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**Phase Equilibrium Data for the Hydrogen Sulphide + Methane System at
Temperatures from 186 to 313 K and Pressures up to about 14 MPa.**

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Isothermal vapour-liquid equilibrium data have been measured for the methane - hydrogen sulphide (CH₄ + H₂S) binary system at five temperatures from 186.25 to 313.08 K, and pressures between 0.043 and 13.182 MPa. The experimental method used in this work is of the static-analytic type, taking advantage of two pneumatic capillary samplers (Rolsi™, Armines' patent) developed in the CTP laboratory. The data were obtained with the following maximum expanded uncertainties ($k = 2$): $u(T) = 0.06$ K, $u(P) = 0.006$ MPa and the maximum uncertainty for compositions $u(x, y) = 0.010$ for molar compositions. The data have been satisfactorily represented with the classical Peng and Robinson equation of state.

Keywords: VLE and LLE data, High-pressures, Modelling, Hydrogen Sulphide, Methane.

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Introduction

In the past three decades a number of sour natural gases and gas condensates fields have been discovered around the world. Some of these fields have been classified as heavy natural gases. Some of them contain great amount of sulphur compounds like hydrogen sulphide. In some cases, the amount of H_2S can be greater than 30 molar percent. Whatever the concentration over a defined value, it is necessary to treat such acid gases to eliminate all traces of toxic sulphur compounds before their uses. Regulation imposes that sweet gas must contain less than 4 ppmv of H_2S . In most industrial plants, the removal acid gases (H_2S) achieved by chemical or physical absorption with solvent. Petroleum industry needs reliable and accurate vapour-liquid equilibrium data for mixtures of hydrocarbons and hydrogen sulphide in order to develop accurate models for calculating thermodynamic properties of natural gases requested for plants designs. Hydrogen sulphide and methane are also present in other energy contexts: for example they are present in gases produced from coals or biomass products from which H_2S must be eliminated. H_2S – methane binary system is very interesting for the petroleum industry, then it is useful to have high accuracy experimental data on a large range of temperatures and pressures.

Few data concerning methane and hydrogen sulphide are available in the literature. We have only found data of Reamer et al. [1], Kohn and Kurata [2], and Yarym-Agaev et al. [3]. Reamer et al. [1] measured data in the 278 - 444 K range. Kohn and Kurata [2] have measured vapour – liquid, vapour – solid, liquid – solid, liquid – vapour – solid, liquid – liquid – solid data between 89 and 422 K. Good consistency has been pointed out between these two sources of data (see ref [2]). Yarym-Agaev et al. [3] have measured data at 222.20, 239.90, 252.00 and 273.20 K. Moreover, Reamer et al. and Kohn and Kurata have measured data on the critical curve from 267 to 361 K and from

193 to 364 K, respectively. In the DECHEMA handbook [4], interaction parameter has been determined for this system using the Peng and Robinson equation of state (PR EoS) [5] with the classical mixing rule ($k_{ij} = 0.08$). This system can be classified as a type III according to the classification of Scott and van Konynenburg [6]. This behaviour is confirmed by the data on the critical locus measured by Reamer et al. and Kohn and Kurata.

In this paper, we present new experimental data and their modelling with classical cubic equation of state. Measurements have been carried out at low temperature in order to complete the literature data. The Peng and Robinson Equation of state (PR EoS) is used with a constant binary interaction parameter and with a binary interaction parameter function of the temperature.

Experimental Section.

All the details concerning the chemicals used are presented in Table 1.

The apparatus used in this work is based on a “static-analytic” method with liquid and vapour phase sampling. It is similar (see Figure 1) to that described by Courtial et al. [7] and Théveneau et al. [8].

The equilibrium cell is immersed inside a regulated liquid bath (Lauda RUK 90). Temperatures are measured with two platinum resistance thermometer probes (Pt100) inserted inside the top and bottom parts of the equilibrium cell. They were calibrated against a 25- Ω reference platinum probe (TINSLEY Precision Instrument) calibrated by the Laboratoire National d'Essais (Paris) following the 1990 International Temperature Scale protocol.

Pressures are measured using pressure transducers (Druck, type PTX611). They were calibrated against a dead weight pressure balance (5202S model from Desgranges &

Huot). Pressure and temperature data are recorded on a computer connected to a HP data acquisition unit (HP34970A).

The data were measured at two different time periods and so two separate campaigns of measurement were done.

-For the first campaign, measurements were done at 223.17, 273.54 and 313.08 K. Two pressures transducers were used and selected in relation to the pressure ranges: 0–10 and 0-30 MPa. After calibrations, the expanded uncertainties ($k=2$) on pressures are not higher than $u(P) = 0.0025$ MPa and $u(P) = 0.006$ MPa respectively. The expanded uncertainty concerning the temperature is $u(T) = 0.06$ K.

-For the second campaign, measurements were done at 186.25 and 203.40 K. The pressure transducer was selected in relation to the pressure ranges: 0 – 15 MPa. After calibrations, the expanded uncertainties ($k=2$) are not higher than $u(T) = 0.02$ K and $u(P) = 0.0025$ MPa.

The analytical work was carried out using a gas chromatograph (VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system (BORWIN ver 1.5, from JMBS, France). The analytical column is PORAPAK Q, 80/100 Mesh (1/8" silcosteel tube, 2 m length, from Restek, France). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through liquid and gas type syringes directly into the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and dispersions of analyses, the resulting accuracies in vapour and liquid mole numbers are estimated to be less than ± 1.0 % and less than 2.5 % for the first and second campaigns, respectively. Consequently, calibration expanded uncertainties ($k=2$) on the mole fractions are less than $u(x, y) = 0.010$.

C) Experimental Procedure

At room temperature, the equilibrium cell and its loading lines are evacuated down to 0.1 Pa. The cell (volume of the cell around 31 cm³) is first loaded with liquid H₂S (about 5 cm³). Equilibrium temperature is assumed to be reached when the two Pt100 probes give equivalent temperature values within their temperature uncertainty for at the least 10 minutes. Also, equilibrium is assumed when the total pressure remains unchanged within ± 1.0 kPa during a period of 10 min under efficient stirring.

After recording the vapour pressure of the H₂S (the heavier component) at the equilibrium temperature, about ten P, x, y points (liquid and vapour) of the two-phase envelopes are determined. For this purpose methane (the lighter component) is introduced step by step, leading to successive equilibrium mixtures of increasing overall methane composition (T, P, x and y).

Besides constancy of T and P, it is necessary to check also for phase compositions constancy. For these purposes, various samples of phases are withdrawn using the ROLSITM pneumatic samplers [9] and analysed. When equilibrium is reached and capillary purged the measured compositions remain constant within experimental uncertainty. Then for each observed equilibrium condition, at least five more samples of both vapour and liquid phases are withdrawn and analysed in order to check for the measurement repeatability.

Modelling by equation of state:

The critical temperatures (T_C), critical pressures (P_C), and acentric factors (ω), for each of the two pure components are provided in Table 2. We have used herein the PR EoS [5]. In order to have accurate representation of vapour pressures of each component,

we have used the Mathias-Copeman alpha function [10] expressed in eq 1. With its three adjustable parameters it was especially developed for polar compounds.

$$\alpha(T) = \left[1 + c_1 \left(1 - \sqrt{\frac{T}{T_C}} \right) + c_2 \left(1 - \sqrt{\frac{T}{T_C}} \right)^2 + c_3 \left(1 - \sqrt{\frac{T}{T_C}} \right)^3 \right]^2 \quad (1)$$

When $T > T_C$, Eq. 1 must be replaced by Eq. 2,

$$\alpha(T) = \left[1 + c_1 \left(1 - \sqrt{\frac{T}{T_C}} \right) \right]^2 \quad (2)$$

The three (c_1 , c_2 and c_3) adjustable parameters are reported in Table 3. For VLE representation, we chose the Van der Waals mixing rules, i.e. :

$$b = \sum_i x_i b_i \quad (3)$$

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (4)$$

The binary parameter k_{ij} can be a constant or temperature dependent as expressed in Eq. 5

$$k_{ij} = k_{ij}^a + \frac{k_{ij}^b}{T} \quad (5)$$

The adjustment of the binary interaction parameter is performed through a modified Simplex algorithm [11] using the objective function:

$$F = \frac{100}{N} \left[\sum_1^N \left(\frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)^2 \right] \quad (6)$$

Where N is the number of data points, P_{exp} is the measured pressure (experimental pressure value), P_{cal} is the calculated pressure through bubble point calculations. From our tests, using an objective function based on both pressures and vapour compositions did not significantly improve modelling. With the objective function given in Eq. 6 we have determined binary interaction parameters that allow calculating vapour compositions

in very good agreement with experimental ones within our determined experimental uncertainties.

Results and discussion:

Tables 4 and 5 report our measurements. The repeatability of the measurements is better than 1%. At our lowest temperature (186.25 K), we observe a liquid – vapour equilibrium for the pressures up to 3.671 MPa and a liquid – liquid equilibrium for the higher pressures. The same behaviour is observed 203.40 K. For higher temperatures, only vapour – liquid phase diagrams have been observed in our experimental pressure range. Figures 2 and 3 show the experimental data at respectively 186.25 and 203.40 K and the curves calculated with the PR Model and binary parameters adjusted on our experimental data at these temperatures. The other data related to classical liquid – vapour behaviours are not drawn.

Table 6 gives the values of binary parameters for each temperature. This enables determining a temperature dependent binary parameter:

$$k_{ij} = 0.0523 + \frac{8.733}{T / K} \quad (7)$$

Finally, the new experimental data have been added to the literature ones and a new temperature-dependent expression for the binary interaction parameter was obtained for the whole ensemble of data:

$$k_{ij} = 0.0390 + \frac{12.30}{T / K} \quad (8)$$

The deviations on pressures and compositions are given in table 7.

In this section, absolute deviations on pressures and compositions, are defined by:

$$Deviation = (100 / N) \sum |(U_{cal} - U_{exp}) / U_{exp}| \quad (9)$$

Where N is the number of data points, and $U = P$, or y .

The result shows a good agreement of the model with all the available experimental data. Moreover we have used the PPR78 predictive model from Privat et al. [12]. The prediction is very good and so confirms the high quality of the data.

Conclusion

In this paper we present VLE and LLE data for the system methane + H₂S at 5 temperatures. We used a “static-analytic” method to obtain our experimental data. We chose the Peng-Robinson EoS, with the Mathias-Copeman alpha function and the classical mixing rules.

The experimental results are given with following maximum expanded uncertainties ($k = 2$): $u(T) = 0.06$ K, $u(P) = 0.006$ MPa and $u(x, y) = 0.017$ for vapour and liquid mole fractions. Comparisons are done with literature data and the phase diagram is determined and classified as type III according to Scott and van Konynenburg classification.

The next work will consist of a comparison of thermodynamic models frequently used for industrial applications. Equation of state combined with excess Gibbs model and Huron Vidal type mixing rule can be used to present the phase diagram of the system. Also, H₂S can be considered as an associating fluid and so associative equations (like CPA or PC-SAFT) can be used to represent the data.

Concerning the study at 186.25 K, the temperature was close to triple point temperature of H₂S (190.86 K from [13], 187.62 K from [14]). Experimentally we did not detect any presence of solid at the lowest studied pressure. SLV-EoS [15, 16] for the simultaneous representation of solid, liquid, and vapour phases will be compared to the other models for the representation of experimental data. This equation will be used for the prediction of phase diagrams especially in the solid-fluid equilibrium region (separation of H₂S from natural gas by solidification process). By this way we will

present the correct phase diagram at 186.25 K (solid – vapour equilibrium is expected at low pressures) and highlight metastability for some data. Such work will be the subject of future paper.

Acknowledgments

The authors thank Dr. Clémence Nikitine for technical assistance. The authors wish to thank Prof. Jean-Noël Jaubert for fruitful discussions and utilisation of PPR78 model.

List of symbols:

a	Parameter of the equation of state (energy parameter [$\text{J} \cdot \text{m}^3 \cdot \text{mol}^{-2}$])
b	Parameter of the equation of state (molar co volume parameter [$\text{m}^3 \cdot \text{mol}^{-1}$])
c	Mathias-Copeman coefficient
F	Objective function
k	Binary interaction parameter
N	<i>Number of data points</i>
P	Pressure [MPa]
T	Temperature [K]
x	Liquid mole fraction
y	Vapour mole fraction

Greek letters

ω	Acentric factor
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Subscripts

c	Critical property
cal	Calculated property
exp	Experimental property
i,j	Molecular species
1	Methane
2	H ₂ S

Superscript

Li	Liquid phase i
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Figure 1: Flow diagram of the equipment: C: Carrier Gas, EC: Equilibrium Cell, FV: Feeding Valve, LB: Liquid Bath, LS: Liquid Sampler, PP: Platinum Probe, MC: Methane Cylinder, PT: Pressure Transducer, HC: Hydrogen sulphide Cylinder, SM: Sampler Monitoring, ST: Sapphire Tube, TCi: Thermal Compressor i, Th: Thermocouple, TR: Thermal Regulator, VP: Vacuum Pump, VS: Vapour Sampler, VSS: Variable Speed Stirring System.

Figure 2: Pressure as a function of CH₄ mole fraction in the CH₄ (1) + H₂S (2) mixture at 186.25 K. Solid lines: calculated with PR EoS (our model) and $k_{ij} = 0.099$. Dashed lines: calculated with PPR78. Symbols : Δ = experimental data, \bullet = pure methane vapour pressure.

Figure 3: Pressure as a function of CH₄ mole fraction in the CH₄ (1) + H₂S (2) mixture at 203.40 K. Solid lines: calculated with PR EoS (our model), and $k_{ij} = 0.098$. Dashed lines: calculated with PPR78. Symbols = experimental data.

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Table 2: Critical parameters and acentric factors for hydrogen sulphide and methane [12] from DIPPR database

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Table 5: “Vapour-liquid” equilibrium pressures and phase compositions (campaign 1) for the Methane (1) - H₂S (2) mixture at 223.17, 273.54 and 313.08 K.

For pressure lower than 10 MPa, $u(P, k=2) = 0.0025$ MPa and for pressure greater than 10 MPa, $u(P, k=2) = 0.006$ MPa, $u(T, k=2) = 0.06$ K and $u(x_1, y_1, k=2) = 0.004$.

Remark: For some VLE points, only bubble pressures and liquid compositions are indicated

Table 6: Values of the binary parameters adjusted at each temperature.

Table 7: Deviations on pressure and compositions for each set of data.

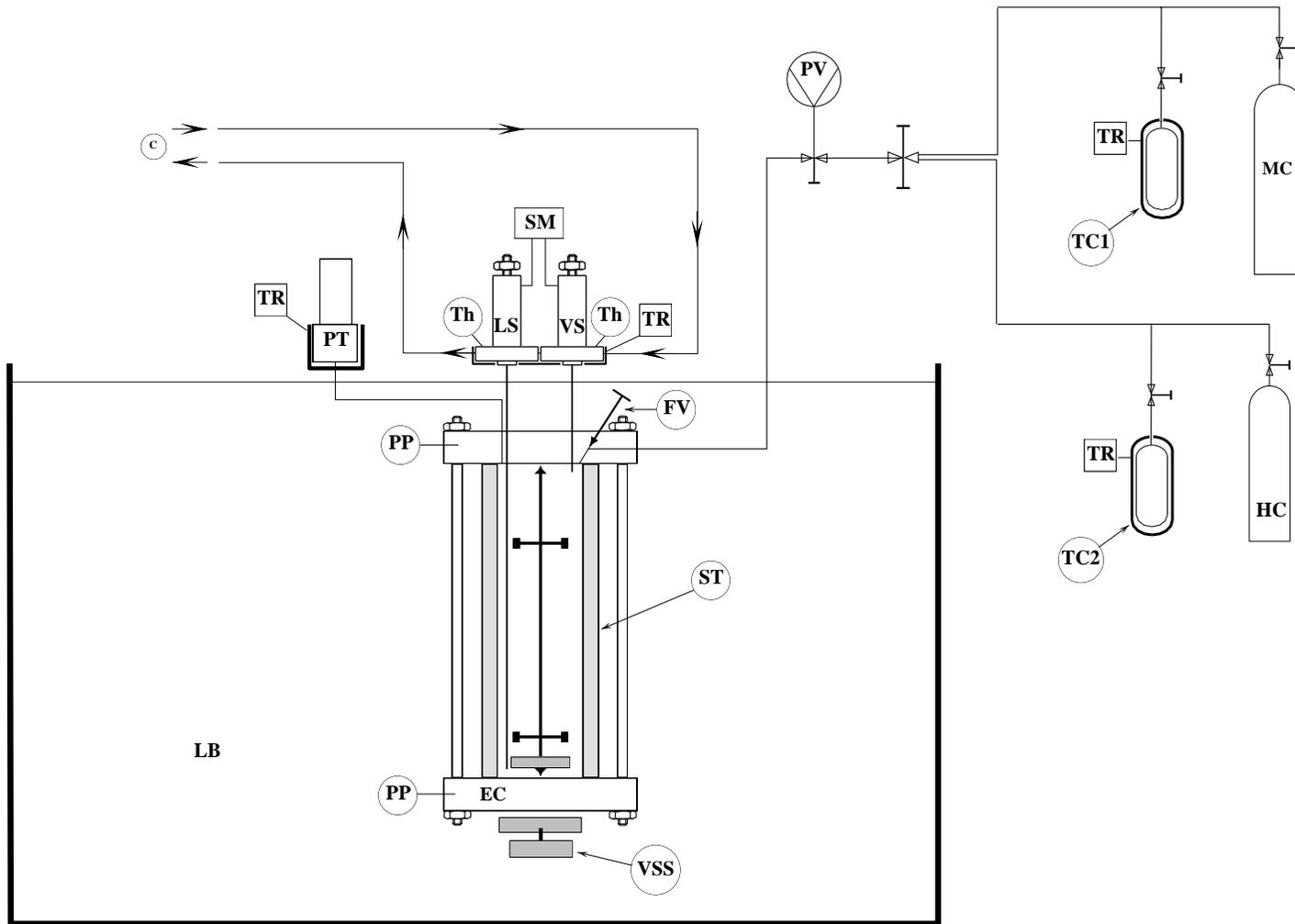


Figure 1

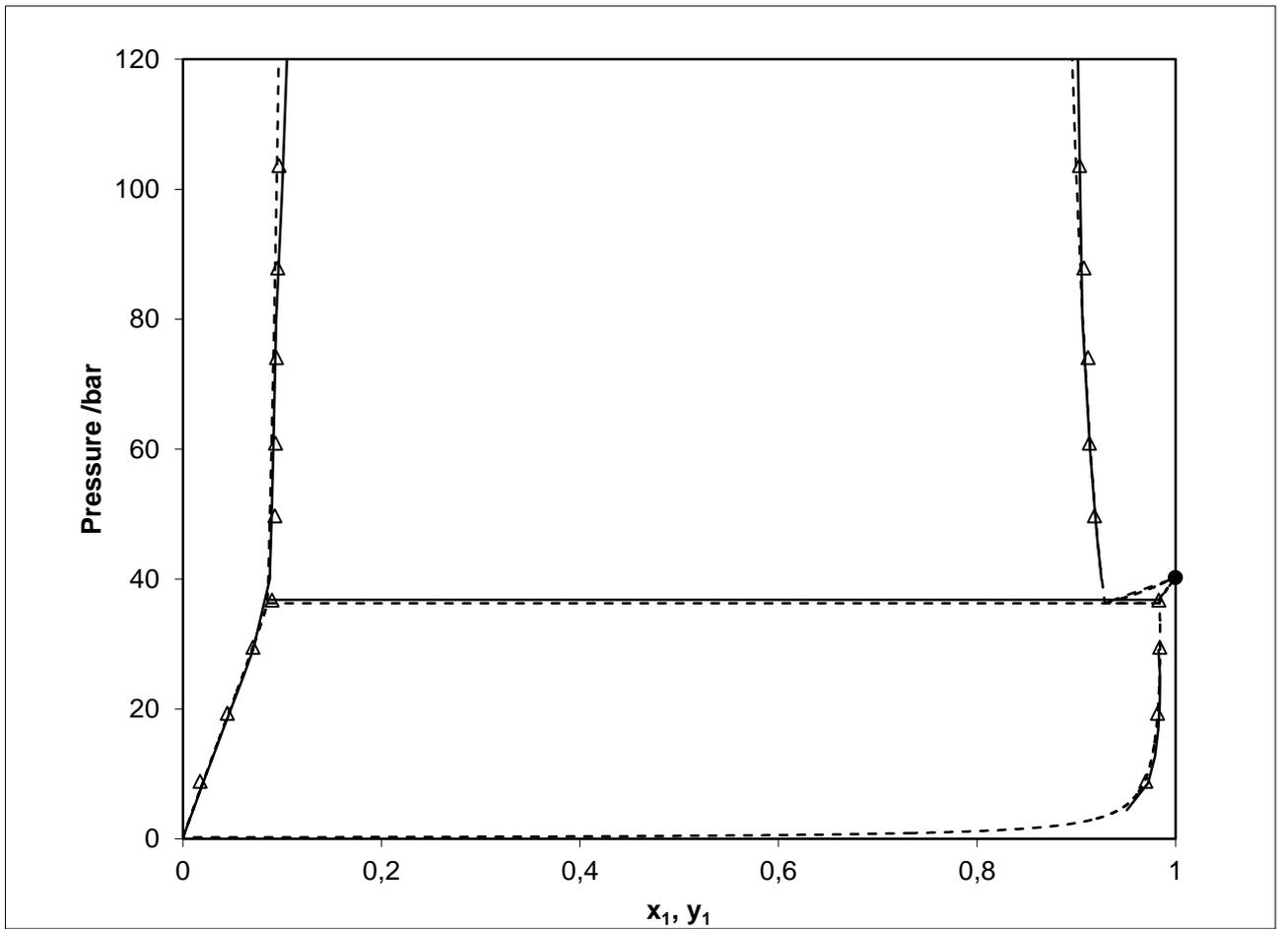


Figure 2

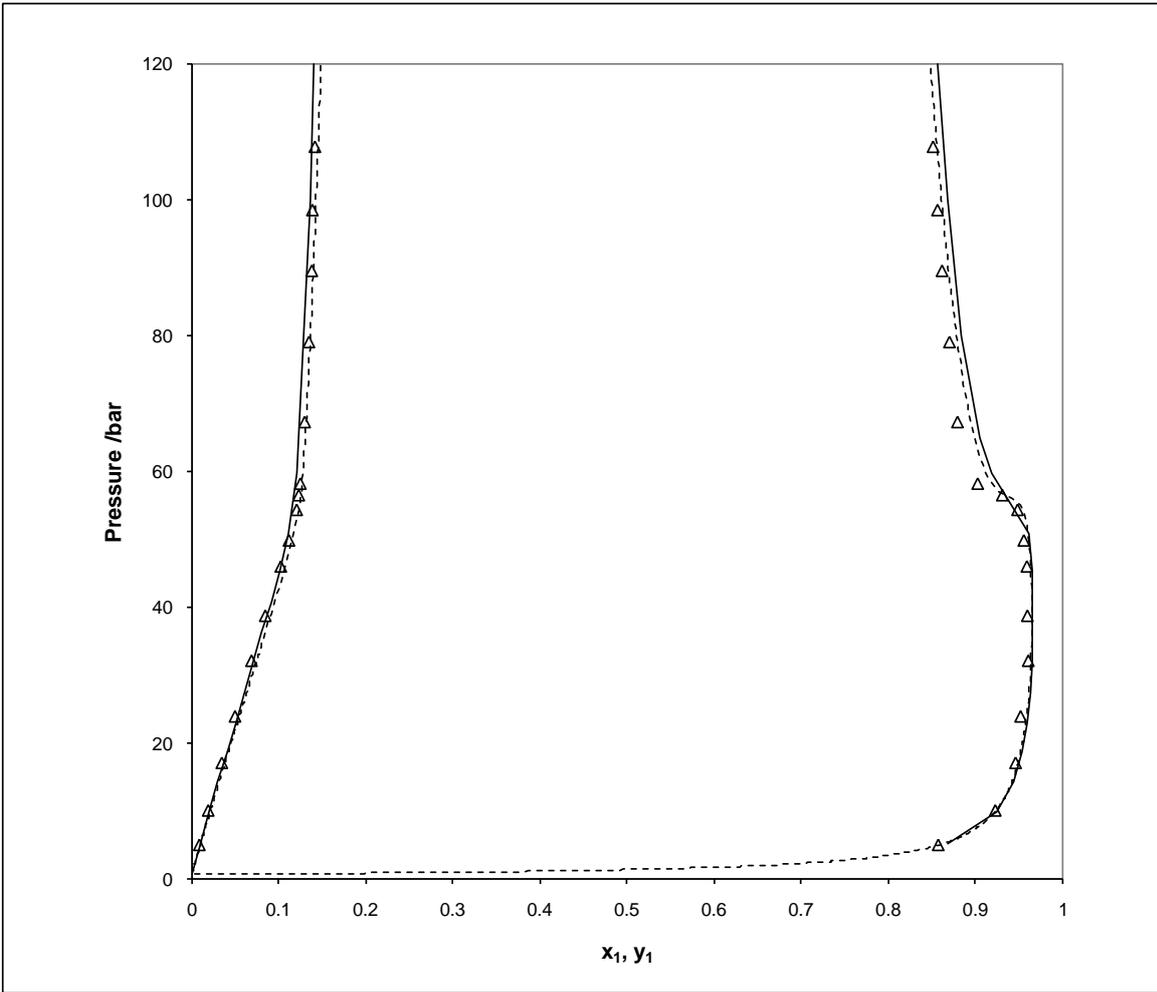


Figure 3

Table 1:

Chemical Name	Source	Initial Vol. Fraction Purity	Purification Method	Final Mole Fraction Purity	Analysis Method
Methane	Air Liquide	0.99995	none	-	SM ^a
Hydrogen Sulphide	Air Liquide	0.995	none	-	SM

a Supplier Method

Table 2

Compound	T_c/K	P_c/MPa	ω
H ₂ S	373.53	8.963	0.094168
CH ₄	190.56	4.599	0.011548

Table 3

EoS	Peng-Robinson	
Coefficients for $T < T_C$	H ₂ S	CH ₄
c_1	0.507354	0.4515742
c_2	0.00757658	-0.172651
c_3	0.342291	0.348424

Coefficients for $T > T_C$	H ₂ S	CH ₄
c_1	0.517478	0.392414

Table 4

P_{exp} /MPa	x_1	y_{1exp}
“Vapor liquid“ equilibria		
$T= 186.25$ K		
0.885	0.017 ₃	0.970 ₃
1.931	0.045 ₀	0.982 ₁
2.948	0.070 ₉	0.984 ₂
3.671	0.089 ₈	0.983 ₃
“Liquid – liquid” equilibria		
P /MPa	x_1^{L1} _{exp}	x_1^{L2} _{exp}
4.970	0.092 ₇	0.918 ₄
6.089	0.093 ₆	0.913 ₅
7.407	0.094 ₃	0.912 ₂
8.787	0.095 ₇	0.908 ₀
10.364	0.097 ₀	0.903 ₆
“Vapor - liquid“ equilibria		
$T= 203.40$ K		
0.043	0	0
0.510	0.009 ₁	0.858 ₅
1.017	0.019 ₃	0.923 ₉
2.402	0.050 ₂	0.953 ₀
3.222	0.069 ₂	0.961 ₈
1.718	0.035 ₀	0.947 ₂
3.884	0.085 ₁	0.960 ₈
4.611	0.103 ₀	0.960 ₂
4.994	0.112 ₄	0.956 ₇
5.444	0.121 ₃	0.949 ₅
5.660	0.123 ₇	0.932 ₀
5.830	0.125 ₅	0.903 ₈
“Liquid – liquid” equilibria		
P /MPa	x_1^{L1} _{exp}	x_1^{L2} _{exp}
6.737	0.130 ₅	0.880 ₆
7.915	0.135 ₄	0.871 ₄
8.964	0.138 ₇	0.862 ₉
9.859	0.139 ₄	0.857 ₇
10.791	0.142 ₃	0.852 ₆

Table 5:

P_{exp}/MPa	x_1	y_{1exp}
$T= 223.17 \text{ K}$		
0.172	0	0
0.442	0.005 ₄	0.590 ₃
0.470	0.006 ₁	0.619 ₁
0.579	0.008 ₃	0.661 ₉
0.753	0.011 ₆	0.742 ₁
1.517	0.027 ₉	0.862 ₉
2.562	0.051 ₈	0.902 ₉
6.538	0.144 ₆	0.923 ₁
8.561	0.191 ₁	0.861 ₈
8.598	0.190 ₄	0.855 ₅
$T= 273.54 \text{ K}$		
5.297	0.080 ₇	0.704 ₅
8.168	0.153 ₈	-
8.174	-	0.745 ₁
12.463	0.312 ₉	0.665 ₄
13.182	0.347 ₅	-
$T= 313.08 \text{ K}$		
3.714	0.014 ₈	0.169 ₆
4.494	0.029 ₂	0.273 ₉
5.156	0.041 ₉	0.335 ₄
5.782	0.054 ₃	0.378 ₆
6.649	0.072 ₆	0.421 ₂
7.485	0.092 ₅	0.456 ₂
8.503	0.116 ₉	0.475 ₇
9.478	0.144 ₇	0.491 ₉
10.620	0.181 ₈	-
11.531	0.216 ₂	-
12.393	0.258 ₅	0.457 ₂
3.714	0.014 ₈	0.169 ₆
4.494	0.029 ₂	0.273 ₉

Table 6:

<i>Reference</i>	<i>T /K</i>	<i>k₁₂</i>
	186.25	0.099
This work	203.40	0.098
	223.17	0.088
	273.54	0.083
	313.08	0.081

Table 7:

<i>References</i>	<i>T /K or range of T /K</i>	<i>Dev. %, P</i>	<i>Dev. % Y (CH₄)</i>	<i>Dev. % Y (H₂S)</i>
	186.90*	6.0	0.2	5.9
	203.40*	11.1	0.8	14.6
This work ; k_{ij} from table 6	223.17	4.3	1.2	4.2
	273.54	4.9	2.7	5.7
	313.08	5.0	3.6	2.1
This work ; k_{ij} given by eq. 7	[186 – 313]	10.3	2.6	16.9
	[186 – 189]*	14.6	0.4	14.3
	[203.4]*	20.8	1.3	20.6
	[210.93]	15.7	1.5	19.4
	[222 – 223]	8.71	2.1	14.2
	[233.15]	13.32	3.7	13.4
	[239.9]	10.13	4.1	12.5
This work	[252]	3.31	2.4	7.2
+ literature ;	[255.38]	9.49	8.2	10.3
k_{ij} given by eq. 8	[273 -274]	5.08	3.6	3.7
	[277.6]	3.65	3.5	3.0
	[299.81]	4.10	3.6	2.3
	[310 -313]	4.42	5.5	2.7
	[322.03]	5.12	9.7	4.3
	[344.26]	3.17	16	3.6

[186 -345]	8.11	5.7	9.5
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* Only VLE data have been considered.