

NBSIR 77-867

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A COMPARISON OF MATHEMATICAL MODELS FOR THE PREDICTION OF LNG DENSITIES

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Prepared for:
American Gas Association, Inc.
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A COMPARISON OF MATHEMATICAL MODELS FOR THE PREDICTION OF
LNG DENSITIES*

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Four mathematical models of the equation of state for LNG like mixtures are compared. Each model has been optimized to the same experimental data set. The experimental data consist of over 175 new PVTx data points taken in this laboratory. The objective of the study was to obtain a mathematical model which would predict LNG densities to within 0.1% of the true value. The extent to which the objective has been achieved is not clear at this time. Additional experimental data are needed to resolve some discrepancies between the present data and all models investigated to date. Computer program listings for all four models are presented.

Key words: Computer program; density; equation of state; LNG; mixtures; PVTx.

1. Introduction

The purpose of this study was to optimize and compare several different mathematical models using the experimentally determined PVTx density data of Haynes, et al. (1976), Haynes and Hiza (1976), Hiza, et al. (1976) and Hiza (1976). These data are for the liquid phase of methane, ethane, propane, normal butane, isobutane and nitrogen and various mixtures thereof. The temperature range of the correlations was limited (95-150 K) and the pressures to those of saturation, the range of which was about 0 to 20 atmospheres. The goals of the study were to produce one or more computer models which would predict a density of LNG (liquefied natural gas) to within 0.1% of the true value, when the temperature, pressure and composition of the LNG are specified. The goal of predicting LNG densities with an accuracy of 0.1% has most probably been achieved. The data from the above references include nine multicomponent (three or more components) mixtures in addition

* This work was carried out at the National Bureau of Standards under the sponsorship of British Gas Corp., Chicago Bridge and Iron Co., Columbia Gas Service Corp., Distrigas Corp., Easco Gas LNG, Inc., El Paso Natural Gas., Gaz de France, Marathon Oil Co., Mobil Oil Corp., Natural Gas Pipeline Co., Phillips Petroleum Co., Shell International Gas, LTD., Sonatrach, Southern California Gas Co., Tennessee Gas Pipeline, Texas Eastern Transmission Co., Tokyo Gas Co., Ltd., and Transcontinental Gas Pipe Line Corp., through a grant administered by the American Gas Association, Inc.

to the binary mixture data in Appendix A. One of the methods (the extended corresponding states) predicts all of the densities to within the 0.1% objective except in the case of the methane-normal butane data on page 18 and one point of the propane-nitrogen data on page 22. Haynes, et al. (1976) estimate the uncertainty of these data to be greater than that of the other binary data. A comparison with an independent set of mixture data (68 data points) for mixtures of the same components due to Rodosevich (1973) resulted in no deviations between experimental and predicted (using extended corresponding states) densities greater than 0.1% (see Appendix A). The Rodosevich data include binary mixtures data for the methane-normal butane system.

The choice of models to use in this study was a difficult one, because there are many possible models and methods to choose from. Since no mathematical model is suitable for every need and needs vary greatly from application to application, an effort was made to choose the models to be tested in such a way as to provide useful information to as diversified an audience as possible and still achieve the stated objective of the study. In an effort to achieve these ends, the choice of models was made on the basis of the following criteria: popularity, degree of complexity, type of approach and likelihood of success, with of course the likelihood of success being the most important factor of consideration.

The models and/or methods which are considered here are: the extended corresponding states method (Leach, 1967 and Rowlinson and Watson, 1969); a hard sphere model by Rodosevich and Miller (1975); a cell model proposed by Echert, et al. (1967) as modified by Albright (1973); and a graphical method by Klosek and McKinley (1968). All of the optimization and testing was performed in the Cryogenics Division of NBS at Boulder, Colorado except in the case of the cell model which was done by M. A. Albright at Phillips Petroleum in Bartlesville, Oklahoma. The details of the optimization of the cell model will be published by Albright (1976) elsewhere.

A general discussion of the performance of each model is given in the following sections. A separate section is devoted to each model considered. The appendices give comparisons of calculated and experimental densities for all the models as well as listings of the computer programs for each model.

2. Extended Corresponding States Method

This method was selected because it seemed to offer an excellent possibility for achieving the objective of predicting the densities of LNG to within 0.1% of the true value.

The extended corresponding states method is labeled as a method rather than a model because it differs from the customary meaning of model in that it is not an equation of state but rather a transformation function which

maps the equation of state of a fluid into the equation of state of another. The thermodynamic equations for the extended corresponding states method are developed in a paper by Rowlinson and Watson (1969) and only a very brief description will be given here. Leach (1967) developed transformation functions for hydrocarbons which are called shape factor functions. Mollerup (1976) and Mollerup and Rowlinson (1974) combined the earlier work with the equation of state for methane by Goodwin (1974) to produce a computer program to calculate the density of LNG mixtures. This method for calculating the densities of LNG was estimated by Mollerup (1975) to be accurate to 0.1%; however, a copy of the computer program obtained from Mollerup produced densities for LNG-like mixtures which are as much as 3% different from those measured in this laboratory. Figure 1 shows the deviations between the densities from the computer program of Mollerup and the PVTx measurements mentioned earlier. The open circles represent deviations using the Mollerup (1976) computer program and the solid circles show deviations for the same data points using the computer program given in Appendix B, i.e., the same program after optimization to the new data.

The computer program in Appendix B for the calculation of LNG densities based on the extended corresponding states method is an extensive revision of the Mollerup program.

The extended corresponding states method is defined by the following equations:

$$Z_i[P,T] = Z_o[P h_{ii,o}/f_{ii,o}, T/f_{ii,o}] \quad (1)$$

$$G_i[P,T] = f_{ii,o} G_o[P h_{ii,o}/f_{ii,o}, T/f_{ii,o}] - RT \ln(h_{ii,o}) \quad (2)$$

where Z is the compressibility factor, G is the Gibbs free energy, P is pressure and T is temperature. The subscript o denotes the reference fluid and the subscript i denotes the fluid for which properties are to be obtained via the equation of state for the reference fluid and the transformation functions $f_{ii,o}$ and $h_{ii,o}$. The double subscript ii is introduced now to allow extension of the method to mixtures. The two defining equations (1) and (2) are necessary since there are two transformation functions. In this case the equation of state for methane by McCarty (1974) was chosen for the reference fluid. During the course of the study it was necessary to modify the equation of state by McCarty (1974). The equation of state was modified to give a realistic vapor liquid phase boundary down to a temperature of 43 K. This modification was necessary to accommodate the very low reduced temperatures of the heavier hydrocarbons and was accomplished without changing the performance of the equation of state above the triple point of methane. The equation of state is given in Appendix B.

The $f_{ii,o}$ and $h_{ii,o}$ are defined as

$$f_{ii,o} = (T_{ii}^C/T_O^C) \theta_{ii,o} (T_r, V_r) \quad (3)$$

and

$$h_{ii,o} = (V_{ii,o}^C/V_O^C) \phi_{ii,o} (T_r, V_r) \quad (4)$$

where

$$\theta_{ii,o} = 1 + (w_i - w_o) [a_1 - a_2 \ln T_{r_i} + (a_3 - a_4/T_{r_i}) (V_{r_i} - a_5)] \quad (5)$$

and

$$\phi_{ii,o} = \frac{Z_O^C}{Z_i^C} [1 + (w_i - w_o) [b_1 (V_{r_i} - b_2) - b_3 (V_{r_i} - b_4) \ln T_{r_i}]] \quad (6)$$

The V_{r_i} and T_{r_i} are reduced temperature and volume, (i.e., $T_{r_i} = T/T_{ii}^C$ and $V_{r_i} = V/V_{ii}^C$) and w_i is a fluid dependent parameter estimated using experimental data. The a_j 's and b_j 's are fluid independent parameters, estimated with experimental data and the Z_O^C/Z_i^C is the ratio of the compressibility factors at the critical point. The parameters a_j , b_j , w_i and Z_{ii} are given in Appendix A. All of these parameters were estimated using the experimental PVT data set from this laboratory and least squares estimation techniques.

The extension of the above to mixtures is now accomplished by the following application of the following combining rules

$$h_{x,o} = \sum_i \sum_j x_i x_j h_{ij,o} \quad (7)$$

$$f_{x,o} h_{x,o} = \sum_i \sum_j x_i x_j f_{ij,o} h_{ij,o} \quad (8)$$

$$f_{ij,o} = \xi_{ij} (f_{ii,o} f_{jj,o})^{1/2} \quad (9)$$

$$h_{ij,o} = \eta_{ij} \left(\frac{1}{2} h_{ii,o}^{1/3} + \frac{1}{2} h_{jj,o}^{1/3} \right)^3 \quad (10)$$

The ξ_{ij} and the η_{ij} are binary interaction parameters determined by least squares from the PVT_x data for binary mixtures. These parameters are given in Appendix A.

This method works quite well as may be seen in the comparisons in Appendix A. It has indeed reproduced all of the present experimental data

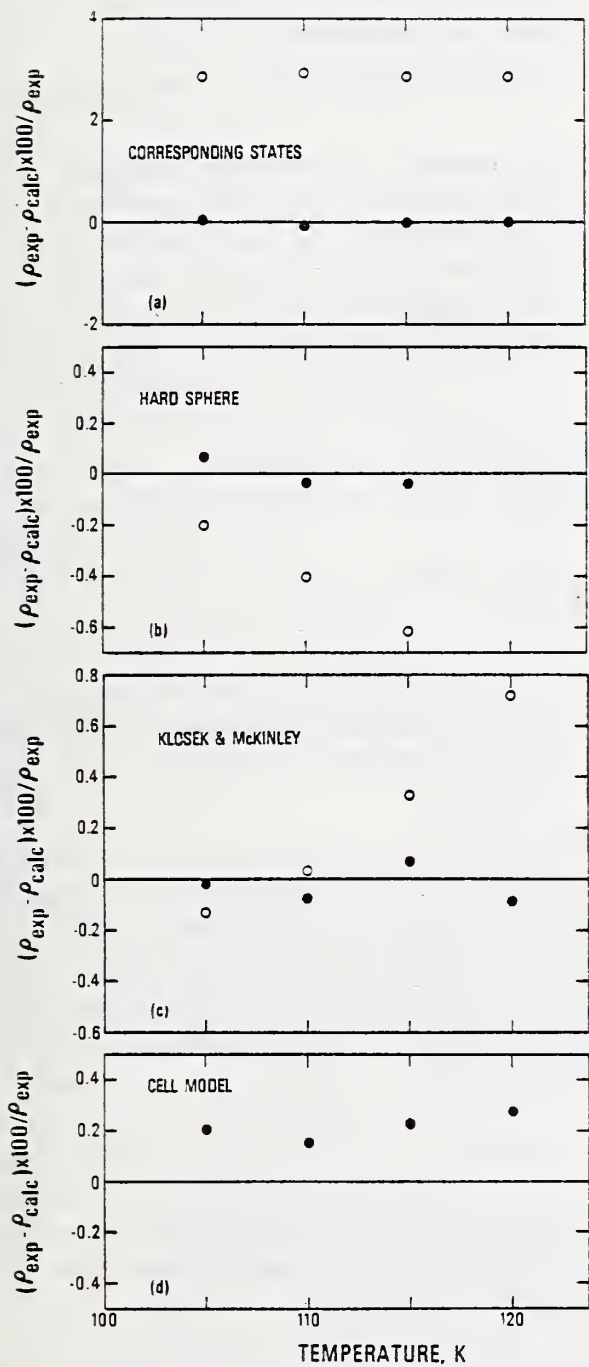


Figure 1. Deviations in density between data from Hiza (1976) and the indicated model. Open circles are for the model before the present work and the closed circles are for the same models after the present work. The composition of the mixture is $0.806 \text{ CH}_4 + 0.047 \text{ C}_2\text{H}_6 + 0.048 \text{ C}_3\text{H}_8 + 0.050 \text{ nC}_4\text{H}_{10} + 0.049 \text{ N}_2$.

set to within $\pm 0.1\%$ except for some of the systems containing butane which are strongly suspected to be in error. Since only binary systems data were used as input to the method, the calculated densities for multicomponent data are, in a sense, predictions on the part of the method.

Figure 1 gives a comparison of the extended corresponding states method before and after modification.

Unfortunately the method has some deficiencies. The method is complex and is not easy to use even with the aid of a computer. Figure 1 shows that it does not perform well when insufficient experimental data are available as input since all of the other models tested show deviations which are much less than those in figure 1 when tested before optimization, i.e., as they were taken from the literature. On the advantages side of the comparison, this method has the most versatility, it handles nitrogen as a component in any concentration, it has the widest PVTx range of any of the methods, and it is probably the most accurate for the calculation of densities. It can also be used to calculate other thermodynamic properties including phase equilibria.

A comparison between the data of Rodosevich and predictions by the extended corresponding states method resulted in no deviations greater than 0.1%. These comparisons were made before any of the Rodosevich data were used as input to the optimization process. The $\text{CH}_4\text{-nC}_4\text{H}_{10}$ and the $\text{CH}_4\text{-iC}_4\text{H}_{10}$ data of Rodosevich were used in the final optimization of the corresponding states model. A complete tabulation of deviations between the various models and the Rodosevich data is given in Appendix A.

3. A Hard Sphere Method

This method was selected for consideration since it currently enjoys wide popularity. The model of Rodosevich and Miller (1975) is one of many modifications of the Longuet-Higgins and Widom (1964) model, and was chosen to be included in this study as a representative example of the application of the hard sphere equation of state concept to the correlation of PVTx data. The equation of state by Rodosevich and Miller (1975) is

$$\frac{PV}{RT} = c \frac{1 + y + y^2}{(1 - y)^3} - \frac{a}{RTV} \quad (11)$$

where the $y = b/4V$ and a , b , and c are adjustable parameters, the PVT and R have the usual meaning. The equation is applied to mixtures by assuming the one-fluid theory and applying the following combining rules.

$$a_m = \sum_i \sum_j a_{ij} x_i x_j \quad (12)$$

$$b_m = \sum_i \sum_j b_{ij} x_i x_j \quad (13)$$

$$c_m = \sum_i \sum_j c_{ij} x_i x_j \quad (14)$$

The mixing rules are:

$$b_{ij} = \left[\frac{b_{ii}^{1/3} + b_{jj}^{1/3}}{2} (1 - j_{ij}) \right]^3 \quad (15)$$

$$a_{ij} = a_{ii} a_{jj}^{1/2} \left[\frac{b_{ij}^2}{b_{ii} b_{jj}} \right]^{1/2} (1 - k_{ij}) \quad (16)$$

$$c_{ij} = \frac{c_{ii} + c_{jj}}{2} \quad (17)$$

The parameters j_{ij} and k_{ij} are in this case the binary interaction parameters. The a's, b's, c's, j_{ij} 's and k_{ij} 's are given in Appendix B. The excess volume is now calculated using the equation of state and

$$V_E = \hat{V}_m - \sum \hat{V}_i X_i \quad (18)$$

where \hat{V}_m and the \hat{V}_i are calculated via the equations 11 through 17 and then

$$V_m = \sum V_i X_i + V_E \quad (19)$$

where the V_E is from equation (18) and the V_i are from experimental data. The V_i in this case were calculated from the equations for the liquid density of the pure fluids given in Appendix C.

The above equations are those of Rodosevich and Miller (1975) and only the j_{ij} 's and k_{ij} 's have been revised on the basis of the present new data set, and only binary systems data were used to estimate via least squares the j_{ij} 's and k_{ij} 's. An attempt to optimize the a, b and c parameters for each pure fluid was made using the new pure fluid data; however the results were disappointing. No appreciable improvement in the prediction of mixture densities was achieved. The results did indicate, however, that any substantial improvement over the a, b and c values given by Rodosevich and Miller (1975) will require some sort of temperature dependence for those parameters.

Figure 1 gives deviations between calculated and experimental densities for the same mixtures but with different parameters for the model as the means of calculating the densities. The open circles show deviations between calculated and experimental densities before the model was optimized using

the present data set. The closed circles represent the deviations for the same data points after optimization. Only binary system data were used in the optimization process. A table of deviations between experimental densities and those calculated via the hard sphere model is given in Appendix A.

The hard sphere model as applied here has some disadvantages when applied to the present problem. The most serious disadvantage is that it is an excess properties method, and therefore when temperatures of the mixture approach the critical temperature of one of the component fluids the method fails. Since the critical temperature of N_2 is about 126 K, calculations for mixtures containing N_2 are limited to temperatures below about 120 K, however at temperatures where the critical temperature of a component does not present a problem, the method works very well. The model is neither the most accurate nor the simplest model investigated, but based on the experience of this study, it is probably the most reliable to extrapolate.

4. A Revised Klosek and McKinley Method

This method (Klosek and McKinley, 1968) is included in the study because it is currently very popular and it seemed at the outset to perform about as well as any of the others chosen. In addition it is one of the easiest methods to apply.

This method is a totally empirical recipe for calculating the density of a LNG-like mixture given the temperature and composition. Pressure is not taken into account. However, this does not seem to be a serious omission. The procedure proposed by Klosek and McKinley (1968) is as follows:

$$V_{\text{mix}} = \sum X_i V_i - k X_{\text{CH}_4} \quad (20)$$

where V_{mix} is the volume of the mixture, X_i and V_i are the mole fraction and volume of the i th component, X_{CH_4} is the mole fraction of methane and k is a correction factor obtained from a table or graph. The V_i and k are obviously temperature dependent and in addition k is dependent upon the molecular weight of the mixture.

Using the present data set k was calculated for all of the experimental data points where methane was present in the mixture and excluding all data points where N_2 was present in greater than 5% concentration. Figure 2 shows a typical isotherm for k . All of the isotherms available show similar behavior, i.e., all of the k 's for mixtures containing nitrogen (of about 5%) fall on one line and all of those for mixtures without nitrogen fall on another. Since all of the mixtures with nitrogen have about the same amount of nitrogen present (about 4.5%), the method was modified by adding a term

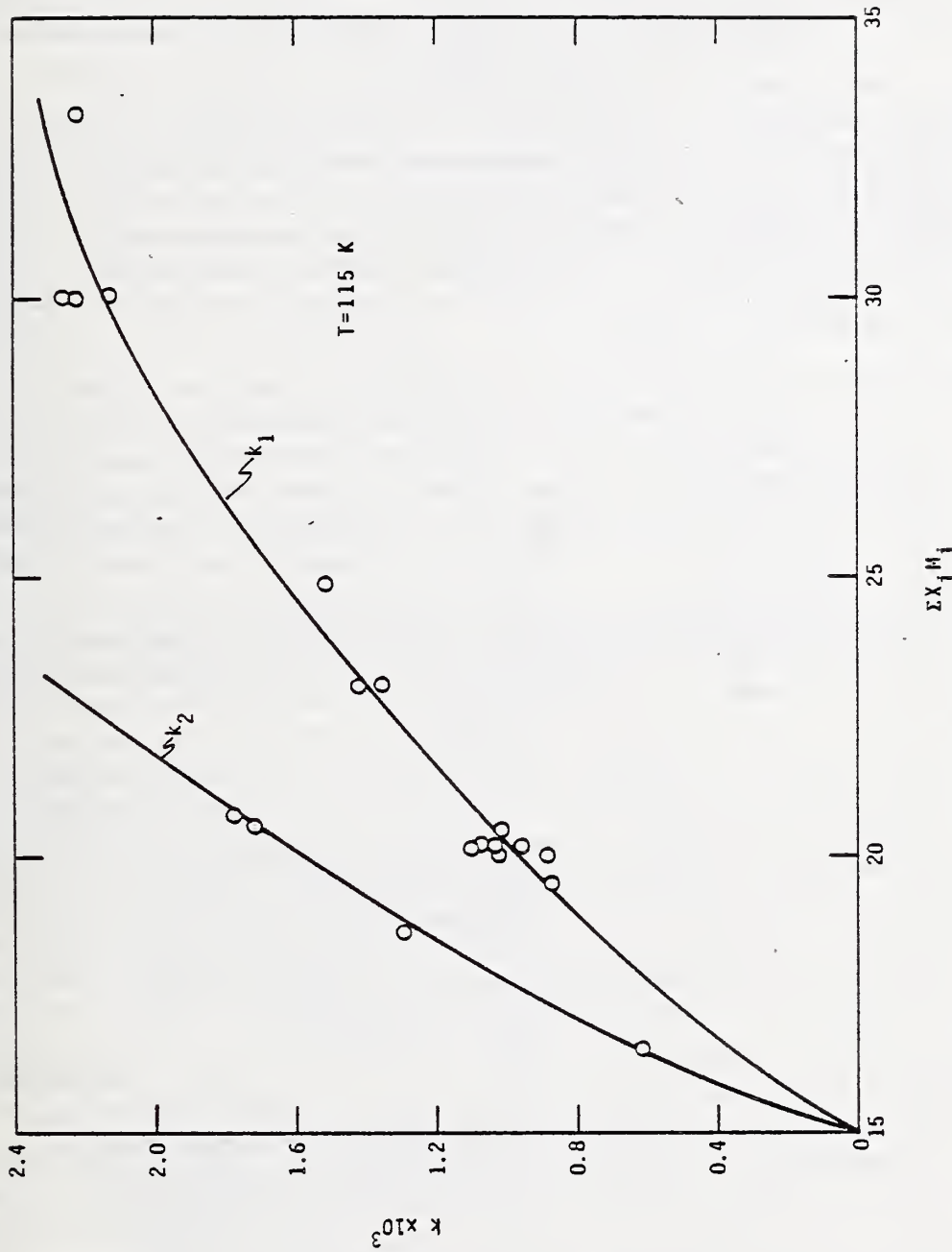


Figure 2. A plot of the correction factors (k_1 and k_2) for the 115 Kelvin Isotherm.

to take into account the nitrogen when it is present. The equation becomes

$$V_{\text{mix}} = \sum X_i V_i - [k_1 + (k_2 - k_1) X_{\text{N}_2} / .0425] X_{\text{CH}_4} \quad (21)$$

where everything is the same as in equation (20) except the k_1 is read from one curve and k_2 is read from the other. Appendix D gives tables of values for the V_i , k_1 and k_2 which are spaced such that linear interpolation is adequate in both variables (i.e., temperature or molecular weight). Using the experimental data it was possible to calculate k directly for the 105, 110, 115, 120 and 125 kelvin isotherms only. A comparison of the linear extrapolation of k to both lower and higher temperatures indicated the extrapolation to be unsatisfactory. Consequently values of k for the 90, 95, 100, 130, and 135 K isotherms were calculated using the extended corresponding states model in section 2.

In the process of calculating k for these additional isotherms it was discovered that for mixtures containing only methane-ethane and propane a table of k 's could be constructed to give values for density almost identical to those of the corresponding states model in section 2, but when either butane or nitrogen were added k became composition dependent. Consequently, it was decided to construct the k_1 and k_2 tables in Appendix C such that they would give results similar to the corresponding states method for methane-ethane and propane mixtures and give the best results for mixtures containing the butanes where the concentrations of the butanes were 5% or less (total) and where the concentration of nitrogen is also less than 5%. The computer comparison of the two models also revealed the following limitation. For the model to predict LNG densities to an accuracy of 0.15% or better, the mixture must contain 80% or more methane and less than 5% butane and nitrogen.

Figure 1 allows a common basis of comparison with the methods given in the other sections. The open circles represent the deviations before optimization and the solid circles show deviations after optimization. The optimization for this model was accomplished with multicomponent data as well as binary mixture data. An extensive tabulation of deviations between calculated and experimental densities is given in Appendix A.

For the purpose of calculating the density of LNG like mixtures, the revised Klosek and McKinley method presented here has one very real advantage over all the others, and that is, it is simple. It is quite easy for almost anyone to use the tables in Appendix C to arrive at an LNG density using only pencil and paper. This is not true of any of the other methods. The value of density arrived at in this manner will be within about 0.15% of the true value in the worst case, and if the composition of the LNG has little or no butane or nitrogen in it, the density will be much better, on the order of

0.1% of the true value. There are, however, some disadvantages. It does not handle nitrogen or butane as a component as well as some of the other methods and if over 5% of either nitrogen or butane is present, it departs rapidly from measured values. It is not as accurate as the extended corresponding states method and it does not extrapolate well.

5. The Cell Model

The cell model considered here was originally proposed by Renon, et al. (1967). In a paper by the same three authors which appeared simultaneously (Eckert, et al., 1967), the cell model was applied to mixtures via Scott's (Scott, 1956) two-fluid theory and a three parameter corresponding states theory. Albright (1973) further modified the method by modifying the mixing rules on the basis of a proposal by Yuan (1971) and by inserting a pressure dependence based on the experimental liquid ethane data by Pope (1971).

As mentioned in the introduction, the optimization of this method was carried out by M. Albright (1976) at Phillips Petroleum Company in Bartlesville, Oklahoma and the details of this work will be published elsewhere. A listing of the optimized computer program together with a comparison with the experimental data are given in Appendices E and A respectively.

Figure 1 shows deviations between densities calculated using the cell model and experimental densities. The experimental densities are those used in the comparisons in the previous sections.

6. Conclusions

As stated earlier the objective of this study was to produce one or more mathematical models which will predict the density of LNG to within 0.1% of the true value. This objective has most probably been achieved as is demonstrated by the ability of the models to predict the experimental PVTx data for LNG-like mixtures to within 0.1%; however all of the four models have been fit to the data of Haynes, et al. (1976) who report that their data may have as much as 0.05% systematic error. Therefore, it is estimated that the densities of LNG-like mixtures as calculated from any one of the four models given here will be within 0.15% of the true density for that mixture.

Each of the models has its particular advantages and disadvantages. The extended corresponding states model has the widest range of pressure, temperature and composition and is probably the most accurate, but it is complex and difficult to use.

The revised Klosek and McKinley method is the easiest to use but it is severely limited in range of composition and temperature (i.e., less than 5% nitrogen or butane).

The hard sphere model works well but is limited to temperatures below 120 K for mixtures containing nitrogen.

The cell model also works well, but does not handle nitrogen at high concentrations (30% or more) as well as the extended corresponding states, and is only slightly less complex.

The last page of Appendix A is a comparison of the performance of various models for actual LNG compositions. The comparison shows that the models perform equally well until the concentration of the butanes exceeds 4%. The largest disagreement between models occurs for the mixture which contains a total of 4.3% of iC_4H_{10} and nC_4H_{10} where the difference between the cell model and the revised Klosek and McKinley method is 0.2%.

All of the other predictions for the other four compositions are within 0.11% of each other, and one of these mixtures includes 2.6% of the butane. It is true that all of these methods were optimized using the same data set, but the methods do differ radically in some cases and one of them (corresponding states) does agree well (0.1%) with the Rodosevich data which represents an independent check. Unfortunately an exhaustive search of the world's literature has not revealed any additional experimental data of compositions which are of interest here and which are of sufficient accuracy and precision to be of use in this correlation, either as input data or as an independent check.

More measurements of LNG like multicomponent mixtures have been scheduled to more precisely determine the concentration limits of nitrogen and butane.

At the request of sponsor, the pentanes (iso and normal) have been added as a possible component in the mixture. These components have been added on the basis of the pure fluid data of Orrit and Olives (1974) only, and no estimate of accuracy of the calculated density for mixtures containing pentane is possible.

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Appendix A. Deviation Tabulations

The deviations tabulated below have been calculated in every case using the following convention:

$$\% \text{ Deviation} = 100 (D_{\text{exp}} - D_{\text{cal}}) / D_{\text{exp}}$$

where D is density in moles/liter, the subscripts exp and cal stand for experimental, and calculated via the model indicated. No entry is given for a particular model when the calculation is not appropriate for that model.

In the case of the corresponding states model there is a deviation tabulated for every data point. For the hard sphere model no deviations are tabulated for the pure fluid data points because the method is an excess volume method and other models were used to calculate the so called ideal volume, i.e., $V_{\text{Ideal}} = \sum X_i V_i$ (see Appendix B). For the revised Klosek and McKinley method deviations have been tabulated for only those mixture data points which contain methane and have less than 5% nitrogen. This is also an excess volume method and the calculation of the ideal volume is outlined in Appendix C.

Saturated Liquid Ethane (Molecular Weight 30.07012)

Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
0.000	21.3408	100.	0.02			-0.07
0.000	21.1585	105.	0.01			-0.03
0.001	20.9746	110.	0.00			-0.00
0.002	20.7927	115.	0.00			0.01
0.004	20.6022	120.	-0.03			0.05
0.007	20.4186	125.	-0.02			0.05
0.013	20.2317	130.	-0.02			0.04
0.023	20.0461	135.	-0.00			0.02
0.038	19.8566	140.	0.00			0.00

Saturated Liquid Propane (Molecular Weight = 44.09721)

0.000	16.3065	100.075	0.01			-0.07
0.000	16.1872	105.075	-0.01			-0.01
0.000	16.0718	110.075	-0.01			-0.01

Saturated Liquid Propane (Continued)

(Molecular Weight = 44.09721)

Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
0.000	15.9557	115.075	-0.00			0.03
0.000	15.8411	120.075	0.01			0.03
0.000	15.7250	125.075	0.01			0.04
0.000	15.6085	130.075	0.01			0.03
0.000	15.4910	135.075	-0.00			0.03
0.000	15.3751	140.075	0.00			-0.00

Saturated Liquid Normal Butane

(Molecular Weight = 58.1243)

0.000	12.6517	135.075	-0.03			-0.01
0.000	12.5706	140.075	-0.02			0.01
0.000	12.4920	145.075	0.01			-0.00

Saturated Liquid Isobutane

(Molecular Weight = 58.1243)

0.000	12.7305	115.075	-0.01			-0.01
0.000	12.6489	120.075	-0.00			0.00
0.000	12.5687	125.075	0.02			-0.00
0.000	12.4850	130.075	0.01			0.02
0.000	12.4015	135.075	-0.00			0.02
0.000	12.3215	140.075	0.02			-0.01
0.000	12.2353	145.075	-0.01			0.01

Saturated Liquid Nitrogen

(Molecular Weight = 28.0134)

5.257	25.6624	95.075	0.02			0.05
7.715	24.6207	100.075	-0.02			0.00
10.744	23.4841	105.075	0.01			-0.08
14.544	22.1840	110.075	0.00			0.06
19.222	20.6490	115.075	0.01			1.93
21.927	19.7356	117.575	0.02			5.22
24.898	18.6525	120.075	0.02			8.64

Methane-Ethane Mixtures
 0.35457 CH₄ + 0.64543 C₂H₆

Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
0.252	23.1032	105.	-0.07	-0.05		-0.04
0.387	22.8777	110.	-0.05	-0.04		-0.05
0.572	22.6478	115.	-0.03	-0.02		-0.05
0.815	22.4035	120.	-0.07	-0.06		-0.11
1.131	22.1872	125.	0.03	0.04		-0.02
1.53	21.9441	130.	0.02	0.03		-0.03

0.49325 CH₄ + 0.50675 C₂H₆

0.321	23.9619	105.	0.07	0.07		0.10
0.496	23.6937	110.	0.03	0.03		0.03
0.739	23.4328	115.	0.03	0.01		0.01
1.06	23.1559	120.	-0.03	-0.02		-0.06
1.49	22.8933	125.	-0.00	0.00		-0.04
2.02	22.6290	130.	0.03	0.04		-0.01
2.69	22.3581	135.	0.05	0.06		0.02
3.51	22.0765	140.	0.04	0.05		0.03

0.68006 CH₄ + 0.31994 C₂H₆

0.411	25.1027	105.	0.07	0.05	0.09	0.08
0.637	24.7802	110.	0.01	-0.01	0.04	0.00
0.950	24.4612	115.	-0.03	-0.04	0.00	-0.04
1.36	24.1402	120.	-0.05	-0.06	-0.02	-0.06
1.90	23.8212	125.	-0.05	-0.05	-0.01	-0.05
2.59	23.5007	130.	-0.02	-0.01	0.02	-0.00

Methane Propane Mixtures

0.29538 CH₄ + 0.70462 C₃H₈

0.267	18.5132	105.	-0.12	-0.08		-0.08
0.404	18.3624	110.	-0.12	-0.09		-0.12

0.49637 CH₄ + 0.50363 C₃H₈

Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
0.379	20.4909	105.	-0.03	0.01		0.02
0.584	20.3046	110.	-0.03	0.01		-0.01
0.863	20.1180	115.	-0.02	0.01		-0.03
1.23	19.9311	120.	0.00	0.01		-0.04
1.700	19.7471	125.	0.04	0.03		-0.02
2.29	19.5546	130.	0.05	0.01		-0.03

0.74920 CH₄ + 0.25080 C₃H₈

0.472	23.4768	105.	-0.02	0.02	-0.11	0.02
0.728	23.2064	110.	-0.03	0.00	-0.13	-0.02
1.085	22.9364	115.	-0.02	-0.00	-0.13	-0.03
1.561	22.6665	120.	0.01	0.01	-0.12	-0.01
2.187	22.3818	125.	-0.01	-0.04	-0.16	-0.03
2.989	22.1019	130.	0.01	-0.05	-0.14	-0.01

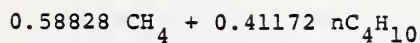
0.85796 CH₄ + 0.14204 C₃H₈

0.510	24.9622	105.	0.07	0.10	-0.02	0.09
0.791	24.6331	110.	0.06	0.08	-0.03	0.07
1.183	24.2941	115.	0.03	0.04	-0.08	0.03
1.70	23.9491	120.	-0.00	-0.00	-0.11	0.01
2.383	23.5941	125.	-0.05	-0.06	-0.19	-0.02
3.257	23.2461	130.	-0.04	-0.06	-0.19	0.01

Methane Normal Butane Mixtures

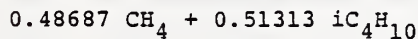
0.91674 CH₄ + 0.08326 nC₄H₁₀

.514	25.1536	105.	0.23	0.25	0.16	0.30
.799	24.7960	110.	0.15	0.16	0.09	0.16
1.200	24.4512	115.	0.15	0.14	0.08	0.10
1.730	24.0910	120.	0.11	0.08	0.04	0.00
2.440	23.7370	125.	0.12	0.08	0.05	-0.03
3.330	23.3789	130.	0.15	0.08	0.06	-0.04
4.450	23.0110	135.	0.17	0.08	0.09	-0.04
5.810	22.6391	140.	0.21	0.10	0.21	-0.02



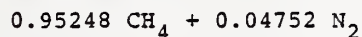
Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
1.615	18.6495	120.	0.00	0.00		0.09
2.251	18.4772	125.	-0.02	- .02		-0.05
2.251	18.4853	125.	0.03	0.03		-0.01
3.141	18.3058	130.	-0.03	-0.07		-0.19

Methane Isobutane Mixtures

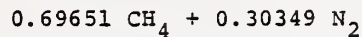


0.621	17.3575	110.	0.02	0.07		-0.02
0.926	17.2076	115.	-0.01	-0.00		-0.05
1.343	17.0639	120.	-0.01	-0.03		-0.03
1.828	16.9156	125.	-0.03	0.10		-0.03

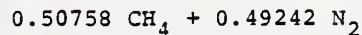
Methane-Nitrogen Mixtures



1.36	26.8476	105.	-0.03	-0.05	-0.06	-0.05
1.96	26.4052	110.	0.04	0.00	0.04	0.00
2.600	25.9374	115.	0.05	0.01	-0.07	0.02
3.45	25.4522	120.	0.06	failed	-0.02	0.03
4.54	24.9496	125.	0.07	failed	0.03	0.04
5.75	24.4210	130.	0.04	-5.69	0.02	0.03
7.20	23.8600	135.	-0.03	-4.00	0.01	-0.01
9.08	23.2809	140.	-0.07	-2.69		-0.02



3.40	26.8735	100.	-0.00	0.06		0.09
4.600	26.3393	105.	0.04	0.02		0.07
6.100	25.7686	110.	-0.00	-0.05		-0.02
7.91	25.1790	115.	-0.03	0.13		-0.08
9.980	24.5737	120.	-0.04	1.88		-0.07

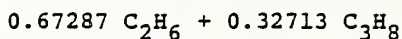


3.260	27.0801	95.	0.04	0.08		0.13
4.59	26.4588	100.	0.02	-0.05		0.04
6.29	25.8106	105.	-0.02	-0.18		-0.06
8.33	25.1387	110.	-0.05	- .21		-0.10

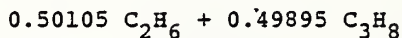
0.50758 CH₄ + 0.49242 N₂ (continued)

Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
10.83	24.4431	115.	-0.03	.24		-0.05
13.800	23.7096	120.	-0.03	3.37		0.07
17.08	22.9315	125.	-0.01	failed		0.25
20.820	22.1005	130.	0.08	-2.29		0.05

Ethane-Propane Mixtures

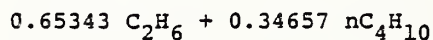


0.000	18.619	125.	0.00	0.02		-0.02
0.000	18.4646	130.	0.01	0.02		-0.00
0.000	18.3059	135.	0.00	0.01		0.00
0.000	18.1509	140.	0.02	0.01		0.05

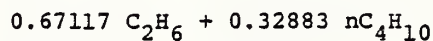


0.000	18.3618	105.	0.02	0.02		0.04
0.000	18.2169	110.	0.00	0.01		0.00
0.000	18.0726	115.	-0.01	-0.00		-0.02
0.000	17.9282	120.	-0.01	-0.01		-0.04
0.000	17.7880	125.	0.00	0.00		-0.03
0.000	17.6412	130.	-0.02	-0.02		-0.04
0.000	17.4988	135.	-0.01	-0.01		-0.01
0.000	17.3526	140.	-0.01	-0.03		0.00

Ethane Normal Butane Mixtures

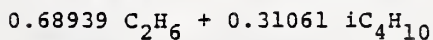


0.000	17.2184	115.	0.00	-0.00		0.00
0.000	17.0824	120.	-0.01	-0.02		-0.03

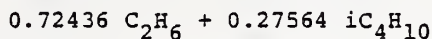


0.000	17.5047	110.	0.00	-0.00		0.01
0.000	17.3706	115.	0.00	0.01		-0.00
0.000	17.1031	125.	0.01	0.02		-0.01
0.000	16.9626	130.	-0.02	-0.01		-0.04
0.000	16.8285	135.	-0.01	-0.00		-0.01
0.000	16.6947	140.	0.01	0.00		0.03

Ethane Isobutane Mixtures



Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
0.000	17.3716	115.	-0.00	-0.01	-0.03	
0.000	17.2344	120.	-0.02	-0.03	-0.05	



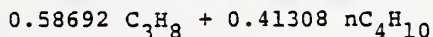
0.000	17.9779	105.	0.00	0.01	0.00
0.000	17.8401	110.	0.01	0.01	-0.01
0.000	17.4235	125.	0.01	0.01	-0.01
0.000	17.2825	130.	0.00	0.00	0.00

Ethane Nitrogen Mixtures

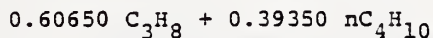


3.800	21.4718	105.	-0.03	-0.02	-0.01
4.57	21.2912	110.	0.03	0.03	0.03
5.400	21.0845	115.	-0.04	-0.01	-0.03
6.300	20.8998	120.	0.00	-0.72	0.02

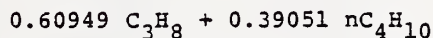
Propane Normal Butane Mixtures



0.000	14.6839	110.	0.01	0.02	0.04
0.000	14.1748	135.	-0.03	-0.03	-0.06
0.000	14.0786	140.	0.00	-0.00	-0.02



0.000	14.1343	140.	-0.00	-0.00	-0.02
0.000	14.0333	145.	-0.00	-0.00	-0.00
0.000	13.9345	150.	0.02	0.02	0.05



0.000	14.6487	115.	-0.01	-0.01	-0.02
0.000	14.5521	120.	0.02	0.02	-0.00

Propane Isobutane Mixtures
 0.49030 C₃H₈ + 0.50970 iC₄H₁₀

Pressure atm	Experimental		Corresponding States	% Deviation		Cell Model
	Density mol/l	Temperature K		Hard Sphere	Revised Klosek and McKinley	
0.000	14.3080	105.	-0.01	-0.01	-0.02	
0.000	14.2136	110.	-0.01	-0.01	-0.03	
0.000	14.1219	115.	0.02	0.02	-0.02	
0.000	14.0257	120.	0.01	0.01	-0.03	
0.000	13.9300	125.	0.00	0.00	-0.03	
0.000	13.8342	130.	-0.01	-0.01	-0.02	

0.50326 C₃H₈ + 0.49674 iC₄H₁₀

0.000	13.9718	125.	0.01	0.01	-0.02
0.000	13.8737	130.	-0.01	-0.01	-0.02

Propane Nitrogen Mixtures

0.93260 C₃H₈ + 0.06740 N₂

6.230	16.8055	100.	0.01	0.04	-0.08
8.680	16.7084	105.	0.18	0.20	0.05

0.96206 C₃H₈ + 0.03794 N₂

4.890	16.4638	105.	0.01	0.02	-0.06
6.620	16.3410	110.	-0.00	0.00	-0.10

0.97986 C₃H₈ + 0.02014 N₂

3.520	16.2131	110.	-0.01	-0.01	-0.07
4.650	16.0931	115.	-0.02	-0.02	-0.10

Normal Butane Isobutane Mixtures

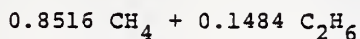
0.52961 nC₄H₁₀ + 0.47039 iC₄H₁₀

0.000	12.6943	125.	-0.01	-0.01	-0.02
0.000	12.6133	130.	0.01	0.01	-0.01
0.000	12.5271	135.	-0.01	-0.01	-0.04
0.000	12.4447	140.	0.00	0.00	-0.02

Comparison of Models to Rodosevich Data



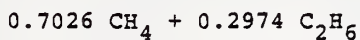
Density mol/l	Experimental		Corresponding States	% Deviation		Cell Model
	Temperature K			Hard Sphere	Revised Klosek and McKinley	
27.7678	91.09		-0.00	-0.04	0.01	-0.01
27.0621	100.01		-0.02	-0.06	0.01	-0.05
26.4026	108.08		-0.02	-0.06	0.02	-0.06
25.7573	115.60		-0.04	-0.07	0.02	-0.06



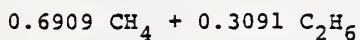
27.1003	91.01		-0.04	-0.09	-0.00	-0.01
26.4711	100.01		-0.01	-0.05	0.05	-0.01
25.8859	108.02		-0.05	-0.08	0.02	-0.06
25.3620	115.13		-0.02	-0.05	0.07	-0.03



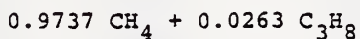
26.4131	91.13		-0.01	-0.05	0.03	0.05
25.8398	100.01		-0.05	-0.08	-0.02	-0.03
25.3235	108.01		-0.03	-0.06	0.01	-0.04



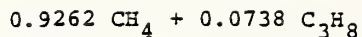
26.0647	91.00		-0.03	-0.07	-0.01	0.04
25.0144	108.00		-0.09	- .11	-0.06	-0.09
24.5712	115.00		-0.09	- .10	-0.05	-0.10



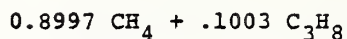
25.9997	91.00		0.03	-0.01	0.05	0.10
25.4466	100.00		-0.04	-0.06	-0.02	-0.01
24.9476	108.00		-0.08	-0.10	-0.05	-0.08
24.5104	115.00		-0.07	-0.09	-0.04	-0.09



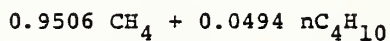
27.6870	90.99		-0.01	-0.02	-0.03	-0.01
26.9709	100.03		-0.01	-0.03	-0.03	-0.04
26.3352	107.87		-0.02	0.00	0.00	-0.02
25.7294	114.99		0.02	-0.00	0.01	-0.01



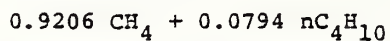
Density mol/l	Experimental		Corresponding States	% Deviation		Cell Model
	Temperature K			Hard Sphere	Revised Klosek and McKinley	
26.9121	91.01		0.01	0.03	-0.02	0.05
26.2667	100.06		0.02	0.03	-0.01	0.03
25.6819	108.01		0.03	0.03	-0.01	0.02
25.1553	114.97		0.04	0.04	0.01	0.04



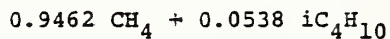
26.4774	91.02		-0.02	0.01	-0.06	0.04
25.8692	100.05		-0.01	0.02	-0.06	0.02
25.3165	108.01		0.01	0.02	-0.06	0.01
24.8207	114.98		0.03	0.04	-0.04	0.03



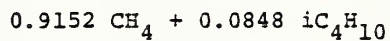
26.5731	95.00		0.03	0.04	0.00	0.13
26.2075	100.00		0.01	0.01	-0.01	0.06
25.6121	108.00		-0.01	-0.02	-0.03	-0.03
25.0771	115.00		-0.02	-0.04	-0.03	-0.09



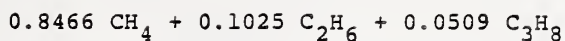
25.3126	103.00		-0.00	0.02	-0.07	0.09
24.9776	108.00		0.01	0.02	-0.06	0.04
24.4906	115.00		0.00	-0.01	-0.07	-0.05



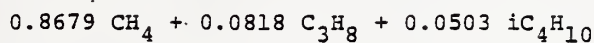
25.4233	108.00		-0.00	-0.01	-0.21	0.17
26.0010	100.00		-0.03	-0.01	-0.22	0.10
24.8843	115.00		-0.04	-0.08	-0.26	0.18



25.5931	95.00		0.03	0.09	-0.23	0.20
25.2653	100.00		0.03	0.07	-0.26	0.21
24.7274	108.00		0.02	0.02	-0.30	0.25
24.2436	115.00		0.01	-0.04	-0.34	0.30



Density mol/l	Experimental Temperature K	Corresponding States	% Deviation Hard Sphere	Revised Klosek and McKinley	Cell Model
25.9821	100.01	-0.02	-0.03	-0.03	-0.00
25.4311	108.01	-0.02	-0.03	-0.03	-0.02
25.4278	108.02	-0.03	-0.04	-0.04	-0.03
24.9401	115.00	-0.01	-0.01	-0.01	-0.01



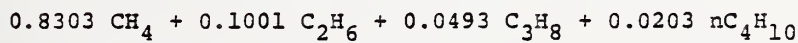
24.9240	100.00	-0.01	0.04	-0.19	0.12
24.4194	108.00	-0.02	0.00	-0.22	0.12
23.9670	115.00	-0.02	-0.03	-0.25	0.14



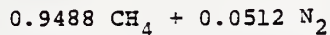
27.3493	91.00	-0.06	-0.03	0.10	0.07
25.4706	115.00	-0.06	-0.11	0.03	0.01
26.0417	108.00	-0.04	-0.07	0.02	0.02
26.6667	100.00	-0.05	-0.06	0.10	0.03



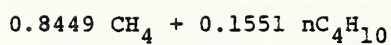
27.2725	91.00	-0.03	0.03	0.03	0.09
25.9410	108.00	-0.01	-0.01	-0.09	0.06



25.5434	100.00	-0.02	-0.00	-0.05	0.03
25.0313	108.00	0.02	0.03	-0.01	0.03
24.5507	115.00	-0.03	-0.02	-0.06	-0.04

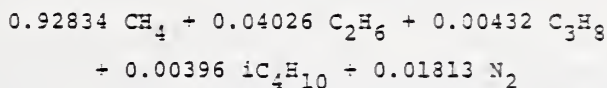


28.0702	91.00	-0.03	0.01	-0.08	0.02
27.2896	99.99	-0.03	-0.02	-0.04	-0.02
26.5717	108.01	0.01	-0.02	-0.03	-0.02
25.9282	114.98	0.06	0.01	-0.12	0.02

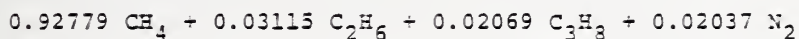


<u>Experimental</u> Density mol/l	<u>Temperature</u> K	Corresponding States	<u>% Deviation</u> Hard Sphere	Revised Klosek and McKinley	Cell Model
27.9666	91.058	-0.02	0.12		0.16
27.0973	100.35	-0.01	0.04		0.06
26.3387	108.13	-0.00	-0.03		0.01
25.6469	115.05	0.06	0.04		0.03

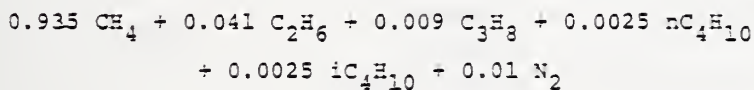
Comparison of Models for Typical LNG Compositions.
 Corresponding States Model Was Taken as a Reference



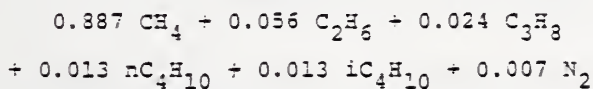
Density from Corresponding States Method, mol/l	Temperature K	Hard Sphere	$\frac{1}{3}$ Difference Revised Klosek and McKinley	Cell Model
27.2677	95	0.00	0.03	0.03
26.8737	100	-0.01	0.04	0.02
26.4716	105	-0.02	0.02	0.01



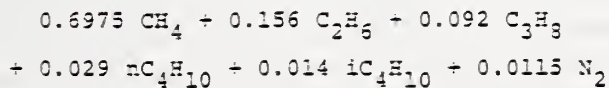
26.4540	105	-0.01	0.03	0.01
26.8562	100	-0.00	0.04	0.01
27.2504	95	0.01	0.04	0.03



27.252	95	-0.01	0.02	0.02
26.8616	100	-0.02	0.03	0.00
26.4632	105	-0.02	0.02	-0.00



25.6800	105	0.01	-0.04	0.05
26.0342	100	0.02	-0.03	0.06
26.3821	95	0.03	-0.03	0.08



24.3315	95	0.03	-0.05	0.15
24.0648	100	0.07	-0.05	0.11
23.7942	105	0.07	-0.03	0.08

Appendix B. Program Listing for the Extended Corresponding States Model

The program listing that follows is for the extended corresponding states method described in section 2. To use the program in its present form one must make one of the two possible calls to SUBROUTINE PDMIX(P,D,T,X). The two possible calls are

```
CALL PDMIX(P,D,T,X)
```

or

```
CALL PMIX(P,D,T,X)
```

When the call to PDMIX(P,D,T,X) is made the input variables are: P (pressure in atmospheres); T (temperature in degrees kelvin); and X which is a matrix of the mole fraction of the components of the mixture in the following order

```
X(1) = mole fraction of methane
X(2) = mole fraction of ethane
X(3) = mole fraction of propane
X(4) = mole fraction of normal butane
X(5) = mole fraction of isobutane
X(6) = mole fraction of nitrogen
X(7) = mole fraction of normal pentane
X(8) = mole fraction of isopentane
```

No other components are allowed and if one or more of the above components are absent, a zero should be inserted in the appropriate matrix element. The program then calculates a density and it is returned in the argument list as D (density in moles/liter).

When a call to PMIX(P,D,T,X) is made all of the above are the same except that the roles of P and D are interchanged, i.e., D is an input variable and P is calculated by the program.

The range of the program is 90 to 150 kelvin for the saturated liquid phase of any of the pure components of CH₄, C₂H₆, C₃H₈, nC₄H₁₀, iC₄H₁₀, N₂, nC₄H₁₂ or iC₄H₁₂ or any mixture of those fluids. The program will extrapolate to higher pressures (higher than saturation pressure) but the user is reminded that such a calculation is an extrapolation and should be used with caution.

```

SUBROUTINE PDMIX(P,D,T,X)
FOR A CALL TO PDMIX, P,T AND X ARE INPUT. P IS IN ATM,T IS IN
KELVIN AND D IS OUTPUT IN THE UNITS OF MOLES/LITER
FOR A CALL TO P MIX, D,T AND X ARE INPUT AND P IS OUTPUT, THE
UNITS ARE THE SAME
THE X MATRIX MUST CONTAIN THE MOL FRACTION OF THE ALLOWABLE FLUIDS
IN THE FOLLOWING ORDER, 1=C1,2=C2, 3=C3,4=NC4,5=IC4,6=N2
PLACE A ZERO IN THE ELEMENTS OF X WHERE THAT PARTICULAR GAS IS NOT
PRESENT
DIMENSION ZATA(10,10),ATA(10,10),TC(10),VC(10),ZC(10),AC(10),W(10)
1,PC(10),CF(9)
DIMENSION THETA(10,10),TH(10,10),PHI(10,10),PH(10,10),F(10,10),FH
1(10,10),H(10,10),HH(10,10),VR(10,10),TR(10,10),X(10)
COMMON/DATA M/ZATA,ATA,TC,VC,W,TCO,VCO,ACO,ZCO,RR,R,OMEGA,AC,ZC,N
1,PC,CF
DATA(IE=0)
D=0.0
GO TO 4
ENTRY PMIX
P=0.0
IP=1
GO TO 5
4 IP=0
5 CONTINUE
IF(IE.GT.0)GO TO 6
IE=1
CALL DATA CH4
IBASE=L=1
CALL MIX DATA(IBASE)
6 CONTINUE
DO 1 I=1,N
F(I,I)=H(I,I)=1.
THETA(I,I)=1.
1 PHI(I,I)=1.
DO 30 J=1,30
HX=FXHX=0.0
DO 10 I=1,N
FH(I,I)=F(I,I)
HH(I,I)=H(I,I)
IF(X(I).LT..0001)GO T O 10
F(I,I)=(TC(I)/TC(L))*THETA(I,I)
H(I,I)=(VC(I)/VC(L))*PHI(I,I)
10 CONTINUE
DO 11 IA=1,N
DO 11 IB=1,N
IF(X(IA).LT..0001)GO TO 11
IF(X(IB).LT..0001)GO TO 11
FAB=ZATA(IA,IB)*(F(IA,IA)* F(IB,IB))**.5
HAB=ATA(IA,IB)*(.5*H(IA,IA)**(1./3.)+.5*H(IB,IB)**(1./3.))**.3
HX=HX+X(IA)*X(IB)*HAB
FXHX=FXHX+X(IA)*X(IB)*HAB*FAB
11 CONTINUE
FX=FXHX/HX
PRO=P*HX/FX
TRO=T/FX
DEN=D*HX
IF(IP.EQ.1)GO TO 8
DD=SATL(TRO)*1000.+1.
9 DEN=FIND M(PRO,TRO,DD)
8 CONTINUE
IF(DEN.LE.0.0) GO TO 33
VRO=1000./DEN

```



```

DO 12 I=1,N
IF(X(I).LT..0001)GO TO 12
VR(I,I)=VRO*PHI(I,I)/VCO
TR(I,I)=TRO*THETA(I,I)/TCO
IF(VR(I,I).GT.2.)VR(I,I)=2.
IF(VR(I,I).LT..5)VR(I,I)=.5
TH(I,I)=THETA(I,I)
THETA(I,I)=1.*(AC(I)-OMEGO)*(CF(1)-CF(2)*ALOG(TR(I,I))+(CF(3)-CF(4)
1)/TR(I,I))*(VR(I,I)-CF(5))
PH(I,I)=PHI(I,I)
PHI(I,I)=(1.*(AC(I)-OMEGO)*(CF(6)*(VR(I,I)-CF(7))-CF(8)*(VR(I,I)
1-CF(9))*ALOG(TR(I,I))))*ZCO/ZC(I)
12 CONTINUE
DO 13 I=1,N
IF(X(I).LT..0001)GO TO 13
IF(ABS((FH(I,I)-F(I,I))/F(I,I)).GT..001)GO TO 30
IF(ABS((HH(I,I)-H(I,I))/H(I,I)).GT..001)GO TO 30
IF(ABS((TH(I,I)-THETA(I,I))/THETA(I,I)).GT..001)GO TO 30
IF(ABS((PH(I,I)-PHI(I,I))/PHI(I,I)).GT..001)GO TO 30
13 CONTINUE
GO TO 31
30 CONTINUE
33 PRINT 100,P,DEN,T
100 FORMAT(* ITERATION FAILED AT*,3F10.4)
STOP
31 D=OEN/HX
THC=THETA(6,6)
IF(IP.EQ.0)GO TO 32
CALL PRESS(P,DEN,TRO)
P=P*FX/HX
32 RETURN
END

```

```

SUBROUTINE MIX DATA(IBASE)
DIMENSION ZATA(10,10),ATA(10,10),TC(10),VC(10),ZC(10),AC(10),W(10)
1,PC(10),CF(9)
COMMON/DATA M/ZATA,ATA,TC,VC,W,TCO,VCO,ACO,ZCO,RR,R,OMEGO,AC,ZC,N
1,PC,CF
DATA(PC=45.35647,96757,41.89008,37.79462,36.40758,33.10393)
DATA(TC=190.555,305.5,370.425,408.1,126.2)
DATA(W=16.04303,30.07012,44.09721,58.1243,58.1243,28.0134)
DATA(VC=98.522,146.2,200.251,62,263.00,89.827)
DATA(AC=.0109,.110427,.154837,.176372,.150115,.0291791)
DATA(R=82.05606),(RR=8.3144),(N=6)
DATA(CF=-.109495,.919454,-4.01525,-4.14192,.444850,.356808,
11.02619,.893323,.761533)
DATA(ATA(1,2)=1.00514),(ATA(1,3)=1.01922),(ATA(1,4)=1.04454),
1(ATA(1,5)=1.04931),(ATA(1,6)=1.01009),
A(ATA(2,3)=1.00599),(ATA(2,4)=1.01616),
2(ATA(2,5)=1.02369),(ATA(2,6)=1.02127),(ATA(3,4)=1.00172),
3(ATA(3,5)=1.01140),(ATA(3,6)=1.04606),(ATA(4,5)=.997114),
4(ATA(4,6)=1.13889),(ATA(5,6)=1.13889)
DATA(ZATA(1,2)=1.01127),(ZATA(1,3)=.988608),(ZATA(1,4)=.987281),
1(ZATA(1,5)=.979315),(ZATA(1,6)=.953430),(ZATA(2,3)=.999951),
2(ZATA(2,4)=.972223),(ZATA(2,5)=.998886),(ZATA(2,6)=.939622),
3(ZATA(3,4)=.985547),(ZATA(3,5)=1.03099),(ZATA(3,6)=.912209),
4(ZATA(4,5)=.976416),(ZATA(4,6)=.857310),(ZATA(5,6)=.857310)
L=IBASE
N=9
NI=N-1

```



```
PC(7)=33.37
PC(8)=31.57
TC(7)=469.6
TC(8)=460.39
VC(7)=304.
VC(8)=306.
W(7)=72.15139
W(8)=72.15139
AC(7)=.234320
AC(8)=.288886
ATA(1,7)=ATA(1,8)=1.04
ATA(2,7)=ATA(2,8)=1.02
ATA(3,7)=ATA(3,8)=1.01
ATA(4,7)=ATA(4,8)=1.
ATA(5,7)=ATA(5,8)=1.
ATA(6,7)=ATA(6,8)=1.
ATA(7,8)=1.
ZATA(1,7)=ZATA(1,8)=.95
ZATA(2,7)=ZATA(2,8)=.99
ZATA(3,7)=ZATA(3,8)=.99
ZATA(4,7)=ZATA(4,8)=.99
ZATA(5,7)=ZATA(5,8)=.99
ZATA(6,7)=ZATA(6,8)=.99
ZATA(7,8)=1.
DO 3 J=1,N1
  JI=J+1
  DO 3 K=J1,N
    ZATA(K,J)=ZATA(J,K)
  3 ATA(K,J)=ATA(J,K)
  DO 4 I=1,N
    4 ATA(I,I)=ZATA(I,I)=1.
  PCO=PC(L)
  VCO=VC(L)
  TCO=TC(L)
  OMEGO=AC(L)
  ZCO=PCO*VCO/TCO/R
  DO 5 I=1,N
    5 ZC(I)=PC(I)*VC(I)/TC(I)/R
  RETURN
END
```

SUBROUTINE PROPS(PP,DD,TT)

DIMENSION X(33)

DIMENSION B(33),G(32)

EQUIVALENCE (B,X)

COMMON/DATA/G,R,GAMMA

DATA(ID=1)

DATA(IZ=1)

1 CONTINUE

D=DD

P=PP

T=TT

GM=GAMMA

D2=D*D

D3=D2*D

D4=D3*D

D5=D4*D

D6=D5*D

D7=D6*D

D8=D7*D

D9=D8*D

D10=D9*D

D11=D10*D

D12=D11*D

D13=D12*D

TS=SQRT (T)

T2=T*T

T3=T2*T

T4=T3*T

T5=T4*T

F=EXP (GM*D2)

GO TO (100,200),K

ENTRY PRESS

K=1

GO TO 1

100 CONTINUE

B(1)=D2*T

B(2)=D2*TS

B(3)=D2

B(4)=D2/T

B(5)=D2/T2

B(6)=D3*T

B(7)=D3

B(8)=D3/T

B(9)=D3/T2

B(10)=D4*T

B(11)=D4

B(12)=D4/T

B(13)=D5

B(14)=D6/T

B(15)=D6/T2

B(16)=D7/T

B(17)=D8/T

B(18)=D8/T2

B(19)=D9/T2

B(20)=D3*F/T2

B(21)=D3*F/T3

B(22)=D5*F/T2

B(23)=05*F/T4
B(24)=07*F/T2
B(25)=07*F/T3
B(26)=09*F/T2
B(27)=09*F/T4
B(28)=011*F/T2
B(29)=011*F/T3
B(30)=013*F/T2
B(31)=013*F/T3
B(32)=013*F/T4

102 P=0

00 101 I=1,32

101 P=P+B(I)*G(I)

P=P+R*0*T

PP=P

RETURN

ENTRY OP00

K=2

GO TO 1

200 CONTINUE

F1=2.00*F*GM*D

F21=3.000*F*D2 +F1*D3

F22=5.000*F*D4 +F1*D5

F23=7.000*F*D6 +F1*D7

F24=9.000*F*D8 +F1*D9

F25=11.00*F*D10+F1*D11

F26=13.00*F*D12+F1*D13

B(1)=2.00*0*T

B(2)=2.00*0*TS

B(3)=2.00*0

B(4)=2.00*0/T

B(5)=2.00*0/T2

B(6)=3.00*02*T

B(7)=3.00*02

B(8)=3.00*02/T

B(9)=3.00*02/T2

B(10)=4.00*03*T

B(11)=4.00*03

B(12)=4.00*03/T

B(13)=5.00*04

B(14)=6.00*05/T

B(15)=6.00*05/T2

B(16)=7.00*06/T

B(17)=8.00*07/T

B(18)=8.00*07/T2

B(19)=9.00*08/T2

B(20)=F21/T2

B(21)=F21/T3

B(22)=F22/T2

B(23)=F22/T4

B(24)=F23/T2

B(25)=F23/T3

B(26)=F24/T2

B(27)=F24/T4

B(28)=F25/T2

B(29)=F25/T3

B(30)=F26/T2

```
B(31)=F26/T3
B(32)=F26/T4
202 P=Q
DO 201 I=1,32
201 P=P+B(I)*G(I)
P=P+R*T
PP=P
RETURN
END
```

SUBROUTINE DATA CH4

```
DIMENSION G(32),VP(9),GI(11)
COMMON/DATA/G,R,GAMMA,VP,DTP
DIMENSION A(10)
COMMON/SATC/A
R=.08205616
GAMMA=-.0096
A(1)=190.555
A(2)=10.23
A(3)=18.404156472
A(4)=7.3498921512
A(5)=-1.4313160833
A(6)=A(7)=0.0
G( 1)=-.187027997685E-01
G( 2)= .103387118009E+01
G( 3)=-.155387625619E+02
G( 4)= .772311478564E+03
G( 5)=-.377103300895E+05
G( 6)= .846818843475E-03
G( 7)=-.496415884529E+00
G( 8)= .869909352414E+02
G( 9)=-.322821592493E+05
G(10)=-.395843026318E-04
G(11)= .266772318035E-01
G(12)=-.304010057839E+01
G(13)= .191584507536E-03
G(14)=-.195587933458E-03
G(15)= .607479967879E+01
G(16)=-.529609525984E-03
G(17)= .152264286004E-04
G(18)=-.109952182842E-01
G(19)= .191395549929E-03
G(20)= .386470003746E+05
G(21)=-.157930582612E+07
G(22)= .195270144401E+03
G(23)= .165996081629E+07
G(24)= .603051146711E+00
G(25)= .376485162808E+02
G(26)= .125593680622E-02
G(27)=-.343570032513E+02
G(28)=-.540945094139E-05
G(29)= .185622284663E-02
G(30)= .770786979245E-03
G(31)=-.286868318650E-05
G(32)= .372376961647E-04
END
```

```

FUNCTION SATL(T)
DIMENSION A(10)
COMMON/SATC/A
IF(T.GT.A(1))GO TO 1
X=(1.-T/A(1))
SATL=A(2)+A(3)*X**(.35)+A(4)*X+A(5)*X**(.4./3.)+A(6)*X**(.5./3.
1)+A(7)*X**2
SATL=SATL/1000.
RETURN
1 SATL=1.E20
RETURN
END

```

```

FUNCTION FIND M(P,T,0)
DD=0
TT=T
DO 10 I=1,50
CALL PRESS(PP,DD,TT)
P2=PP
IF(ABS (P-P2)-1.E-7*P) 20,20,1
1 CALL CPDD(PP,DD,TT)
DP=PP
CORR=(P2-P)/DP
IF(ABS (CORR)-1.E-7*00) 20,20,10
10 DD=DD-CORR
FIND M=0
RETURN
20 FIND M=DD
RETURN
END

```

Appendix C. Program Listing for the Hard Sphere Model

The program listing that follows is for the hard sphere model described in section 3. To use the program in its present form one must make the following reference to the computer program

$$\text{DEN} = \text{RODEN}(\text{P}, \text{T}, \text{X})$$

where DEN is density in moles/liter, P is pressure in atmospheres, T is temperature in degrees kelvin, and X is a matrix of the mole fractions of the components of the mixture in the following order

- X(1) = mole fraction of methane
- X(2) = mole fraction of ethane
- X(3) = mole fraction of propane
- X(4) = mole fraction of normal butane
- X(5) = mole fraction of isobutane
- X(6) = mole fraction of nitrogen
- X(7) = mole fraction of isopentane
- X(8) = mole fraction of methylpentane

Note: The inclusion of the pentanes is due to Rodosevich and Miller (1975) and no checking or optimization of parameter has been included in this work for mixtures with pentane as a component.

The range of the program is 90 to 150 kelvin for the saturated liquid phase of mixtures of CH_4 , C_2H_6 , C_3H_8 , $i\text{C}_4\text{H}_{10}$, $n\text{C}_4\text{H}_{10}$ and N_2 . The program will calculate densities of any of the pure components but they will be from a different model (i.e., some from an equation of state (CH_4 and N_2) and some from the equations for saturated liquid densities. Therefore in its present form, extrapolation to higher pressures is possible but the reliability of the results is questionable.

FUNCTION RODEN(P,T,X)

DIMENSION X(10)

CALL FM(P,T,X,V,G)

D=28.

V=V+V ICEL(P,C,T,X)

RODEN=1000./V

RETURN

END

SUBROUTINE FM(Q,T,X,V9,G9)

PREDICTION OF EXCESS PROPERTIES WITH LHM POTENTIAL, COMP 1-METH

ANE,COMP 2-ETHANE,COMP 3-PROPANE,COMP 4 N-BUTANE,COMP 5-I-BUT

ANE, COMP 6-NITROGEN, COMP 7-ISOPENTANE,COMP 8-METHYLPENTANE

ADV CRYO ENGR. VOL. 19 (1973)-REPROGRAMED BY R. MCCARTY,2/22/74

ARGUMENTS ARE X-MOLE FRACTIONS,T-TEMPERATURE,Q-PRESSURE,V9-EXCESS

VOLUME,G9-EXCESS GIBBS ENERGY, FIRST THREE ARE INPUT, LAST TWO ARE

OUTPUT, INPUT IS IN KELVINS AND ATM,

DIMENSION A(8),B(8) ,S(8),V(8),G(8),C(8,8),D(8,8),K(3,8),

1J(8,8),E(8),Y(8),O(8),X(10)

TYPE REAL J,K,N1

DATA(KEY=1)

DATA(J(1,2)=-.00388616),(J(1,3)=-.0120932),(J(1,4)=-.0180737),

A(J(1,5)=-.0181962),(J(1,6)=-.00997547),(J(1,7)=-.0326),(J(1,8)=

B=-.0458),(J(2,4)=-.00400910),(J(2,5)=-.00812712),(J(2,6)=-.0143976)

C,(J(2,7)=-.003),(J(2,8)=-.004),(J(3,4)=+.0007615710),(J(3,5)=-.003

083743),(J(3,6)=-.024014),(J(3,7)=0.0),(J(3,8)=0.0),(J(4,5)=.002221

E50),(J(4,7)=.0),(J(4,8)=.0),(J(5,6)=-.0576043),(J(4,6)=-.0576043),

F(J(5,7)=.0),(J(5,8)=0.0),(J(6,7)=-.04),(J(5,8)=-.05),(J(7,8)=.0)

G ,(J(2,3)=-.002162)

DATA(K(1,2)=.00298830),(K(1,3)=.0597378),(K(1,4)=.1189470),(

AK(1,5)=.116009),(K(1,6)=.0197290),(K(1,7)=.14),(K(1,8)=.1745),

B(K(2,4)=.0677703),(K(2,5)=.0346632),(K(2,6)=.0529034),(K(2,7)=

C.02),(K(2,8)=.03),(K(3,4)=.0249291),(K(3,5)=-.00838212),(K(4,5)=.0

D199213),(K(4,6)=.154365),(K(4,7)=.0),(K(4,8)=.0),(K(5,6)=.154365)

E,(K(5,7)=.0),(K(5,8)=.0),(K(6,7)=.15),(K(6,8)=.18),(K(7,3)=0.0)

F,(K(2,3)=.014527),(K(3,6)=.14719),(K(3,7)=0.0),(K(3,8)=0.0)

DATA(S=3.676E-8,4.158E-8,4.644E-8,5.051E-8,5.056E-8,3.546E-8,

15.389E-8,5.706E-8)

DATA(A=2.755E+5,7.773E+5,14.165E+5,22.733E+5,21.279E+5,1.718E+5,

130.550E+5,42.946E+5)

DATA(O=1.,1.5,1.67,1.83,1.79,1.03,1.91,2.11)

THESE ARE THE ACENTRICITY FACTORS (FOR MOLECULAR SHAPES, ETC.) *****

DATA(Y=35.,45.,60.,75.,75.,40.,90.,105.)

DATA(P1=3.14159),(N1=6.025E+23),(R=8.3143)

IF(KEY.EQ.0)GO TO 1

KEY=0

DO 2 I=1,8

J(I,I)=0.0

K(I,I)=0.0

DO 2 M=I,8

J(M,I)=J(I,M)

2 K(M,I)=K(I,M)

1 CONTINUE

P=Q*.101325

IW=8

DO 10 I=1,IW

10 E(I)=0(I)

DO 15 I=1,IW

15 B(I)=(2./3.)*P1*N1*S(I)**3

DO 20 I=1,IW

DO 20 M=1,IW

O(I,M) = ((B(I)**(1./3.) + B(M) ** (1./3.)) / 2.) + (1. - J(I,M)))

1 **3

20 C(I , M) = (1. - K(I , M)) * (A(I) * A(M)) ** (1. / 2.) *

1(D(I , M) **2 / (B(I) * B(M))) ** (1./2.)

```

A2=0 $ B2=0
E2=0 $ V2=0
DO 25 I=1,IW
V2=V2+X(I)*Y(I)
DO 25 M=1,IW
E2=E2+X(I)*X(M)*(E(I)+E(M))/2.
A2 = A2 + X(I) * X(M) * C( I, M )
25 B2=B2+X(I)*X(M)*D(I,M)
V6=V2
DO 30 I = 1, IW
A3 = A(I)
B3 = B(I)
E3 = E(I)
V2 = Y(I)
V1 = FIND V1( A3, B3, E3, R, V2, P, T )
G1 = FIND G1( A3, B3, E3, R, V2, P, T )
V(I) = V1
30 G(I) = G1
A3=A2
B3=B2
E3=E2
V2=V6
V1=FIND V1(A3,B3,E3,R,V2,P,T)
G1=FIND G1(A3,B3,E3,R,V2,P,T)
V7=V1
G7=G1
EXCEAS VOLUME AND GIBS ENERGY
V9=0
G9=0
DO 35 I=1,IW
V9=V9-X(I)*V(I)
35 G9=G9-X(I)*G(I)
W9 = -V9
H9 = -G9
V9=V9+V7
G9=G9+G7
VIWW=V(IWW)
RETURN
END

```

FUNCTION FIND V1(A3, B3, E3,R, V2, P, T)
A2 IS THE CONSTANT A, B2 IS THE CONSTANT B, E3 IS THE ACENTRICITY FACTOR.

```

INDEX = 0
1 V1 = V2
X1 = B3 / ( 4. * V1 )
F2 = (( 1. + X1 + X1**2) / ( 1. - X1)**3) * E3 -A3 / ( V1 * R * T )
1- (P * V1) / ( R*T)
F3 = A3 / (R*T*V1**2) - P/ (R*T)
F3 = F3 - ((( X1 + 2.* X1**2) * ( 1 - X1) + 3* ( 1. + X1 + X1**2)
1* X1) / (( 1. - X1 )**4 * V1)) * E3
V2 = V1 - F2/ F3
IF( ABS( (V2 - V1) / V2) .LT. .00001 ) GO TO 2
INDEX = INDEX + 1
IF( INDEX .LT. 250 ) GO TO 1
FLAG = ABS( (V2 - V1) / V2 )
5 FORMAT(28H0 ABS( (V2 - V1) / V2 ) = 1F10.5 )
2 V1 = V2
FIND V1 = V2
RETURN
END

```

```

FUNCTION FIND G1( A3, B3, E3,R, V2, P, T )
V1 = V2
X1 = B3 / ( 4. * V1 )
G1 =ALOG( 1. / ( 1. - X1 ) ) +(3. *X1) / ( 1. - X1 ) + ( 3. * X1**2)
1 / (2. * ( 1. - X1 )**2)
G1 = G1 - A3 / ( E3 * R * T*V1 ) + ( P * V1 ) / ( E3 * R * T ) -1.0
1 - ALOG( V1 )
G1 = R * T * E3 * G1
FIND G1 = G1
RETURN
END

```

```

FUNCTION EXCESS(P,DD,T,X)
DIMENSION X(10),F(10)
KR=0
GC TO 1
ENTRY V IDEL
KF=1
1 CONTINUE
CALL ZERO(F)
IF(X(1).LE..000001)GO TO 2
CALL DATA CH4
IF(T.GT.190.555)GO TO 12
PM=VPM(T)+.00001
DELP=P-PM
D=SAT(T,1)
CALL DPDD(OP,D,T)
D.FD=DELP/DP
D=DELD+D
F(1)=X(1)*1000./D
GO TO 2
12 D=FINO M(P,T,DD)
IF(D.LE.0.0)D=1000.
F(1)=X(1)*1000./D
2 IF(X(2).LE. .000001)GO TO 3
F(2)=X(2)*1000./SAT(T,2)
3 IF(X(3).LE..000001)GO TO 4
F(3)=X(3)*1000./SAT(T,3)
4 IF(X(4).LE..000001)GO TO 5
F(4)=X(4)*1000./SAT(T,4)
5 IF(X(5).LE..000001)GO TO 6
F(5)=X(5)*1000./SAT(T,5)
6 IF(X(6).LE..000001)GO TO 8
CALL DATA N2
IF(T.GT.126.6)GO TO 7
PN=VPM(T)+.000001
DELP=P-PM
D=SAT(T,6)
CALL DPCD(OP,D,T)
F(6)=X(6)*1000./D+DELP/DP)
GO TO 8
7 D=FINO M(P,T,DD)
IF(D.LE.0.0)D=1000.
F(6)=X(6)*1000./D
8 V=1000./OD
V:=0
D( 21 I=1,6
21 VS=VS+F(I)
EXCESS=V-VS
IF(KR.GT.0)EXCESS=VS
CALL DATA CH4
RETURN
END

```

PROGRAM DATA 42
COMMON/DATA/G,R,GAMMA,VP,OTP
DIMENSION G(32),VP(9)
R=3.205390-2
GAMMA=.3256

G(1)= 0.136224769272827E-02
G(2)= 0.107332463998591E-00
G(3)= -0.243901721871413E 01
G(4)= 0.341397449376470E 02
G(5)= -0.4223743094666167E 04
G(6)= 0.195390600246494E-03
G(7)= -0.112594826522081E-01
G(8)= 0.142600799270907E-03
G(9)= 0.194998501609007E 05
G(10)= 0.811140002503776E-07
G(11)= 0.233011645038006E-02
G(12)= -0.517752536351386E-03
G(13)= 0.485327881931214E-04
G(14)= -0.113556764119364E-22
G(15)= -0.707430273540575E 00
G(16)= 0.751727643352620E-24
G(17)= -0.111614119537424E-05
G(18)= 0.353736562237495E-03
G(19)= -0.201317691347729E-05
G(20)= -0.199717444795349E 05
G(21)= -0.119719240044192E 06
G(22)= -0.975213272033201E 02
G(23)= 0.554630713151823E 05
G(24)= -0.179920450443470E 00
G(25)= -0.256582926077184E 01
G(26)= -0.413707715090789E-03
G(27)= -0.256245415300293E 00
G(28)= -0.124222373740063E-06
G(29)= 0.103556535840165E-04
G(30)= -0.535699166553303E-09
G(31)= -0.757415412839596E-08
G(32)= 0.545367177019521E-07

VP(1)=5.1113192394 \$ VP(2)=6.482667539E-1
VP(3)=-1.5103739915E-1 \$ VP(4)=7.4328493342E-1
VP(5)=1.5 \$ VP(6)=.123 \$ VP(7)=63.15 \$ VP(8)=126.26
VP(9)=3.0
OTP=31.0
RETURN \$ END

```

SUBROUTINE DATA CH4
DIMENSION G(32),VP(3)
COMMON/DATA/G,P,GAMMA,VP,DTP
P=.33205615
GAMMA=-.0095

```

```

G( 1)= .117127997385E+01
G( 2)= .107387106309E+01
G( 3)= -.155337525619E+02
G( 4)= .772314473564E+03
G( 5)= -.377133394395E+05
G( 6)= .346818343475E-03
G( 7)= -.438415384929E+00
G( 8)= .369909352414E+02
G( 9)= .322321592493E+05
G(10)= -.795843026318E-04
G(11)= .256772313935E+01
G(12)= -.304010167339E+01
G(13)= .131536367536E+05
G(14)= -.125547933453E-03
G(15)= .897479927379E+01
G(16)= -.529609525984E-03
G(17)= .152264236934E-05
G(18)= -.109952132842E-01
G(19)= .132339549323E+05
G(20)= .33647003746E+05
G(21)= -.157335232612E-07
G(22)= .195270144401E+03
G(23)= .155936301620E+03
G(24)= .603051446711E+00
G(25)= .374482153335E+02
G(26)= .125593680622E-02
G(27)= -.347571232613E+02
G(28)= -.540945094139E-05
G(29)= .145622284663E+02
G(30)= .770735379245E-03
G(31)= .236463914853E-03
G(32)= .372376361647E-04
VP(1)=1.77743333
VP(2)=1.75065363
VP(3)=1.56733333
VP(4)=1.32706231
VP(5)=1.5
VP(6)=.1153993
VP(7)=93.63
VP(8)=100.555
VP(9)=3.3

```

```

RETURN
END

```

```

SUBROUTINE CPDD (P,DD,IT)

```

```

DD=0

```

```

DO 10 I=1,50

```

```

CALL CPDD(P,DD,IT)

```

```

P2=PP

```

```

PP=(P-PP)*1.E-10/20./20./

```

```

1 CALL CPDD(PP,DD,IT)

```

```

PP=PP

```

```

CPP=(P2-PP)/PP

```

```

PP=(PP*(1+CPP)-1.E-10)/20./20./

```

```

17 DD=DD-CPP

```

```

PP=PP

```

```

RETURN

```


22 FIND M=30

RETURN

END

SUBROUTINE= PPOPS(PP,DD,TT)

DIMENSION X(33)

DIMENSION B(33),G(32)

EQUIVALENCE (B,X)

COMMON/DATA/G,R,GAMMA

1 CONTINUE

B=DD

P=PP

T=TT

GM=GAMMA

B2=B*0

B3=B2*0

B4=B3*0

B5=B4*0

B6=B5*0

B7=B6*0

B8=B7*0

B9=B8*0

B10=B9*0

B11=B10*0

B12=B11*0

B13=B12*0

T0=S0*T (T)

T2=T*T

T3=T2*T

T4=T3*T

T5=T4*T

F=EXP (GM*02)

GO TO (100,200),K

ENTRY PPOPS

K=1

GO TO 1

100 CONTINUE

B(1)=02*T

B(2)=02*T2

B(3)=02

B(4)=02/T

B(5)=02/T2

B(6)=03*T

B(7)=03

B(8)=03/T

B(9)=03/T2

B(10)=04

B(11)=04

B(12)=04/T

B(13)=05

B(14)=05/T

B(15)=06/T2

B(16)=07/T

B(17)=08/T

B(18)=07/T2

B(19)=09/T2

B(20)=07*F/T2

B(21)=07*F/T3

B(22)=05*F/T2

B(23)=05*F/T4

B(24)=07*F/T2


```

B(25)=07*F/T3
B(26)=09*F/T2
B(27)=09*F/T4
B(28)=011*F/T2
B(29)=011*F/T3
B(30)=013*F/T2
B(31)=013*F/T3
B(32)=013*F/T4
P=0
09 101 I=1, T2
101 P=P+B(I)*G(I)
P=P+B*G/T
PP=0
DEFUN
ENTRY OPDO
K=2
GO TO 1
200 CONTINUE
F1=2.00*F*GM*D
F21=7.000*F*02 +F1*03
F22=5.000*F*04 +F1*05
F23=7.000*F*06 +F1*07
F24=9.000*F*08 +F1*09
F25=11.000*F*10 +F1*11
F26=13.000*F*12 +F1*13
B( 1)=2.00*02/T
B( 2)=2.00*03*TS
B( 3)=2.00*04
B( 4)=2.00*05/T
B( 5)=2.00*06/T2
B( 6)=3.00*02*T
B( 7)=3.00*03
B( 8)=3.00*02/T
B( 9)=3.00*03/T2
B(10)=4.00*03*T
B(11)=4.00*04
B(12)=4.00*03/T
B(13)=5.00*04
B(14)=6.00*05/T
B(15)=6.00*05/T2
B(16)=7.00*06/T
B(17)=8.00*07/T
B(18)=8.00*07/T2
B(19)=9.00*08/T2
B(20)=F21/T2
B(21)=F21/T3
B(22)=F22/T2
B(23)=F22/T3
B(24)=F23/T2
B(25)=F23/T3
B(26)=F24/T2
B(27)=F24/T4
B(28)=F25/T2
B(29)=F25/T3
B(30)=F26/T2
B(31)=F26/T3
B(32)=F26/T4

```

```

P=0
DO 201 I=1,32
201 P=P+R(I)*G(I)
P=P+P*I
PP=P
RETURN
END

```

```

FUNCTION SAT(T,I)
UNITS ARE DEG K AND MOLES/LITER
DIMENSION A(7,5)
DATA((A(I),I=1,7)=190.555,10.16,18.65812322,6.712030737,
1-.9472319712,3.3,0.0)
DATA((A(I),I=8,14)=305.33,
1 6.85,12.55219121,13.47244373,-19.38461866,11.37715985,0.0)
DATA((A(I),I=15,21)=369.82,5.8,684458671,18.04085714,-29.46261356
1.14,43599114,3.3)
DATA((A(I),I=22,28)=425.16,7.92,
1 7.285162567,11.96337859,-19.37591962,
211.50211932,1.0)
DATA((A(I),I=29,35)=488.13,3.8,
1 7.657535400,3.145251283,-13.10582462,
21.14519,131,3.3)
DATA((A(I),I=36,42)=126.2,11.21,19.39216835,26.01408462,-39.497587
131.23,32877312,3.0)
IF(T.GT.A(1,I))GO TO 1
X=(1.-T/A(1,I))
SAT=(A(2,I)+1(A(3,I)*X**(.35)+A(4,I)*X+A(5,I)*X**(.4/.3.)
1+1(A(6,I)*X**(.5/.3.))
RETURN
1 SAT=1.0E+23
RETURN
END

```

```

FUNCTION VP(T)
DIMENSION G(12),VP(3)
COMMON/DATA/G,P,GAMMA,VP,DT
X=(1.-VP(7)/T)/(1.-VP(7)/VP(8))
7P=VP(5)-X**2(VP(1)*X+VP(2)*X**2+VP(3)*X**3+VP(9)*X**4+VP(4)*X
1(1.-X)**VP(5)
22 DEN
1 VP=.01
22 DEN
END

```

```

SUBROUTINE ZERO(X)
DIMENSION X(10)
DO 1 I=1,10
1 X(I)=0.1
RETURN
END

```

Appendix D. Program Listing for the Revised Klosek and McKinley Model

The program listing and tables that follow are for the Revised Klosek and McKinley model described in section 4. The method may be used in two ways. First using the equation

$$V_{\text{mix}} = \sum X_i V_i - [k_1 + (k_2 - k_1) X_{N_2} / 0.0425] X_{CH_4} \quad (C-1)$$

The V_i , k_1 and k_2 may be obtained from tables 1, 2 and 3 and the volume of the mixture calculated. For example given the mixture of 0.8130 CH_4 + 0.0475 C_2H_6 + 0.0487 C_3H_8 + 0.0242 nC_4H_{10} + 0.0241 iC_4H_{10} + 0.0425 N_2 and a temperature of 105 kelvin.

The $\sum X_i V_i$ is obtained from table 1.

$$\begin{aligned} \sum X_i V_i &= (.8130)(.037112) + (.0475)(.047266) + (.0487)(.061766) \\ &+ (.0242)(.076100) + (.0241)(.077538) + (.0425)(.042560) \end{aligned}$$

$$\begin{aligned} \text{Then the } \sum X_i W_i &= (.8130)(16.04303) + (.0475)(30.07012) + (.0487)(44.09721) \\ &+ (.0242)(58.1243) + (.0241)(58.1243) + (.0425)(28.0134) \\ &= 20.6168 \text{ the molecular weight of the mixture} \end{aligned}$$

$$\text{from table 2 } k_1 = .730 \times 10^{-3}$$

$$\text{from table 3 } k_2 = .849 \times 10^{-3}$$

plugging all this into equation (C-1) gives

$$V_{\text{mix}} = .040944$$

$$1/V_{\text{mix}} = \rho_{\text{mix}} = 24.858 \text{ moles/liter}$$

This compares to the experimental values of 24.850 (see last page of Appendix E) to within 0.03%.

The same result may be obtained by using the computer program in the following way

$$D = \text{FMKM}(T, X)$$

where T is temperature in kelvins and X is a matrix of mole fractions of the components in the following order:

X(1) = mole fraction of methane
X(2) = mole fraction of ethane
X(3) = mole fraction of propane
X(4) = mole fraction of normal butane
X(5) = mole fraction of isobutane
X(6) = mole fraction of nitrogen
X(7) = mole fraction of normal pentane
X(8) = mole fraction of isopentane

for the example: $T = 105.$, $X(1) = .8130$, $X(2) = .0475$, $X(3) = .0487$,
 $X(4) = .0242$, $X(5) = .0241$ and $X(6) = .04256$.

Table 1. Volumes of Saturated Liquid of the Pure Components in

liters/mole.

T, K	CH ₄	C ₂ H ₆	C ₃ H ₈	nC ₄ H ₁₀	IC ₄ H ₁₀	N ₂	nC ₅ H ₁₂	IC ₅ H ₁₂
90.	.035441	.046081	.060461	.074708	.076084	.037543	.089173	.089243
92.	.035649	.046235	.060632	.074891	.076274	.038081	.089379	.089454
94.	.035861	.046390	.060804	.075075	.076466	.038650	.089586	.089666
96.	.036077	.046547	.060977	.075259	.076659	.039254	.089793	.089878
98.	.036298	.046704	.061151	.075445	.076853	.039897	.090000	.090091
100.	.036524	.046863	.061325	.075631	.077047	.040586	.090208	.090304
102.	.036755	.047023	.061501	.075818	.077243	.041327	.090416	.090518
104.	.036992	.047185	.061677	.076006	.077440	.042128	.090624	.090733
106.	.037234	.047348	.061855	.076194	.077637	.043002	.090833	.090948
108.	.037481	.047512	.062033	.076384	.077836	.043963	.091042	.091163
110.	.037735	.047678	.062212	.076574	.078035	.045031	.091252	.091379
112.	.037995	.047845	.062392	.076765	.078236	.046231	.091462	.091596
114.	.038262	.048014	.062574	.076957	.078438	.047602	.091673	.091814
116.	.038536	.048184	.062756	.077150	.078640	.049179	.091884	.092032
118.	.038817	.048356	.062939	.077344	.078844	.050885	.092095	.092251
120.	.039106	.048529	.063124	.077539	.079049	.052714	.092307	.092470
122.	.039404	.048704	.063309	.077734	.079255	.054679	.092520	.092690
124.	.039710	.048881	.063496	.077931	.079462	.056797	.092733	.092911
126.	.040025	.049059	.063684	.078128	.079671	.059085	.092947	.093133
128.	.040350	.049239	.063873	.078327	.079880	.061565	.093161	.093355
130.	.040685	.049421	.064063	.078526	.080091	.064263	.093376	.093578
132.	.041031	.049605	.064254	.078727	.080303	.067208	.093591	.093801
134.	.041389	.049790	.064446	.078928	.080516	.070435	.093807	.094026
136.	.041760	.049978	.064640	.079130	.080730	.073989	.094024	.094251
138.	.042144	.050167	.064835	.079334	.080946	.077919	.094241	.094477
140.	.042542	.050359	.065031	.079538	.081162	.082291	.094459	.094704
142.	.042956	.050552	.065229	.079744	.081380	.087183	.094678	.094932
144.	.043387	.050748	.065427	.079950	.081600	.092693	.094897	.095160
146.	.043836	.050946	.065628	.080158	.081821	.098947	.095117	.095389
148.	.044304	.051146	.065829	.080367	.082043	.106105	.095338	.095620
150.	.044794	.051348	.066032	.080577	.082266	.114380	.095560	.095851

Table 2. Correction Factor $k_1 \times 10^3$

T/W	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
90.	-.005	.12	.22	.34	.43	.51	.59	.66	.75	.82	.88	.93	.98	1.03	1.08
95.	-.006	.14	.26	.38	.49	.58	.67	.75	.85	.92	.99	1.05	1.10	1.15	1.20
100.	-.007	.15	.30	.42	.54	.65	.75	.86	.96	1.04	1.11	1.17	1.23	1.28	1.34
105.	-.007	.17	.34	.46	.62	.73	.84	.96	1.08	1.16	1.24	1.31	1.37	1.43	1.49
110.	-.008	.19	.38	.54	.70	.82	.93	1.06	1.21	1.30	1.39	1.47	1.53	1.60	1.67
115.	-.009	.22	.42	.61	.79	.93	1.06	1.20	1.36	1.47	1.56	1.65	1.71	1.79	1.86
120.	-.010	.25	.50	.70	.90	1.04	1.23	1.40	1.54	1.65	1.75	1.85	1.92	2.00	2.08
125.	-.013	.30	.59	.79	1.02	1.18	1.38	1.60	1.73	1.86	1.97	2.08	2.15	2.24	2.33
130.	-.015	.35	.70	.92	1.14	1.36	1.60	1.73	1.96	2.09	2.22	2.34	2.42	2.52	2.62
135.	-.017	.40	.80	1.06	1.39	1.51	1.77	1.90	2.23	2.38	2.52	2.64	2.74	2.85	2.95

Table 3. Correction Factor $k_2 \times 10^3$

T/W	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
90.	-.004	.10	.22	.35	.50	.60	.69	.78	.86	.95	1.03	1.12	1.20	1.27	1.35
95.	-.005	.12	.28	.43	.59	.71	.83	.94	1.05	1.14	1.22	1.28	1.37	1.45	1.54
100.	-.007	.16	.34	.49	.64	.79	.94	1.08	1.17	1.27	1.37	1.47	1.57	1.67	1.77
105.	-.010	.24	.42	.61	.75	.91	1.05	1.19	1.33	1.45	1.58	1.69	1.81	1.92	2.03
110.	-.015	.32	.59	.77	.92	1.07	1.22	1.37	1.52	1.71	1.83	1.97	2.10	2.23	2.36
115.	-.024	.55	.72	.95	1.15	1.22	1.30	1.45	1.65	2.00	2.17	2.32	2.47	2.63	2.79
120.	-.032	.75	.91	1.23	1.43	1.63	1.85	2.08	2.30	2.45	2.60	2.77	2.95	3.13	3.32
125.	-.043	1.00	1.13	1.48	1.73	1.98	2.23	2.48	2.75	2.90	3.10	3.30	3.52	3.74	3.96
130.	-.058	1.34	1.46	1.92	2.20	2.42	2.68	3.00	3.32	3.52	3.71	3.95	4.20	4.46	4.74
135.	-.075	1.75	2.00	2.40	2.60	3.00	3.40	3.77	3.99	4.23	4.47	4.76	5.05	5.36	5.69


```

FUNCTION FMKM(T,X)
DIMENSION TM(150),TN(150),X(10),Q(8)
DATA(Q=16.04303,30.07012,44.09721,58.1243,58.1243,28.0134,72.1513
19.72,15139)
DATA((TM(I),I=1,15)=-.005,.A2,.22,.34,.43,.51,.59,.66,.75,.82,
A.88,.93,.98,1.03,1.08)
DATA((TM(I),I=16,30)=-.006,.14,.26,.38,.49,.58,.67,.75,.85,.92,
A.99,1.05,1.1,1.15,1.2)
DATA((TM(I),I=31,45)=-.007,.15,.3,.42,.54,.65,.75,.86,.95,1.04,
A1.11,1.17,1.23,1.28,1.34)
DATA((TM(I),I=46,60)=-.007,.17,.34,.46,.62,.73,.84,.96,1.08,1.16,
A1.24,1.31,1.37,1.43,1.49)
DATA((TM(I),I=61,75)=-.008,.19,.38,.54,.7,.82,.93,1.06,1.21,1.3,
A1.39,1.47,1.53,1.6,1.67)
DATA((TM(I),I=76,90)=-.009,.22,.42,.61,.79,.93,1.06,1.2,1.36,1.47,
A1.56,1.65,1.71,1.79,1.86)
DATA((TM(I),I=91,105)=-.01,.25,.5,.7,.9,1.04,1.23,1.4,1.54,1.65,
A1.75,1.85,1.92,2.,2.08)
DATA((TM(I),I=106,120)=-.013,.3,.59,.79,1.02,1.18,1.38,1.6,1.73,
11.86,
A1.97,2.08,2.15,2.24,2.33)
DATA((TM(I),I=121,135)=-.015,.35,.7,.92,1.14,1.36,1.6,1.73,1.96,
A2.09,2.22,2.34,2.42,2.52,2.62)
DATA((TM(I),I=136,150)=-.017,.4,.80,1.06,1.39,1.51,1.77,1.9,2.23,2
A.38,2.52,2.64,2.74,2.85,2.95)
DATA((TN(I),I=1,15)=-.004,.1,.22,.35,.5,.6,.69,.78,.86,.95,
A1.03,1.12,1.20,1.27,1.35)
DATA((TN(I),I=16,30)=-.005,.12,.28,.43,.59,.71,.83,.94,1.05,1.14,
A1.22,1.28,1.37,1.45,1.54)
DATA((TN(I),I=31,45)=-.007,.16,.34,.49,.64,.79,.94,1.08,1.17,1.27,
A1.37,1.47,1.57,1.67,1.77)
DATA((TN(I),I=46,60)=-.01,.24,.42,.61,.75,.91,1.05,1.19,1.33,1.45,
A1.58,1.69,1.81,1.92,2.03)
DATA((TN(I),I=61,75)=-.015,.32,.59,.77,.92,1.07,1.22,1.37,1.52,
11.71,
A1.83,1.97,2.1,2.23,2.36)
DATA((TN(I),I=76,90)=-.024,.55,.72,.95,1.15,1.22,1.3,1.45,1.65,2.,
A2.17,2.32,2.47,2.63,2.79)
DATA((TN(I),I=91,105)=-.032,.75,.91,1.23,1.43,1.63,1.85,2.08,2.3,
12.45
A.26,2.77,2.95,3.13,3.32)
DATA((TN(I),I=106,120)=-.043,1.,1.13,1.48,1.73,1.98,2.23,2.48,2.75
1,
A2.9,3.1,3.3,3.52,3.74,3.96)
DATA((TN(I),I=121,135)=-.058,1.34,1.46,1.92,2.2,2.42,2.63,3.,
A3.32,3.52,3.71,3.95,4.2,4.46,4.74)
DATA((TN(I),I=136,150)=-.075,1.75,2.,2.4,2.6,3.,3.4,3.77,
A3.99,4.23,4.47,4.76,5.05,5.36,5.69)
IF(X(I).LT..00001)GO TO 20
AW=0.0
DO I I=1,8
1 AW=AW+X(I)*Q(I)
VI=VIDEAL(T,X)
J=1
IF(T.GE.95.)J=16
IF(T.GE.100.)J=31
IF(T.GE.105.)J=46
IF(T.GE.110.)J=61
IF(T.GE.115.)J=76
IF(T.GE.120.)J=91
IF(T.GE.125.)J=106

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IF (T.GE.130.)J=121
JJ=J+14
W=15.
DO 5 I=J,JJ
W=W+1.
IF(AW.GT.W)GO TO 5
GO TO 6
5 CONTINUE
I=JJ
6 DIF1=AW-W
J=I-1
FK=(TM(I)-TM(J))*DIF1+TM(I)
FK1=(TM(I+15)-TM(J+15))*DIF1+TM(I+15)
IT=(T+.00001)/5.
DIF2=T-IT*5
IF(T.GE.135.)DIF2=T-130.
IF(T.LT.90.)DIF2=T-90.
FK=FK+(FK1-FK)*DIF2/5.
IF(X(6).LT..0001)GO TO 17
FKN=(TN(I)-TN(J))*DIF1+TN(I)
FK1=(TN(I+15)-TN(J+15))*DIF1+TN(I+15)
FKN=FKN+(FK1-FKN)*DIF2/5.
FK=FK+(FKN-FK)*X(6)/.0425
17 FK=FK/1000.
FMKM=1./(VI-FK*X(1))
RETURN
20 FMKM=0.0
RETURN
END

```

```

FUNCTION V IDEAL(T,X)
DIMENSION X(10)
V=0
J=0
IF(X(6).GT..0001.AND.T.GT.115.)J=1
DO 10 I=1,8
IF(X(I).LE..000001)GO TO 10
IF(J.GT.0.AND.I.EQ.6)GO TO 10
V=V+X(I)/SAT(T,I)
10 CONTINUE
IF(J.EQ.1)V=V+X(6)/SATN2(T)
VIDEAL=V
RETURN
END

```

```

FUNCTION SATN2(T)
IF(T.LT.115.)GO TO 1
DELT=(T-115.)
SATN2=SAT(115.,6)+DELT*(SAT(115.05,6)-SAT(114.95,6))/.1
RETURN
1 SATN2=SAT(T,6)
RETURN
END

```

```

FUNCTION SAT(T,I)
UNITS ARE DEG K AND MOLES/LITER
DIMENSION A(7,8)
DATA((A(I),I=1,7)=190.555,10.16,18.65812322,6.712030737,
1-.9472019702,0.0,0.0)
DATA((A(I),I=8,14)=305.33,
1 6.86,12.55205121,13.43284373,-19.00461066,11.07715985,0.0)
DATA((A(I),I=15,21)=369.82,5.8,6.84458671,18.04085714,-29.46261356
1,15.43559114,0.0)
DATA((A(I),I=22,28)=425.16,3.92,
1 7.286062567,11.96307859,-19.87591962,
211.60211932,0.0)
DATA((A(I),I=29,35)=408.13,3.8,
1 7.657535400,8.145251293,-13.10582462,
28.145894091,0.0)
DATA((A(I),I=36,42)=126.2,11.21,19.39216835,26.01408462,-39.497587
191.23,32977312,0.0)
DATA((A(I),I=43,49)=469.6,3.285,-.0362004993,59.00202990,
1-93.44193819,43.66780833,0.0)
DATA((A(I),I=50,56)=460.39,3.271,2.946310456,35.50770979,
1-57.41242993,28.15898339,0.0)
IF(T.GT.A(1,I))GO TO 1
X=(1.-T/A(1,I))
SAT=(A(2,I)+A(3,I)*X**(.35)+A(4,I)*X+A(5,I)*X**(4./3.)
1+A(6,I)*X**(5./3.))
RETURN
1 SAT=1.E+20
RETURN
END

```


10	DO 11 I = 1,NC	LNGD
	TEI(I) = T / TS(I)	LNGD
	CALL VOLUME(TBI(I),VBI(I),JPUR,NC)	LNGD
	TBIM(I) = T / TSIM(I)	LNGD
	CALL VOLUME(TBIM(I),VBIM(I),JMIX,NC)	LNGD
11	CONTINUE	LNGD
	VM = 0.0	LNGD
	DO 12 I = 1,NC	LNGD
	VM = VM + (X(I)*VBIM(I)*VSIM(I))	LNGD
12	CONTINUE	LNGD
	IMP = (T * 1.8) - (459.67)	LNGD
	DO 13 I = 1,NC	LNGD
	VHOLD(I) = VBI(I)	LNGD
	VFHOLD(I) = VBIM(I)	LNGD
	PP = (P*TS(I))/US(I)	LNGD
	VBIMP(I) = VBI(I)	LNGD
	CALL PRES(PP,VBIMP(I),TBI(I),NC)	LNGD
	VBI(I) = VBIMP(I)	LNGD
	PP = (P * TSIM(I)) / USIM(I)	LNGD
	VBIMP(I) = VBIM(I)	LNGD
	CALL PRES(PP,VBIMP(I),TBIM(I),NC)	LNGD
	VBIM(I) = VBIMP(I)	LNGD
13	CONTINUE	LNGD
	VMP = 0.0	LNGD
	DO 14 I = 1,NC	LNGD
	VMP = VMP + (X(I)*VBIMP(I)*VSIM(I))	LNGD
	PO(I) = VBIMP(I) * VSIM(I)	LNGD
14	CONTINUE	LNGD
	DENS = MWM/VMP	LNGD
	DOUT=DENS*1000./MWM	LNGD
	RETURN	
19	DOUT=0.0	
	RETURN	
	END	
	SUBROUTINE ZERO1	
	COMMON /RUN/A(361)	ZERO
	COMMON /DAY/B(224)	ZERO
	DO 1 I = 1,361	ZERO
1	A(I) = 0.0	ZERO
	DO 2 I = 1,224	ZERO
2	B(I) = 0.0	ZERO
	RETURN	ZERO
	END	ZERO
	SUBROUTINE VOLUME(T,V,J,NC)	VOL
	TR = T	VOL
	IF(TR.GT.(1.00)) GO TO 4	VOL
	V = 0.5	VOL
1	VT = (1.0) + (0.1*TR*V**(4.0))	VOL
	ERR = (1.0) - (V/VT)	VOL
	TEST = ABS(ERR)	VOL
	IF(TEST.LE.(0.00001)) GO TO 2	VOL
	V = VT	VOL
	GO TO 1	VOL
2	V = V**(3.0)	VOL
3	RETURN	VOL
4	V = ((((((10.06600 *TR)-24.79837)*TR)+23.260722)*TR)-5.686880)	VOL
	GO TO 3	VOL
	END	VOL


```

SUBROUTINE INPUT(Q)
DIMENSION NNO( 6),SIGM( 6),EPSI( 6),LAMB( 6),NAME(2, 6),SNO( 6),MOIN
1L( 6),CT( 6),TCH( 6),VCH( 6),ECH( 6),AR( 6),AZ( 6),Q(6)
COMMON /RUN/ID(12),X(12),NAM(2,12),C12(12,12),P(12),Z(12),S(12),VSTN
1(12),TS(12),US(12),SG(12),EP(12),LAM(12),NC,MW(12),AIJ(12,12),PST(IN
2(12),TCT(12)
COMMON /DAT/TBI(12),VBI(12),TBIM(12),VBIM(12),C(12),SGIM(12),SIM(1IN
12),EPTM(12),PTM(12),STN(12),VSTM(12),USTM(12),TSTM(12),DVBM(12),PTN
2D(12),PV(12),RHO(12),VBIMP(12),TTM(12),MWM,CNT1,CNT2,TOLD(12),INCRIN
3(12),SWITCH,JPG,JPCS,JMTX,DENS,VFX,HEX,GEX,TMP,VMP,TP
COMMON/PAR/KIJ( 6, 6),AJI( 6, 6)
TYPE REAL MW,LAM,MWM,INCP,KIJ,MOL,LAMB
TYPE INTEGER CNT1,CNT2,SWITCH
DATA SIGM/
*0.991000,1.029000,1.155000,1.278000,1.388752,1.392995/
DATA EPSI/
*0.640000,0.909000,1.69800,2.237000,2.705262,2.545907/
DATA LAMB/
*1.053604,0.986325,1.227117,1.408519,1.473346,1.461676/
DATA MCL/
*28.01600,16.04200,30.06800,44.09400,58.12000,58.12000/
DATA SNO/
*10.00000,10.00000,10.00000,10.00000,10.00000,10.00000/
DATA CT/
*126.0600,190.5600,305.4300,369.8200,425.1600,408.0300/
DATA TCH/
*112.7699,170.9645,256.8311,294.7255,340.7867,322.6109/
DATA VCH/
*25.01846,29.04010,40.88188,54.60301,68.72075,69.44272/
DATA ECH/
*1393.000,1977.000,3695.000,4867.000,5886.652,5539.895/
DATA AR/
*1.000000,1.000000,1.000000,1.000000,1.000000,1.000000/
DATA AZ/
*10.00000,10.00000,10.00000,10.00000,10.00000,10.00000/
DO 4 I=2,6
4 X(I)=Q(I-1)
X(1)=Q(6)
NC=0
DO 1 I=1,6
IF(X(I).LE.0.0)GO TO 1
NC=NC+1
X(NC)=X(I)
ID(NC)=I
1 CONTINUE
DO 2 I = 1,NC
J = ID(I)
R(I) = AR(J)
Z(I) = AZ(J)
S(I) = SNO(J)
TS(I)= TCH(J)
US(I)= ECH(J)
SG(I) = SIGM(J)
T(T(I)) = CT(J)
EP(I) = EPSI(J)
LAM(I) = LAMB(J)
VS(I) = VCH(J)

```


MW(I) = MOL(J)	IN
2 CONTINUE	IN
DO 3 I = 1,NC	IN
DO 3 J = 1,NC	IN
M = ID(I)	IN
L = ID(J)	IN
C12(I,J) = KIJ(M,L)	IN
C12(J,I) = KIJ(L,M)	IN
AIJ(I,J) = AJI(M,L)	IN
AIJ(J,I) = AJI(L,M)	IN
3 CONTINUE	IN
RETURN	IN
END	IN
SUBROUTINE PRES(A,B,C,NC)	PRES
TYPE REAL H,P,V,T,K1,K2,K3,VT,PT,K4	
P = A	PRES
V = B	PRES
T = C	PRES
H=.01	
IF(H.GT.P) H = P	PRES
ASSIGN 3 TO KK	PRES
1 CALL BETA(P,K1,T,V,NC)	PRES
K1 = H * K1	PRES
VT=V+K1/2.	
PT=P+H/2.	
CALL BETA(PT,K2,T,VT,NC)	PRES
K2 = K2 * H	PRES
VT=V+K2/2.	
CALL BETA(PT,K3,T,VT,NC)	PRES
K3 = K3 * H	PRES
PT = P + H	PRES
VT = V + (K3)	PRES
CALL BETA(PT,K4,T,VT,NC)	PRES
K4 = K4 * H	PRES
V=V+(K1+2.*K2+2.*K3+K4)/6.	
P = P - H	PRES
IF(P.EQ.(0.0)) GO TO 4	PRES
IF(P.LT.(0.0)) GO TO 2	PRES
GO TO 1	PRES
2 GO TO KK , (3,4)	PRES
3 P = P + H	PRES
H = P	PRES
ASSIGN 4 TO KK	PRES
GO TO 1	PRES
4 A = P	PRES
B = V	PRES
C = T	PRES
RETURN	PRES
END	PRES

SUBROUTINE PZERO(TRT)	PZER
COMMON /RUN/ID(12),X(12),NAM(2,12),C12(12,12),R(12),Z(12),S(12),VSPZER	PZER
1(12),TS(12),US(12),SG(12),EP(12),LAM(12),NC,MW(12),AIJ(12,12),PST(PZER	PZER
212),TCT(12)	PZER
COMMON /DAT/TBI(12),VBI(12),TBIM(12),VBIM(12),C(12),SGIM(12),SIM(1PZER	PZER
12),EPIM(12),PIM(12),SIN(12),VSIM(12),USIM(12),TSIM(12),DVBIM(12),PPZER	PZER
2D(12),PV(12),RHO(12),VBIMP(12),ITM(12),MWM,CNT1,CNT2,TOLO(12),INCRPZER	PZER
3(12),SWITCH,JPC,JPCS,JMIX,DENS,VEX,HEX,GEX,TMP,VMP,TP	PZER
COMMON/PAR/KIJ(6, 6),AJI(6, 6)	PZER
COMMON /UNITS/ITC,IPC,T,TMAX,DT,P,PMAX,DP,PS	PZER
TYPE REAL MW,LAM,MWM,INCR,KIJ,MOL,LAMB	PZER
TYPE INTEGER CNT1,CNT2,SWITCH	PZER
IF(NC.EQ.1) TRT = T/TCT(1)	PZER
IF(NC.GT.1) CALL TCM(TRT)	PZER
IF(NC.GT.1) TRT = T/TRT	PZER
IF(NC.EQ.1) CALL PURE(TRT,TRT,R(1),RXX)	PZER
DO 1 I = 1,NC	PZER
TCXX = T/TCT(I)	PZER
IF(NC.GT.1) CALL PURE(TCXX,TRT,R(I),RTR)	PZER
JPC = 0	PZER
IF(TRT.GT.(.87)) JPC = 2	PZER
IF(TPT.GT.(1.0)) JPC = 1	PZER
IF(NC.EQ.1) RTR = RXX	PZER
THERE ARE SEVERAL OTHER FORMS OF THESE EQUATIONS	PZER
REFER TO ORIGINAL ARTICLES FOR VALUES TO USE	PZER
S(I) = RTR * Z(I) - 2. * RTR + 2.	PZER
SIM(I) = S(I)	PZER
SG(I) = (VS(I)/RTR) ** (1./3.)	PZER
EP(I) = US(I) / S(I)	PZER
C(I) = LAM(I) * (2176./((185.6)*(1.98726)))	PZER
ITM(I) = TS(I)	PZER
TOLO(I) = TS(I)	PZER
INCR(I) = (20.0)	PZER
1 CONTINUE	PZER
JFUR = 0	PZER
CNT1 = 1	PZER
CNT2 = 1	PZER
JMIX = 0	PZER
2 DEN = 0	PZER
DO 3 I = 1,NC	PZER
DEN = DEN + (X(I) * SIM(I))	PZER
3 CONTINUE	PZER
DO 4 I = 1,NC	PZER
PIM(I) = (X(I) * SIM(I)) / DEN	PZER
4 CONTINUE	PZER
DO 6 I = 1,NC	PZER
SGIM(I) = 0.0	PZER
DO 6 J = 1,NC	PZER
M = I	PZER
N = J	PZER
IF(I.GT.J) M = J	PZER
IF(I.GT.J) N = I	PZER
IF(I.EQ.J) GO TO 5	PZER
TRUOX = (AIJ(N,M)/(T/ITM(I)))	PZER
IF(TRUOX.LT.(-180.0)) GO TO 5	PZER
SGIM(I) = SGIM(I) + (((PIM(J) * (((SG(I)**(1./3.) + SG(J)**(1./3.))	PZER
1/(2.0)) **3)) * (AIJ(M,N) * EXP(AIJ(N,M)/(T/ITM(I))))	PZER

GO TO 6	PZER
5 SGIM(I) = SGIM(I) + (PIM(J) * (((SG(I)**(1./3.) + SG(J)**(1./3.)) 1/(2.0))**3)	PZER
6 CONTINUE	PZER
DEN = 0.0	PZER
DO 7 I = 1,NC	PZER
DEN = DEN + (PIM(I) * SGIM(I) * SGIM(I))	PZER
7 CONTINUE	PZER
DO 8 I = 1,NC	PZER
SIN(I) = (S(I) * (SGIM(I)**(2.))) / DEN	PZER
8 CONTINUE	PZER
DO 9 I = 1,NC	PZER
TEST = (1.0) - (SIM(I) / SIN(I))	PZER
TEST = ABS (TEST)	PZER
IF (TEST.GT.(0.00001)) GO TO 10	PZER
9 CONTINUE	PZER
GO TO 12	PZER
10 DO 11 I = 1,NC	PZER
SIM(I) = (SIM(I) + SIN(I)) / (2.0)	PZER
11 CONTINUE	PZER
CNT1 = CNT1 + 1	PZER
IF (CNT1.GT.250) GO TO 12	PZER
GO TO 2	PZER
12 DO 14 I = 1,NC	PZER
SIM(I) = SIN(I)	PZER
EPIM(I) = 0.0	PZER
DO 14 J = 1,NC	PZER
K = I	PZER
L = J	PZER
IF (J.LT.I) K = J	PZER
IF (J.LT.I) L = I	PZER
IF (I.EQ.J) GO TO 13	PZER
TRUDX = C12(L,K) / (T/TTM(I))	PZER
IF (TRUDX.LT.(-100.0)) GO TO 13	PZER
EPIM(I) = EPIM(I) + ((PIM(J) * SQRT(EP(I)*EP(J))) * 1(C12(K,L) * EXP((C12(L,K) / (T/TTM(I))))))	PZER
GO TO 14	PZER
13 EPIM(I) = EPIM(I) + (PIM(J) * SQRT(EP(I) * EP(J)))	PZER
14 CONTINUE	PZER
ASSUME NUMBER OF MOLS OF MIXTURE = 1.0	PZER
DO 15 I = 1,NC	PZER
VSIM(I) = R(I) * (SGIM(I)**(3.0))	PZER
USIM(I) = SIM(I) * EPIM(I)	PZER
TSIM(I) = USIM(I) / ((1.98726) * C(I))	PZER
15 CONTINUE	PZER
DO 16 I = 1,NC	PZER
TEST = (1.0) - (TSIM(I)/TTM(I))	PZER
TEST = ABS(TEST)	PZER
IF (TEST.GT.(0.00001)) GO TO 17	PZER
16 CONTINUE	PZER
RETURN	PZER
17 DO 20 I = 1,NC	PZER
IF (TSIM(I) - TTM(I)) 18,20,19	PZER
18 TNEW = TTM(I) - INCR(I)	PZER
IF (TNEW.EQ.TOLD(I)) INCR(I) = INCR(I) / (2.0)	PZER
IF (TNEW.EQ.TOLD(I)) GO TO 18	PZER
TOLD(I) = TTM(I)	PZER

SUBROUTINE TCM(TMC)	TCM
TYPE REAL MW,LAM,MWM,INCR,KIJ,MOL,LAMB,NUM	
TYPE INTEGER CNT1,CNT2,SWITCH	
DIMENSION VCI(6),TH(12)	TCM
COMMON /RUN/ID(12),X(12),NAM(2,12),C12(12,12),R(12),Z(12),S1(12),VSTCM	
1(12),TS(12),US(12),SG(12),EP(12),LAM(12),NC,MW(12),AIJ(12,12),PST(TCM	
2(12),TCT(12)	TCM
COMMON /DAT/TBI(12),VBI(12),TBIM(12),VBIM(12),C(12),SGIM(12),SIM(1TCM	
12),EPIM(12),PIM(12),SIN(12),VSIM(12),USIM(12),TSIM(12),DVBIM(12),PTCM	
2D(12),PV(12),PHO(12),VBIMP(12),TTH(12),MWM,CNT1,CNT2,TOLD(12),INCRTCM	
3(12),SWITCH,JPC,JPCS,JMIX,DENS,VEX,HEX,GEX,TMP,VMP,TP	TCM
COMMON/PAR/KIJ(6, 6),AJI(6, 6)	TCM
COMMON/UNITS/ITC,IPC,T,THAX,DT,P,PHAX,DP,PS	TCM
DATA VCI/ 1.44,1.59,2.27,3.18,4.03,4.21/	TCM
DC 1 I = 1,NC	TCM
J = ID(I)	TCM
V = VCI(J)**(2./3.)	TCM
TH(I) = X(I) * V	TCM
1 CONTINUE	TCM
ITZ = 0.0	TCM
DO 2 I = 1,NC	TCM
ITZ = ITZ + TH(I)	TCM
2 CONTINUE	TCM
DO 3 I = 1,NC	TCM
TH(I) = TH(I) / ITZ	TCM
3 CONTINUE	TCM
SUM1 = 0.0	TCM
SUM2 = 0.0	TCM
K = NC - 1	TCM
DO 5 I = 1,K	TCM
L = I + 1	TCM
DO 4 J = L,NC	TCM
TTZ = (TCT(I)-TCT(J))/(TCT(I)+TCT(J))	TCM
ITZ= ABS(TTZ)	TCM
T12 = ((((((TTZ*(-3.038)))+(5.443))*TTZ)+(-1.343))*TTZ)	TCM
1 + (0.287))*TTZ) - (.0076)	TCM
T12 = T12*(TCT(I) + TCT(J)) * (0.9)	TCM
SUM2 = SUM2 + ((2.)*TH(I)*TH(J)*T12)	TCM
4 CONTINUE	TCM
SUM1 = SUM1 + (TH(I)*TCT(I)*(1.8))	TCM
5 CONTINUE	TCM
TMC = SUM1 + SUM2 + (TH(NC)*TCT(NC)*(1.8))	TCM
V = 0.0	TCM
DO 6 I = 1,NC	TCM
J = IB(I)	TCM
TH(I) = X(I) * VCI(J)	TCM
V = V + TH(I)	TCM
6 CONTINUE	TCM
DO 7 I = 1,NC	TCM
TH(I) = TH(I) / V	TCM
7 CONTINUE	TCM
TDM=0.0	
DO 9 I = 1,NC	TCM
DO 8 J = 1,NC	TCM
M = ID(I)	TCM
N = ID(J)	TCM
NUM = (VCI(M)**(1./3.)) * (VCI(N)**(1./3.))	TCM

NUM = SQRT(NUM)	TCM
DEN = (0.5)*((VCI(M)**(1./3.))+(VCI(N)**(1./3.)))	TCM
NUM = NUM / DEN	TCM
NUM = NUM**(3.)	TCM
AKIJ = (1.0) - NUM	TCM
TCIJ = (1.0 - AKIJ) * SQRT(TCT(I)*TCT(J)*1.8*1.8)	TCM
TDM=TDM+TH(I)*TH(J)*TCIJ	
3 CONTINUE	TCM
9 CONTINUE	TCM
TCMP=TDM+10.	
ICT = 0	TCM
TPO=TDM+10.	
10 TR = (T*1.8)/TCMP	TCM
NUM = (2901.01) -((5738.92)*TR) +((2849.85)*TR*TR)	TCM
1 + ((1.74127)/(1.01 - TR))	TCM
NUM = NUM * (TR - (1.0))	TCM
IF(NUM.LT.(-180.)) DD = 0	TCM
IF(NUM.LT.(-180.)) GO TO 11	TCM
DD = EXP(NUM)	TCM
THE STATEMENT ABOVE MAY RESULT IN AN UNDERFLOW SENSE LIGHT	
ON SOME OPERATING SYSTEMS WHEN THE NUMBER NUM IS A LARGE	
NEGATIVE NUMBER. THE LARGE NEGATIVE VALUE IS PROPER AND	
THE CORRECT ANSWER FOR DD IS ZERO.	
11 TCMP = TDM + ((TDM-TDM)*DD)	
TEST = (1.0) - (TCMP/TPO)	TCM
TEST = ABS(TEST)	TCM
IF(TEST.LT.(.0001)) GO TO 12	TCM
ICT = ICT + 1	TCM
IF(ICT.GT.250) GO TO 12	TCM
TPO = TCMP	TCM
GO TO 10	TCM
12 TMC = TCMP/(1.8)	TCM
RETURN	TCM
END	TCM
SUBROUTINE BLOCK	
TYPE REAL KIJ,AJI	
DIMENSION KIJ(6,6),AJI(6,6)	
COMMON /PAR/ KIJ,AJI	
DATA KIJ/	DATA
*0.000000,.293E-07,.988E-07,.584E-06,0.001000,0.001000,1.088608,	DATA
*0.000000,.0537605,.744E-06,.278E-08,.154E-05,1.088264,1.029639,	DATA
*0.000000,.403E-07,.224E-06,.251E-06,.9906540,1.139564,1.010192,	DATA
*0.000000,.440E-07,.495E-07,0.995000,1.337262,.9867502,.9688072,	DATA
*0.000000,.310E-05,0.995000,1.121902,1.016260,.9992935,.9435220,	DATA
*0.000000/	DATA
DATA AJI/	DATA
*0.000000,.161E-04,.988E-06,.448E-05,0.001000,0.001000,1.014967,	DATA
*0.000000,.0002462,.336E-06,.998E-06,.0000297,1.007314,1.008772,	DATA
*0.000000,.603E-05,.0000226,.666E-06,1.001711,1.010832,1.001911,	DATA
*0.000000,.622E-05,.280E-05,0.995000,1.027909,1.003225,.9997213,	DATA
*0.000000,.317E-05,0.995000,1.015870,1.005915,1.001421,.9963974,	DATA
*0.000000/	DATA
RETURN	
END	DATA

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 77-867	2. Gov't Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE A COMPARISON OF MATHEMATICAL MODELS FOR THE PREDICTION OF LNG DENSITIES		5. Publication Date October 1977	6. Performing Organization Code 275.02
7. AUTHOR(S) Robert D. McCarty		8. Performing Organ. Report No.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234		10. Project/Task/Work Unit No. 2751574	11. Contract/Grant No. BR-50-11
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) American Gas Association 1515 Wilson Boulevard Arlington, VA 22209		13. Type of Report & Period Covered	14. Sponsoring Agency Code
15. SUPPLEMENTARY NOTES			
<p>16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)</p> <p>Four mathematical models of the equation of state for LNG like mixtures are compared. Each model has been optimized to the same experimental data set. The experimental data consist of over 175 new PVTx data points taken in this laboratory. The objective of the study was to obtain a mathematical model which would predict LNG densities to within 0.1% of the true value. The extent to which the objective has been achieved is not clear at this time. Additional experimental data are needed to resolve some discrepancies between the present data and all models investigated to date. Computer program listings for all four models are presented.</p>			
<p>17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)</p> <p>Computer program; density; equation of state; LNG; mixtures; PVTx.</p>			
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		<p>20. SECURITY CLASS (THIS PAGE)</p> <p>UNCLASSIFIED</p>	<p>22. Price</p> <p>\$5.25</p>

