram was useless for any analysis. We therefore set out to determine the maximum concentration of the coal liquid that would not overload the detector. Samples of various concentrations were analyzed and the following sample concentrations (volume basis) were determined for chromatographic analysis.

Wilsonville SRC-1	10%
Lummus ITSL	10%
H-Coal Run #8	40%
H-Coal Run #10	30%

The chromatogram corresponding to the four liquids are given in Figures 2-5. The elution time range for most of the liquids was 2.20 min - 5.65 min, with the Lummus ITSL liquid exhibiting a somewhat narrower chromatogram than the other three.

FRACTION COLLECTION

It was decided to divide the separated coal liquid into 10-16 fractions and collect these fractions using the Gilson fraction collector. The objective was such that these fractions may be analyzed for elemental and functional group composition.

Before collecting the fractions, it was first necessary to calibrate the fraction collector. Fraction collectors generally operate in either peak mode or in time mode. In peak mode, the fraction collector responds to the detector peak response and collects fractions corresponding to the peaks in accordance with the delay time and the peak width which need to be programmed into the collector. The delay time is the time necessary for the solvent to flow from the detector to the first vial of the fraction collector. For this process a relay is necessary to send the signal from the detector to the fraction collector. Our fraction collector was not fitted with this option, so we had to operate in the time mode. Here, the time period after injection necessary for the sample to appear at the first vial of the fraction collector needs to be determined. This was determined in two ways. First, by simply calculating the volume between the injection port and the collector and calculating the delay time by dividing this by the volumetric flow rate of 3 mL/min. This calculation was then checked by experimenting with a pure sample quinoline and making sure that all the sample could be collected by using the delay time. A delay time of 2.07 minutes was used for all coal liquid fraction collections.

The method used for coal liquid fraction collections was exactly the same as the one used for the chromatographic analysis except that the samples were 100 microliters of pure coal liquid. This was done to minimize the number of runs necessary to collect enough fractions for analysis. Even so with our analytical LC at 3 mL/min, over 100 runs had to be made for each coal liquid. The usage of pure sample did not cause any problems with the fraction collection, because the tests showed that the chromatogram width was not affected by the concentration of the sample. Table 5 gives the summary of the fraction collections for the four coal liquids.

Figure 2: Chromatogram of Wilsonville SRC-1

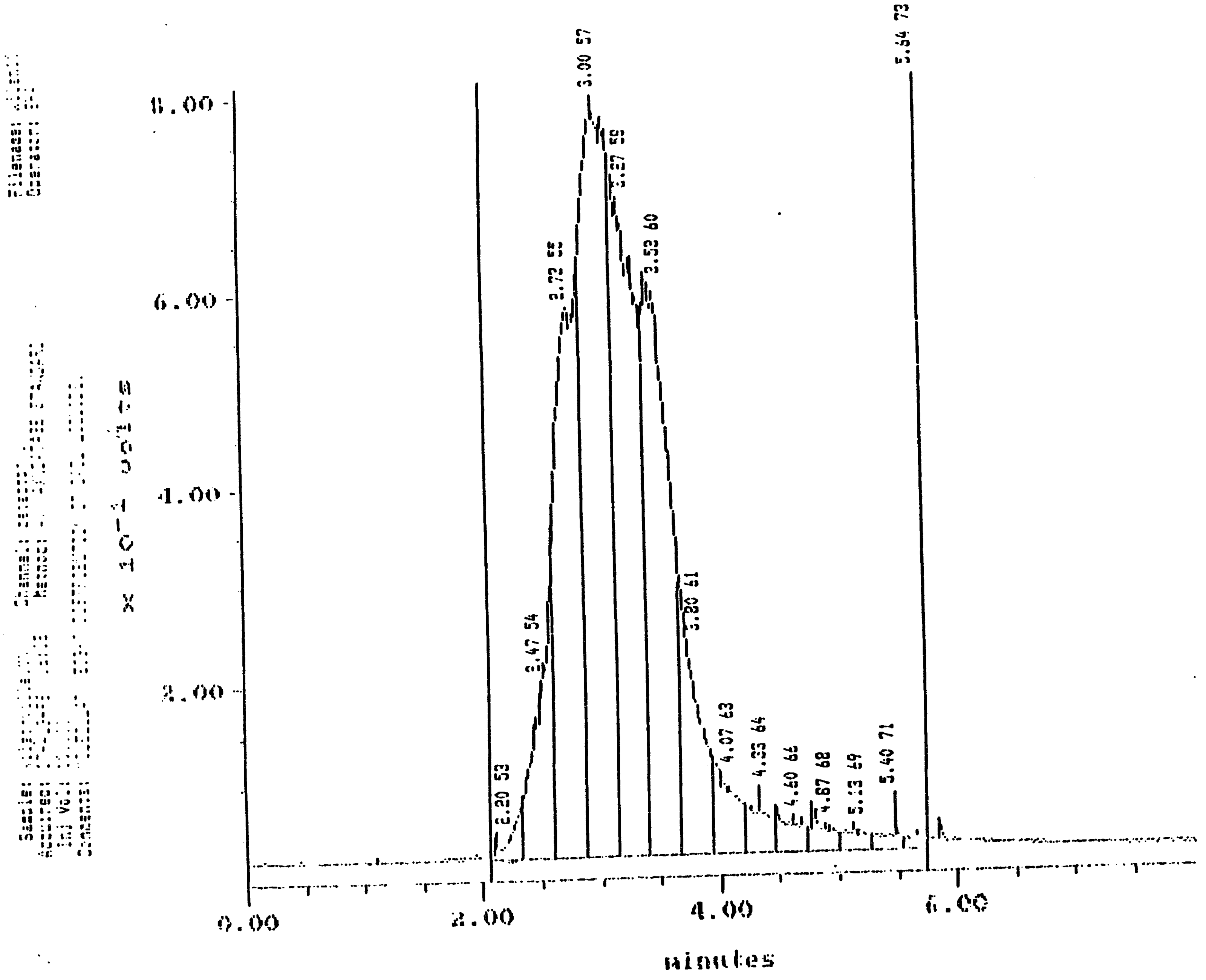


Fig # 49

Sample: Lumas 10%
Acquired: 10-AUG-92 14:05
Inj Vol: 100.00
Comments: MOLECULAR WEIGHT DISTRIBUTION OF CAGL LIQUIDS.

Channel: detector 1
Method: C:\MAX\DATA92\STND-FUR

Filename: lumas10%
Operator: SHA

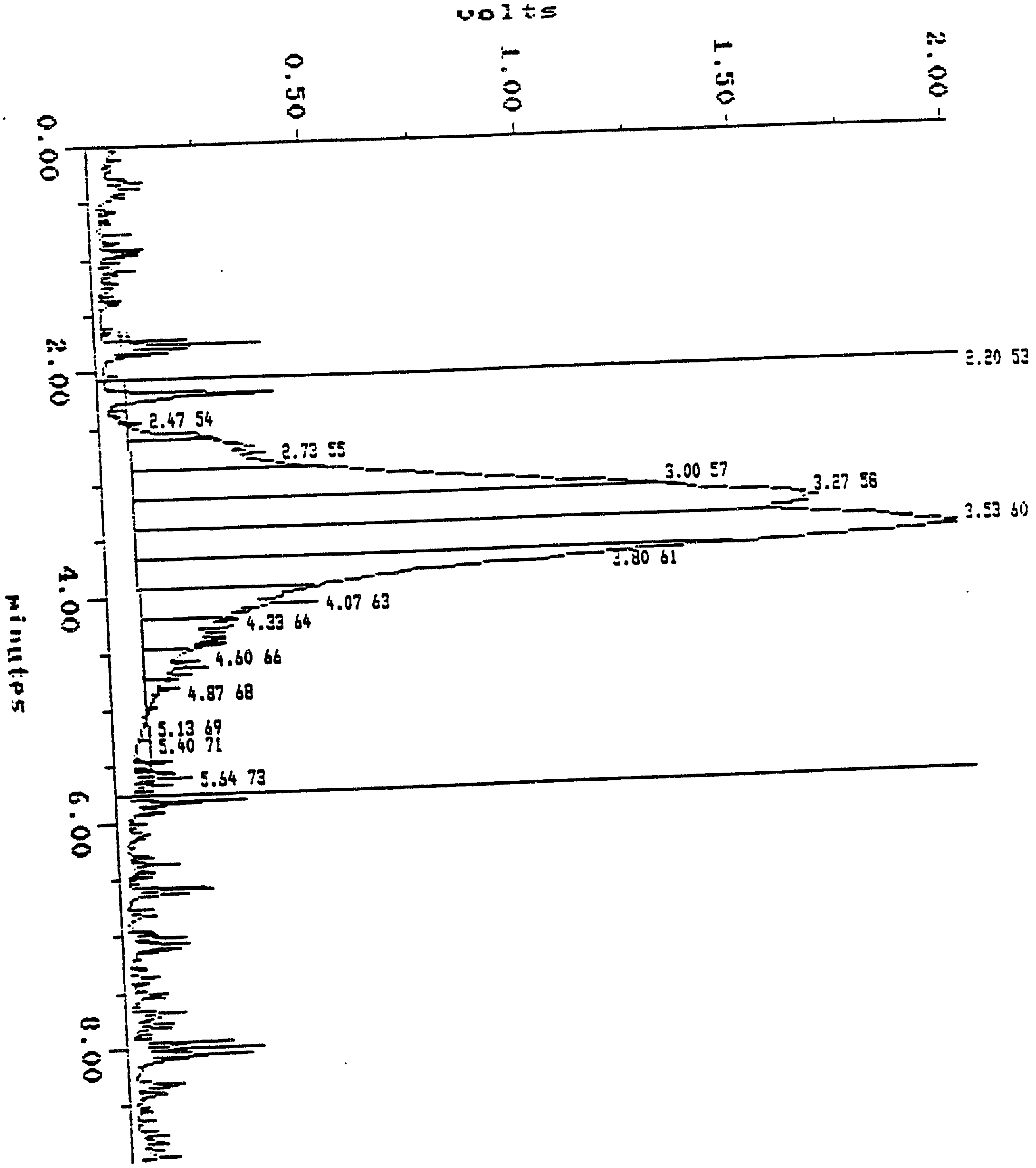


Figure 3: Chromatogram of Lummus ITSL distillate

Fig #492

Sample: H-Coal Run#8-40 Channel: detector 1 Filename: HC#8-40
Acquired: 31-AUG-92 0:15 Method: A:\MAX\DATA\GENSTANDARD Operator: BHA
Inj Vol: 100.00
Comments: MOLECULAR WEIGHT DISTRIBUTION OF COAL LIQUIDS.

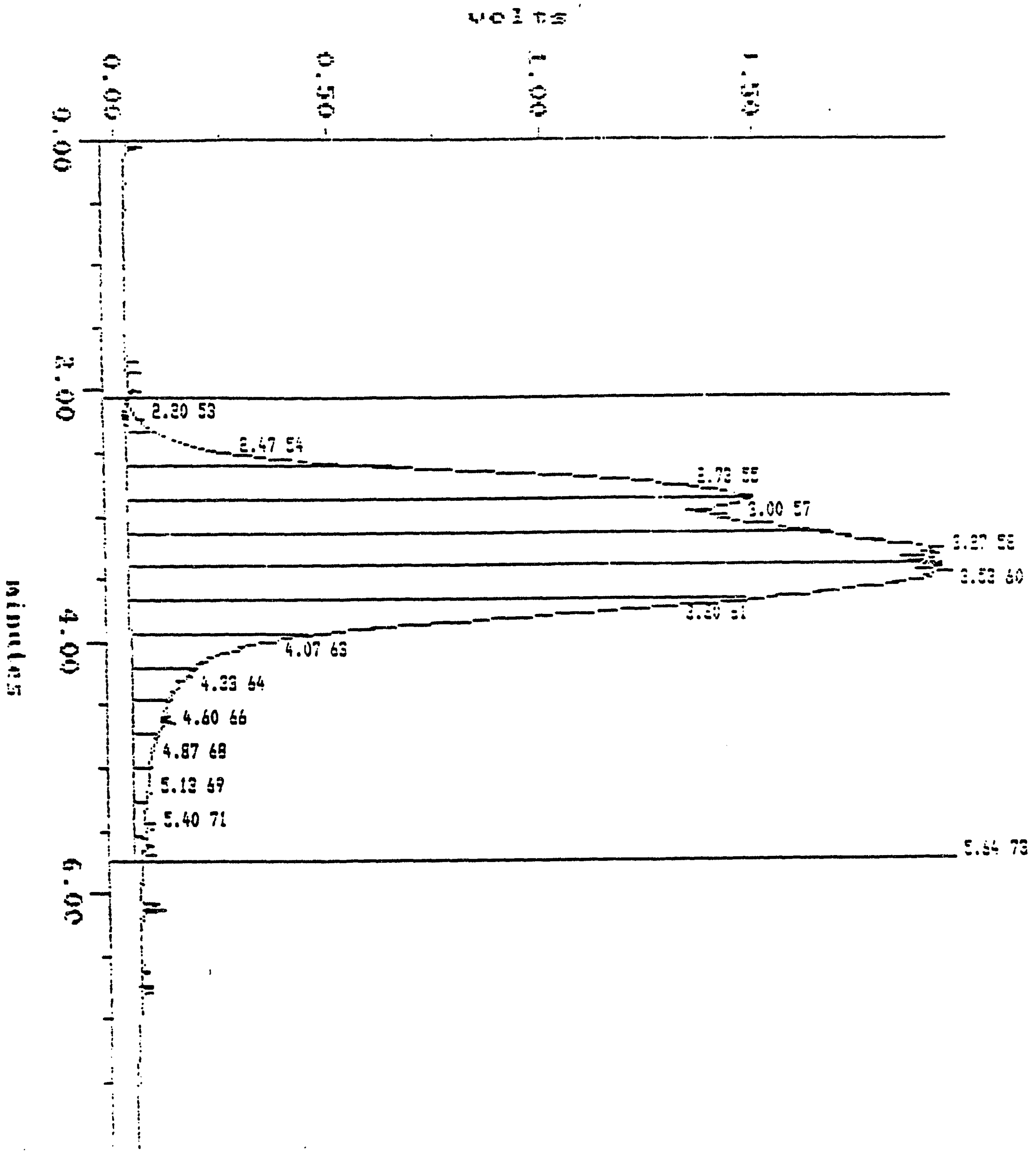


Figure 4: Chromatogram of H-Coal Run #8

Fig #493

Sample: H-CoalRun#10SOX   Channel: detector 1   Filename: HC#10SOX
Acquired: [illegible]   Method: [illegible]   Operator: SHA
Inj Vol: 100.00
Comments: MOLECULAR WEIGHT DISTRIBUTION OF COAL LIQUIDS.

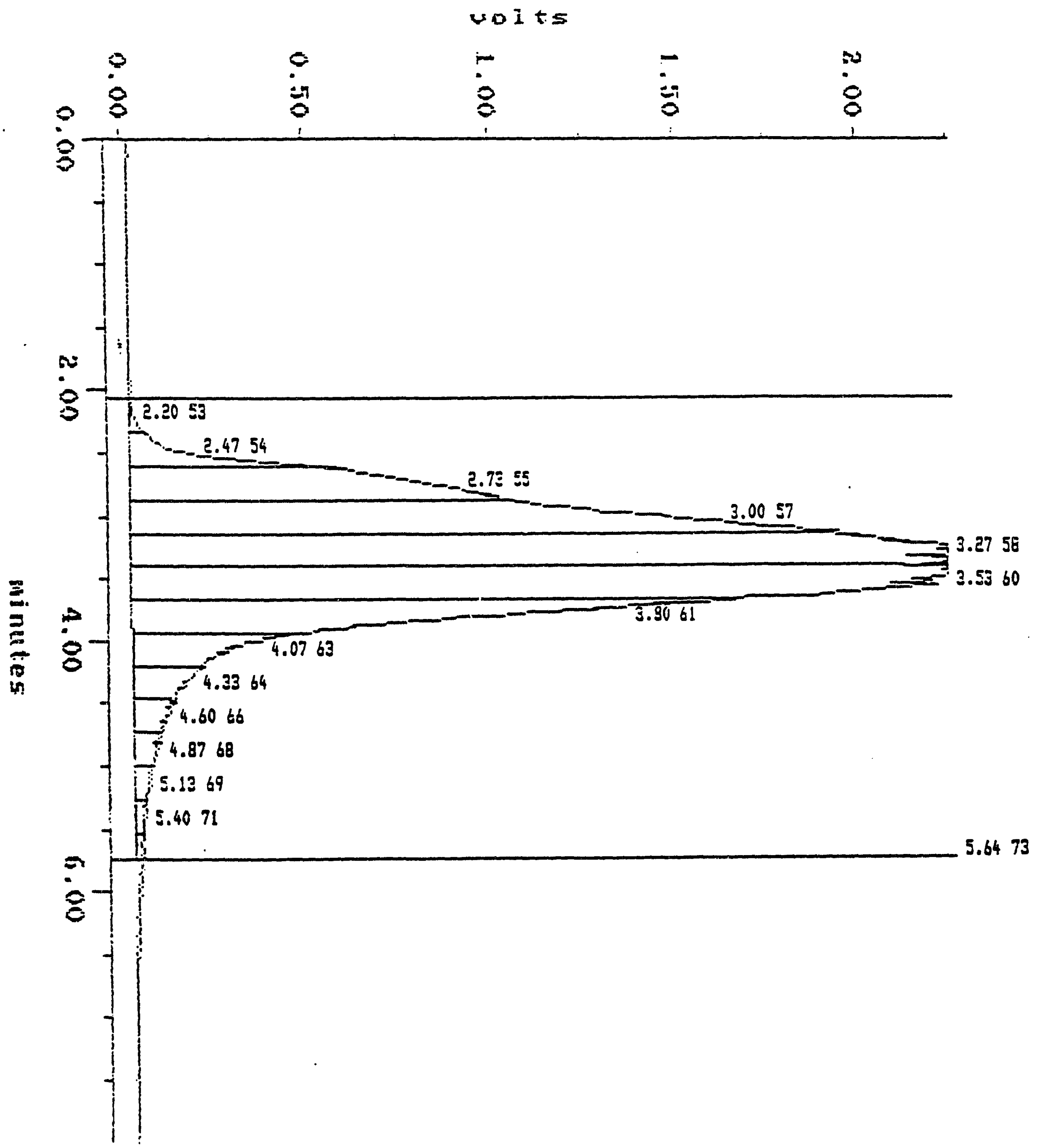


Figure 5: Chromatogram of H-Coal Run #10

Fig. # 494

Table 5
Summary of Fraction Collections for Coal Liquids

Coal Liquid	Number of fractions	Start time	End time	Time period of each collection
Wilsonville SRC-1	14	2.07 min	5.80 min	16 sec
Lummus ITSL	10	2.45 min	5.12 min	16 sec
H-Coal Run #8	14	2.07 min	5.80 min	16 sec
H-Coal Run #10	14	2.07 min	5.80 min	16 sec

For the characterization procedure, it was important to know the peak responses corresponding to the fractions collected for chromatograms shown in figures 2 - 5. These were obtained using Waters Maxima software and are given in Table 6.

CHARACTERIZATION PROCEDURE

Although elemental analysis and FTIR data on fractions collected are not yet available, we have formulated a detailed procedure to determine the true molecular weight distribution of the coal liquid and distributions of phenolic and pyridinic compounds. The stepwise procedure is given below:

1. Obtain the chromatogram of the coal liquid. divide the chromatogram into 10-12 slices according to elution times. Determine peak responses corresponding to each slice. Using a fraction collector collect enough of fraction corresponding to each slice for elemental and FTIR analysis.

2. Determine the elemental compositions and FTIR spectrum of each fraction.

3. For each slice, using an average elution time calculate the molecular weights of hydrocarbon material, phenolic material and pyridinic material from the linear calibration equations 1, 2, and 3.

4. Assume all oxygen is phenolic and all nitrogen is pyridinic (Justification: data of White and Cowokers, Fuel, 67, 119, 1988). Also assume one -OH group per molecule and one pyridinic ring per molecule. From molecular weights and elemental analysis determine relative compositions of hydrocarbons, phenols, and pyridines in each slice.

5. Next, injection concentrations of hydrocarbon, phenolic, and pyridinic material in each slice is calculated by trial and error. First, a concentration is assumed for hydrocarbon

TABLE 6: Peak Responses for LC Fractions of Coal Liquids

SLICE #	WILLSONVILLE SRC - 1		LUMMUS ITSL DIST.		H-COAL RUN #8		H-COAL RUN #10	
	SLICE AREA microvolts-sec x 10^{-6}	CUM. AREA %	SLICE AREA microvolts-sec x 10^{-6}	CUM. AREA %	SLICE AREA microvolts-sec x 10^{-6}	CUM. AREA %	SLICE AREA microvolts-sec x 10^{-6}	CUM. AREA %
1	0.39	0.85	7.40	2.91	0.41	0.33	0.20	0.15
2	2.61	6.57	42.21	19.48	3.91	3.42	3.11	2.50
3	8.15	24.47	57.57	42.08	18.60	18.13	1.30	12.35
4	11.52	49.75	57.52	64.66	22.98	36.31	23.69	30.31
5	9.78	71.21	52.18	85.15	28.98	59.22	34.40	56.37
6	7.54	87.76	19.25	92.70	28.17	81.50	32.86	81.28
7	2.50	93.24	9.31	96.36	14.45	92.93	14.66	92.39
8	1.02	95.48	5.00	98.32	3.88	96.00	4.21	95.57
9	0.64	96.88	2.74	99.40	1.78	97.41	2.24	97.27
10	0.44	97.85	1.54	100.0	1.19	98.35	1.41	98.33
11	0.37	98.66			0.74	98.93	0.93	99.00
12	0.26	99.23			0.55	99.37	0.60	99.50
13	0.23	99.73			0.45	99.72	0.41	99.81
14	0.12	100.0			0.35	100.0	0.25	100.0

material. The concentrations of phenolic and pyridinic materials are obtained using results in step 4. Peak responses corresponding to these three concentrations are calculated using peak response calibration curves. These are added and the result compared to the experimental peak response. Concentrations are increased or decreased until the experimental and calculated peak responses are in agreement. This is repeated for all the slices.

6. Thus we have generated data that divides coal liquids into hydrocarbon, phenolic, and pyridinic homologous series and gives molecular weights and corresponding injection concentrations for each of them.

7. This information is now used to generate the overall true molecular weight distributions, and individual molecular weight distributions of hydrocarbons, phenolics, and pyridines.

Once elemental analysis and FTIR data are available for the fractions collected, the above procedure will be used to generate molecular weight distributions for hydrocarbons, phenols, and pyridines in coal derived liquids. The procedure may be extended later to include other homologous series. Figure 6 gives a depiction of the typical results that may be expected from this procedure. The distributions shown in Figure 6 are probability density distributions which may be normalized in any convenient manner. These distributions would be very valuable and convenient for usage with continuous distribution methods for property prediction of coal liquids. One such thermodynamic model was presented in part I of this report.

CONTINUING WORK

Further work is necessary to demonstrate the utility of the characterization procedure formulated here. Work is necessary in the following areas:

1. Extend the standards base to obtain better and more extensive elution time and peak response analysis.

2. Analyze the collected coal liquid fractions by elemental analysis and FTIR.

3. Use all the data to obtain the true molecular weight distribution for various homologous series by the characterization procedure developed in this work.

All this work is currently on-going and will be completed shortly.

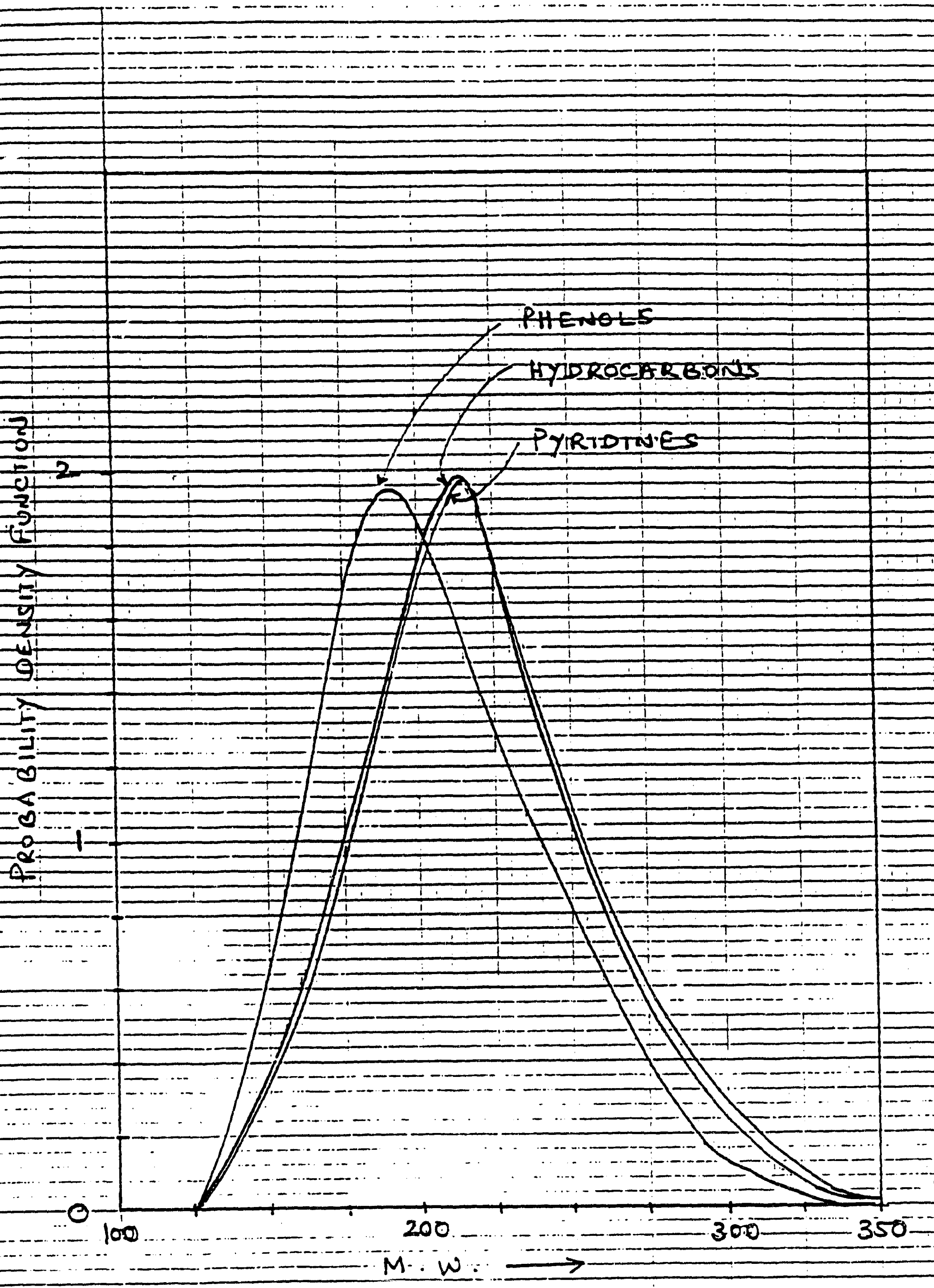


FIGURE 6 : MOLECULAR WEIGHT DISTRIBUTIONS OF HYDROCARBONS, PHENOLS AND PYRIDINES

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