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Phase Behavior of System Methane + Hydrogen Sulfide

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Abstract

An accurate description of the phase behavior of the CH₄+H₂S system is given for temperatures from 70 K to the critical temperature of H₂S and pressures up to 250 MPa. The study includes the solid phases of CH₄ and H₂S. A global pressure-temperature diagram is presented. The types of temperature-composition and pressure-composition phase diagrams that can be encountered in the studied temperature and pressure ranges have been described. The temperature and pressure ranges where the phase behavior of the system changes have been identified and a representative phase diagram is presented for each range. Phase diagrams have been obtained through the solid-liquid-vapor equation of state proposed by Yokozeki. The parameters of the equation of state have been regressed on all the available phase equilibrium data for the considered system.

Keywords: Natural gas purification, Methane-hydrogen sulfide mixture, Equation of state, Phase diagram, Solid-liquid-vapor equilibrium

Introduction

The global energy demand is expected to increase rapidly over the next twenty years. The rise of the primary energy demand is predicted to be 41% between 2012 and 2035.¹ Among fossil fuels consumptions, the natural gas ones are projected to have the most rapid growth trend.¹

Recent studies have shown that 40% of the remaining natural gas reserves are sour² and/or with high CO₂ content³ (15%-80%). In these low quality gas fields, the hydrogen sulfide content in certain gas reservoirs could be high, even up to about 15%.⁴

In this scenario, a detailed description of the phase behavior of systems containing methane and hydrogen sulfide is necessary to perform the correct process design of new gas purification technologies⁵⁻¹⁹ that are required to allow the profitable production of commercial-grade gas from low quality natural gas reserves.²⁰⁻²¹

In the range of temperature and pressure investigated in this work (T from 70 K to the critical temperature of H₂S and P up to 250 MPa), the system CH₄ (1) + H₂S (2) can present two liquid phases (L₁, rich in CH₄, and L₂, rich in H₂S) and two solid phases (S₁, rich in CH₄, and S₂, rich in H₂S) in addition to the vapor phase (V).

Several authors have studied the methane - hydrogen sulfide system from the experimental point of view. The first literature work presenting experimental values for the methane - hydrogen sulfide mixture was published by Reamer et al.²² in 1951. The authors investigated the critical locus and the vapor-liquid equilibrium of the mixture at 277.59 K, 310.93 K and 344.26 K.²²

A total of 6 experimental values of VL₂E were measured by Robinson and coauthors: the correspondent temperatures are 310 K, Robinson and Bailey,²³ and 277 K, Robinson et al.²⁴

A more complete experimental investigation of the phase behavior of the system down to 170 K was carried out by Kohn and Kurata in 1958.²⁵ The different mixture compositions under study leaded the authors inferring the presence of two different solid₂-liquid-vapor equilibrium loci and a solid₂-liquid₂-liquid₁-vapor Quadruple Point (QP). The first S₂LVE locus has a methane rich liquid phase (S₂L₁VE), the second a hydrogen sulfide rich liquid phase (S₂L₂VE). From the QP, a

L_2L_1VE and a $S_2L_2L_1E$ curves originate. The L_2L_1VE curve ends to a first Upper Critical EndPoint (UCEP₁), $L_2(L_1=V)$. Kohn and Kurata treated the solid phase S_2 as pure H_2S .²⁵

Furthermore, Kohn and Kurata argued the presence of a $L_2=V$ critical locus, which is continuous with a $L_1=L_2$ critical locus at high pressure. This latter ends to a second Upper Critical EndPoint at high pressure (UCEP₂), $S_2(L_1=L_2)$, where the critical curve meets the $S_2L_1L_2E$ curve. In addition to these points, same authors claimed the presence of a second quadruple point at a temperature close to the triple point temperature of methane, where two solid phases (S_1 and S_2), a CH_4 -rich liquid phase, and a vapor phase coexist in equilibrium.²⁵

The system described by Kohn and Kurata is then of Type - III according to the classification of phase diagrams of Van Konynenburg and Scott,²⁶ or $1^P A_{In} Q$ according to the one by Bolz et al.²⁷ Furthermore, the mixture presents two totally immiscible solid phases (S_1 and S_2) in the low temperature region.

Cheung and Zander²⁸ reported few experimental points for the S_2L_1E region, while in 1991 supplementary VL_2E values were obtained by Yarim-Agaev et al.²⁹ for temperatures ranging from 222 K up to 273 K. More recently, Coquelet et al.³⁰ have experimentally investigated the VL_2E behavior together with the immiscibility gap in the liquid phase at 186.25 K and 203.4 K, thus proposing the first literature values of L_1L_2E .

From the modeling point of view, different approaches have been used in the literature to represent the phase behavior of the mixture of interest in this work. Equations of state have been largely used to this scope. Examples are the works by Huron et al.,³¹ Adachi et al.,³² Mohsen-Nia et al.,³³ and Sakoda and Uematsu.³⁴⁻³⁵

Huron et al.³¹ used the Soave-Redlich-Kwong Equation of State (EoS); Adachi et al.³² adopted a cubic EoS with four parameters; Mohsen-Nia et al.³³ made use of a two constant cubic EoS; an EoS in the Helmholtz free energy form was used by Sakoda and Uematsu³⁴⁻³⁵ for representing the phase behavior and thermal properties of the system. Same authors investigated the Pressure-Temperature

(PT) diagram including only equilibria between fluid phases (namely VL₂E, L₂L₁VE and the critical locus of the system), without any extension to phase equilibria involving solid phases.³⁴⁻³⁵

Privat et al.³⁶ used a temperature dependent k_{ij} parameter within the group contribution model PPR78 and compared the calculated values with literature data of equilibria involving fluid phases.

Tsivintzelis et al.³⁷ studied the methane-hydrogen sulfide system with the CPA EoS considering four different association schemes for H₂S. As in the works by Sakoda and Uematsu,³⁴⁻³⁵ and Privat et al.,³⁶ Tsivintzelis et al.³⁷ represented only fluid phases.

In 2010, Tang and Gross²⁸ have published the first modeling work involving also the apparition of the solid phase at low temperature. The authors used the PCP-SAFT EoS and the PC-SAFT EoS for the fluid phases and a fugacity equation for the solid phase considered as pure H₂S. Nevertheless, the presented study is limited to temperatures higher than the temperature of the S₂L₂L₁V quadruple point.³⁸

In this work the detailed phase behavior of the CH₄ + H₂S system has been investigated using the analytical equation of state for Solid, Liquid and Vapor phases, SLV EoS.³⁹ The phase diagram has been studied for temperatures from 70 K up to the critical temperature of H₂S and for pressures up to 250 MPa. The CH₄ + H₂S phase behavior has been investigated for the first time in a so wide range of temperature and pressure. With respect to the cited literature works on the phase behavior of the CH₄ + H₂S system, this work adds new information about the phase diagram, especially for the low temperature region and the high pressure region. Isothermal P-x diagrams and isobaric T-x diagrams are presented for all the P-T regions in which the system changes qualitatively the phase behavior. For a chosen temperature and pressure in the investigated P-T range, the reader can find a P-x or T-x diagram representative of the behavior of the system. In practice, this work provides a map of the CH₄ + H₂S phase behavior that can be used for the process design, crystallization risk evaluation, or other purposes that need a reliable representation of the phase behavior of the system.

Solid Transitions in Pure CH₄ and H₂S

From the authors' knowledge, the work by Kohn and Kurata²⁵ is the first dealing with the solid phases of the methane-hydrogen sulfide system. As stated in the previous section, these authors described the phase diagram of the mixture taking into account two solid phases made of pure CH₄ (S₁) and pure H₂S (S₂), respectively.

Nevertheless, these components present different phase transitions in the solid phase. The orders and the types of the transitions that occur in the molecular crystals of methane and hydrogen sulfide have been widely discussed in the literature⁴⁰⁻⁴³, and agreements have been reached about the solid-solid transition temperatures and the related thermodynamic properties.

According to Colwell et al.⁴⁰ methane has two possible crystal lattices (α and β) resulting in a solid _{α} -solid _{β} transition and a related solid _{α} -solid _{β} -vapor triple point located at 20.5 K and vapor pressure ($P \approx 0$). Crystal lattices α and β have been stated to have a face-centered cubic (fcc) structure, and the solid transition involves uniquely changes in the degree of orientational order of the fcc structure.⁴⁰ In 1957, Stevenson⁴¹ used a strong cylindrical container for measuring pressure-volume isotherms and found two additional solid phases (γ and δ). As a consequence, the pressure-temperature diagram of pure methane presents other three solid-solid transition boundaries (β - γ , α - γ , and γ - δ) and a solid _{α} -solid _{β} -solid _{γ} triple point located at about 32 K and 260 MPa. In the low temperature region, the β - γ and γ - δ phase equilibrium curves do not match any other phase transition curve, and they go toward absolute zero at about 90 MPa and 210 MPa, respectively. Furthermore, the γ - δ boundary extends in the high pressure region remaining always located at temperatures lower than 35 K.⁴¹

In 1936, Giauque and Blue⁴² carried out experimental measurements for pure H₂S by means of a calorimetric apparatus and observed two solid-solid transitions in addition to the freezing transition. Authors observed a region of considerable energy absorption at 126 K and a sharp transition at 103.5 K. The former solid-solid transition was explained as an orientational ordering with respect to the rotational vibrations of the hydrogen atoms, whereas a drop in the dielectric constant was

associated to the latter. Giaque and Blue⁴² underlined then the presence of three fcc structures (α , β , and γ) for solid H_2S , and suggested three triple points (solid $_{\alpha}$ -liquid-vapor, solid $_{\alpha}$ -solid $_{\beta}$ -vapor, and solid $_{\beta}$ -solid $_{\gamma}$ -vapor) at vapor pressure ($P \approx 0$). Successively, Stevenson⁴³ showed the presence of other two solid phases (δ and κ) of H_2S in the high pressure region by a volume discontinuity method. The slopes of the related solid-solid boundaries are such as to originate four solid-solid-solid triple points between 110 K and 160 K, and 400 MPa and 900 MPa.⁴³

All the solid-solid-solid triple points of pure methane and hydrogen sulfide occur at pressures higher than 250 MPa,⁴⁰⁻⁴³ then this limit has been considered for the application of the thermodynamic model used in this work. With respect to the low pressure region and the solid-solid-vapor triple points, only pure H_2S presents more than one solid phase in the range of temperature chosen in this work (70 – 373K). Nevertheless, these solid-solid transitions do not involve a meaningful change in the solid-fluid equilibria of the mixture seeing that the solid phase S_2 is always made of fcc crystals of pure H_2S . This aspect has been pointed out in the last section of this work, where the presence of two additional solid phases for pure H_2S have been qualitatively taken into account in a temperature-composition diagram and compared with the case of considering a single solid phase.

Thermodynamic Model

The pressure-explicit equation of state proposed by Yokozeki in 2003 is presented in Eq. 1.³⁹

$$P(T, v) = \frac{RT}{v-b} \frac{v-d}{v-c} - \frac{a}{v^2 + qbv + rb^2} \quad (1)$$

In Eq. 1, P is the pressure, R is the gas constant, T is the temperature, v is the molar volume, a keeps into account the attractive forces among molecules, c is the liquid covolume, b is the solid covolume, d is molar volume for which the repulsive term in Eq. 1 is null, q and r are parameters of the attractive term. The van der Waals attractive term ($q, r = 0$) has been considered in this work.

According to Yokozeki, parameters a and b in Eq. 1 are temperature dependent functions whose functional forms are given in Eqs. 2 and 3:

$$a(T) = \frac{(RT_c)^2}{P_c} \left[a_0 + a_1 T_r \exp(-a_2 T_r^n) \right] \quad (2)$$

$$b(T) = v_c \left[b_0 + b_1 \exp(-b_2 T_r^m) \right] \quad (3)$$

where $T_r = T/T_c$ is the reduced temperature, $a_0, a_1, a_2, n, b_0, b_1, b_2,$ and m are parameters, R is the gas constant, and $T_c, P_c,$ and v_c are temperature, pressure, and volume at the critical point.

The application of Eqs. 1-3 for the representation of the phase equilibrium behavior of a pure component requires the previous evaluation of 11 parameters (the critical volume v_c or equivalently the critical compressibility coefficient $Z_c, a_0, a_1, a_2, n, b_0, b_1, b_2, m, c,$ and d). The procedure deeply illustrated by Stringari et al.⁴⁴ has been used to this scope.

This procedure is based on the analytical representation of the critical and triple points of a pure component, and on the minimization of an objective function based on the isofugacity conditions along the saturation, sublimation, and melting curves. The fugacities of the coexisting phases are evaluated at the experimental conditions (temperature and pressure) of equilibrium.

For CH_4 , pseudo-experimental temperature-pressure couples for vapor-liquid, solid-vapor, and solid-liquid equilibria have been generated from accurate auxiliary equations⁴⁵ considering these values as true equilibrium values. Therefore, it has been considered that comparing the model with

the values obtained from the auxiliary equations (referred to as auxiliary values) is equivalent to compare the model to experimental data, seeing that these auxiliary equations are precise correlations of the available experimental data.

For H₂S, only the auxiliary equation for the vapor-liquid equilibrium is available⁴⁵. Experimental values of sublimation have been proposed by Stevenson,⁴³ and Clark et al.,⁴⁶ while temperature-pressure couples of solid-liquid equilibrium have been generated by means of Eq. 4.

$$P^{SLE} = P_t + \frac{\Delta H^{SLE}}{\Delta v^{SLE}} \left(1 + \frac{T_t}{T} \right) \quad (4)$$

Eq. 4 has been obtained from the expression relating the solid and the liquid fugacities of a pure component, also known as “classic approach”.⁴⁷ In Eq. 4, P_t is the triple point pressure, T_t is the triple point temperature, $\Delta H^{SLE}=H_L-H_S$ and $\Delta v^{SLE}=v_L-v_S$ are latent heat of fusion and the volume change upon melting at the triple point, whose values are 2.377 kJ/mol,⁴⁸ and 3.892 cm³/mol,⁴⁹ respectively.

The references of VLE, SLE, and SVE data needed for the regression of parameters of the pure components are summarized in Table 1.

Table 1. Summary of the data sources used for SVE, SLE, and VLE of pure methane and hydrogen sulfide.

<i>Substance</i>	<i>VLE</i>	<i>SLE</i>	<i>SVE</i>
CH ₄	auxiliary values ⁴⁵	auxiliary values ⁴⁵	auxiliary values ⁴⁵
H ₂ S	auxiliary values ⁴⁵	generated values, Eq. 4	experimental values ^{43,46}

For sake of simplicity, the term data has been henceforth used to group all the kind of values: auxiliary values obtained from auxiliary equations,⁴⁵ experimental values of SVE for H₂S,^{43,46} and SLE values calculated by Eq. 4 for H₂S,⁴⁷.

Values of pressure and temperature at critical and triple points for methane and hydrogen sulfide are presented in Table 2.⁴⁵

Table 2. Temperature and pressure of triple and critical points of methane and hydrogen sulfide.⁴⁵

<i>Substance</i>	P_t / kPa	T_t / K	P_c / MPa	T_c / K
CH ₄	11.697	90.694	4.5992	190.56
H ₂ S	22.3	187.7	9	373.1

For each substance, the P-T range used for the regression of the parameters within the SLV EoS extends from a minimum on the sublimation branch to a maximum on the melting branch. These values are presented in Table 3.

Table 3. Temperature and pressure ranges for the regression of the parameters for methane and hydrogen sulfide.

<i>Substance</i>	<i>SVE</i>		<i>SLE</i>	
	T_{min} / K	P_{min} / kPa	T_{max} / K	P_{max} / MPa
CH ₄	60	0.0164	200	594
H ₂ S	130	0.0417	400	2741

Regressed parameters are Z_c , a_0 , a_1 , a_2 , n , b_0 , b_1 , b_2 , m , c , and d for CH₄ and H₂S are reported in Table 4. Values for CH₄ are the same presented by Stringari et al.,⁴⁴ and here reported for the reader convenience.

Table 4. Parameters of Eqs. 1-3 for methane and hydrogen sulfide.

<i>Substance</i>	Z_c (x10 ²)	a_0 (x10 ²)	a_1	a_2	n	b_0	b_1	b_2	m	c (x10 ²)	d (x10 ²)
CH ₄	37.50400	3.903	21.983	4.051	0.381	0.335	-0.334	4.201	0.682	4.468	4.422
H ₂ S	37.50023	0.998	11.043	3.289	0.503	0.334	-0.236	5.160	1.370	4.430	4.426

The comparison of the phase equilibrium values calculated with Eq. 1 and data is presented in Table 5 in terms of Absolute Average Deviation, Bias, and Maximum Absolute Deviation. Table 5 represents the deviations obtained calculating the equilibrium pressure at fixed temperature; for each kind of equilibrium, N is the number of data used for the comparison. Values for CH₄ are the same presented by Stringari et al.⁴⁴

Table 5. Summary of the statistical errors in calculating equilibrium pressures at fixed temperatures for CH₄ and H₂S.

Errors are evaluated with respect to the auxiliary values of VLE, SLE, SVE of CH₄ and of VLE of H₂S, to the experimental values of SVE of H₂S, and to the values generated from Eq. 4 for SLE of H₂S.

<i>Substance</i>	<i>VLE</i>				<i>SVE</i>				<i>SLE</i>			
	<i>AAD</i> %	<i>Bias</i> %	<i>MAD</i> %	<i>N</i>	<i>AAD</i> %	<i>Bias</i> %	<i>MAD</i> %	<i>N</i>	<i>AAD</i> %	<i>Bias</i> %	<i>MAD</i> %	<i>N</i>
CH ₄	0.11	-0.07	0.26	131	0.03	0.01	0.06	32	0.26	0.00	1.37	141
H ₂ S	0.19	0.85	4.08	118	4.08	1.99	12.38	18	8.08	7.20	13.32	215

According to Table 5, the SLV EoS agrees well with the auxiliary values⁴⁵ of melting, saturation, and sublimation obtained for CH₄. Considering all the kind of equilibrium, the AAD is always lower than 0.3%, the Bias is close to zero, and the highest MAD of about 1.4% is obtained for the SLE.

Similar results are related to the comparison between the SLV EoS and the auxiliary values⁴⁵ of saturation of H₂S; the AAD is 0.19%, the Bias lower than 1%, the MAD is about 4%.

Higher deviations are obtained for the quantitative comparison between calculated and experimental pressures of SVE and SLE of H₂S. With respect to the SVE, the highest deviation (12.38%) occurs at 130K where the experimental pressure is lower than 5×10^{-5} MPa. For the SLE, the AAD, Bias and MAD are about 8%, 7%, and 13%, respectively. It should be remembered that the pressure of melting have been calculated by means of Eq. 4, which is a simple approximation of the solid-liquid equilibrium.

Pressure-temperature equilibrium behaviors obtained with the SLV EoS are represented in Figures 1-2 for CH₄ and H₂S, respectively; empty symbols are selected data of VLE, SLE, and VLE.

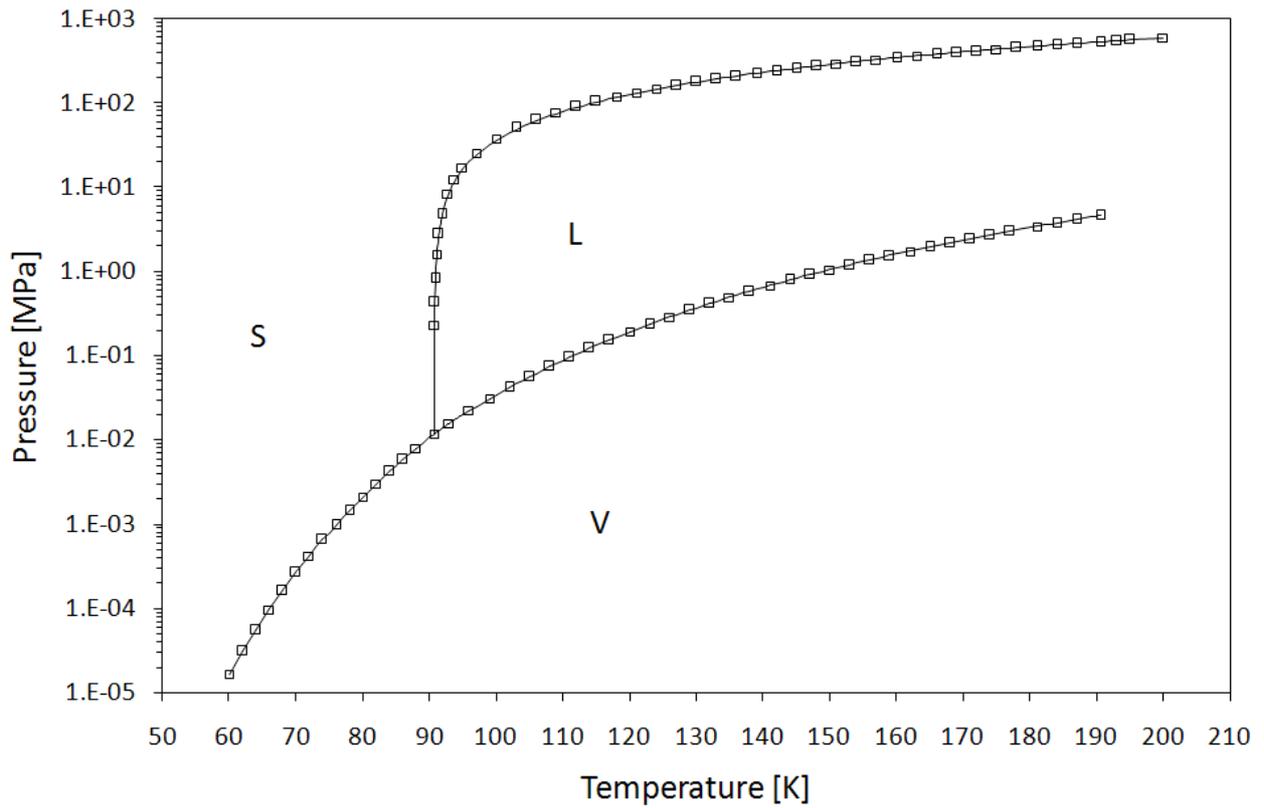


Figure 1. Pressure-temperature phase diagram of CH_4 .
 —: SLV EoS; \square : auxiliary values⁴⁵ for SVE, SLE, and VLE.

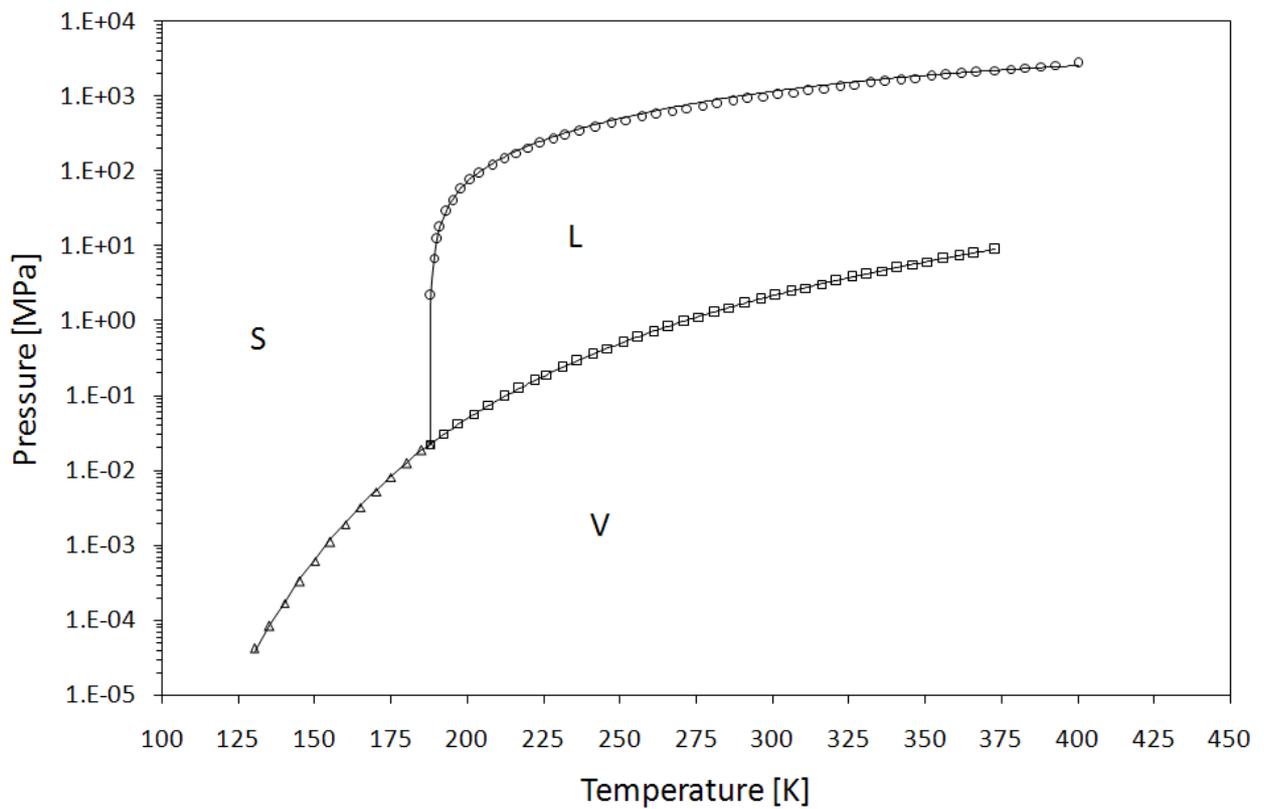


Figure 2. Pressure-temperature phase diagram of H_2S .
 —: SLV EoS; \square : VLE auxiliary values⁴⁵; \circ : SLE generated values, Eq. 4; Δ : SVE experimental values,^{43,46}.

Extension of Eq. 1 to the binary mixture has been considered using the mixing rules proposed by Yokozeki³⁹, Eqs. 5-8. The consistency test for the adopted mixing rules has been presented in Ref. 44.

$$a = \sum_{i,j=1}^{NC} \sqrt{a_i a_j} (1 - k_{ij}) x_i x_j \quad (5)$$

$$b = \sum_{i=1}^{NC} b_i x_i \quad (6)$$

$$c = \sum_{i=1}^{NC} c_i x_i \quad (7)$$

$$d = \sum_{i=1}^{NC} d_i x_i \quad (8)$$

The binary interaction parameter k_{ij} has been regressed by minimization of an objective function defined as the sum of the absolute difference between the calculated and experimental methane compositions, averaged with respect to the total number N of VL₂E, L₂L₁E and S₂L₁E data, Eq. 9.

$$fob = \left[\frac{1}{N} \sum_{i=1}^N \left| x_{CH_4}^{calc} - x_{CH_4}^{exp} \right| \right] \quad (9)$$

In Eq. 9, each calculated composition of methane refers to the equilibrium composition at VL₂E or L₂L₁E obtained by the model by means of a PT flash calculation at imposed experimental temperature and pressure.

In spite of the complex phase equilibrium behavior, a not temperature dependent value for k_{ij} ($k_{ij} = 0.058$) has been found to allow the complete description of the methane-hydrogen sulfide system from 70 K up to the critical temperature of H₂S.

Section 4 presents the comparisons between experimental values of equilibrium and the SLV EoS, while Section 5 illustrates the complete phase diagram of the binary mixture in the temperature and pressure ranges of this work.

As it is possible to observe in the figures presented in the following sections, the solid phases S₂ and S₁ calculated by the model are not always pure phases. This discrepancy with what is expected

according to the literature depends heavily on the functional form of Eqs. 5-8. Because the mixing rules used for the volumetric parameter b , c , and d are of the type developed for the fluid phase, it follows that the solid phase is treated as a liquid-like phase, which entails the solubility in the solid phase. The fact that the solid phases are not constituted by a pure component does not affect the quality of the representation of the temperature-pressure-composition data of the fluid phases in equilibrium with the solid.

Model Validation

This section has the scope to assess the accuracy and reliability of the developed SLV EoS in representing the existing phase equilibrium data. Once the SLV EoS validated, it will be used in Section 5 for predicting the phase equilibrium behavior of the $\text{CH}_4 + \text{H}_2\text{S}$ system in the considered range of temperature and pressure.

The quantitative comparison between the values calculated by means of Eq. 1, with the mixing rules of Eqs. 5-8, and the experimental values proposed in the literature is illustrated in Table 6.

The first part of Table 6 presents the comparison between calculated and experimental values of VL_2E , $\text{L}_1\text{L}_2\text{E}$, and $\text{S}_2\text{L}_1\text{E}$; errors are in terms of the compositions of methane in the liquid and the vapor phase, obtained by means of a PT flash calculation at imposed experimental temperature and pressure.

The second part of Table 6 portrays the comparison with respect to the experimental values of temperature and pressure related to the three-phase equilibria $\text{S}_2\text{L}_1\text{VE}$, $\text{S}_2\text{L}_2\text{VE}$, $\text{L}_2\text{L}_1\text{VE}$, and $\text{S}_2\text{L}_2\text{L}_1\text{E}$. Errors in terms of temperature have been obtained comparing the experimental value with the temperature calculated imposing the experimental pressure of three-phase equilibrium. Errors in terms of pressure have been obtained comparing the experimental value with the pressure calculated imposing the experimental temperature of three-phase equilibrium.

Finally, the last two rows present the comparison along the Critical Curve (CC) of the mixture; errors have been evaluated comparing experimental and calculated values of temperature and pressure at fixed composition of methane.

Table 6. Quantitative comparison of equilibrium compositions, temperatures and pressures of three-phase equilibria, and critical temperatures and pressures for the system $x\text{CH}_4+(1-x)\text{H}_2\text{S}$.

Reference	N	Kind of data	T K	P MPa	x	y	PT FLASH		
							x	y	
Reamer et al. 1951 ²²	59	VL ₂ E TP _{xy}	277-344	1.4-13.4	0.0057-0.55	0.059-0.73	N calc	57	57
							AAD%	10.03	5.24
							Bias%	4.36	-1.43
							MAD%	33.70	28.17
Robinson and Bailey 1957 ²³	3	VL ₂ E TP _{xy}	310	4.1-12.4	0.033-0.26	0.29-0.51	N calc	3	3
							AAD%	16.48	5.38
							Bias%	9.83	-1.93
							MAD%	24.41	9.69
Kohn and Kurata 1958 ²⁵	54	VL ₂ E TP _{xy}	188-344	1.4-11.0	0.005-0.24	0.10-0.97	N calc	51	51
							AAD%	18.31	4.29
							Bias%	13.62	-2.71
							MAD%	87.17	31.17
Robinson et al. 1959 ²⁴	3	VL ₂ E TP _{xy}	277	2.8-11.0	0.023-0.26	0.51-0.72	N calc	3	3
							AAD%	20.56	0.31
							Bias%	20.56	-0.26
							MAD%	43.52	0.85
Cheung and Zander 1968 ²⁸	6	S ₂ L ₁ E T _x	119-162		0.98-0.99		N calc	6	
							AAD%	1.23	
							Bias%	-1.23	
							MAD%	2.57	
Yarim-Agaev et al. 1991 ²⁹	42	VL ₂ E TP _{xy}	222-273	0.7-11.8	0.001-0.36	0.14-0.90	N calc	42	27
							AAD%	16.34	3.53
							Bias%	13.14	3.27
							MAD%	261.53	6.45
Coquelet et al. 2014 ³⁰	14	VL ₂ E TP _{xy}	186-203	0.5-5.8	0.0091-0.13	0.86-0.98	N calc	13	13
							AAD%	4.34	0.81
							Bias%	-4.11	0.71
							MAD%	13.17	1.77
	10	L ₁ L ₂ E TP _{xx}	186-203	6.7-10.8	0.090-0.14	0.85-0.98	N calc	11	11
							AAD%	10.37	1.15
							Bias%	-10.37	-0.92
							MAD%	16.56	5.75
Reference	N	Kind of data	T K	P MPa	THREE-PHASE EQ.				
					T	P			
Kohn and Kurata 1958 ²⁵	3	S ₂ L ₁ VE ¹	167-168	2.05-2.2			N calc	3	3
							AAD%	0.56	3.16
							Bias%	0.56	-3.16
							MAD%	0.83	4.69
	8	S ₂ L ₂ VE ¹	184-186	0.04-2.01			N calc	8	8
							AAD%	0.93	>100
							Bias%	0.93	>100
							MAD%	1.46	>100
	3	L ₂ L ₁ VE ¹	186-200	3.6-5.3			N calc	3	3
							AAD%	0.42	1.99
							Bias%	0.27	-1.32
							MAD%	0.64	2.93
	10	S ₂ L ₂ L ₁ E ¹	183-185	6.03-13.7			N calc	10	2
							AAD%	0.52	28.15
							Bias%	0.52	-28.15
							MAD%	0.88	46.40

Reference	N	Kind of data	Tc K	Pc MPa	x	CRITICAL POINTS		
						Tc	Pc	
Reamer et al. 1951 ²²	6	CC TPx	267-361	10.2-13.4	0.1-0.6	N calc	5	5
						AAD%	1.22	1.60
						Bias%	1.05	-0.02
						MAD%	2.00	3.09
Kohn and Kurata 1958 ²⁵	4	CC TPx	193-364	4.8-12.0	0.067-0.97	N calc	4	4
						AAD%	1.89	4.58
						Bias%	1.89	1.01
						MAD%	2.70	6.32

¹ Values evaluated from pressure-temperature diagrams prepared from experimental isotherms by cross-plotting at constant percentage of liquid.

According to Table 6, the critical values of Reamer et al. and Kohn and Kurata²⁵ are well represented by the model; the maximum MAD considering the two sources of experimental values is about 6%.

The model agrees well also with the values of S₂L₁E of Cheung and Zander,²⁸ and the L₂L₁E values of Coquelet et al.³⁰ In this last case, a MAD of about 17% is found at 186 K and 3.7 MPa for a composition of methane in the liquid phase lower than 0.1.

Considering all the VL₂E experimental values, the methane composition in the vapor phase is represented within an overall AAD of about 5%, the Bias% is between about -3% and 4%, while the highest values of MAD of about 30% are found with respect to the data of Reamer et al.²² and Kohn and Kurata²⁵ for two compositions lower than 0.1. Taking into account the deviations in Table 6 related to the composition of the liquid phase mole fraction, it is possible to state that the AAD is always lower than about 21%, and that the MAD is higher than in the vapor phase. Higher percentage deviations are encountered in the liquid phase because of the low CH₄ mole fraction. For instance, the MAD of about 34% (Reamer et al.²²), 87% (Kohn and Kurata²⁵), and 260% (Yarim-Agaev²⁹) are related to experimental liquid compositions of methane of 0.0057, 0.0125, and 0.001, respectively.

With respect to phase equilibria involving three phases, a good agreement is achieved along the S₂L₁VE and L₂L₁VE boundaries. The extent to which the pressures of S₂L₂L₁E and S₂L₂VE calculated by the SLV EoS deviate from the experimental pressures is a direct consequence of the

difference between the calculated and the experimental temperature at the quadruple point, as discussed later in this section.

Table 7 presents the quantitative comparison between the SLV EoS and the experimental values (composition of methane, temperature, and pressure) proposed by Kohn and Kurata²⁵ concerning the Quadruple Point ($S_2L_2L_1VE$) and the Upper Critical EndPoint $L_2(L_1=V)$.

With respect to the QP, the relative percentage errors between calculated and literature values are about -0.6%, -32%, and 2% for the composition of CH_4 in the liquid L_1 , liquid L_2 , and vapor phase, respectively; the temperature and pressure of the QP are reproduced by the model within 1% of deviation. It should be noted that in Ref. 25 the solid phase S_2 is treated as pure H_2S , whereas the calculated mole fraction of methane in the S_2 phase is 0.046.

With respect to the UCEP₁, the deviations related to the experimental temperature and pressure are about 1.3% and 2.6%, respectively. For the composition of methane, the errors are -1.28% for the $L_1=V$ phase and 14% for the L_2 phase.

Improved representations could have been obtained using more complex mixing rules involving binary interaction parameters instead of Eqs. 6-8 and/or introducing temperature dependent binary interaction parameters, but authors decided to use a single binary interaction parameter, k_{ij} , constant with temperature, to increase the prediction capability of the model. The model is applied in the next section for representing the whole and complex phase diagram of the mixture in a wide range of temperature and pressure even for regions where data are scarce or not at all available. The chosen parameterization of the SLV EoS is then a compromise between the accuracy in representing the existing experimental values and the robustness of the model with respect to extrapolation for predicting the phase diagrams at temperatures and pressures for which experimental values are not available.

Table 7. Comparison between calculated and the experimental²⁵ singular points for the methane-hydrogen sulfide system.

	x_{CH_4} in S_2	x_{CH_4} in L_1	x_{CH_4} in L_2	x_{CH_4} in V	T / K	P / MPa
QP ($S_2L_1L_2VE$)						
Ref. 25	0	0.935	0.104	0.967	182.21	3.38
SLV EoS	0.046	0.929	0.071	0.988	183.92	3.40
err%	/	-0.64	-31.73	2.17	0.94	0.59
UCEP ₁ $L_2(L_1=V)$						
Ref. 25	/	0.935	0.1	0.935	199.76	5.30
SLV EoS	/	0.923	0.114	0.923	202.25	5.44
err%	/	-1.28%	14.00	-1.28%	1.25	2.64

Figures 3-7 portray some qualitative comparisons between selected experimental values and the model.

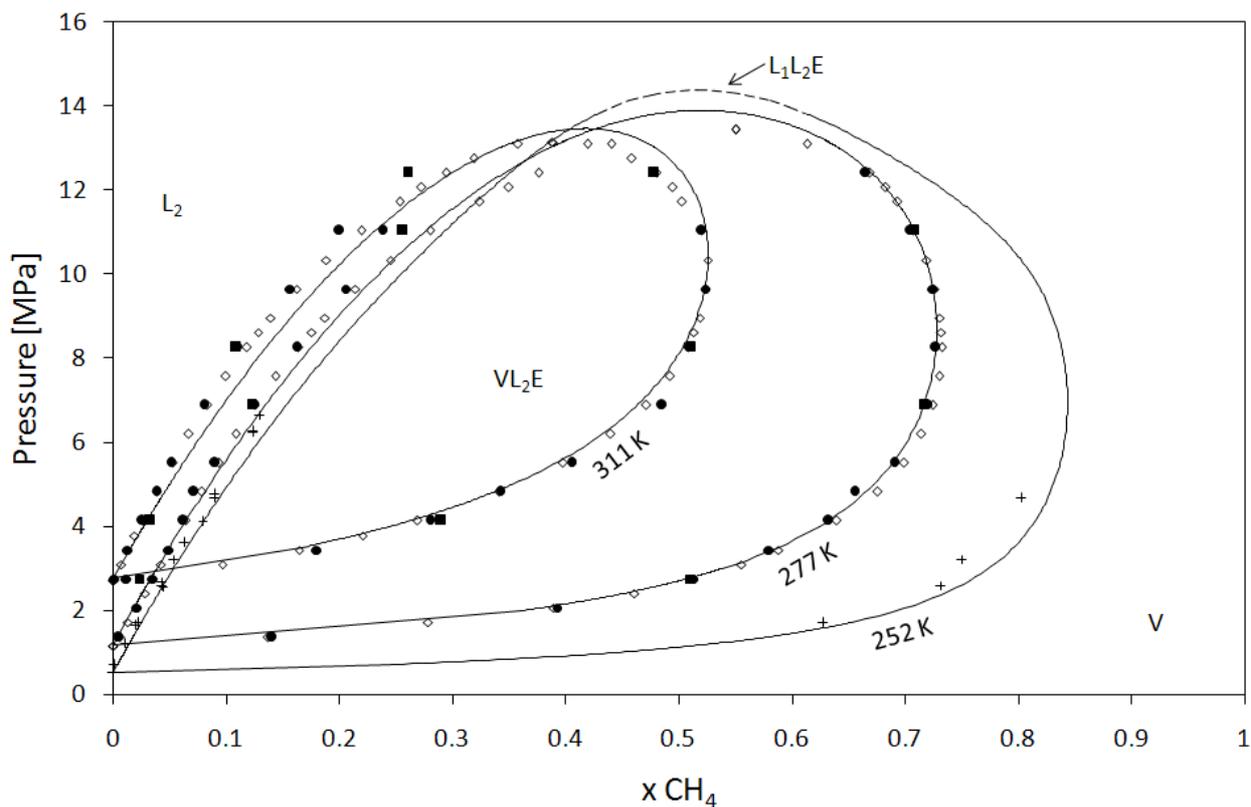


Figure 3. Pressure-composition diagram at 252K, 277 K, and 311 K.

Data: \diamond : Reamer et al.²²; \bullet : Kohn and Kurata²⁵; \blacksquare : Robinson et al.²⁴, Robinson and Bailey²³; $+$: Yarim-Agaev²⁹. SLV EoS: —: VL_2E , - -: L_1L_2E .

The pressure-composition cross sections in Figure 3 show the agreement of the SLV EoS with VL_2E data in the range 252 – 311 K. Data in Figure 3 are rather consistent among them, and the

model slightly deviates from the experimental composition of methane in the L_2 phase when the temperature increases approaching the critical temperature of pure H_2S .

In Figure 3, the isotherms at 277 K and 311 K end at a $V=L_2$ critical point. To the contrary, at 252 K the VL_2E becomes a L_1L_2E at about 13.8 MPa and the isotherm ends at a $L_1=L_2$ critical point, thus explaining the odd shape of the isotherm at this temperature with respect to the behaviors at the higher temperatures shown in Figure 3. The dashed line in Figure 3 represents the L_1L_2E at 252 K.

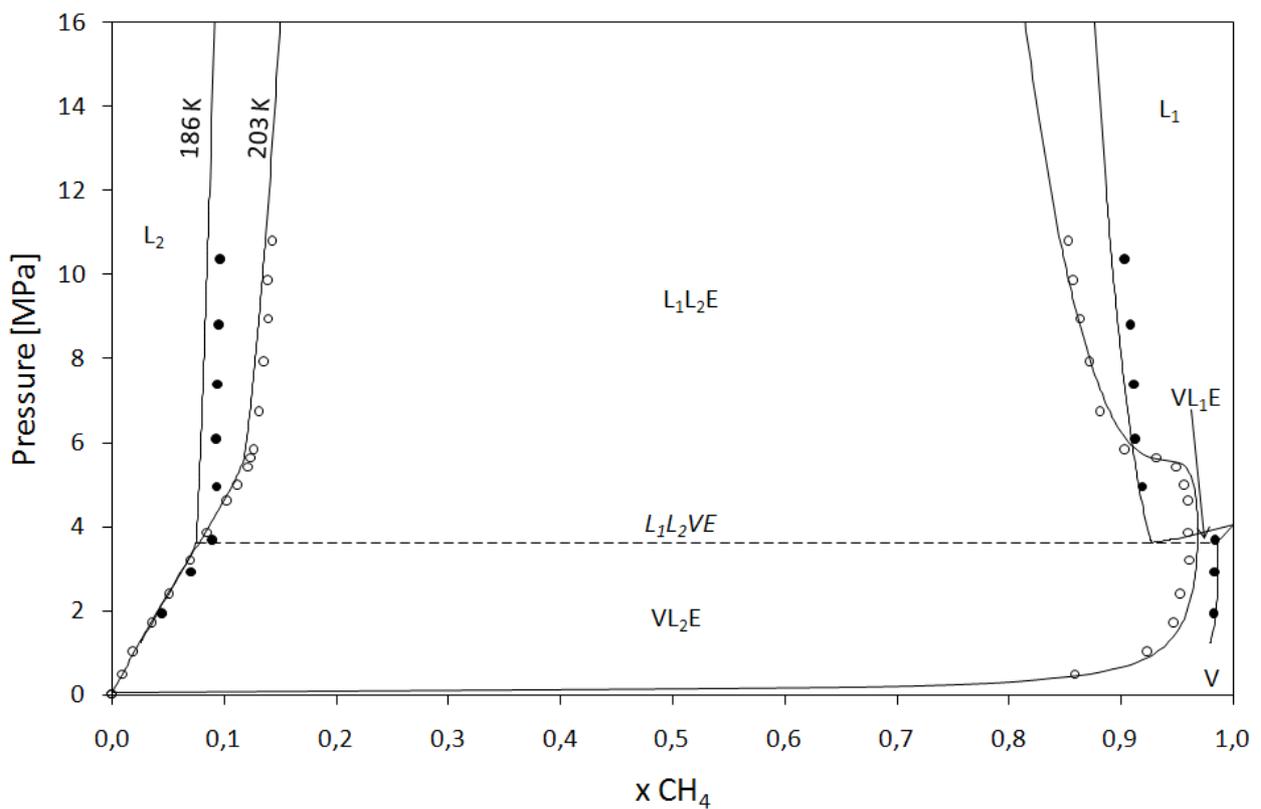


Figure 4. Pressure-composition diagram at 186 K and 203 K.

SLV EoS: — : VL_1E , VL_2E , and L_2L_1E ; -- : L_2L_1VE . Data of Coquelet et al.³⁰: ● : 186 K; ○ : 203 K.

Figure 4 presents the qualitative comparison at 186 and 203 K; data are from Coquelet et al.³⁰ At 203 K the system presents immiscibility between two liquid phases (L_1 and L_2), and the one rich in methane (L_1) becomes a vapor phase in the low pressure region. Being this temperature higher than the calculated temperature of the $UCEP_1$ (202.25 K from Table 7), the transition from L_1 to the vapor does not involve neither a VL_1E nor a critical point $L_1=V$.

A VL₁E occurs at any temperature lower than the critical temperature of methane (190.56 K) and higher than the calculated temperature of the quadruple point QP₁ (183.92 K from Table 7), as for 186 K in Figure 4. Furthermore, a L₂L₁VE appears because of the immiscibility gap in the liquid phase. The isotherm at 186K has not been presented in Figure 4 in the low pressure region seeing that a solid phase and related solid-fluid equilibria are involved there. Nevertheless, next section presents the complete phase equilibrium behavior.

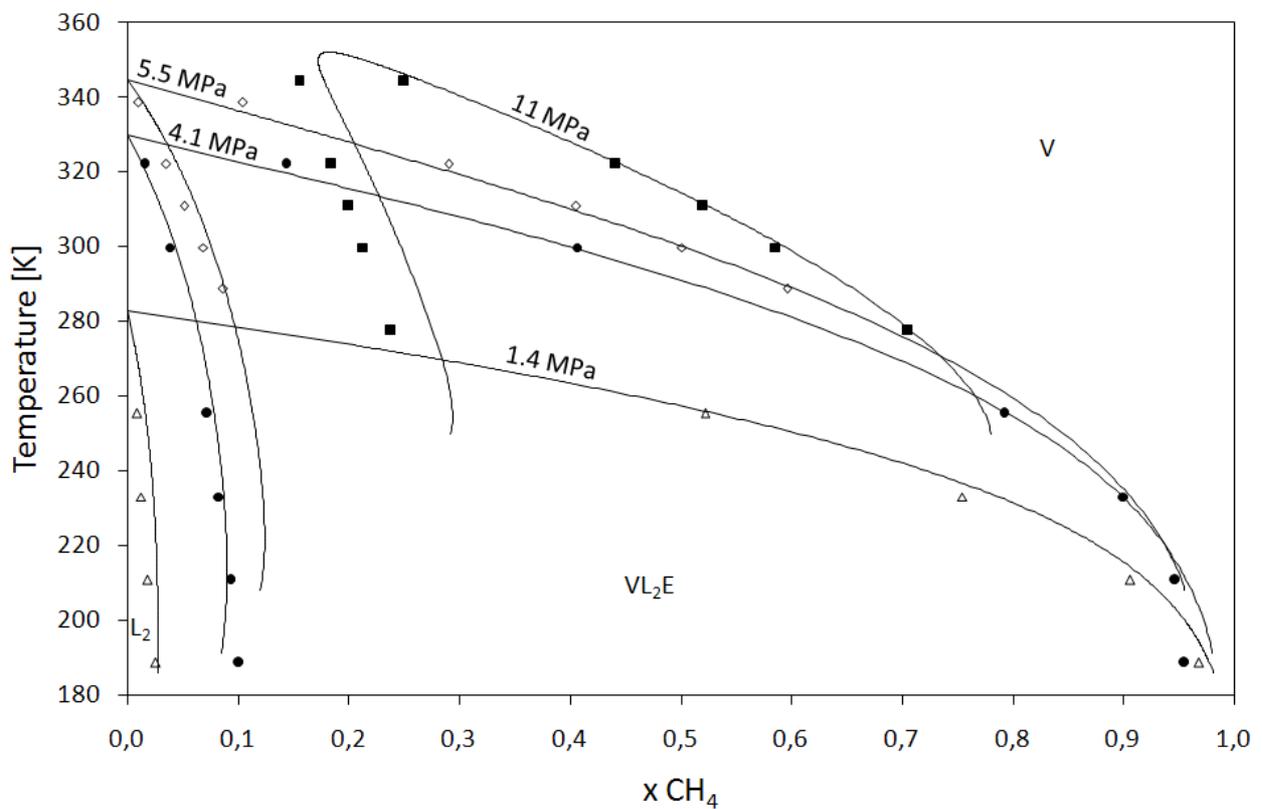


Figure 5. Temperature-composition diagram at 1.4, 4.1, 5.5, and 11 MPa.
 — : SLV EoS. Data of Kohn and Kurata²⁵: ■ : 11 MPa; ◇ : 5.5 MPa; ● : 4.1 MPa; △ : 1.4 MPa.

The temperature-composition cross sections of Figure 5 show the phase equilibrium behavior of the CH₄+H₂S system between 1.4 MPa and 11 MPa. Only the VL₂E has been presented in Figure 5, whereas the low temperature equilibria have been added and discussed in the next section. According to Figure 5, the SLV EoS is in a quite good agreement with data, except for the deviation with respect to the composition of methane in the L₂ phase at 11 MPa. As a consequence, the

calculated $L_2=V$ critical point appears to have a higher methane content than what can be inferred from the experimental values.

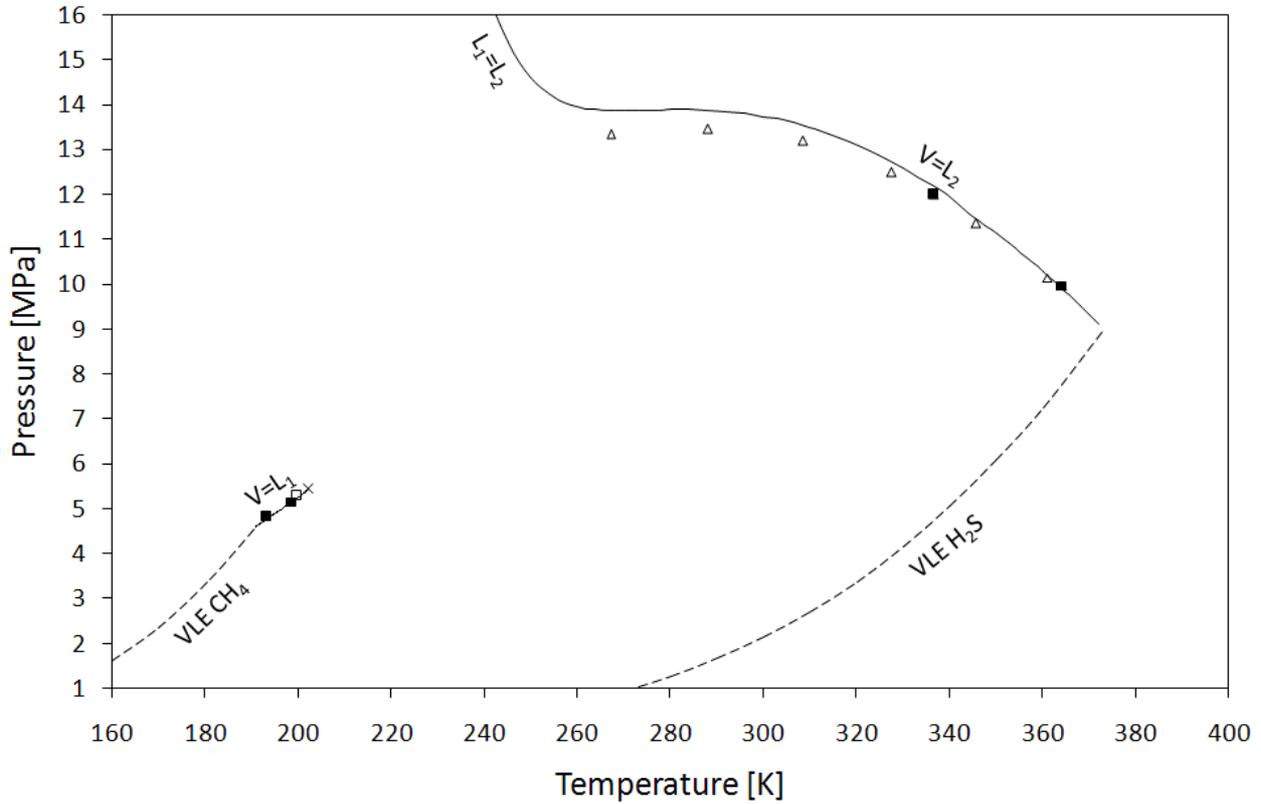


Figure 6. Vapor-liquid and liquid-liquid critical loci for the $\text{CH}_4+\text{H}_2\text{S}$ system.
 Data: $V=L_1$ and $V=L_2$: ■ : Kohn and Kurata²⁵; Δ : Reamer et al.²²; $L_2(L_1=V)$: □ : Kohn and Kurata²⁵.
 SLV EoS: - - : VLE of CH_4 and H_2S ; — : $V=L_1$, $V=L_2$ and $L_1=L_2$; × : $L_2(L_1=V)$.

Figure 6 illustrates the comparison between calculated and experimental values of the critical points of the mixture. Considering the left-branch of the critical curve (mixtures at higher methane content), deviations concerning the calculated (cross) and experimental (empty square) UCEP_1 have been already presented in Table 7. The calculated $L_1=V$ critical curve exits the critical point of methane (see Table 2) and rises up to the UCEP_1 .

The calculated $L_2=V$ critical curve originates from the critical point of H_2S (see Table 2) and reaches firstly a local maximum and then a local minimum in pressure while extending toward the low temperature region. These values (respectively 13.9 MPa and 13.87 MPa) are located at temperatures higher than about 266 K, temperature where, in the critical curve, the vapor phase

becomes a liquid phase rich in methane (phase L_1). As a consequence, the $L_2=L_1$ critical curve replaces the $L_2=V$ one for temperature lower than 266 K, and it develops in the high pressure region for decreasing temperatures. This $L_2=L_1$ critical curve ends in the singular point $S_2(L_2=L_1)$, $UCEP_2$, as discussed in the next section.

With respect to the data of Reamer et al.,²² the calculated critical curve develops at pressures slightly higher than the experimental values before reaching the inflection point and the $L_2=L_1 - L_2=V$ transition.

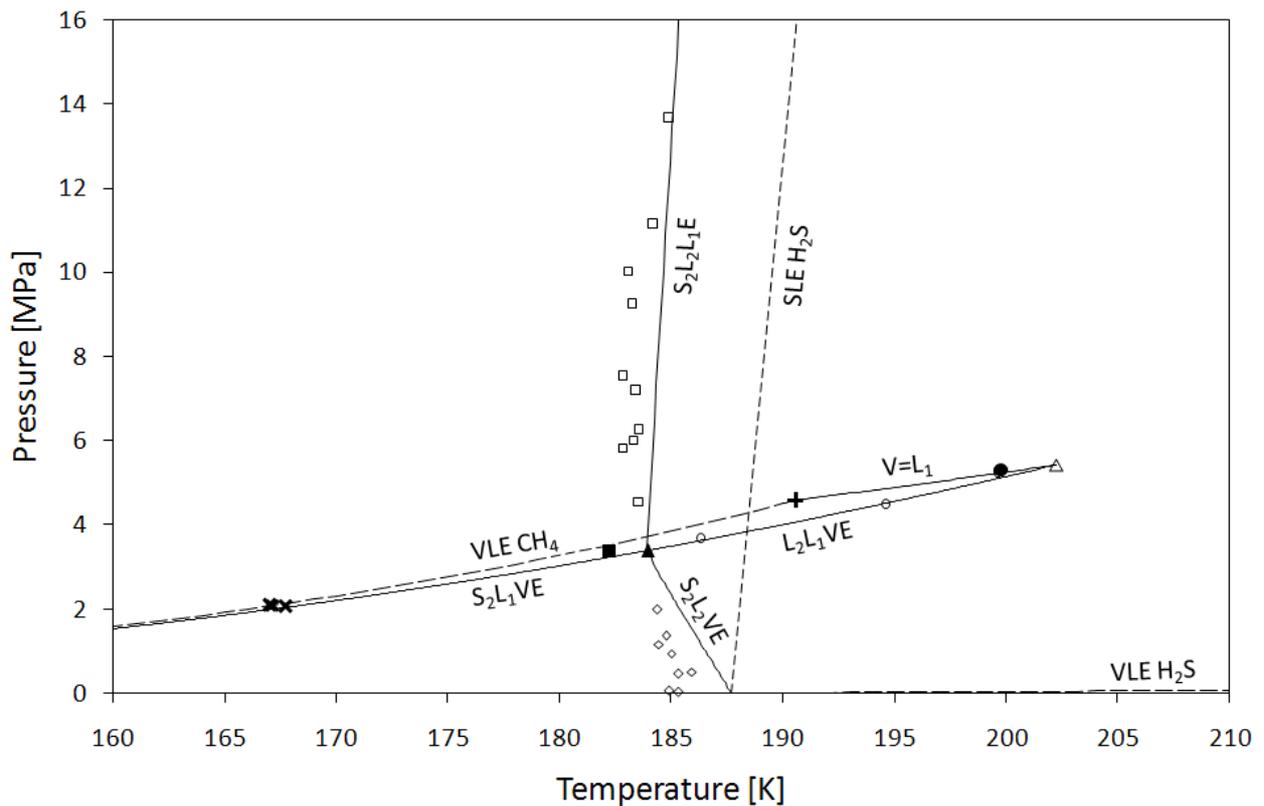


Figure 7. Pressure-temperature phase diagram of the CH_4+H_2S system in proximity of the QP_1 .

Data of Kohn and Kurata²⁵: \diamond : S_2L_2VE ; \circ : L_2L_1VE ; \square : $S_2L_2L_1E$; \times : S_2L_1VE ; \blacksquare : QP_1 ; \bullet : $UCEP_1$.

SLV EoS : — : three-phase equilibrium and $V=L_1$ curve; - - : VLE of CH_4 , SLE and VLE of H_2S ;

+ : critical point of CH_4 ; \blacktriangledown : triple point of H_2S ; \blacktriangle : QP_1 ; \triangle : $UCEP_1$.

Figure 7 groups all the three-phase equilibria of the binary mixture occurring at temperatures higher than 160 K and pressures up to 16 MPa. It should be remarked that being the data in Figure 7 not available numerically, they have been obtained from graphs²⁵ by means of a specific software.

Filled square and circle represent the experimental temperature-pressure couples for the quadruple point and the UCEP₁, respectively; correspondent calculated values are the filled triangle and the empty triangle. The dashed curves in Figure 7 are the saturation curves of CH₄ and H₂S, and the melting curve of H₂S as calculated by the SLV EoS.

Four three-phase boundaries originate from the calculated QP; the S₂L₁VE curve which extends down to 160 K remaining close to the saturation curve of methane; the L₂L₁VE curve ending at the calculated UCEP₁; the S₂L₂L₁E curve which rapidly extends in the high pressure region; the S₂L₂VE curve which joins the triple point of H₂S (▼). For sake of completeness, the V=L₁ critical curve has been added in Figure 7; it exits the critical point of CH₄ (+) and joins the UCEP₁ (Δ).

The deviation between the calculated S₂L₂L₁E and S₂L₂VE boundaries and the experimental trends which can be inferred from the correspondent available data (respectively empty squares and diamonds) can be related to the deviation between the calculated and experimental temperature of the QP (see Table 7). Furthermore, the S₂L₂VE data²⁵ seem not to extend in the low pressure region towards the triple point temperature of pure H₂S (187.7 K, 22.3 kPa). In fact, the experimental points tend to a temperature of about 185 K in the zero-pressure limit, temperature that is about 3 degrees lower than the triple point temperature of H₂S proposed in Ref. 45. This explains the remarkable deviations for the S₂L₂L₁E and S₂L₂VE presented in Table 7.

As previously stated, next section aims at presenting an overview of the phase equilibrium behavior of the CH₄+H₂S system by means of several isotherms and isobars. With respect to this section, solid phases and correspondent equilibria have been added in cross sections and P-T diagrams in order to present the whole phase equilibrium behavior.

Description of the Phase Diagram of the Methane-Hydrogen Sulfide System

This section has the scope of describing the pressure-temperature phase diagram and all the possible types of pressure-composition and temperature-composition phase diagrams that can be encountered in the investigated range of temperature and pressure. This analysis aims to be helpful to the process engineer who needs to understand how the CH₄+H₂S system behaves at a certain temperature and pressure.

Figure 8 presents the pressure-temperature phase diagram of the CH₄+H₂S mixture for temperatures from 70 K up to the critical temperature of H₂S and pressures up to 250 MPa.

According to the available experimental values and the results of the SLV EoS, in these ranges the mixture presents two Quadruple Points and two Upper Critical EndPoints. The QPs are related to the S₂S₁L₁VE (QP₂) and the S₂L₂L₁VE (QP₁); the UCEPs are related to the singular points L₂(L₁=V), UCEP₁, and the S₂(L₂=L₁), UCEP₂.

The phase equilibrium behavior involves then 7 three-phase equilibrium boundaries (S₂S₁VE, S₂S₁L₁E, S₁L₁VE, S₂L₁VE, S₂L₂VE, S₂L₂L₁E, and L₂L₁VE) and 5 phases (S₂, S₁, L₂, L₁, and V).

Taking into account the huge range of pressure considered in this work, the y-axis in Figure 8 has been cut twice (at 0.5 MPa and 19 MPa) for easing the comprehension of the equilibria occurring in proximity of the QP₂, of the points QP₁-UCEP₁, and the high-pressure equilibria located near the UCEP₂. Furthermore, a zoom of Figure 8 has been presented in Figure 9 in order to show the phase equilibrium behavior in the low-pressure region, namely in proximity of the QP₂ and the triple point of CH₄.

In the low pressure region of Figure 8, 0-0.5 MPa, the QP₂ almost overlaps the triple point of pure methane, than the saturation, melting, and sublimation curves of pure CH₄ are not clearly visible being overlapped by the S₂S₁VE, S₂S₁L₁E, and S₂L₁VE curves. The S₂L₂VE curve originates at the triple point of H₂S, and extends at higher pressures with a negative slope.

The more complex part of the phase equilibrium behavior concentrates between 0.5 MPa and 19 MPa. The S₂S₁L₁E remains close to the SLE of CH₄, while the S₂L₁VE boundary distances itself

from the saturation curve of CH_4 while approaching the filled triangle, which represents the QP_1 . The $\text{S}_2\text{L}_2\text{VE}$, curve originating at the triple point of H_2S , also ends at the QP_1 . The other three-phase equilibria joining the QP_1 are the $\text{L}_2\text{L}_1\text{VE}$ and the $\text{S}_2\text{L}_2\text{L}_1\text{E}$. The former reaches the UCEP_1 , namely the empty triangle in Figure 8, the latter extends rapidly at high pressures with a positive slope. In addition to that, two critical boundaries occur: the $\text{V}=\text{L}_1$ loci leaving the critical point of CH_4 to end in the UCEP_1 , and the $\text{V}=\text{L}_2$ loci originating from the critical point of H_2S and becoming the $\text{L}_2=\text{L}_1$ loci at low temperatures.

In the high pressure region of Figure 8, the $\text{S}_2\text{S}_1\text{L}_1\text{E}$ starts to deviate from the SLE of CH_4 , and the $\text{L}_2=\text{L}_1$ loci meets the $\text{S}_2\text{L}_2\text{L}_1\text{E}$ curve at the empty square, namely the UCEP_2 (208.98 K and 224.09 MPa). As a consequence, the L_2 and L_1 phases become a unique liquid phase for any pressure higher than the pressure at the UCEP_2 , $\text{S}_2(\text{L}_2=\text{L}_1)$.

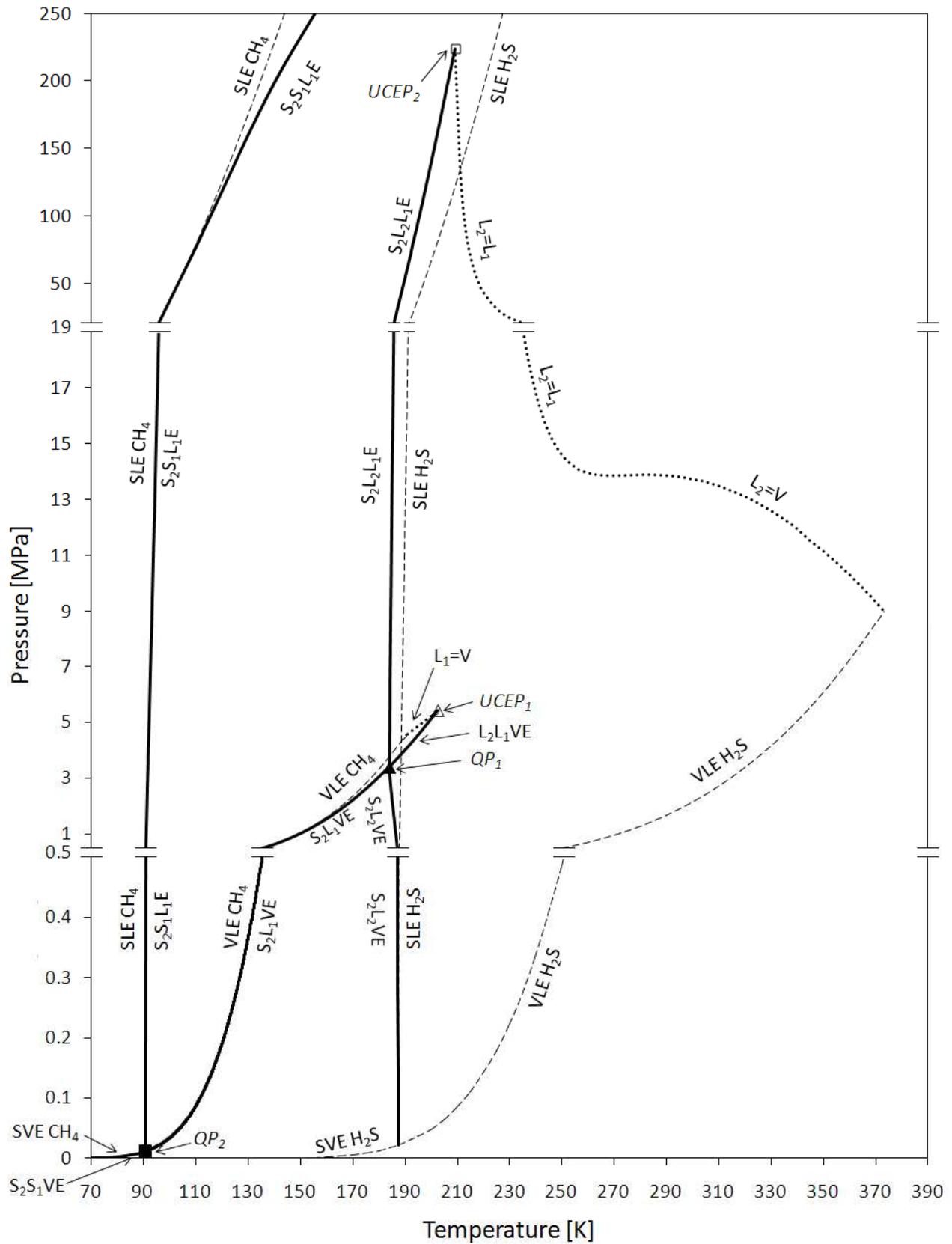


Figure 8. Calculated pressure-temperature phase diagram of the CH_4+H_2S system.

— : three-phase equilibrium boundaries; \cdots : critical curves; - - : SVE, VLE and SLE of CH_4 and H_2S ;
 \blacksquare : QP_2 ; \blacktriangle : QP_1 ; \triangle : $UCEP_1$; \square : $UCEP_2$.

The three-phase equilibrium boundaries related to the QP_2 , calculated at 90.75 K and 11.77 kPa, can be appreciated in Figure 9. From the QP_2 , the S_2S_1VE curve extends in the low temperature region, the $S_2S_1L_1E$ extends in the high pressure region, the S_2L_1VE curve develops in such a way to end in the QP_1 , the S_1L_1VE joins the triple point of CH_4 . Dashed curves represent the sublimation, saturation, and melting curves of pure CH_4 .

It should be stated that any experimental evidence has been provided in the literature concerning the precise position of the QP_2 , thus the calculated QP_2 is a simple result of the SLV EoS with a binary interaction parameter regressed with respect to the available data at high temperatures. The calculated QP_2 is at a temperature slightly higher than the triple point temperature of methane, and this feature results in a solid-fluid equilibrium behavior of the peritectic type, as it has been discussed in the following.

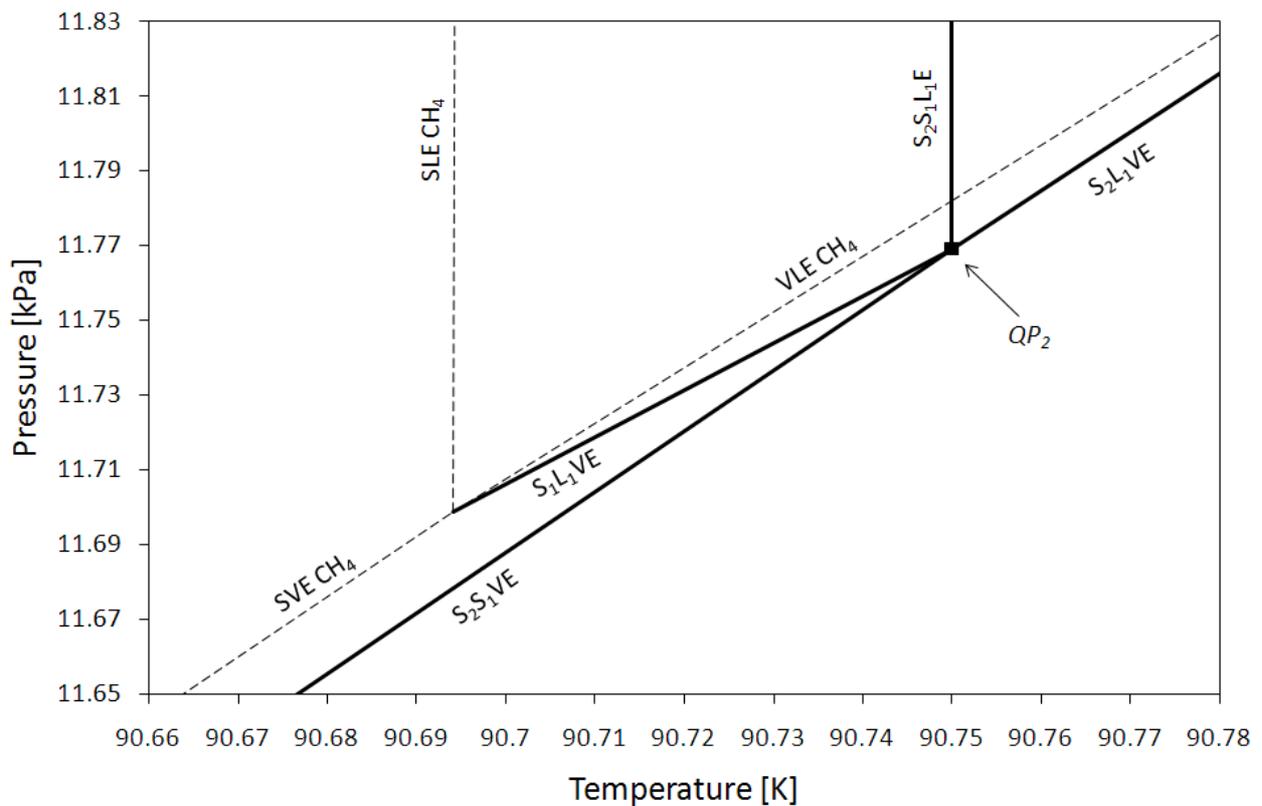


Figure 9. Calculated pressure-temperature phase diagram of the CH_4+H_2S system in proximity of the QP_2 .

■ : QP_2 ; — : three-phase equilibrium boundaries; - - : VLE, SVE, and SLE of CH_4 .

Figures 10-15 present a series of cross sections at constant temperature and pressure that have been selected in the PT phase diagram (Figure 8) in order to describe all the phase equilibrium behaviors of the mixture in the wide ranges of temperature and pressure considered in this work.

As it has already been stated, the objective is to provide the reader with a mapping of the phase diagram and the possibility of rapidly obtaining an overview of the phase equilibrium behavior according to the system temperature and pressure.

A set of temperature and pressure couples has been selected in order to follow the qualitative changes of the phase behavior, as summarized in Tables 8 and 9.

Table 8 presents all the main regions of temperature (listed from 1T to 13T) where the correspondent pressure-composition cross section does not change from a qualitative point of view. A lower and an upper temperature limit have been fixed for each region of temperature, and a representative temperature (T_{ref}) has been chosen for each interval in order to describe its qualitative phase diagram. The last column of Table 8 indicates the figure presenting the cross section correspondent to the chosen representative temperature. In some cases, either the lower or the upper limit or both temperature limits are represented by the temperature where two phase boundaries meet or cross each other. For instance for the region 4T, the lower limit is the temperature at the quadruple point QP_1 , whereas the upper is the temperature where the saturation curve of CH_4 (VLE CH_4) crosses the $S_2L_2L_1E$ curve.

Table 8. Temperature ranges presenting different qualitative pressure-composition phase equilibrium behaviors for the methane-hydrogen sulfide system, and the selected representative temperature (T_{ref}).

<i>Region</i>	<i>Lower limit (T / K)</i>	<i>Upper limit (T / K)</i>	<i>T_{ref} / K</i>	<i>Figure</i>
1T	Low-temperature limit (70)	T _t CH ₄ (90.694)	85	10A
2T	T _t CH ₄ (90.694)	T QP ₂ (90.75)	90.7	10B
3T	T QP ₂ (90.75)	T QP ₁ (183.92)	140	10C
4T	T QP ₁ (183.92)	T cross VLE CH ₄ /S ₂ L ₂ L ₁ E (184.13)	183.94	10D
5T	T cross VLE CH ₄ /S ₂ L ₂ L ₁ E (184.13)	T _t H ₂ S (187.7)	186.25	10E
6T	T _t H ₂ S (187.7)	T cross SLE H ₂ S/L ₂ L ₁ VE (188.47)	188	10F
7T	T cross SLE H ₂ S/L ₂ L ₁ VE (188.47)	T cross VLE CH ₄ /SLE H ₂ S (188.56)	188.48	11A
8T	T cross VLE CH ₄ /SLE H ₂ S (188.56)	T _c CH ₄ (190.56)	189.5	11B
9T	T _c CH ₄ (190.56)	T UCEP ₁ (202.25)	195	11C
10T	T UCEP ₁ (202.25)	T UCEP ₂ (208.98)	203.4	11D
11T	T UCEP ₂ (208.98)	T cross SLE H ₂ S/L ₂ =L ₁ (210.71)	210	11E
12T			230	11F
13T	T cross SLE H ₂ S/L ₂ =L ₁ (210.71)	T _c H ₂ S (373.1)	300	12

A S₂VE, a S₁VE, and a S₂S₁E occur at any temperature higher than 70 K and lower than the triple point temperature of methane, as shown in the Pressure-composition (Px) cross section at 85 K, Figure 10A. At this temperature, the binary mixture presents a region of S₂VE for all pressures lower than 4.911 kPa down to the sublimation pressure of pure H₂S. An equilibrium between the phases S₂, S₁, and V occurs at 4.911 kPa. Then, the S₂S₁E extends up to 250 MPa, while the S₁VE ends at the sublimation pressure of pure CH₄ (4.913 kPa).

With respect to the range 1T, any Px cross section in the range 2T presents one additional pressure of three-phase equilibrium. This is related to the S₁L₁VE.

Figure 10B shows the phase equilibrium behavior at 90.7 K: the S₂S₁V₁E and S₁L₁VE are at 11.694 kPa and 11.705 kPa, respectively. The S₂VE extends again from the sublimation pressure of H₂S (1.3×10^{-6} kPa) up to the pressure of S₂S₁VE, and the S₂S₁E extends up to 250 MPa and beyond. In this case, the S₁VE ends at the S₁L₁VE rather than at the sublimation of CH₄; the VL₁E and the S₁L₁E end respectively at the saturation (11.708 kPa) and melting (40.13 kPa) pressures of pure CH₄.

Any Px cross section in the range 3T is qualitatively represented in Figure 10C, which has been calculated at 140 K. The S₂VE originating at the sublimation pressure of H₂S ends now at the pressure of S₂L₁VE (0.635 MPa): from this pressure, the VL₁E joins the saturation pressure of CH₄

(0.647 MPa), while the S_2L_1E extends in the high pressure region up to the $S_2S_1L_1E$ (198 MPa). From this three-phase equilibrium, the S_1L_1E ends at the melting pressure of CH_4 (230 MPa), the S_2S_1E extends in the high pressure region.

When the system temperature exceeds 183.92 K, namely the temperature of QP_1 , a liquid phase L_2 appears in order to provide the S_2L_2VE , the L_2L_1VE , the $S_2L_2L_1E$, and the related two-phase equilibria. The P_x cross section at 183.94 K in Figure 10D presents a S_2VE ending at the pressure of S_2L_2VE (3.374 MPa). The system is at S_2L_2E between this pressure and the pressure of $S_2L_2L_1E$ (3.645 MPa) only for compositions of CH_4 between about 0.04 and 0.07. To the contrary, the VL_2E and L_2L_1E occur for higher contents of CH_4 , and the transition between these equilibria involves the L_2L_1VE (3.402 MPa). The S_2L_1E originates from the $S_2L_2L_1E$ and extends up to 250 MPa and beyond, while a VL_1E runs from the pressure of L_2L_1VE and the saturation pressure of CH_4 (3.768 MPa).

In the region 4T the saturation pressure of CH_4 is higher than the pressure of $S_2L_2L_1E$, while the contrary occurs in the region 5T, where the phase L_2 develops and reaches higher pressures thus making the $S_2L_2L_1E$ occurring at higher pressures. For instance at 186.25 K (Figure 10E), the pressure of $S_2L_2L_1E$ is 23.449 MPa, higher than the saturation pressure of CH_4 (4.045 MPa).

In general, all the solid-liquid-vapor equilibria occur once the temperature is higher than the triple point temperature of CH_4 ; the S_2L_2E develops between the pressures of S_2L_2VE and $S_2L_2L_1E$ in regions 4T and 5T, whereas it starts at the melting pressure of H_2S in all the PT cross sections from the region 6T to higher temperatures. For instance at 188 K, Figure 10F, the S_2L_2E exits the melting pressure of H_2S (1.632 MPa) and ends at the $S_2L_2L_1E$ (37.439 MPa); furthermore, the VL_2E extends from the L_2L_1VE (3.808 MPa) down to the saturation pressure of H_2S (0.0228 MPa).

The underlying difference between the phase equilibrium behaviors in the regions 6T-8T is the reciprocal positions of the melting pressure of H_2S , the pressures of L_2L_1VE , and the saturation pressure of CH_4 .

In the region 6T, the melting pressure of H₂S is lower than the pressure of L₂L₁VE and the saturation pressure of CH₄. In the region 7T, the melting pressure of H₂S exceeds the pressure of L₂L₁VE remaining lower than the saturation pressure of CH₄. For instance, in the Px cross section at 188.48 K, Figure 11A, these values are 4.222 MPa, 3.859 MPa, and 4.326 MPa, respectively.

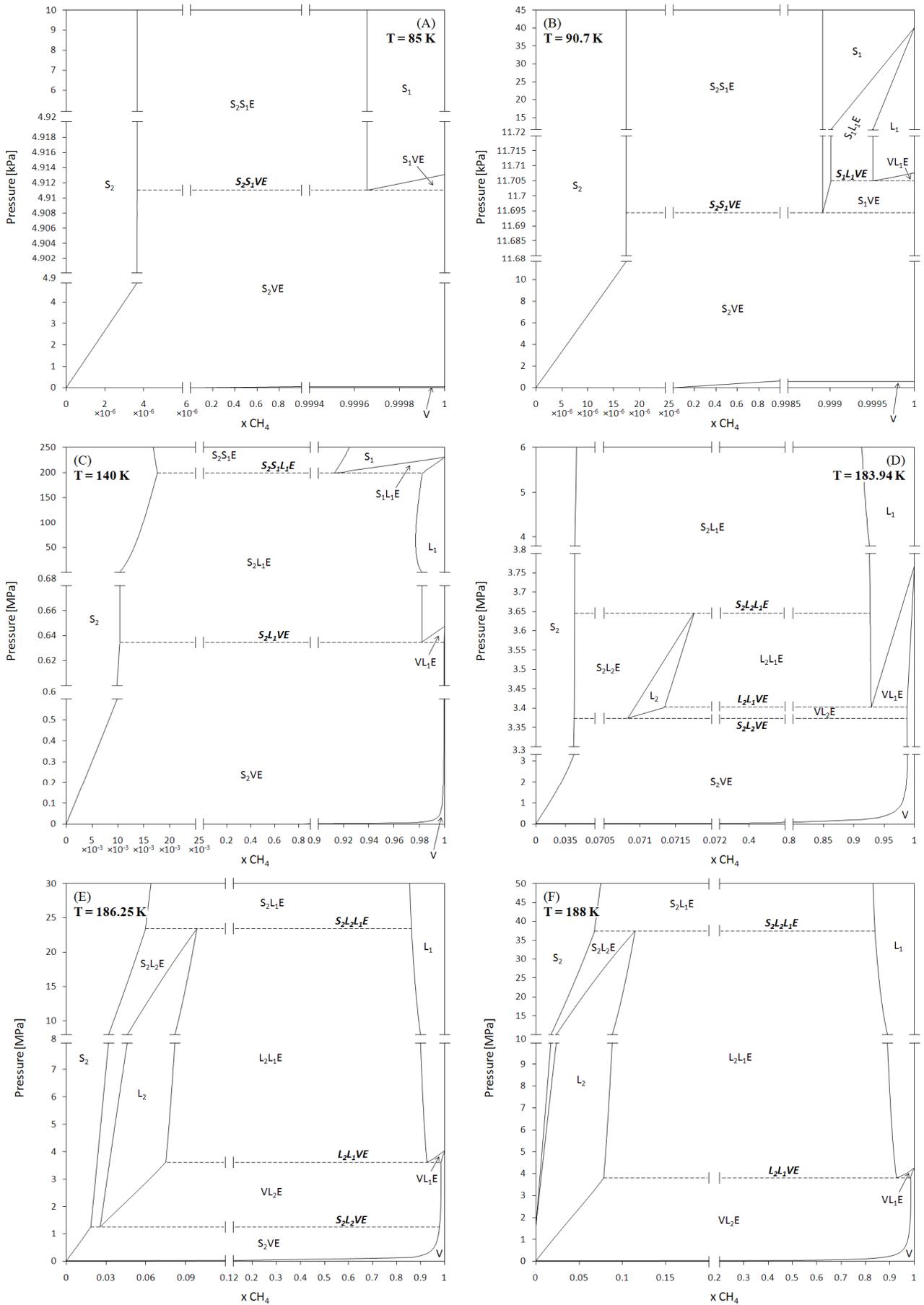


Figure 10. Calculated pressure-composition (P_x) cross sections for the regions 1T-6T.

The melting pressure of H₂S exceeds also the saturation pressure of pure CH₄ in the region 8T; for instance, in the P_x cross section at 189.5 K (Figure 11B) these values are 9.786 MPa (SLE H₂S), 4.458 MPa (VLE CH₄), and 4.326 MPa (L₂L₁VE), respectively.

The upper temperature related to the region 8T is the critical temperature of CH₄. As a consequence, the VL₁E ends at the saturation pressure of pure CH₄ in all the P_x cross sections in the range of temperatures corresponding to the regions from 2T to 8T. The VL₁E ends instead at a critical point L₁=V in region 9T, as it can be appreciated in Figure 11C which shows the P_x cross section at 195 K. At this temperature, the calculated L₂L₁VE and the S₂L₂L₁E are at 4.57 MPa and 94.718 MPa, respectively.

According to the PT diagram of Figure 9, the L₂L₁VE boundary ends at the singular point UCEP₁. Consequently, the transition between the V and L₁ phases becomes continuous for temperatures higher than 202.25 K. For instance, the P_x cross section at 203.4 K portrayed in Figure 11D illustrates the absence of the VL₁E and of the critical point L₁=V. The difference between the VL₂E and the L₂L₁E is the consequence of a change in density of the phase at equilibrium with the phase L₂. Furthermore, the S₂L₂L₁E occurs at 169.717 MPa.

No critical point exists for the mixture in the region 10T; to the contrary, the L₂=L₁/V=L₂ critical curve is crossed at each temperature higher than the temperature at the UCEP₂ (208.98 K).

At 210 K, Figure 11E, the VL₂E originates at the saturation pressure of H₂S, and the L₂L₁E ends at a critical point L₂=L₁ (176.4 MPa). The S₂L₂E exits the melting pressure of H₂S (139.74 MPa) and extends in the high pressure region. It should be noted that the melting pressure of H₂S is lower than the pressure of the critical point L₂=L₁ at 210 K, and so for all the temperatures in the region 11T.

In the region 12T the critical point of the system is placed at a pressure lower than the melting pressure of pure H₂S; for instance at 230 K, Figure 11F, the L₂L₁E ends at about 23 MPa, which represents a critical point L₂=L₁; the solid-liquid equilibria are located at pressures higher 250 MPa.

Finally, the extent of the L_2L_1E reduces for temperatures approaching the critical temperature of H_2S , and the critical point $L_2=L_1$ becomes a critical point $L_2=V$, as shown in Figure 12 by the Px cross section at 300 K.

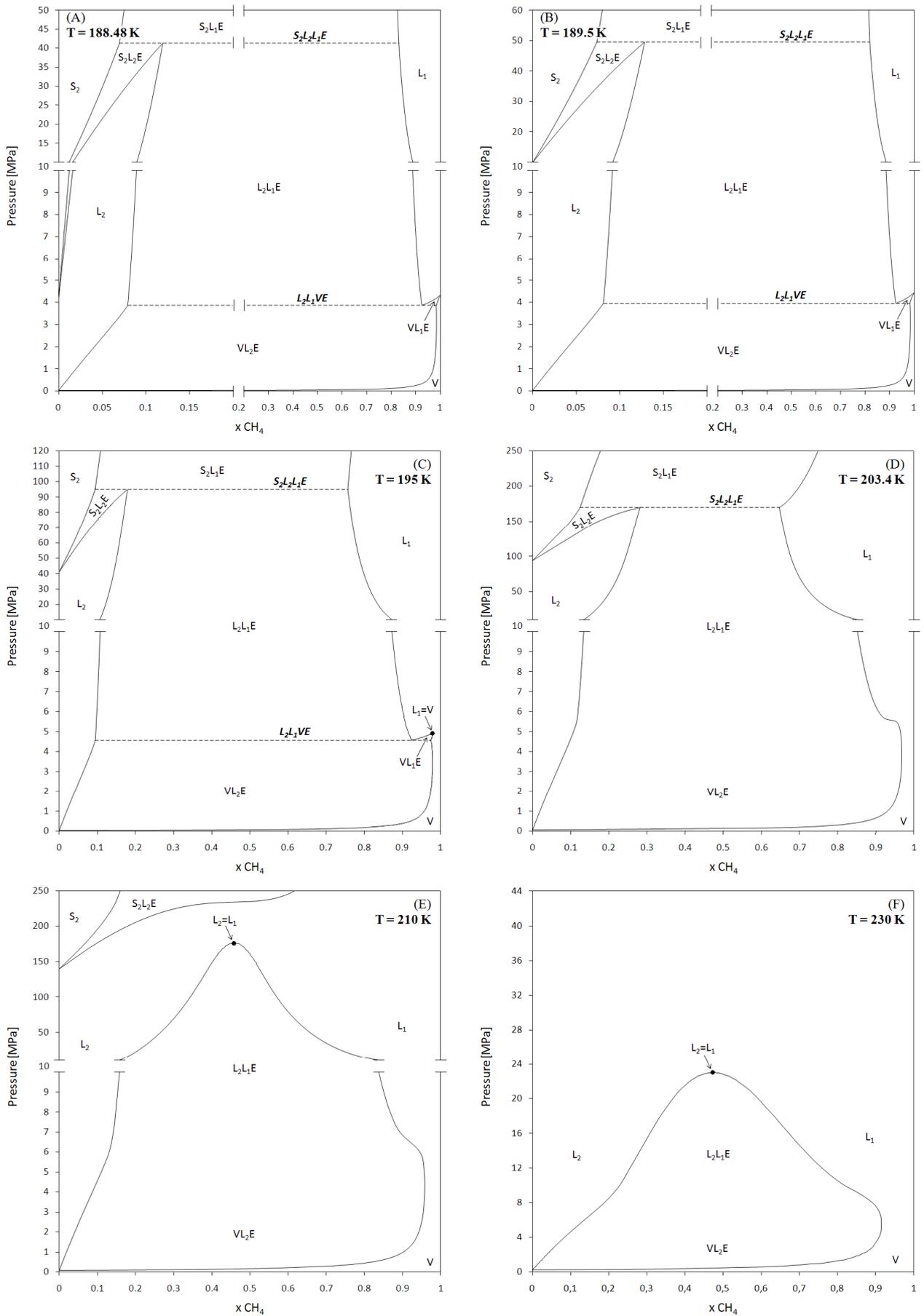


Figure 11. Calculated pressure-composition (Px) cross sections for the regions 7T-12T.

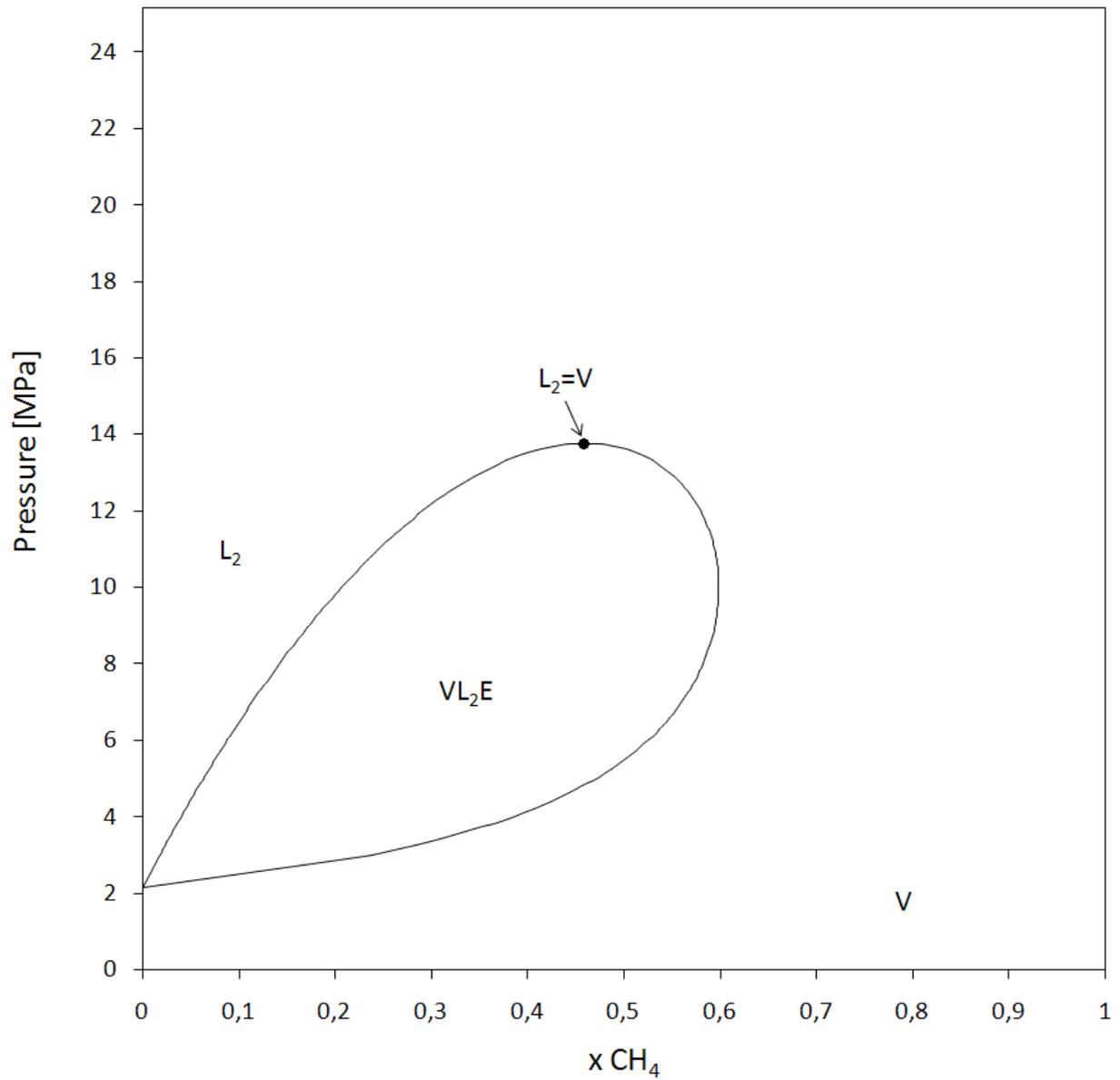


Figure 12. Calculated pressure-composition (Px) cross section at 300 K, i.e. the reference temperature for the region 13T.

A similar study has been carried out with respect to the qualitative changes of the temperature-composition cross sections with pressure. Table 9 summarizes the main pressure regions listed from 1P to 13P. Lower and upper pressure limits and a reference pressure have been fixed for each region of pressure, whereas the last column of Table 9 indicates the number of the figure presenting the correspondent cross section.

In some case, either the lower or the upper limit or both pressure limits are represented by the pressure where two phase boundaries cut cross each other. For instance, the lower limit for the region 5P is the pressure at the quadruple point QP_1 , whereas its upper limit is the pressure where the melting curve of H_2S (SLE H_2S) crosses the L_2L_1VE curve.

Table 9. Pressure ranges presenting different qualitative temperature-composition phase equilibrium behaviors for the methane-hydrogen sulfide system, and the selected representative pressure (*P_{ref}*).

<i>Region</i>	<i>Lower limit (P / MPa)</i>	<i>Upper limit (P / MPa)</i>	<i>P_{ref} / MPa</i>	<i>Figure</i>
1P	Low-pressure limit (0)	$P_t CH_4$ (0.011697)	0.009	13A
2P	$P_t CH_4$ (0.011697)	$P QP_2$ (0.01177)	0.0117335	13B
3P	$P QP_2$ (0.01177)	$P_t H_2S$ (0.0223)	0.02	13C
4P	$P_t H_2S$ (0.0223)	$P QP_1$ (3.4)	1.37	13D
5P	$P QP_1$ (3.4)	P cross SLE H_2S/L_2L_1VE (3.8)	3.75	13E
6P	P cross SLE H_2S/L_2L_1VE (3.8)	P cross VLE $CH_4/S_2L_2L_1E$ (3.85)	3.825	13F
7P	P cross VLE $CH_4/S_2L_2L_1E$ (3.85)	P cross VLE $CH_4/SLE H_2S$ (4.34)	4.14	14A
8P	P cross VLE $CH_4/SLE H_2S$ (4.34)	$P_c CH_4$ (4.5992)	4.5	14B
9P	$P_c CH_4$ (4.5992)	$P UCEP_1$ (5.44)	5	14C
10P	$P UCEP_1$ (5.44)	$P_c H_2S$ (9)	7.5	14D
11P	$P_c H_2S$ (9)	P cross SLE $H_2S/L_2=L_1$ (144.46)	15	14E
12P	P cross SLE $H_2S/L_2=L_1$ (144.46)	$P UCEP_2$ (224.09)	200	14F
13P	$P UCEP_2$ (224.09)	High-pressure limit (250)	235	15

At 9 kPa (Figure 13A) the system CH_4+H_2S presents a S_2S_1VE at 88.906 K; a S_2S_1E extends down to 70 K, whereas the S_2VE and the S_1VE ends at the sublimation temperature of pure H_2S (175.957 K) and CH_4 (88.902 K), respectively. The Temperature-composition (Tx) cross section of Figure 13A is representative of the region 1P, whose upper pressure limit is the triple point of CH_4 .

At any pressure in the region 2P, namely between the triple point pressure of CH_4 (11.697 kPa) up to the pressure of the QP_2 (11.77 kPa), the S_1VE exists between a S_1L_1VE and a S_2S_1VE . For instance at 11.7335 kPa, Figure 13B, the S_1VE is confined in the high-methane content region

between 90.72 K (temperature of S_1L_1VE) and 90.722 K (temperature of S_2S_1VE). From the S_1L_1VE , a S_1L_1E and a VL_1E originate and join the melting temperature (90.695 K) and the saturation temperature (90.718 K) of pure CH_4 , respectively. The S_2VE originating at the S_2S_1VE always ends at the sublimation temperature of H_2S (179.22 K in the case of Figure 13B).

A $S_2S_1L_1E$ and a S_2L_1VE appear when the system pressure exceeds the pressure at QP_2 remaining lower than the triple point pressure of H_2S , as shown in the Tx cross section at 0.02 MPa portrayed in Figure 13C. Figure 13C is representative of the phase equilibrium behavior in the region 3P, and the temperatures of $S_2S_1L_1E$ and a S_2L_1VE at 0.02 MPa are 90.748 K and 95.14 K, respectively.

The S_1VE does not exist for pressures higher than the pressure of the QP_2 , and for increasing pressures the $S_2S_1L_1E$ remains located almost at the same temperature while the S_2L_1VE moves to higher values. Furthermore, a S_2L_1E appears for the first time in the region 3P and it will never disappear in the Tx cross sections at higher pressures. With respect to the behavior in the region 2P (Figure 13B) where the S_1L_1E and a VL_1E both join the temperature of S_1L_1VE , in the region 3P the S_1L_1E and a VL_1E reach two different three-phase equilibria. According to Figure 13C, the S_1L_1E ranges from the melting temperature of CH_4 (90.694 K) and the temperature of $S_2S_1L_1E$, while the VL_1E extends from the saturation temperature of CH_4 (95.136 K) and the temperature of S_2L_1VE .

A third three-phase equilibrium, the S_2L_2VE , is encountered for pressures in the region 4P, namely from the triple point pressure of H_2S (22.3 kPa) up to the pressure of QP_1 (3.4 MPa). This additional equilibrium and its related two-phase equilibria (S_2L_2E and VL_2E) are the consequence of the appearance of the liquid phase L_2 in the Tx cross section, as shown at 1.37 MPa in Figure 13D. Thus, in the region 4P, the phase equilibrium behavior changes qualitatively in the high temperature region. With respect to Figure 13C, in Figure 13D the S_2VE reaches the S_2L_2VE (157.132 K), from which the S_2L_2E and VL_2E continue up to the melting temperature (186.112 K) and saturation temperature (282.753 K) of H_2S , respectively.

The S_2L_1VE and S_2L_2VE cease to occur when the system pressure becomes higher than the pressure of QP_1 , while the $S_2S_1L_1E$ persists at low temperatures. To the contrary, two different three-phase equilibria turn out, at least for pressures lower than the pressure of $UCEP_1$ (5.44 MPa).

For instance at 3.75 MPa, whose Tx cross section is presented in Figure 13E, the system is characterized by a $S_2S_1L_1E$ (91.778 K), a $S_2L_2L_1E$ (183.95 K), and a L_2L_1VE (187.428 K), and related two-phase equilibria. Consequently, it can be stated that the immiscibility between the L_1 and L_2 phases occurs only for pressures higher than the pressure of QP_1 , according obviously to the value of the system temperature. The Tx cross sections in Figures 13F, 14A, and 14B are qualitatively of the same kind of Figure 13E. The difference among the correspondent phase equilibrium behaviors (respectively at 3.75 MPa, 3.825 MPa, 4.14 MPa, and 4.5 MPa) is the position of the saturation and/or melting temperatures of the pure components.

At 3.75 MPa, Figure 13E, the melting temperature of H_2S (188.393 K) is higher than the temperature of L_2L_1VE (187.428 K), which in turns is higher than the temperatures of $S_2L_2L_1E$ (183.95 K) and saturation of CH_4 (183.787 K).

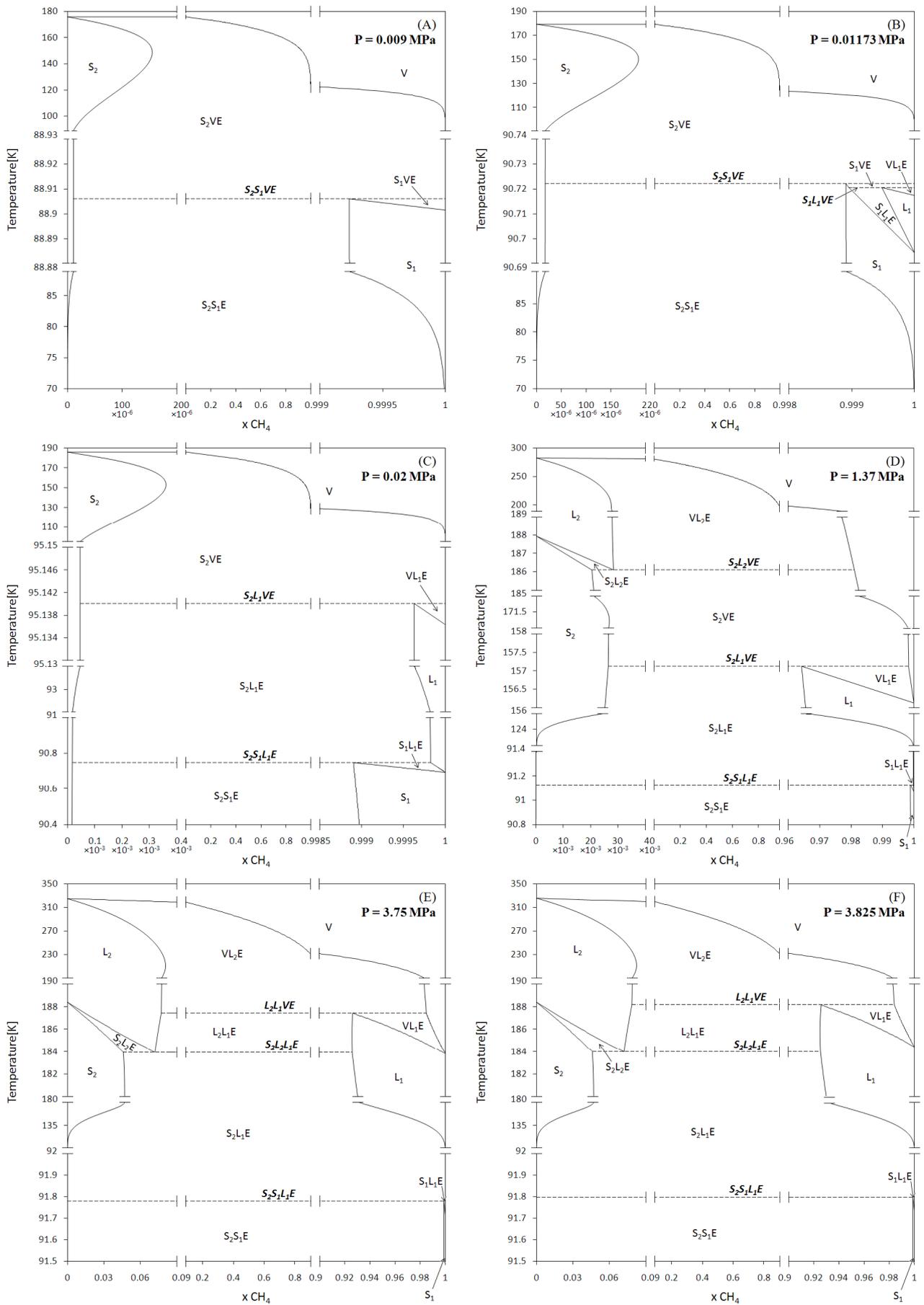


Figure 13. Calculated temperature-composition (T_x) cross sections for the regions 1P-6P.

At 3.825 MPa, Figure 13F, the melting temperature of H₂S (188.407 K) is still higher than the temperature of L₂L₁VE (188.156 K), and the saturation temperature of CH₄ (184.425 K) is in this case lower than the temperature of L₂L₁VE but higher than the temperature of S₂L₂L₁E (183.958 K).

At 4.14 MPa, Figure 14A, the temperature of L₂L₁VE (191.09 K) exceeds the melting temperature of H₂S (188.464 K); the saturation temperature of CH₄ (186.99 K) and the temperature of S₂L₂L₁E (183.98 K) are again lower than the melting temperature of H₂S.

At 4.5 MPa, Figure 14B, the temperatures of L₂L₁VE (194.379 K) and saturation of CH₄ (189.815 K) are both higher than the temperatures of melting of H₂S (188.531 K) and of S₂L₂L₁E (184.022 K).

The region 9P involves the appearance of the critical point L₁=V. The Tx cross section at 5 MPa in Figure 14C is representative of the phase equilibrium behavior in this region of pressure. In this case, the VL₁E joining the L₂L₁VE at 198.672 K does not end at the saturation temperature of CH₄ seeing that the system pressure is now higher than the critical point pressure of same component (4.5992 MPa). Therefore the VL₁E ends at a critical point L₁=V at about 197.093 K.

It should be noted that in Figures 13D-13F and 14A-14C the S₁L₁E is confined in the region of high-methane content, and that the temperature of S₂L₂L₁E changes from 91.125 K at 1.37 MPa (Figure 13D) to 92.12 K at 5 MPa (Figure 14C).

In the Tx cross section, a L₁=V critical point occurs at each pressure between the critical point pressure of CH₄ and the pressure of UCEP₁ (5.44 MPa). It means that for higher pressures, as in the region 10P represented by the diagram at 7.5 MPa in Figure 14D, the transition between the L₁ and the vapor is continuous, thus the L₂L₁VE ceases to exist.

Nevertheless, a critical point exists when the pressure is higher than the critical pressure of H₂S (9 MPa) and lower than the pressure of UCEP₂ (224.09 MPa). This critical point represents either a L₂=V or a L₂=L₁ equality according to pressure. For instance, at 15 MPa, Figure 14E, the VL₂E

ends at a critical point $L_2=V$ (363.3 K), while at 200 MPa, Figure 14F, the VL_2E has disappeared and the L_2L_1E ends directly at a critical point $L_2=L_1$ (209.53 K).

In Figures 14C-14F, the solid-liquid equilibria S_2L_2E and S_1L_1E join the $S_2L_2L_1E$ and the $S_2S_1L_1E$, respectively. The S_2L_2E ends at the melting temperature of H_2S , the S_1L_1E ends at the melting temperature of CH_4 .

Because the immiscibility in the liquid phase ceases at pressures higher than the pressure of $UCEP_2$ (224.09 MPa), it follows that the $S_2L_2L_1E$ does not persist in the region 13P, as it happens at 235 MPa, Figure 15. This feature leads to have a homogeneous liquid phase and a S_2LE extending in the low temperature region down to the $S_2S_1L_1E$.

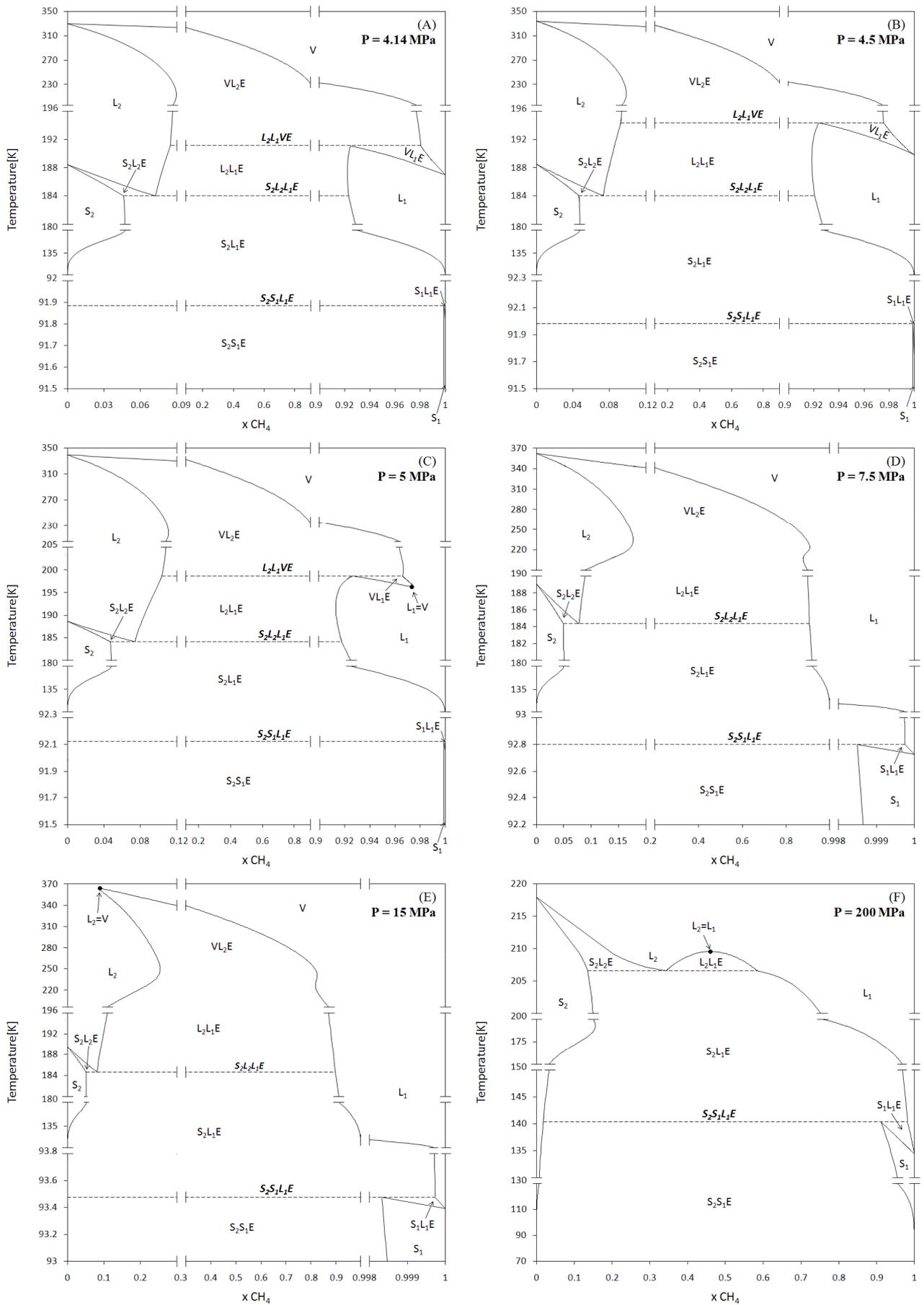


Figure 14. Calculated temperature-composition (T_x) cross sections for the regions 7P-12P.

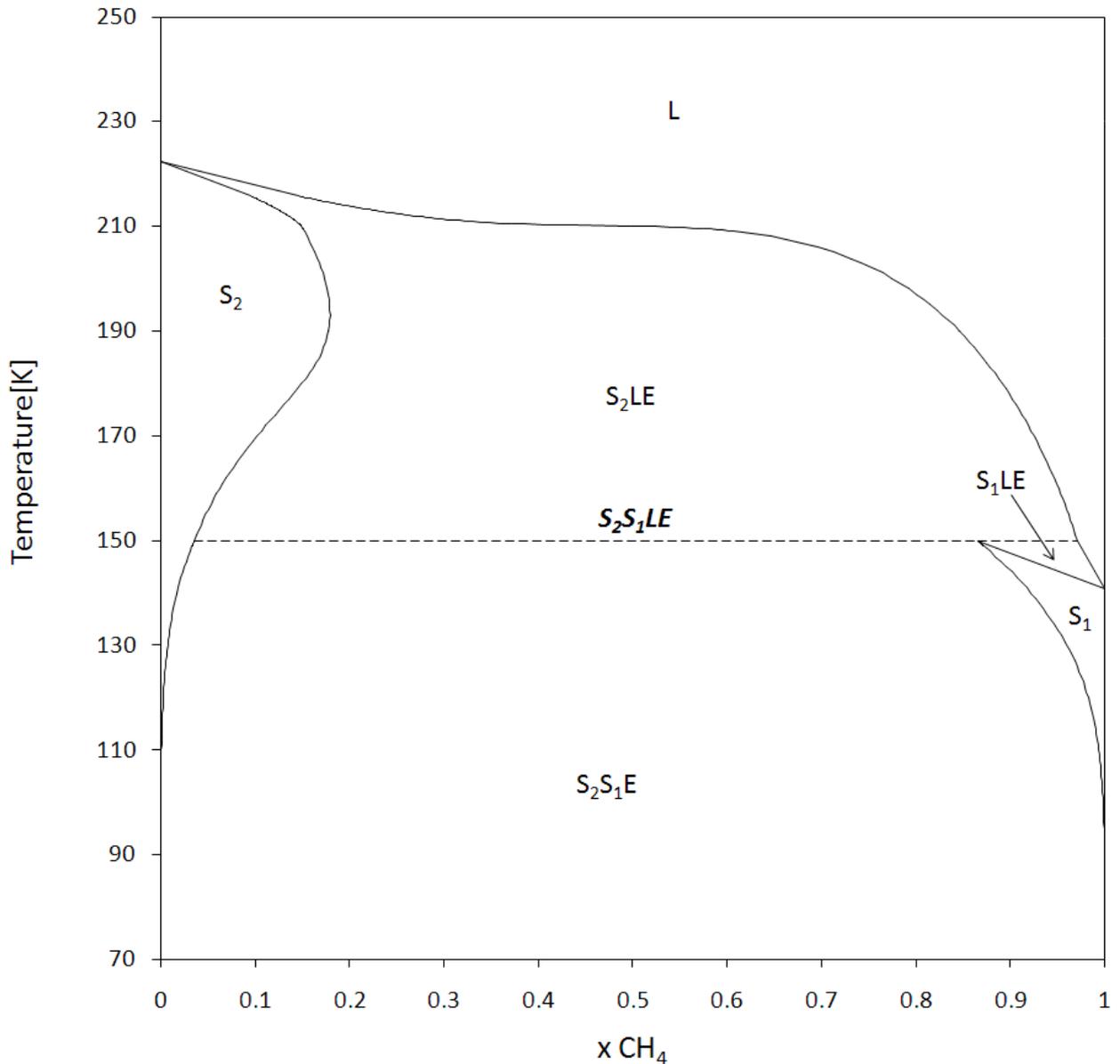


Figure 15. Calculated temperature-composition (Tx) cross sections at 235 MPa, i.e. the reference pressure for the region 13P.

Miscibility of the Solid Phases and Allotropic Behavior of H₂S

The first comment concerning the Px and Tx cross sections calculated by the SLV EoS concerns the purity of the solid phases S₁ and S₂. As stated in Section 3, using the mixing rules developed for fluid phases presented in Eqs. 5-8 results in obtaining not pure solid phases, as it can be observed for instance in Figure 15. The Tx cross section at 235 MPa presents a solid phase S₂ rich in H₂S with a maximum mole fraction of methane of 0.18, and a solid phase S₁ rich in CH₄ where the mole fraction of hydrogen sulfide reaches a maximum of 0.13. As already stated, any evidence has been

provided yet in the literature concerning the purity of the solid phases in the methane + hydrogen sulfide system, and the results here presented resulted from the mere application of the cited mixing rules in the SLV EoS.

Moreover, as previously introduced in this section, also the position of the $S_2S_1L_1VE$ (QP_2) has not been determined yet. The kind of the solid-liquid equilibrium of the system of interest strictly depends on the exact position of the quadruple point, QP_2 . The binary mixture of CH_4 and H_2S presents immiscibility in the solid phase, but this feature could result in a solid-liquid equilibrium either of the eutectic type or the peritectic type. The discerning aspect is comparison between the mole fraction for instance of CH_4 in the liquid phase L_1 (x_{L_1}) and those in the solid phases S_1 and S_2 (x_{S_1} and x_{S_2}): x_{L_1} is lower than x_{S_1} but higher than x_{S_2} in the eutectic behavior, it is higher than both x_{S_1} and x_{S_2} in the peritectic behavior.

According to the results presented in Figures 10C, 14C-14F, and 15, it clearly appears that the mole fraction of CH_4 in the liquid phase L_1 is higher than the mole fractions in the solid phases S_1 and S_2 . This is a direct consequence of the position of the singular point QP_2 in the PT diagram. No binary interaction parameter has been regressed in order to match an eutectic behavior seeing that there is no literature evidence of this feature for the CH_4+H_2S system.

The last analysis concerning the results of the SLV EoS is related to the three different crystal structures of H_2S that should be considered for obtaining the real behavior of the system. As introduced in Section 2, H_2S presents a triple point of solid $_{\gamma}$ -solid $_{\beta}$ -vapor equilibrium at 103.5 K and triple point of solid $_{\beta}$ -solid $_{\alpha}$ -vapor equilibrium at 126 K in addition to the common triple point of solid $_{\alpha}$ -liquid-vapor at 187.7 K.⁴² The triple points at low temperature are stated to occur at the zero-pressure limit, while the solid-liquid-vapor equilibrium is at 22.3 kPa.⁴⁵

Being the SLV EoS in Eq. 1 a fourth-degree polynomial in the variable volume, a single root can be associated to the solid volume, being the other roots related to the fluid phases. In dealing with mixtures, this solid volume correspond to a solid phase rich in either H_2S or CH_4 , which explains

the possibility of representing the phases S_2 and S_1 . To the contrary, the possibility of representing several solid phases for each pure component is outside the range of applicability of this EoS.

Nevertheless, the way the pure H_2S solid phases γ and β affect the phase equilibrium behavior of the mixture can be added relatively easily in both Tx and Px cross sections. For instance, Figures 16A and 16B present the Tx cross sections at 4.14 MPa in the range 91.8 K – 196 K considering a single phase for the solid H_2S , S_2 , and two additional solid-solid transitions occurring in pure H_2S at 103.5 K and 126 K, respectively.

One can notice at once that the phase S_α in Figure 16B takes the role of the phase S_2 in Figure 16A. In addition to that, the $S_2S_1L_1E$ is replaced by the $S_\gamma S_1L_1E$ at about 91.9 K, while two new three-phase equilibria appear. A $S_\gamma S_\beta E$ originating at 103.5 K ends at the temperature of the former, the $S_\gamma S_\beta L_1E$ at about 92 K, and a $S_\beta S_\alpha E$ originating at 126 K ends at the temperature of the latter, namely the $S_\beta S_\alpha L_1E$ placed at about 108 K. The temperatures of these SSL_1E have been randomly fixed and supposed lower than the correspondent solid-solid transitions of pure H_2S .

As it is possible to observe in Figure 16, the inclusion of different crystal structures of H_2S does not modify the solid-fluid equilibria, although the different solid phases imply the presence of supplementary solid-solid and solid-solid-fluid equilibria.

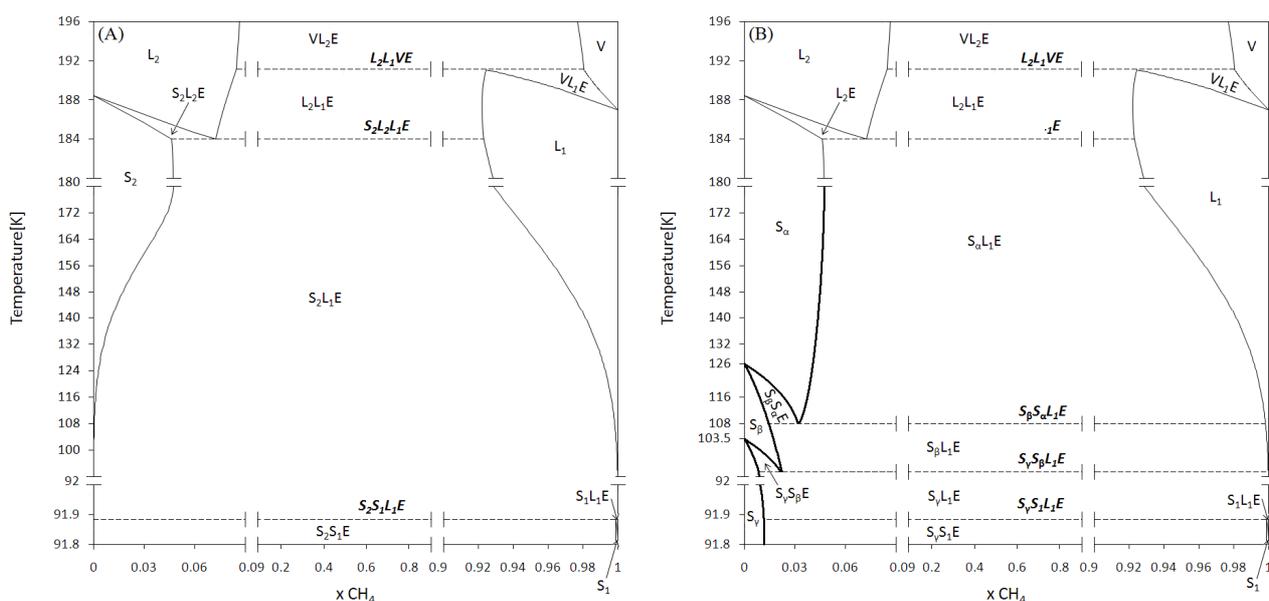


Figure 16. Comparison between the Tx cross sections at 4.14 MPa without (A) and with (B) the solid_α-solid_β and solid_β-solid_γ transitions of H_2S .

Conclusions

The increasing global energy demand and the availability of highly sour natural gas reserves establish the need of a detailed description of the phase behavior of systems containing methane and hydrogen sulfide in order to properly tune thermodynamic models and, most of all, to perform the correct process design of new gas purification technologies (particularly the low temperature ones) that are required to allow the commercialization of such a kind of low quality natural gas reserves.

Different authors studied the phase behavior of the system methane - hydrogen sulfide considering only fluid phases, whereas few works considered the presence of a pure solid phase of H₂S. The experimental works proposed in the last 60 years investigated the phase behavior of the system in a large proportion of the Pressure-Temperature (PT) diagram down to about 180 K. In particular, the work by Kohn and Kurata presented qualitative representations of the PT diagram and highlighted the complexity of the phase equilibrium behavior.

Nevertheless, no work has been proposed to reproduce the PT diagram of the mixture down to the triple point of methane by means of a unified thermodynamic model for both fluid and solid phases. In addition to that, literature data never exceed 14 MPa.

In this work, the complete PT diagram of the methane - hydrogen sulfide system has been investigated down 70 K and for pressures up to 250 MPa thanks to a model based on the analytic Solid-Liquid-Vapor Equation of State (SLV EoS) proposed in 2003 by Yokozeki. The parameters within the model have been tuned and validated against the available experimental data.

The calculated PT diagram and isobaric/isothermal cross sections show the complexity of the phase equilibrium behavior; immiscibility in both the liquid and solid phases characterizes the system and results in the presence of two quadruple points and two upper critical endpoints.

In addition to that, this work aims at proposing a map of the phase equilibrium behavior thus providing a rapid access to the evaluation of the change of the equilibria as function of pressure and temperature. 13 regions of both pressure and temperature have been found to resume all the possible

schemes of the equilibrium behavior that can be encountered in dealing with the process simulation and/or plant design.

One of the strength of the model here applied is the possibility of representing the rather complex phase equilibrium behavior of the system by means of a single binary interaction parameter. This point better highlights also the simplicity of the approach, enforcing the validity and the effective industrial interest of a simple thermodynamic tool, reliable in a wide region of possible operating conditions.

According to model results for the phase behavior of the system $\text{CH}_4 - \text{H}_2\text{S}$, it is possible to identify areas where further experimental investigations are needed. A region of interest extends from temperatures below the UCEP_1 and pressures up to 15 MPa. These experimental studies will be useful to better investigate the L_2VE , L_1VE , $\text{L}_1\text{L}_2\text{E}$, $\text{S}_2\text{L}_2\text{E}$, $\text{S}_2\text{L}_1\text{E}$ and S_2VE regions where complete datasets (T, P and fluid phase compositions) are missing and phase behavior is complex. Particularly, it can be of interest to determine experimentally the existence of the narrow L_2 area present at temperatures between the QP_1 and the triple point of pure H_2S . $\text{TP}_{x_2x_1y}$ data along the $\text{L}_1\text{L}_2\text{VE}$ locus, TP_{xy} data along the $\text{S}_2\text{L}_2\text{VE}$ and $\text{S}_2\text{L}_1\text{VE}$ loci and $\text{TP}_{x_2x_1}$ data along the $\text{S}_2\text{L}_2\text{L}_1\text{E}$ locus are also of paramount importance. These experimental data will provide useful information also for the validation and proper design of low-temperature process technologies for the purification of highly acid and/or sour natural gases and biogas.

Nomenclature

List of symbols

a	Equation of state parameter
a_0	Parameter in Eq. 2
a_1	Parameter in Eq. 2
a_2	Parameter in Eq. 2
b	Solid covolume

b_0	Parameter in Eq. 3
b_1	Parameter in Eq. 3
b_2	Parameter in Eq. 3
c	Liquid covolume
d	Equation of state parameter
k	Binary interaction parameter
N	Number of points (experimental or auxiliary)
NC	Number of components in the mixture
P	Pressure
R	Gas constant
T	Temperature
v	Molar volume
x	Mole fraction
Z	Compressibility factor

Subscript

c	Critical point property
i	Relative to the substance i
j	Relative to the substance j
ij	Relative to the interaction between substance i and the substance j
r	Reduced property
t	Triple point property
1	Relative to methane
2	Relative to hydrogen sulfide

Superscript

$calc$	Calculated value
exp	Experimental value

m Parameter in Eq. 3

n Parameter in Eq. 2

Acronyms

AAD Average Absolute Deviation

EoS Equation of State

L Liquid phase

LLE Liquid - Liquid Equilibrium

LLVE Liquid - Liquid - Vapor Equilibrium

MAD Maximum Absolute Deviation

QP Quadruple Point

S Solid phase

SLE Solid - Liquid Equilibrium

SLL Solid - Liquid - Liquid Equilibrium

SLVE Solid - Liquid - Vapor Equilibrium

SSE Solid - Solid Equilibrium

SSLE Solid - Solid - Liquid Equilibrium

SSVE Solid - Solid - Vapor Equilibrium

SVE Solid - Vapor Equilibrium

V Vapor phase

VLE Vapor - Liquid Equilibrium

UCEP Upper Critical EndPoint

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