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IMPACT OF IMPURITIES ON CO₂ STORAGE IN SALINE AQUIFERS: MODELLING OF GASES SOLUBILITY IN WATER

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Flue gas captured contains different impurities (N₂, O₂, SO₂, NO etc) and their concentrations depend on the capture process and the industrial sector. Moreover, the presence of impurities may change the thermophysical properties of the stream and therefore impact the conditions of CO₂ storage. The aim of the paper is to investigate the solubility in water of carbon dioxide and some chosen impurities. In this work VLE calculations using a geochemical model (Corvisier, 2013) and two group contribution (GC-PR-CPA (Group Contribution-Peng Robinson-Cubic Plus Association) (Hajiw, 2014 and Hajiw et al., 2015) and E-PPR78 (Qian et al., 2013) equations of state) models are compared.

Keywords: Water/gas solubility; CO₂; Co-injected impurities; Group contribution method

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1. INTRODUCTION

Combustion of fossil fuels and industrial processes are the principal anthropological sources of greenhouse gases emissions (carbon dioxide, methane, NO_x, SO_x...) to the atmosphere.

Emissions of carbon dioxide, estimated at 35 gigatons in 2013 (Agency P.N.E.A., 2014), are considered to be the major cause of global warming. Carbon Capture and Storage (CCS) is a solution proposed to avoid emissions of carbon dioxide. Conditions for CO₂ storage are considered to be in this study in the temperature and pressure range of 300-423 K and 6-30 MPa (Liebscher et al., 2013).

Depending on the capture process and the industrial field, the flue gases contain different impurities, with various compositions. Three examples, from a thermal power plant (Case A), a cement plant (Case B) (Meunier et al., 2014) and a coal IGCC (Integrated Gasification Combined Cycle) plant (Case C) (European Communities, 2011) are presented in Table 1. In all plants, coal is used as the major fuel.

[Table 1]

In this study, the major focus is the solubility of these impurities in water. Indeed, their presence in the flue gas may change CO₂ thermophysical properties (density, viscosity) and phase diagram behaviour (solubility). As an example of the effect of different impurities on phase diagrams, phase envelopes of pure CO₂ and mixtures given in Table 1 are drawn on Figure 1.

[figure 1]

Depending on the binary system, there are more or less data (Table 2). To the knowledge of the authors, no experimental data has been found for VLE of NO-H₂O and NO₂-H₂O under pressure. On the contrary, VLE data are abundant for CO₂-H₂O, N₂-H₂O and CH₄-H₂O systems. References for these systems are presented in Table 2.

[Table 2]

To predict phase diagrams, it is necessary to have robust models. In this paper, three models are applied and compared on binary systems: two group contribution models (GC-PR-CPA (Hajiw et al., 2015) and E-PPR78 (Qian et al., 2013) EoS or equations of state) and a geochemical model (Corvisier, 2013). All three models have the Peng-Robinson EoS (Peng and Robinson, 1976) in common. Few data have been found in the open literature for ternary systems with water. Therefore, only three systems (i.e. two ternary systems CO₂-CH₄-H₂O and CO₂-N₂-H₂O and a quaternary CO₂-CH₄-H₂S-H₂O) are presented and used to validate all three models.

2. THERMODYNAMIC MODELLING

2.1. Group Contribution Models

In group contribution models, molecules can be divided into groups and interactions between groups are taken into account rather than between molecules (e.g. UNIFAC model (Fredenslund et al., 1975)). However, in this study, molecules of interest are small and can therefore be considered also as groups.

The PR-CPA EoS (Hajiw et al., 2015) has been used in this work. This model is composed of the cubic Peng Robinson EoS and the Wertheim term (Wertheim, 1984) which takes into account the presence of H-bonds due to the presence of associating molecules like water (equation 1)

$$P = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} - \frac{1}{2} \frac{RT}{v} \left(1 + \rho \frac{\partial \ln(g)}{\partial \rho} \right) \sum_{i=1}^N x_i \sum_{A_i} (1 - X_{A_i}) \quad (1)$$

The Peng-Robinson (PR) EoS is used in both E-PPR and GC-PR-CPA EoS. Therefore, when considering systems of non-associating compounds, the GC-PR-CPA EoS is reduced to the E-PPR78 EoS. Therefore, the attractive parameter a_i and the co-volume b_i for non-associating compounds are described by the same equations (Jaubert et al., 2014).

In E-PPR78, there are two adjustable group interaction parameters (A_{kl} and B_{kl}), that can be found in the paper of (Xu et al., 2015). As for the GC-PR-CPA EoS, different steps of adjustment have been taken into account. First, five parameters of the PR-CPA EoS (attractive

parameter a_0 , co-volume b , parameter C_l , association energy ε and association volume β) have been adjusted for pure water using vapour pressure and saturated liquid density data (see thesis of Hajiw (Hajiw, 2014)). They are recalled in Table 3. Then, group interaction parameters for gases – water binary systems (C_{kl} , D_{kl} and E_{kl}) have been adjusted on solubility data (Table 2). The modified simplex algorithm has been used to minimize the objective function. They are given in Table 4. Equations used in both models are developed in the appendix.

[Table 3]

[Table 4]

2.2. Geochemical Model

The geochemical model presented shortly in this part is implemented in CHESS/HYTEC software (Corvisier, 2013; Corvisier et al., 2013). The dissymmetrical approach γ - φ is used in geochemistry (Equation 2):

$$m_i^{aa} \gamma_i^{aa} K_i^g(T, P^{sat}) \exp\left(v_i^\infty \frac{P - P^{sat}}{RT}\right) = y_i^g \varphi_i^g P \quad (2)$$

where m_i is the molality (mol/kg of water) of the dissolved gaseous component i , γ_i^{aa} its activity coefficient, K_i^g the Henry's law constant at water saturation pressure, v_i^∞ the molar volume of the dissolved gaseous component at infinite dilution, y_i^g the component mole fraction in the gas phase and φ_i^g its fugacity coefficient. For the gas phase, the PR EoS is used. Henry's law constants can be collected from various sources of the literature. Molar volumes, used to correct these latter for pressure, can be obtained from the revised Helgeson-Kirkham-Flowers general equation (Tanger et al., 1988) and the associated parameters are also found in the literature.

Moreover, this last model uses an important database and could solve a large set of mass balance and mass action laws equations to calculate the whole water speciation (i.e. pH, concentrations of species such as HCO_3^- , CO_3^{2-} , SO_4^{2-} ...) and minerals dissolution/precipitation (i.e. carbonates, cement phase...).

Parameters for pure gases and for gas solubilities are given in Table 5. In this model, binary interaction parameters are temperature independent.

[Table 5]

3. RESULTS AND DISCUSSION

3.1. Binary systems with water

Models are compared over experimental data found in the literature for each binary system. However, availability of data is disparate according to the binary system. Deviations are presented in Table 6. Duan and co-workers (Duan et al., 2003; Duan and Mao, 2006; Duan et al., 2007; Mao and Duan, 2006; Geng and Duan, 2006) also developed a model for gas solubility in water. When it is possible, their model is compared to the other three.

[Table 6]

Deviations for the same systems for temperature/pressure conditions from 300 to 423 K, from 6 to 60 MPa are given in Table 7. In general, while the GC-PR-CPA EoS presents lower deviations for higher pressures, E-PPR78 and the geochemical model give similar deviations than the ones presented in Table 6. A reason is that, for the GC-PR-CPA EoS, parameters have been adjusted for high pressures. For SO₂, when low and high pressures data are omitted the deviation for the GC-PR-CPA EoS decreases, whereas the deviations for others are significantly improved. The explanation comes from the fact that fitted (GC-PR-CPA and E-PPR78) or collected (geochemical model) parameters of each model have been adjusted on various data temperature/pressure ranges. Consequently, it shall also be mentioned that results could be improved with adapted and optimized fit.

[Table 7]

Figures 2 and 3 present respectively CO₂ and SO₂ solubilities in water at three temperatures. Water content in CO₂ at three isotherms is shown on Figure 4.

[Figures 2-4]

Table 8 gives deviations between experimental data and predictions for the CO₂-H₂O and SO₂-H₂O binary systems presented on Figures 2 and 4. It reveals that the quality of data is very important for estimation of deviations and evaluation of the performance of the models.

[Table 8]

Based on Tables 6 and 7 and Figures 2 to 4, one may say that the geochemical model and the GC-PR-CPA give similar predictions for gas solubilities in water. Concerning the E-PPR78 EoS, while its predictions are in good agreement with experimental data for carbon dioxide or methane solubilities in water, it gives qualitative rather than quantitative predictions for nitrogen, oxygen and hydrogen solubilities in water. Solubilities and water contents from the geochemical model are satisfactory using literature parameters and once again, it shall be pointed out that the whole water speciation is calculated and potential minerals dissolution/precipitation reactions could also be taken into account.

3.2. Multicomponent gas mixtures + water systems

While fair amount of data are available for binary systems with water, limited data for ternary or multicomponent systems containing carbon dioxide, water and impurities are available in the open literature, particularly at conditions of interest. Scarce data have been found for the CO₂-CH₄-H₂O ternary system (Qin et al., 2008; Chapoy et al., 2016; Song and Kobayashi, 1990; Dhima et al., 1999, Al Ghafri, 2014) (Figures 5 Figure 8), one reference for the CO₂-N₂-H₂O system (Liu et al., 2012) (Figures 9 and 10) and the CO₂-CH₄-H₂S-H₂O quaternary system (Robinson et al., 1982) (Figures 11 and 12).

[Figures 5 and 12]

Deviations between experimental data and models are given in Table 9.

[Table 9]

Based on previous figures, one might observe that the presence of impurities decreases the solubility of carbon dioxide in the water rich phase.

According to Table 9, deviations for multicomponent systems are of the same order of magnitude than for binary systems. However, there are some concerns about the measurements for the CO₂-CH₄-H₂O ternary system. Indeed, for a similar composition of the gas phase (about 50% CO₂-50% CH₄), there are discrepancies between water content data (Figure 7). Moreover, the trend does not follow neither other data (Chapoy et al., 2016) (Figure 8) nor the one given by the PR-CPA EoS with a binary interaction parameter k_{ij} set to 0. Yet, it has been shown in the paper of (Hajiw et al. 2015), that for such systems, adjusted binary interaction parameters are necessary for solubility predictions but not for water content. The modelling of the quaternary system CO₂-CH₄-H₂S-H₂O shows relatively good

results regarding the experimental data (Robinson et al., 1982), and regarding another model from the literature (Zirrahi et al., 2012) as well for our three models. This last comparison tends to demonstrate the ability of these three approaches to handle complex gas mixtures.

4. CONCLUSION

Thermodynamic and geochemical models have been applied to binary and ternary systems with water. Compared to literature data, the geochemical model and the GC-PR-CPA Eos give satisfactory results. However, predictions are strongly dependent on the availability and quality of experimental data, and consequently on the quality of the selected parameters for the geochemical model. Solubility data for SO₂ and O₂ at storage conditions (higher pressures and temperatures) and solubility data for NO are missing. Very few data for multicomponent systems are available in the open literature to validate the three models.

It is noticeable that the three models are built around the same general cubic EOS (i.e. Peng-Robinson) using different methods (i.e. associating term, group contribution, symmetrical/dissymmetrical approach...). Nevertheless, they all demonstrate ability to deal with complex gas mixtures over relatively large temperature and pressure ranges. Providing sufficient experimental data to calibrate their associated parameters, the models are able to handle some computations involving CO₂ and potential impurities within the context of its capture, transport (group contribution models) and geological storage (geochemical model).

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APPENDIX

• Pure compounds

With the presence of water or associating molecules, an associating term (from Wertheim's theory and perturbation theory) is added to the PR EoS. Two functions must be defined: the radial distribution function $g(d)$ of the reference fluid (hard sphere) (eq. A.2) and the fraction of non-bonded associating molecules X^A (eq. A.3):

$$g(d)^{simp} = \frac{1}{1 - 1.9\eta}$$

With

$$\eta = \frac{1}{4} b\rho = \frac{b}{4v}$$

(A.2)

$$X^{A_i} = \frac{1}{1 + \rho \sum_j n_j \sum_{B_i} X^{B_i} \Delta^{A_i B_i}}$$

with

$$\Delta^{A_i B_i} = g(d)^{simp} \left[\exp\left(\frac{\varepsilon^{A_i B_i}}{RT}\right) - 1 \right] \beta^{A_i B_i} b$$

(A.3)

- **Mixtures**

Classical mixing rules are used in both E-PPR78 and GC-PR-CPA EoSs. They are given by equations A.4 and A.5

$$a_{ij}(T) = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \sqrt{a_i(T) a_j(T) (1 - k_{ij})}$$

(A.4)

$$b_{ij} = \sum_{i=1}^N z_i b_i$$

(A.5)

The binary interaction parameter k_{ij} is defined as follow for the E-PPR78 EoS (eq. A.6 and A.7)

$$k_{ij}(T) = \frac{-\frac{1}{2} \times Sum - \left(\frac{\sqrt{\alpha_i(T)}}{b_i} - \frac{\sqrt{\alpha_j(T)}}{b_j} \right)^2}{2 \frac{\sqrt{\alpha_i(T) \alpha_j(T)}}{b_i b_j}}$$

(A.6)

with

$$Sum = \sum_{k=1}^{Ng} \sum_{l=1}^{Ng} (\alpha_{ik} - \alpha_{jk})(\alpha_{il} - \alpha_{jl}) A_{kl} \left(\frac{298.15}{T} \right)^{\left(\frac{B_{kl}}{A_{kl}} - 1 \right)}$$

(A.7)

This binary interaction parameter has been modified when considering water in the GC-PR-CPA EoS. Equation A.7 becomes equation A.8:

$$\begin{aligned}
 Sum_{asso} = & \sum_{k=1}^{H_2O} (\alpha_{ik} - \alpha_{jk}) (\alpha_{iH_2O} - \alpha_{jH_2O}) (C_{kH_2O} T^2 + D_{kH_2O} T + E_{kH_2O}) \\
 & + \sum_{l=1}^{H_2O} (\alpha_{iH_2O} - \alpha_{jH_2O}) (\alpha_{il} - \alpha_{jl}) (C_{H_2Ol} T^2 + D_{H_2Ol} T + E_{H_2Ol})
 \end{aligned}
 \tag{A.8}$$

Finally, combining rules have to be used in the associating term of the GC-PR-CPA EoS. The Combining Rule CR1 (Hajiw et al., 2015) is used in our GC-PR-CPA EoS (eq. A.9 and A.10).

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2}
 \tag{A.9}$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}}
 \tag{A.10}$$

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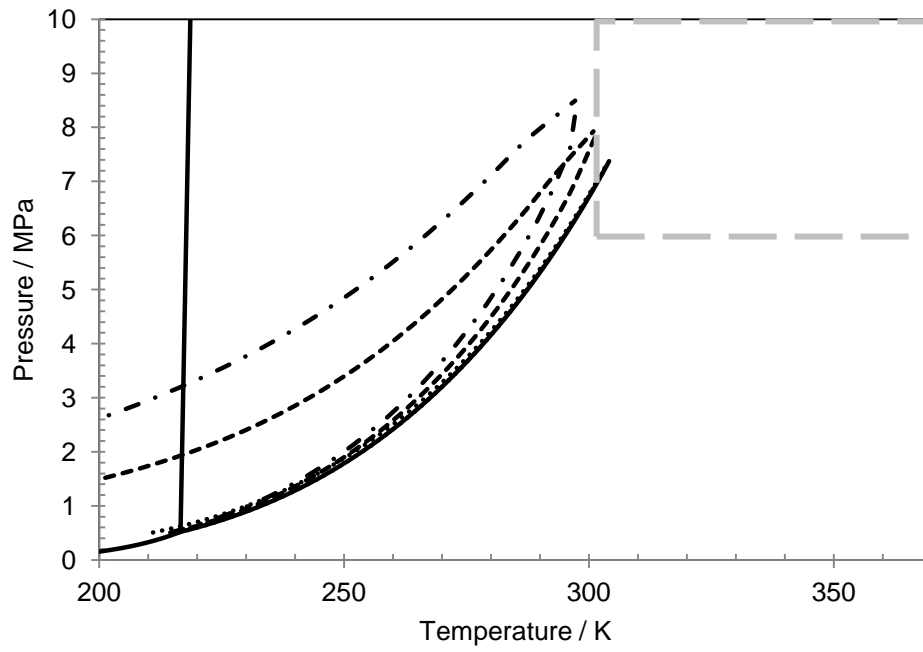


Figure 3: Pressure-Temperature diagram. Solid line: pure CO₂. Broken dotted line: Case A.

Dashed line: Case B. Dotted line: Case C. Grey square: storage conditions in saline aquifers.

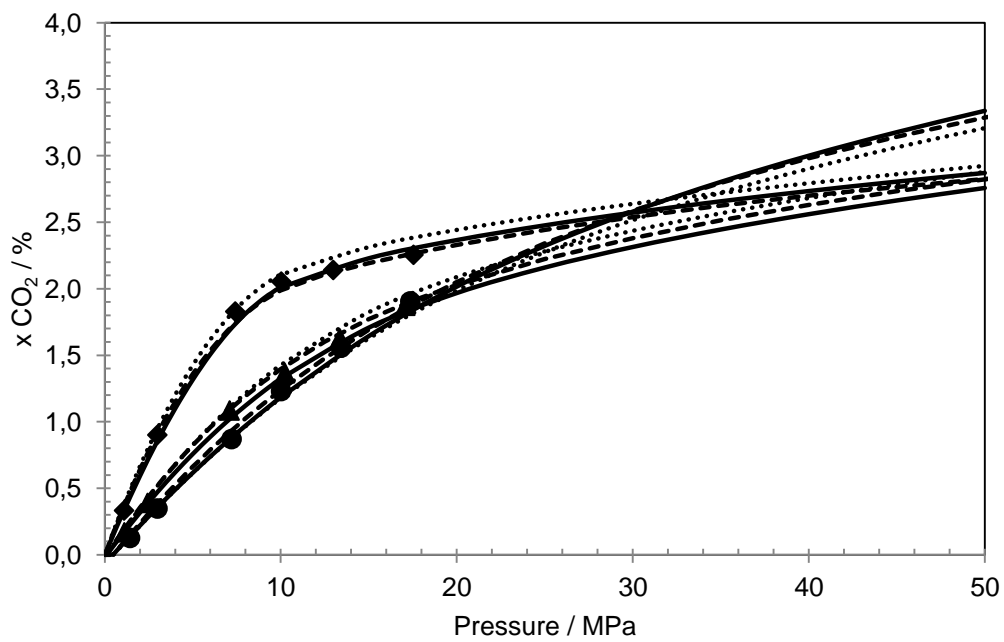


Figure 4: CO₂ solubility in water at 323 K (◆), 373 K (▲) and 423 K (●) (Hou et al. 2013).
 Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78 EoS. Dashed lines: geochemical model

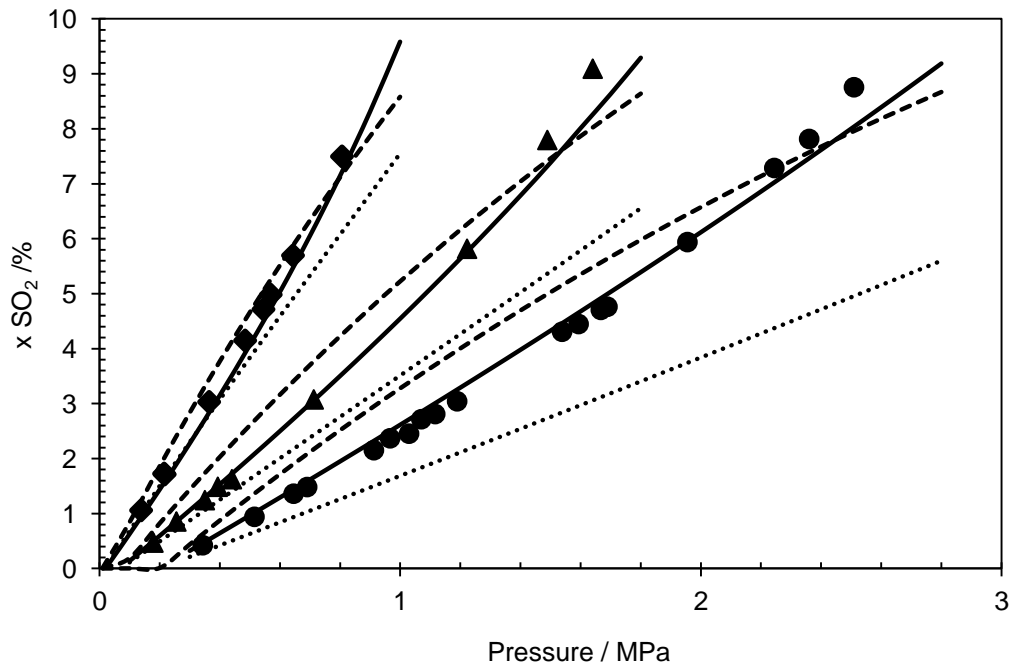


Figure 3: SO₂ solubility in water at 333 K (◆), 363 K (▲) and 393 K (●) (Rumpf and Maurer, 1992). Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78 EoS. Dashed lines: geochemical model

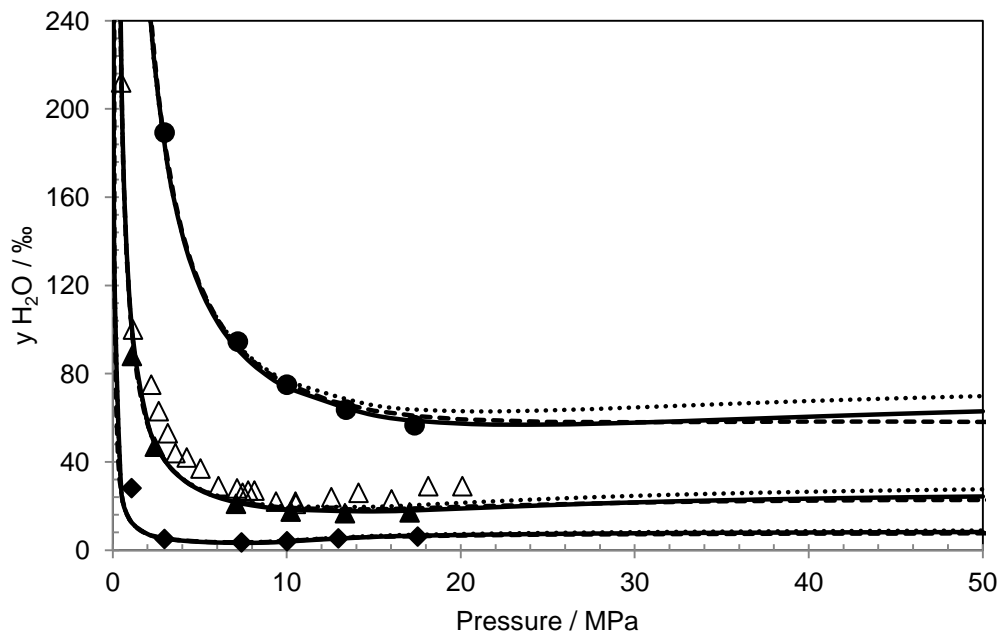


Figure 4: Water content at 323 K (\blacklozenge , (Hou et al. 2013)), 373 K (\blacktriangle , (Hou et al. 2013) and \triangle , (Caumon et al., 2016)) and 423 K (\bullet , (Hou et al. 2013)). Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78 EoS. Dashed lines: geochemical model

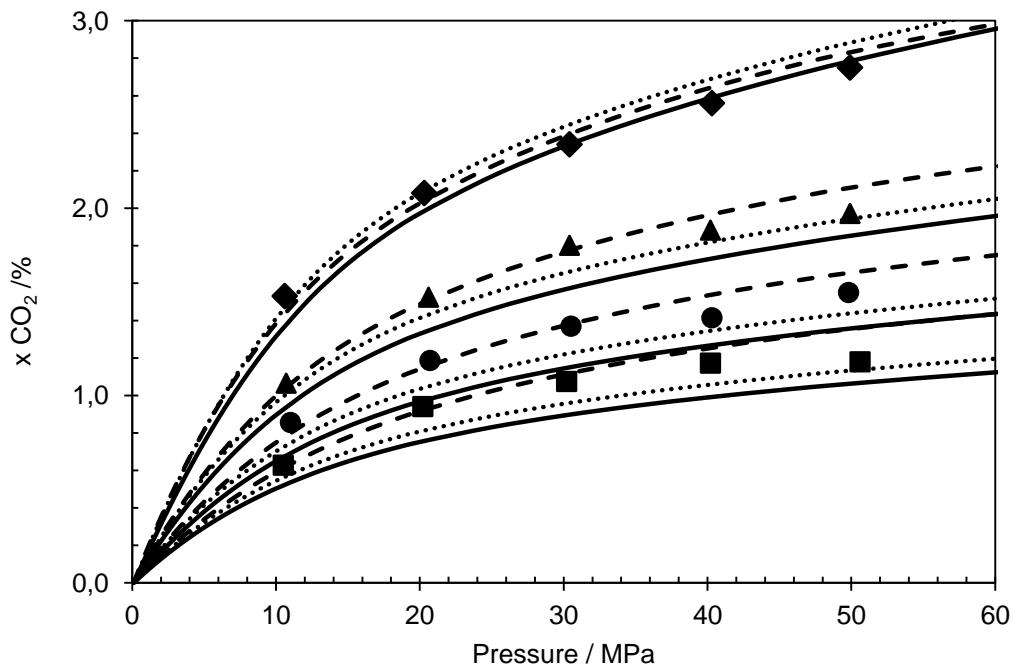


Figure 5: CO₂ aqueous mole fraction versus pressure for the CO₂-CH₄-H₂O system at 375 K. Experimental data (Qin et al., 2008): (◆) pure CO₂, (▲) 72% CO₂, (●) 53% CO₂ and (■) 41% CO₂. Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78. Dashed lines: geochemical model

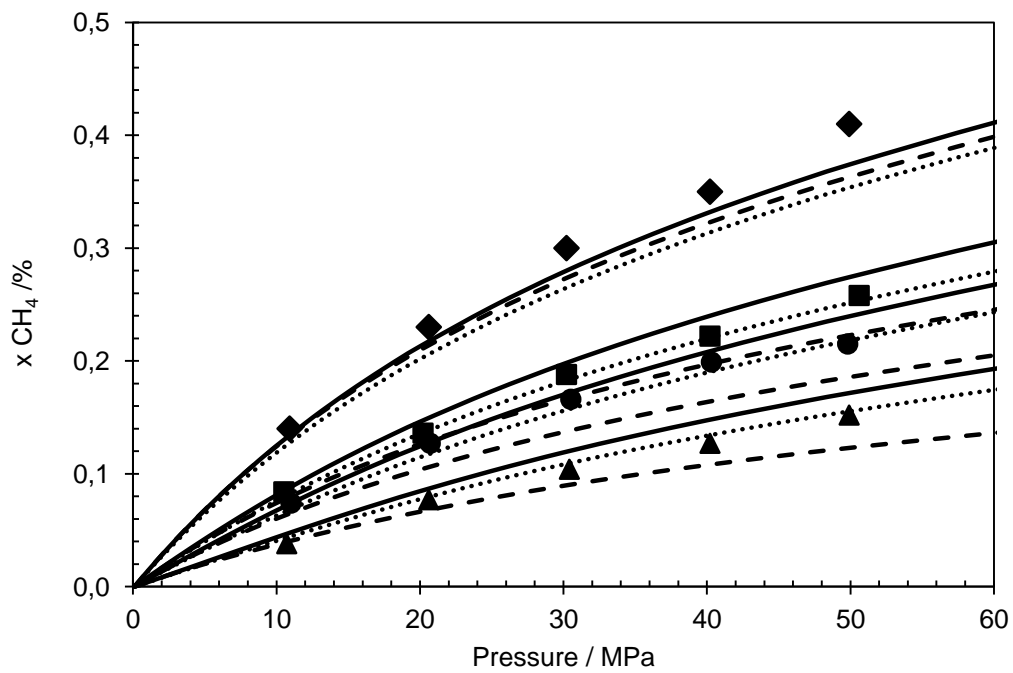


Figure 6: CH₄ aqueous mole fraction versus pressure for the CO₂-CH₄-H₂O system at 375 K. Experimental data (Qin et al., 2008): (♦) pure CH₄, (▲) 72% CO₂, (●) 53% CO₂ and (■) 41% CO₂. Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78. Dashed lines: geochemical model

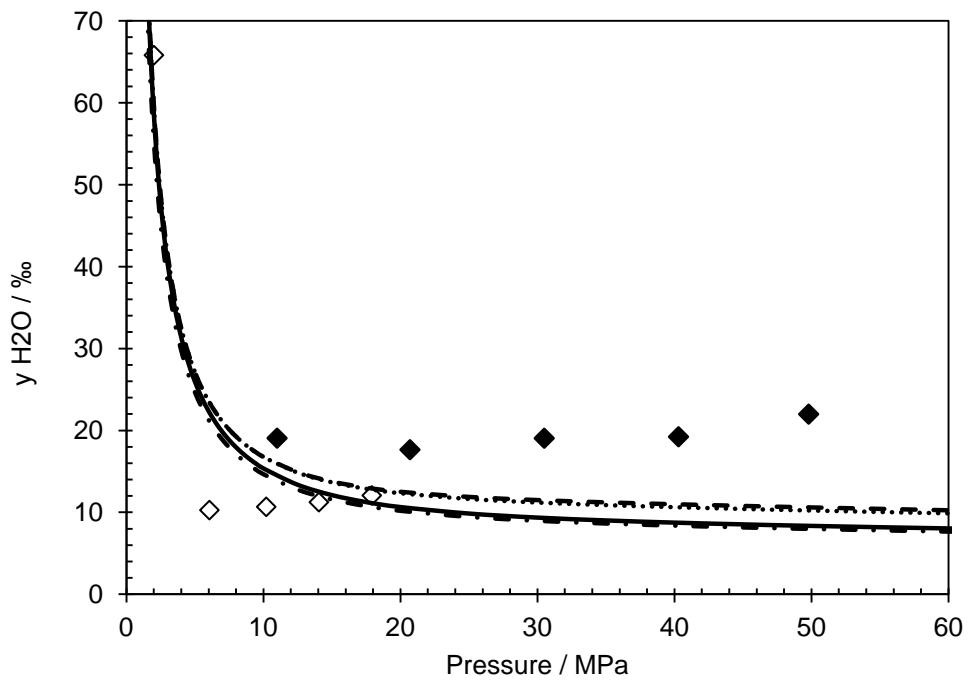


Figure 7: Water content versus pressure for the 50% CO₂-50% CH₄-H₂O system at 373 K. Experimental data: (◆) (Qin et al., 2008) and (◇) (Al Ghafri et al., 2014). Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78. Dashed lines: geochemical model. Broken dotted line: PR-CPA EoS with $k_{ij}=0$.

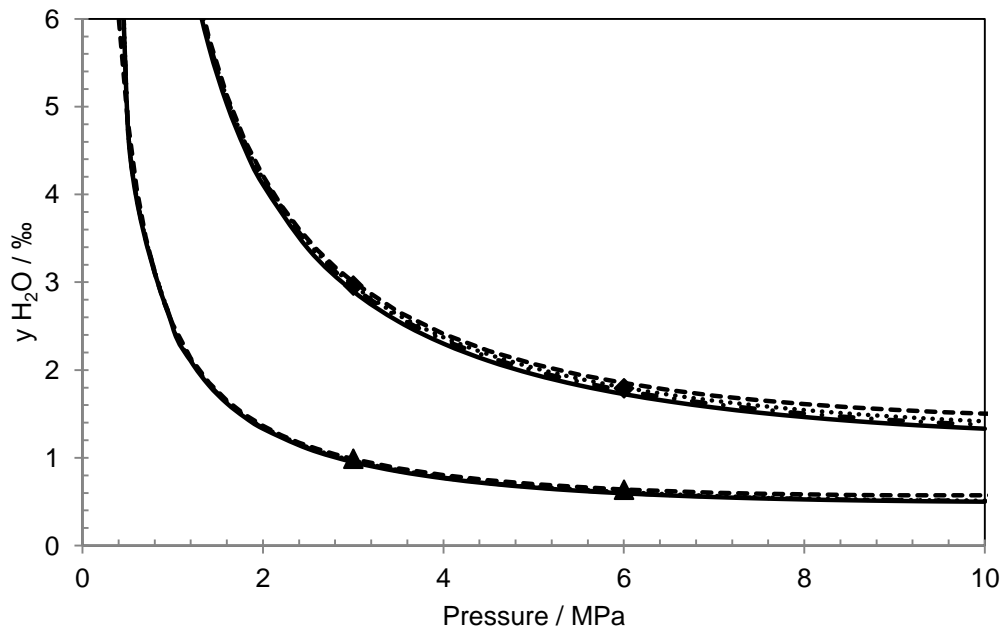


Figure 8: Water content versus pressure for the 50% CO₂-50% CH₄-H₂O system (Chapoy et al., 2016) at 293 (◆) and 313 K (▲). Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78.

Dashed lines: geochemical model. Broken dotted line: PR-CPA EoS with $k_{ij}=0$.

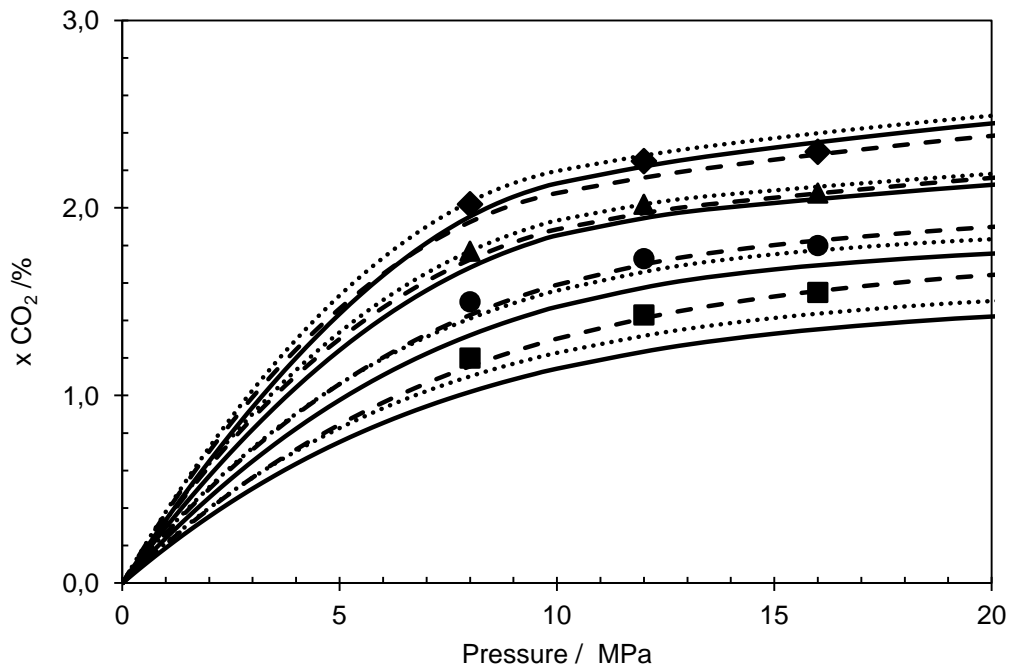


Figure 9: CO₂ aqueous mole fraction versus pressure for the CO₂-N₂-H₂O system at 318 K. Experimental data (Liu et al., 2012): (♦) pure CO₂, (▲) 89% CO₂, (●) 72% CO₂ and (■) 57% CO₂. Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78. Dashed lines: geochemical model

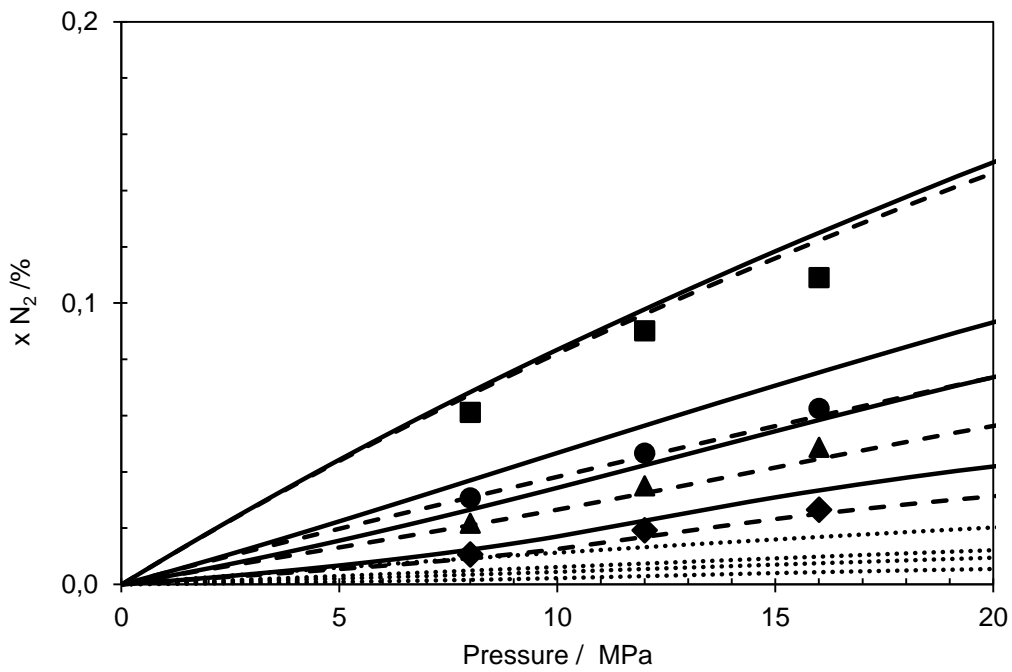


Figure 10: N₂ aqueous mole fraction versus pressure for the CO₂-N₂-H₂O system at 318 K. Experimental data (Liu et al., 2012): (◆) pure N₂, (▲) 89% CO₂, (●) 72% CO₂ and (■) 57% CO₂. Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78. Dashed lines: geochemical model

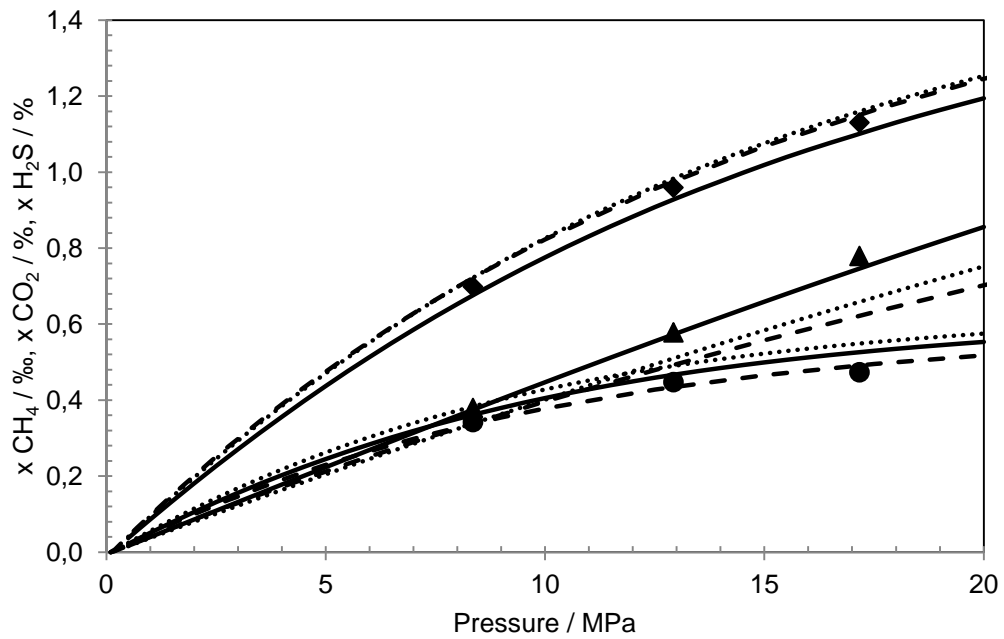


Figure 11: CO₂ (♦), CH₄ (▲) and H₂S (●) aqueous mole fraction versus pressure for the 30% CO₂-15% CH₄-5% H₂S-50% H₂O system at 380 K (Robinson et al., 1982). Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78. Dashed lines: geochemical model

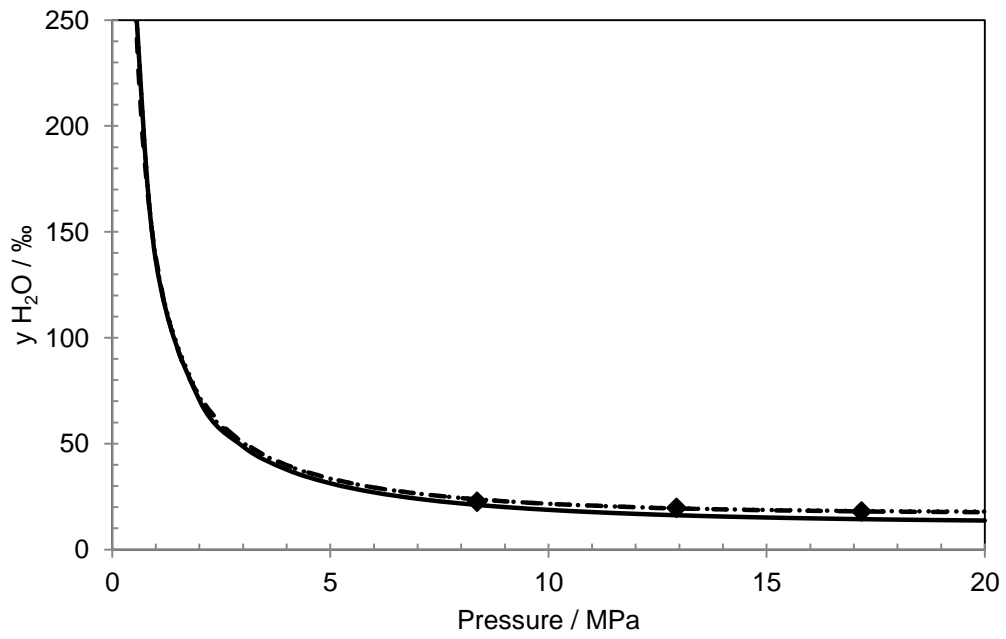


Figure 12: Water content (◆) versus pressure for the 30% CO₂-15% CH₄-5% H₂S-50% H₂O system at 380 K (Robinson et al., 1982). Solid lines: GC-PR-CPA EoS. Dotted lines: E-PPR78. Dashed line: geochemical model

Table 10: Example of compositions of flue gases from thermal power plant (Case A, (Meunier et al., 2014)), a cement plant (Case B, (Meunier et al., 2014)) and a coal IGCC plant (Case C, European Communities, 2011)).

Component	Composition in mole %		
	Case A	Case B	Case C
CO ₂	72	83.13	98.1
H ₂ O	5.6	1	376 ppm
N ₂	14	11.11	196 ppm
O ₂	5.9	3.27	-
Ar	2.4	1.34	178 ppm
CO	-	397 ppm	0.13
NO	320 ppm	861 ppm	-
NO ₂	51 ppm	96 ppm	-
SO ₂	700 ppm	156 ppm	-
H ₂ S	-	-	0.17
CH ₄	-	-	112 ppm
H ₂	-	-	1.5

Table 11: Gas solubility data in pure water.

Component	References	Range of temperatures [K]	Range of pressures [MPa]
CO₂	[1- 6]	273 – 623	0.008 – 150
N₂	[7- 11]	273 – 636.5	0.02 – 101
O₂	[11 - 32]	273 – 616.5	0.02 – 20
Ar	[11, 17, 27, 33-40]	273 – 568	0.02 – 15
CO	[41- 48]	273 – 478	0.06 – 14
NO	-	-	-
NO₂	-	-	-
SO₂	[49, 50]	293 – 393	0.035 – 2
H₂S	[2, 46, 51- 64]	273 – 518	0.01 – 31
CH₄	[42, 65-74]	273 – 523	0.08 – 197
H₂	[15, 43-45, 66, 75- 86]	273 – 498	0.1 – 101

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Table 12: PR-CPA parameters for pure water (Hajiw et al., 2015)

	a₀ [bar.L ² .mol ⁻²]	b [L.mol ⁻¹]	C₁	ε [bar.L.mol ⁻¹]	β [10 ³]	Temperature range [K]	ΔP [%]	Δρ [%]
Water	2.2	0.015	0.64	146.4	68.3	273 – 643	1.1	2.7

Table 13: Group interaction parameters with water (C_{k,H_2O} , D_{k,H_2O} and E_{k,H_2O})

k	$C_{k,H_2O} / 10^3 \text{ Pa.K}^{-2}$	$D_{k,H_2O} / 10^6 \text{ Pa.K}^{-1}$	$E_{k,H_2O} / 10^9 \text{ Pa}$
CO₂	-5.7	4.9	-8.8
N₂	-12.3	10.9	-18.5
O₂	-16.4	14.1	-23.5
Ar	-18.2	15.3	-25.7
CO	210	-141	239
SO₂	-4.5	2.8	-5.9
H₂S	-4.8	3.9	-6.0
CH₄	-11.2	9.7	-15.9
H₂	-10.5	9.5	-14.7

Table 14: Sources for Henry's law constants, HKF parameters for molar volume at infinite dilution, values for critical temperature and pressure, acentric factors and fitted water binary interaction parameters.

Compound	$K_{g,i}(T, P^{sat})$	$v_i^\infty [\text{cm}^3 \cdot \text{mol}^{-1}]$	T_c	P_c	Acentric	k_{i,H_2O}
			[K]	[bar]	factor	
			[1]	[1]	[1]	<i>This study</i>
CO₂	[2]	[9]	304.19	73.82	0.228	0.198
N₂	[3]	[10, 11]	126.10	33.94	0.040	0.455
O₂	[4]	[10, 11]	154.58	50.43	0.022	0.621
Ar	[3]	[10, 11]	150.86	48.98	0.000	0.590
CO	[3]	[10, 11]	132.92	34.99	0.066	0.266
SO₂	[5]	[10]	430.75	78.84	0.245	-
H₂S	[6]	[12]	373.53	89.63	0.083	0.151
CH₄	[7]	[11, 12]	190.58	46.04	0.011	0.507
H₂	[8]	[10]	33.18	13.13	-0.220	0.529

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Table 15: AAE (Absolute Average Error) and AAD (Absolute Average Deviation)) between experimental data and predictions

	GC-PR-CPA		E-PPR78 EoS		Geochemical model		Duan		<i>Number of experimental points</i>
	AAE (mole fraction)	AAD (%)	AAE (mole fraction)	AAD (%)	AAE (mole fraction)	AAD (%)	AAE (mole fraction)	AAD (%)	
x CO₂	1.10 ⁻³	8.9	1.10 ⁻³	6.3	1.10 ⁻³	5.6	6.10 ⁻⁴	4.1	1803
y H₂O	7.10 ⁻³	13.2	8.10 ⁻³	14.3	8.10 ⁻³	9.0	2.10 ⁻²	28.5	413
x N₂	5.10 ⁻⁵	3.7	6.10 ⁻⁴	84.0	5.10 ⁻⁵	3.9	4.10 ⁻⁵	3.8	561
y H₂O	2.10 ⁻³	9.8	2.10 ⁻³	4.7	3.10 ⁻³	5.3	3.10 ⁻³	5.2	163
x O₂	2.10 ⁻⁵	4.4	2.10 ⁻⁴	71.2	3.10 ⁻⁵	4.5	3.10 ⁻⁵	4.8	835
y H₂O	2.10 ⁻⁴	13.0	1.10 ⁻³	69.1	1.10 ⁻⁵	0.6	-	-	14
x Ar	7.10 ⁻⁶	2.6	-	-	1.10 ⁻⁵	2.6	-	-	296
y H₂O	4.10 ⁻⁴	8.9	-	-	1.10 ⁻³	1.3	-	-	28
x CO	4.10 ⁻⁵	9.6	-	-	5.10 ⁻⁵	9.8	-	-	187
y H₂O	3.10 ⁻³	1.9	-	-	7.10 ⁻³	3.0	-	-	17
x SO₂	2.10 ⁻³	17.6	3.10 ⁻³	14.7	2.10 ⁻³	16.7			393
x CH₄	1.10 ⁻⁴	6.8	5.10 ⁻⁴	10.2	1.10 ⁻⁴	6.7	1.10 ⁻⁴	6.3	678
y H₂O	2.10 ⁻³	15.9	2.10 ⁻³	6.5	2.10 ⁻³	6.2	1.10 ⁻³	5.3	319
x H₂S	1.10 ⁻³	6.1	6.10 ⁻⁴	3.4	3.10 ⁻³	9.9	7.10 ⁻⁴	3.5	704
y H₂O	6.10 ⁻³	11.6	6.10 ⁻³	8.1	1.10 ⁻²	7.1	-	-	183
x H₂	4.10 ⁻⁴	7.4	9.10 ⁻²	>100	6.10 ⁻⁴	10.5			571
y H₂O	3.10 ⁻³	5.4	6.10 ⁻³	21.4	8.10 ⁻³	3.3			17

Table 16: AAE (Absolute Average Error) and AAD (Absolute Average Deviation)) between experimental data and predictions at limited pressure conditions

	GC-PR-CPA		E-PPR78 EoS		Geochemical model		Duan		<i>Number of experimental points</i>
	EoS		AAE (mole fraction)	AAD (%)	AAE (mole fraction)	AAD (%)	AAE (mole fraction)	AAD (%)	
	AAE (mole fraction)	AAD (%)							
x CO₂	8.10 ⁻⁴	6.3	8.10 ⁻⁴	5.5	6.10 ⁻⁴	4.1	5.10 ⁻⁴	4.0	725
y H₂O	4.10 ⁻³	13.5	4.10 ⁻³	14.9	3.10 ⁻³	9.4	8.10 ⁻³	24.7	235
x N₂	6.10 ⁻⁵	4.7	8.10 ⁻⁴	74.4	7.10 ⁻⁴	5.1	7.10 ⁻⁵	5.4	152
y H₂O	1.10 ⁻³	7.6	6.10 ⁻⁴	4.9	3.10 ⁻³	5.1	9.10 ⁻⁴	5.9	59
x O₂	5.10 ⁻⁵	5.6	5.10 ⁻⁴	52.9	7.10 ⁻⁵	8.2	5.10 ⁻⁵	6.6	127
y H₂O	3.10 ⁻⁴	10.1	2.10 ⁻³	60.0	2.10 ⁻⁵	0.6	-	-	9
x Ar	6.10 ⁻⁵	3.2	-	-	9.10 ⁻⁵	4.4	-	-	11
y H₂O	4.10 ⁻⁴	3.5	-	-	9.10 ⁻⁵	0.5	-	-	14
x CO	5.10 ⁻⁵	11.2	-	-	6.10 ⁻⁵	12.5	-	-	97
y H₂O	5.10 ⁻⁴	1.8	-	-	4.10 ⁻⁴	1.5	-	-	12
x SO₂	2.10 ⁻³	10.6	1.10 ⁻²	27.6	6.10 ⁻³	25.9			30
x CH₄	1.10 ⁻⁴	7.4	2.10 ⁻⁴	10.0	1.10 ⁻⁴	7.6	1.10 ⁻⁴	7.6	430
y H₂O	2.10 ⁻³	15.6	1.10 ⁻³	5.8	2.10 ⁻³	5.5	1.10 ⁻³	5.2	270
x H₂S	2.10 ⁻³	7.7	8.10 ⁻⁴	3.7	3.10 ⁻³	13.9	1.10 ⁻³	3.8	450
y H₂O	8.10 ⁻³	15.4	9.10 ⁻³	10.6	1.10 ⁻²	9.2	-	-	131
x H₂	1.10 ⁻⁴	6.8	1.10 ⁻¹	>100	2.10 ⁻⁴	10.4	-	-	298
y H₂O	3.10 ⁻³	5.7	6.10 ⁻³	23.4	8.10 ⁻³	3.3	-	-	15

Table 17: Deviations (AAD %) between experimental data and predictions for CO₂-H₂O and SO₂-H₂O binary systems

System	Solubility	GC-PR-CPA EoS (%)	E-PPR78 EoS (%)	Geochemical model (%)	Duan and Sun [101] (%)
CO₂-H₂O	x CO ₂ (Hou et al., 2013)	3.0	5.2	5.0	5.6
	y H ₂ O (Hou et al., 2013 ; Caumon et al., 2016)	15.4	15.1	14.9	15.8
SO₂-H₂O	x SO ₂ (Hou et al., 2013)	5.5	24.6	22.3	-

Table 18: Deviations (AAD %) between experimental data and predictions for ternary systems

System	Solubility	GC-PR-CPA EoS (%)	E-PPR78 EoS (%)	G
CO ₂ -N ₂ -H ₂ O (Liu et al., 2012)	x CO ₂	7.1	3.6	
	x N ₂	18.6	84.4	
CO ₂ -CH ₄ -H ₂ O (Qin et al., 2008)	x CO ₂	11.1	6.9	
	x CH ₄	8.1	6.1	
CO ₂ -CH ₄ -H ₂ O	y H ₂ O (Chapoy et al., 2016)	4.0	1.8	
	y H ₂ O (Qin et al., 2008)	45.7	36.7	
	y H ₂ O (Al Ghafri et al., 2014)	32.8	32.3	
CO ₂ -CH ₄ -H ₂ S-H ₂ O (Robinson et al., 1982)	x CO ₂	3.0	2.9	
	x CH ₄	2.0	12.6	
	x H ₂ S	7.1	12.6	
	y H ₂ O	14.2	2.7	