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PVT analysis for Hydrogen and Methane mixtures for Underground Hydrogen Storage

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Abstract

Hydrogen has been identified as an energy carrier that could play a major role in decarbonization. Large-scale hydrogen storage is required to face future challenges in terms of energy and environmental transition. Underground Hydrogen Storage (UHS) in depleted gas reservoirs is broadly recognized as a promising strategy to safely store large quantities of hydrogen, which can be injected into the porous rocks as a pure component (100% of H₂) or as a mixture with methane. In order to properly design storage activity in a depleted gas reservoir, it is extremely important to define a reliable 3D reservoir dynamic model able to simulate the behavior of the system under all the possible considered operating conditions. To properly represent the interaction between injected hydrogen or mixture with the reservoir fluids, the Equations of State adopted in the compositional simulation must be validated against laboratory data in the pressure and temperature ranges representative of possible operating conditions, and if necessary, properly calibrated.

In this paper, we provide the results of experiments carried out on H₂-CH₄ mixtures within ranges of temperature and pressure conditions representative of depleted gas candidates for storage activities. Constant Mass Expansion (CME) tests were performed using a PVT cell. Pressures up to 300 bar and a temperature range from 30 to 60°C, representing the typical range for a gas storage reservoir in Italy and Europe, were applied. Four different mixtures were considered: pure H₂, 50 mole% H₂-50 mole% CH₄, 10% H₂-90 mole% CH₄, pure CH₄. Results are represented in terms of gas compressibility factor (z factor) curves as a function of pressure for different temperatures and compositions. Furthermore, the obtained results are compared with the GERG-2008 equation of state (EoS).

In the considered pressure and temperature ranges, the GERG-2008 EoS provides a satisfactory match with the experimental data for all the considered cases.

Introduction

In recent years, hydrogen has been pursued as a sustainable energy carrier (Yue et al., 2021). Hydrogen allows for emission-free power generation and aims to reduce the world's dependence on fossil fuels. It has the potential to reduce greenhouse gas emissions and mitigate climate change. When used as a fuel, it does not produce carbon dioxide. Among the list of proposed alternative energy sources, hydrogen appears to be the most promising large-scale fuel due to its high specific energy (Yue et al., 2021), efficient storage over time, and clean combustion (Dunn, 2002). One hydrogen-related approach that has been put forward for making a transition towards a carbon-free economy is adding hydrogen into existing natural gas transport and distribution systems (Melaina et al., 2013; Messaoudani et al., 2016; Polman et al., 2003; Schouten, 2004; Tabak, 2009). (Capocelli & De Falco, 2016) stated that enriched methane is a pathway to introduce hydrogen in the established and consolidated energy infrastructure (Hernández-Gómez, Tuma, Lozano-Martín, et al., 2018). Moreover, hydrogen can be used as an energy carrier to store energy produced from renewable sources for balancing intermittent production; the electrolytic production of hydrogen using excess electricity from renewable energy sources can contribute to a more flexible energy supply and a reduction of the demand for carbonaceous primary energy (Beckmüller et al., 2021). This supply pathway is called Power-to-Gas (P2G). As hydrogen is playing an increasingly important role in future energy scenarios, the concept of a Hydrogen-based Energy Storage System (HydESS) is gaining potential as a cost-effective solution for large-scale RE storage, transport, and export. A vast expansion of the H₂ economy requires a massive storage capacity which can be achieved in geological storage, such as deep aquifers, and depleted oil and gas reservoirs. Underground Hydrogen Storage (UHS) is a challenging process that involves various factors such as containment security (Benetatos et al., 2021; Salina Borello et al., 2024), pore-scale phenomena, and large-scale storage capacity. These factors are greatly influenced by the thermodynamic behavior of hydrogen (H₂) and its mixture with cushion

gases and reservoir fluids. For instance, when the hydrogen storage site is a depleted gas reservoir that has been used for the storage of natural gas (typically, mostly methane), the presence of a mixture of methane and hydrogen is expected in the primary phase of hydrogen storage.

The thermodynamic behavior of hydrogen and its mixtures are needed for the development of theoretical models necessary for the introduction of hydrogen as a promising energy carrier in the near future (Lozano-Martín et al., 2022). This knowledge plays a significant role in designing and operating processes related to hydrogen production, transport, storage, and utilization.

Significant effort has been made to investigate the thermodynamic properties of hydrogen-containing mixtures (Hernández-Gómez, Tuma, Pérez, et al., 2018; Jaeschke et al., 1996; Kritscheveskii & Levchenko, 1941; Magee et al., 1985; Mihara et al., 1977). However, while the knowledge of pure H₂ thermodynamics is well established (Michels & Goudekot, 1941; Seward & Franck, E.U., 1981) published properties of gas mixtures in relation to geological hydrogen storage do not cover the full range of additional gases and often do not encompass the pressures and temperatures encountered within the hydrogen storage system (Hassanpouryouzband et al., 2020).

The current work aims to provide an experimental estimation of the compressibility factor (*z*-factor) of hydrogen, methane, and their binary mixtures, at reservoir pressures and temperatures. To this aim, Constant Mass Expansion (CME) tests were conducted with a PVT cell for different H₂-CH₄ mixtures (pure hydrogen; 10 mole% H₂, and 90 mole% CH₄; 50 mole% H₂ and 50 mole% CH₄, pure methane). Several temperatures in the range of interest of an underground storage system were considered (T = 20, 30, 40, 50, and 60°C). A pressure range of 1-300 bar, representing the typical range for a gas storage reservoir in Italy and Europe, was investigated. The experimental results of the compressibility factor are also compared with the GERG-2008 equation of state (EoS).

Materials and Methods

Theoretical background

An equation of state (EoS) is an analytical expression relating the pressure *p*, the temperature *T*, and the volume *V*. The objective of an EoS is to accurately represent the volumetric behavior, vapor/liquid equilibrium, and thermodynamic properties of a substance in both its liquid and gaseous states.

In 1662, Boyle empirically proved that the volume of the given mass of a dry gas is inversely proportional to its pressure (Boyle & Sharrock, 1662). In 1787, Charles (Levine, 2009) stated empirically that the pressure of the given volume of a dry gas is proportional to its absolute temperature for a fixed volume. In 1802, Gay-Lussac stated empirically that the volume of a dry gas at given pressure is proportional to its absolute temperature (Gay-Lussac, 1802). Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present, at constant pressure and temperature (Avogadro, 1811). Clapeyron summarized the empirical laws above and proposed the ideal gas EoS (Clapeyron, 1834). The mathematical expression of the ideal gas equation of state is expressed as follows:

$$pV = nRT \quad (1)$$

where *p* is the pressure in Pa, *V* is the volume in m³, *n* is the number of moles (mole), *R* is the gas constant (8.314 m³Pa.K⁻¹mol⁻¹), and *T* is the temperature in Kelvin (K).

In this EoS, four assumptions were made (Ahmed, 2007)

- The total volume of the individual molecules is magnitudes smaller than the volume that the gas occupies.
- There are no attractive or repulsive forces between the molecules or the walls of the container.
- Collisions between the molecules are purely elastic, implying no losses on collision.
- The molecules are constantly in motion, and the distance between two molecules is significantly larger than the size of an individual molecule.

This EoS has limitations when describing the behavior of real fluids at a broader range of pressures and temperatures. The generalization to real gases reads:

$$pV = nZRT \quad (2)$$

where *Z* is the compressibility factor. *Z*-factor is considered as the ratio between the volume occupied by a real gas at a specific pressure and temperature to the volume occupied by it under the same thermodynamic conditions if it were ideal.

Z-factor is not a constant but varies with temperature, pressure and fluid composition. Such a trend has to be characterized, either experimentally or by an empirical or analytical model (EoS). At low pressure and high temperature, intermolecular forces become negligible, so real gases approach ideal gas behavior. Thus, at standard conditions $Z = 1$.

Once the behavior of the compressibility factor (Z) is characterized as a function of pressure and temperature, either experimentally or from EoS, density and volume factor can be easily obtained. In fact, from the real gas law, the formation volume factor can be obtained as a function of pressure and temperature as follows:

$$B(p, T) = \frac{V}{V_{sc}} = Z \frac{T}{T_{sc}} \frac{p_{sc}}{p} \quad (3)$$

where $T_{sc} = 15^\circ\text{C}$ and $p_{sc} = 1 \text{ atm}$ are the temperature and pressure at standard conditions, respectively.

Analogously, the gas density can be written as a function of pressure and temperature as follows:

$$\rho(p, T) = \frac{nM}{V} = \frac{pM}{ZRT} \quad (4)$$

where M is the molar mass.

Z factor from experimental data

Experimental data are collected in terms of volumes (V) as a function of pressure (p), temperature (T), and gas composition. According to the real gas law (eq. 2), the Z -factor is calculated from measured volumes as follows:

$$Z(p, T) = \frac{pVT_{sc}}{p_{sc}V_{sc}T} \quad (5)$$

where $T_{sc} = 15^\circ\text{C}$ and $p_{sc} = 1 \text{ atm}$ are temperature and pressure at standard conditions, respectively, and V_{sc} is the volume of the gasometer plus the dead volume of the cell, both reported at standard conditions.

Z factor from GERG-2008 EoS

Z factor obtained from experimental data was compared with the Z -factor from the GERG-2008 equation of state. The GERG-2008 (Kunz & Wagner, 2012) is an empirical EoS for natural gases and mixtures of natural gas components based on a multi-fluid approximation. Developed by the Gas Research Group (GERG), this equation provides an accurate representation of the behavior of multi-component gas mixtures under various thermodynamic conditions. Properties of mixtures over a wide range of compositions of 21 components including hydrogen, methane, nitrogen, and carbon dioxide, are predicted. It was adopted as an ISO Standard (ISO 20765-2) for natural gases and similar mixtures.

Unlike most EoSs, GERG takes density and temperature as the independent variables, while the pressure is calculated by an iterative technique. Helmholtz's free energy definition is the starting point for developing GERG-2008 EoS. For a mixture, the Helmholtz free energy as a function of density (ρ) temperature (T), and compositions (\mathbf{x}) is defined as follows (Kunz & Wagner, 2012):

$$\alpha(\delta, \tau, \mathbf{x}) = \alpha^o(\rho, T, \mathbf{x}) + \alpha^r(\delta, T, \mathbf{x}), \quad (6)$$

where α^o and α^r represents the ideal part and the residual part of the gas mixture, respectively; δ and τ are the reduced fluid mixture density and inverse reduced temperature, respectively:

$$\delta = \frac{\rho}{\rho_r(x_i)}; \tau = \frac{T_r(x_i)}{T} \quad (7)$$

where $1/\rho_r$ and T_r are expressed as a linear combination of the composition. Details are given in (ISO 20765-2:2015, 2015; Kunz & Wagner, 2012).

The ideal part of Helmholtz free energy could be defined by (Kunz & Wagner, 2012):

$$\alpha^0(\rho, T, \mathbf{x}) = \sum_{i=1}^N x_i [\alpha_{oi}^0(\rho, T) + \text{Ln}(x_i)] \quad (8)$$

in which, $\alpha_{oi}^0(\rho, T)$ and $\sum_{i=1}^N x_i \text{Ln}(x_i)$ are the ideal dimensionless Helmholtz free energy and entropy production due to the mixing of component i , respectively; N is the total number of components in the mixture.

The residual part α^r of the reduced Helmholtz free energy of the mixture is given by (Kunz & Wagner, 2012):

$$\alpha^r(\delta, \tau, \mathbf{x}) = \sum_{i=1}^N x_i \alpha_{oi}^r(\delta, \tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta, \tau), \quad (9)$$

Eq.7 takes into account the residual behavior of the mixture at the reduced mixture variables δ and τ . The first sum in this equation is the linear contribution of the reduced residual Helmholtz free energy of the pure substance equations of state multiplied by the mole fractions x_i . The double summation in Eq.7 is the departure function $\Delta\alpha^r(\delta, \tau, \mathbf{x})$ which is the summation over all binary specific and generalized departure functions $\Delta\alpha_{ij}^r(\delta, \tau, \mathbf{x})$ developed for the respective binary mixtures. F_{ij} is the EoS parameters and $\alpha_{ij}^r(\delta, \tau)$ is temperature and density dependence of specific departure functions. $\alpha_{ij}^r(\delta, \tau)$ was developed either for a specific binary mixture or for a group of binary mixtures. Departure functions are expressed as (Kunz & Wagner, 2012):

$$\alpha_{ij}^r(\delta, \tau) = \sum_{k=1}^{K_{pol,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{K=K_{pol,ij}+1}^{K_{pol,ij}+K_{exp,ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp \left[-\eta_{ij,k} (\delta - \varepsilon_{ij,k})^2 - \beta_{ij,k} (\delta - \gamma_{ij,k}) \right] \quad (10)$$

The coefficients $n_{ij,k}$, $d_{ij,k}$ and $t_{ij,k}$, $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ are the EoS parameters and constant. They could be found in ISO 20765–2. Experimental data were used to determine the structures, coefficients, and parameters of the correlation equations (Kunz & Wagner, 2012).

Finally, the compressibility factor could be computed as (Kunz & Wagner, 2012):

$$Z = 1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau, \mathbf{x}} \quad (11)$$

There are two ranges for using the GERG-2008 EoS (Kunz & Wagner, 2012): the normal and the extended range. In the normal range, the temperature is between 90 K and 450 K and the pressure is up to 35MPa. In the extended range, the temperature is between 60 K and 700 K and the pressure can reach 70 MPa. The uncertainty of GERG-2008 in gas-phase density is 0.1 % over the temperature range from 250 to 450 K at pressures up to 35 MPa (Kunz & Wagner, 2012).

(Hassanpouryouzband et al., 2020) used the GERG-2008 EoS to predict the thermo-physical properties of H₂ mixed with a typical natural gas from the North Sea and for binary mixtures of hydrogen with selected components of natural gas (CH₄, N₂, CO₂). The predictions are performed over wide ranges of the mole fraction of H₂ (10–90 mol %), pressures (0.01–100 MPa), and temperatures (200–500 K). Benchmarks comparing various cubic (PR, SRK, BM-PR, VTPR) and noncubic EoS (PC-SAFT and GERG-2008) (Alanazi et al., 2022) individuated GERG-2008 as very accurate in predicting the thermophysical properties of binary and ternary H₂-blend mixtures. (Beckmüller et al., 2021) reported the percentage deviation of homogeneous density data from GERG-2008 for the binary system CH₄ + H₂ with respect to literature experimental data for some mixture proportions.

Test procedure and experimental setup

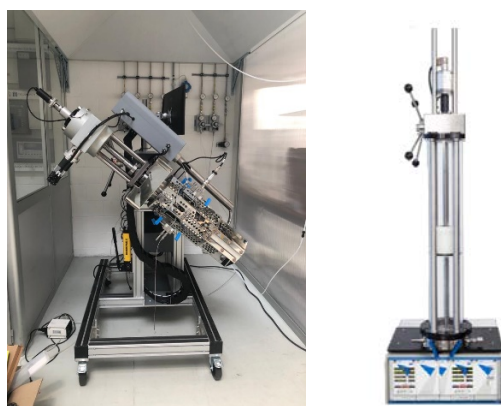
Several temperatures in the range of interest of an underground storage system were considered (T = 20, 30, 40, 50, and 60°C) in a pressure range of 1-300 bar. Different mixtures of hydrogen in methane are considered:

- pure hydrogen (100 mole% H₂)
- 10 mole% H₂ and 90 mole% CH₄
- 50 mole% H₂ and 50 mole% CH₄
- pure methane (100 mole% CH₄)

For each of the considered gas mixtures and each of the target temperatures, a Constant Mass Expansion (CME) test was conducted by adopting a PVT cell. Keeping the desired temperature constant, starting from 300 bar, the pressure is reduced in successive steps ($\Delta p = 20$ bar) by expanding the volume of the cell. At each step, pressure and volume values are recorded, after stabilization is reached.

The PVT cell is an instrument for the study of the thermodynamic properties and phase behavior of fluids. It is equipped with an accurate pressure transducer and an electric heater for temperature control. The internal parts in contact with the fluid are made of Hastelloy to be safely used with hydrogen and its mixtures. The cell also has an external reference pressure sensor that is used to calibrate the internal pressure sensor.

To increase the precision of the volume measurements, the flow at the inlet of the cell is regulated through a mass flow specific for hydrogen mixtures, while at the outlet, the gas volume brought to standard conditions is measured by a gasometer. Adopted instruments are shown in Figure 1 and their specifications are summarized in Table 1.



(a)

(b)

Figure 1: (a) PVT cell; (b) gasometer

Table 1: Instruments specifications and accuracy

PVT cell	Pressure range	1 to 700 bar
	Temperature range	20 to 200 °C
	PVT cell volume	300 ml
	Visual Volume	300 ml
	Pressure Accuracy	± 0.1 bar
	Temperature Accuracy	± 0.1 °C
	Liquid deposit	0.005 ml
	Bubble/Dew point repeatability	± 0.35 bar
	Resisting corrosive abilities	CO ₂ and H ₂ S
Gasometer	Volume	4000 ml
	Pressure range	Vacuum to 2 bar
	Temperature	Ambient
	Volume accuracy	± 0.1 ml
	Pressure accuracy	± 0.1 mbar
	Temperature accuracy	± 0.1 °C
Mass flow	Flow range	0-50 ml/min
	Accuracy (incl. linearity)	$\pm 0,5$ % RD plus $\pm 0,1$ % FS
	Operating pressure	Up to 200 bar
	Operating Temperature	-10 to +70 °C
	Pressure sensitivity	0,01% Rd/bar typical H ₂
	Temperature sensitivity	zero: < 0,05% FS/°C; span: < 0,05% Rd/°C

Results & Discussion

From the volumes measured for changing pressure at fixed temperature and mixture composition, the compressibility factor, density, and formation volume factor were calculated. Z factor results are compared with GERG-2008 EoS in Figure 2. Significantly different trends are shown for different mixtures. Correlation trends and experimental data are in discreet agreement. GERG-2008 slightly overestimates Z values in all scenarios. The corresponding density and volume factor trends, compared with GERG-2008, are shown in Figure 3 and Figure 4, respectively.

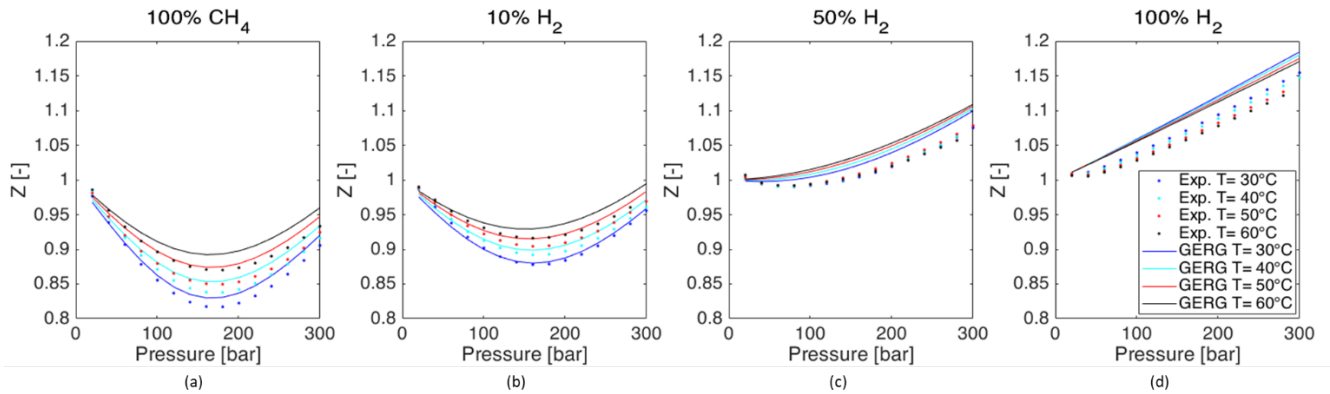


Figure 2: Z factor: comparison between experimental data and GERG2008 correlation for different temperatures and different H₂-CH₄ mixtures: (a) pure methane, (b) 10% H₂, (c) 50% H₂, (d) 100% H₂.

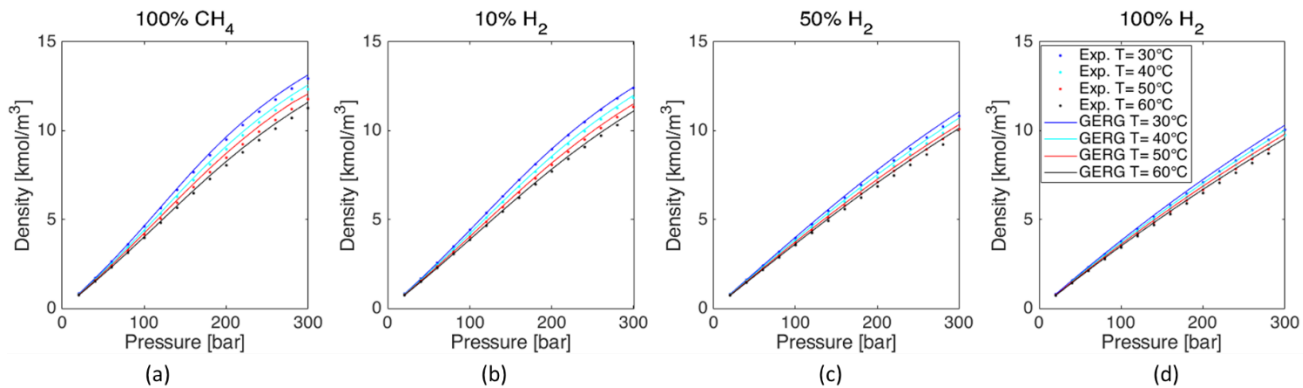


Figure 3: Density as a function of pressure and temperature and for different H₂-CH₄ mixtures: (a) pure methane, (b) 10% H₂, (c) 50% H₂, (d) 100% H₂.

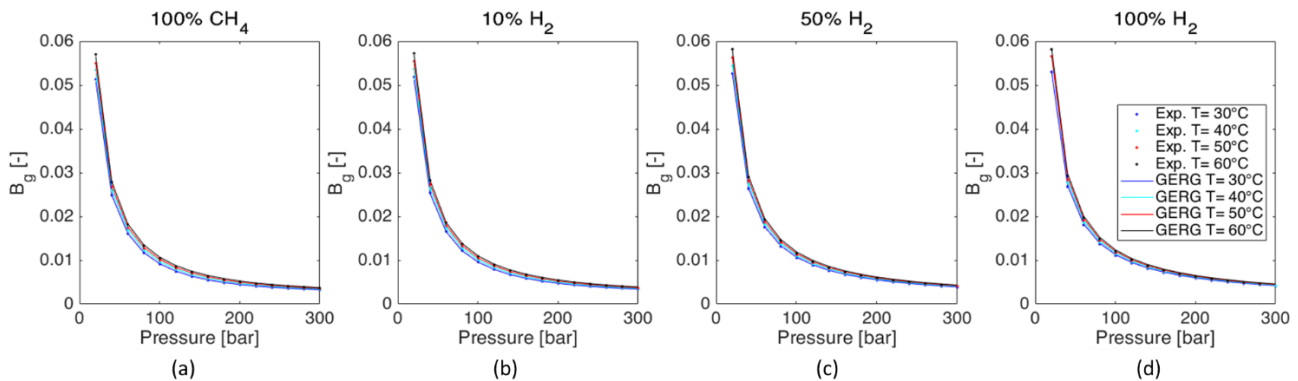


Figure 4: Volume factor as a function of pressure and temperature and for different H₂-CH₄ mixtures: (a) pure methane, (b) 10% H₂, (c) 50% H₂, (d) 100% H₂.

The analysis of the relative discrepancy between the compressibility factor obtained by experimental data (Z_E) and by GERG (Z_G) as a function of temperature and pressure is shown in Figure 5 and a summary boxplot is shown in Figure 6. Notice that, being B and ρ proportional to Z and $1/Z$ respectively (eq. (3) and (4)), the relative deviations on B , and ρ coincide (or almost coincide) with the relative deviations on Z . In fact, from eq. (3) and (4) it follows, respectively:

$$\frac{|B_G - B_E|}{B_E} = \frac{T}{T_{sc}} \frac{p_{sc}}{p} \frac{|Z_G - Z_E|}{Z_E} = \frac{|Z_G - Z_E|}{Z_E} \quad (7)$$

$$\frac{|\rho_G - \rho_E|}{\rho_E} = \frac{pM}{RT} \left(\frac{1}{Z_G} - \frac{1}{Z_E} \right) = \frac{|Z_E - Z_G|}{Z_G Z_E} Z_E = \frac{|Z_G - Z_E|}{Z_G} \quad (8)$$

Discrepancy trend increasing with temperature and pressure (especially for $p > 100$ bar) is observed (Figure 5) in all scenarios. The deviation is always below 4%, mostly lower than 3% (Figure 5 and Figure 6). The maximum discrepancy is observed for 50% H_2 50% CH_4 mixture at the maximum considered temperature, while the minimum discrepancy is observed for 10% H_2 90% CH_4 mixture. The observed discrepancy range is in line with (Beckmüller et al., 2021) who found a deviation of density data within 3% between GERG-2008 and literature experimental data for the binary system $CH_4 + H_2$ in the temperature range of interest.

In the considered pressure and temperature ranges, GERG-2008 is adequate to reproduce the PVT behavior of the mixtures considered.

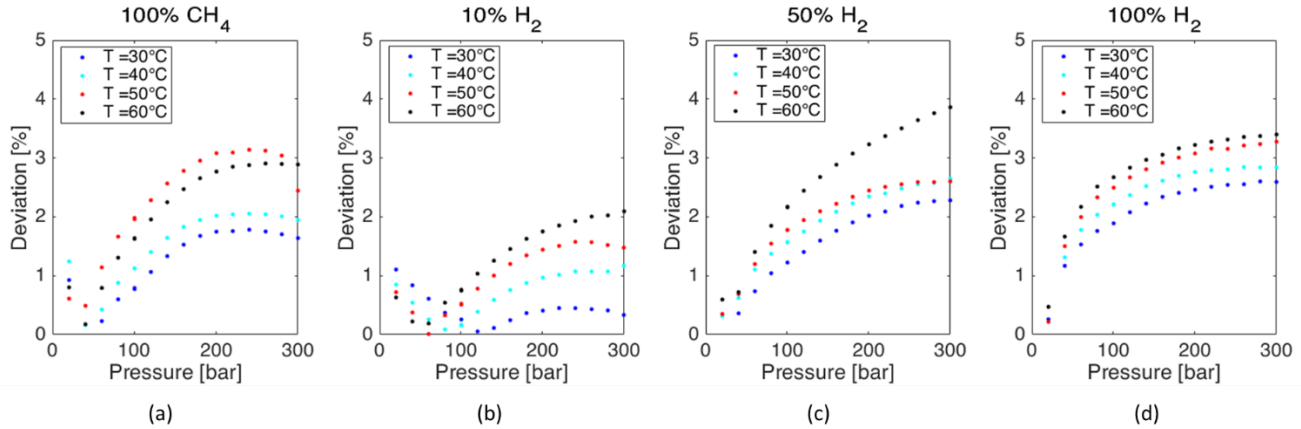


Figure 5: Discrepancy between experimental data and GERG-2008 correlation as a function of temperature and pressure for different H_2 - CH_4 mixtures: (a) pure methane, (b) 10% H_2 , (c) 50% H_2 , (d) 100% H_2 .

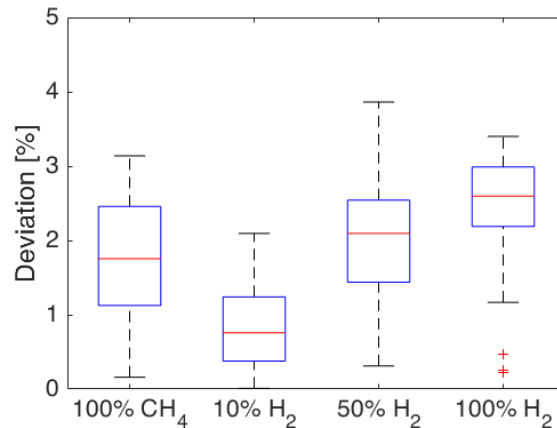


Figure 6: Discrepancy between experimental data and GERG-2008 correlation for different H₂-CH₄ mixtures.

Conclusions

This work provides the results of experiments carried out on H₂-CH₄ mixtures (0%, 10% 50%, and 100% H₂) within ranges of temperature (30-60°C) and pressure (up to 300 bar) conditions representative of depleted gas candidates for storage activities. Tests of Constant Mass Expansion (CME) were performed using a PVT cell. The obtained gas compressibility factor curves as functions of pressures for the different temperatures and compositions are compared with the one obtained by GERG-2008 EoS.

In the pressure and temperature ranges considered, a discreet agreement is observed between experimental data and GERG-2008 EoS for all the considered cases, with a maximum discrepancy of 4%. GERG-2008 was confirmed to be a feasible EoS for the dynamic simulations of the storage cycles of hydrogen-methane mixtures for design purposes. However, considering that GERG EoS is not available in many commercial simulators, a calibration of the most diffused EoS such as Peng and Robinson will be part of our future work.

The experimental results of this study help understand the PVT behavior of the H₂-CH₄ gas mixtures, an essential knowledge in designing and operating processes related to underground hydrogen storage.

References

- Ahmed, T. H. (2007). *Equations of state and PVT analysis: Applications for improved reservoir modeling*. Gulf Pub.
- Alanazi, A., Ali, M., Bawazeer, S., Yekeen, N., & Hoteit, H. (2022). Evaluation of cubic, PC-SAFT, and GERG2008 equations of state for accurate calculations of thermophysical properties of hydrogen-blend mixtures. *Energy Reports*, 8, 13876–13899. <https://doi.org/10.1016/j.egy.2022.10.257>
- Avogadro, A. (1811). Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons, *Journal de physique, de chimie, d'histoire naturelle et des arts*, Volume 73: 58-76. *Journal de physique, de chimie, d'histoire naturelle et des arts*, 73, 58–76.
- Beckmüller, R., Thol, M., Bell, I. H., Lemmon, E. W., & Span, R. (2021). New Equations of State for Binary Hydrogen Mixtures Containing Methane, Nitrogen, Carbon Monoxide, and Carbon Dioxide. *Journal of Physical and Chemical Reference Data*, 50(1), 013102. <https://doi.org/10.1063/5.0040533>
- Benetatos, C., Bocchini, S., Carpignano, A., Chiodoni, A., Cocuzza, M., Deangeli, C., Eid, C., Ferrero, D., Gerboni, R., Giglio, G., Lamberti, A., Marasso, S., Massimiani, A., Menin, B., Moscatello, A., Panini, F., Pirri, C. F., Quaglio, M., Rocca, V., ... Viberti, D. (2021). How underground systems can contribute to meet the challenges of energy transition. *How underground systems can contribute to meet the challenges of energy transition*, 1224(163), 65–80. <https://doi.org/10.19199/2021.163-164.1121-9041.065>
- Boyle, R., & Sharrock, R. (1662). *A defence of the doctrine touching the spring and weight of the air* (1–1 online resource ([12], 122 pages, 1 unnumbered leaf of plates) : illustrations). Printed by F.G. for Thomas Robinson ... London; WorldCat. http://gateway.proquest.com/openurl?ctx_ver=Z39.88-2003&res_id=xri:eebo&rft_val_fmt=&rft_id=xri:eebo:image:57681
- Capocelli, M., & De Falco, M. (2016). Enriched Methane: A Ready Solution for the Transition Towards the Hydrogen Economy. In M. De Falco & A. Basile (A c. Di), *Enriched Methane* (pp. 1–21). Springer International Publishing. https://doi.org/10.1007/978-3-319-22192-2_1

- Clapeyron, E. (1834). Mémoire sur la puissance motrice de la chaleur. *Journal de l'École polytechnique*, XXIII, 153–190.
- Dunn, S. (2002). Hydrogen futures: Toward a sustainable energy system. *International Journal of Hydrogen Energy*, 27(3), 235–264.
[https://doi.org/10.1016/S0360-3199\(01\)00131-8](https://doi.org/10.1016/S0360-3199(01)00131-8)
- Gay-Lussac, J. L. (1802). Recherches sur la dilatation des gaz et des vapeurs. *Annales de Chimie*, 137–175.
- Hassanpouryouzband, A., Joonaki, E., Edlmann, K., Heinemann, N., & Yang, J. (2020). Thermodynamic and transport properties of hydrogen containing streams. *Scientific Data*, 7(1), 222. <https://doi.org/10.1038/s41597-020-0568-6>
- Hernández-Gómez, R., Tuma, D., Lozano-Martín, D., & Chamorro, C. R. (2018). Accurate experimental (p , ρ , T) data of natural gas mixtures for the assessment of reference equations of state when dealing with hydrogen-enriched natural gas. *International Journal of Hydrogen Energy*, 43(49), 21983–21998. <https://doi.org/10.1016/j.ijhydene.2018.10.027>
- Hernández-Gómez, R., Tuma, D., Pérez, E., & Chamorro, C. R. (2018). Accurate Experimental (p , ρ , and T) Data for the Introduction of Hydrogen into the Natural Gas Grid (II): Thermodynamic Characterization of the Methane–Hydrogen Binary System from 240 to 350 K and Pressures up to 20 MPa. *Journal of Chemical & Engineering Data*, 63(5), 1613–1630.
<https://doi.org/10.1021/acs.jced.7b01125>
- ISO 20765-2:2015. (2015). *Natural gas Calculation of thermodynamic properties Part 2: Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application (ISO 20765-2:2015)*. <https://www.iso.org/standard/59222.html>
- Jaeschke, M., Hinze, H.-M., & Humphreys, A. E. (1996). *Supplement to the GERG databank of high-accuracy compression factor measurements. GERG*.
- Kritschevskii, I. R., & Levchenko, G. T. (1941). *Compressibility of gas mixtures. II. PVT data Bin. Ternary Mix. Methane, nitrogen and hydrogen. in Russ. Acta Physicochim.*(UR SS _L4), 271–278.
- Kunz, O., & Wagner, W. (2012). The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004. *Journal of Chemical & Engineering Data*, 57(11), 3032–3091. <https://doi.org/10.1021/je300655b>
- Levine, I. N. (2009). *Physical chemistry* (6th ed). McGraw-Hill.
- Lozano-Martín, D., Moreau, A., & Chamorro, C. R. (2022). Thermophysical properties of hydrogen mixtures relevant for the development of the hydrogen economy: Review of available experimental data and thermodynamic models. *Renewable Energy*, 198, 1398–1429. <https://doi.org/10.1016/j.renene.2022.08.096>
- Magee, J. W., Pollin, A. G., Martin, R. J., & Kobayashi, R. (1985). Burnett—Isochoric P — V — T measurements of a nominal 20 mol% hydrogen—80 mol% methane mixture at elevated temperatures and pressures. *Fluid Phase Equilibria*, 22(2), 155–173.
[https://doi.org/10.1016/0378-3812\(85\)85017-2](https://doi.org/10.1016/0378-3812(85)85017-2)
- Melaina, M. W., Antonia, O., & Penev, M. (2013). *Blending hydrogen into natural gas pipeline networks: A review of key issues* [Tech.rep.]. National Renewable Energy Lab. (NREL).

- Messaoudani, Z. L., Rigas, F., Binti Hamid, M. D., & Che Hassan, C. R. (2016). Hazards, safety and knowledge gaps on hydrogen transmission via natural gas grid: A critical review. *International Journal of Hydrogen Energy*, *41*(39), 17511–17525. <https://doi.org/10.1016/j.ijhydene.2016.07.171>
- Michels, A., & Goudekot, M. (1941). Compressibilities of hydrogen between 0°C and 150°C up to 3000 atmospheres. *Physica*, *8*(3), 347–352. [https://doi.org/10.1016/S0031-8914\(41\)90076-9](https://doi.org/10.1016/S0031-8914(41)90076-9)
- Mihara, S., Sagara, H., Arai, Y., & Saito, S. (1977). The compressibility factors of hydrogen-methane, hydrogen-ethane and hydrogen-propane gaseous mixtures. *JOURNAL OF CHEMICAL ENGINEERING OF JAPAN*, *10*(5), 395–399. <https://doi.org/10.1252/jcej.10.395>
- Polman, E. A., de Laat, J. C., & Crowther, M. (2003). *Reduction of CO2 emissions by adding hydrogen to natural Gas* (IEA Greenhouse Gas R&D Program, p. pp.1-104).
- Salina Borello, E., Bocchini, S., Chiodoni, A., Coti, C., Fontana, M., Panini, F., Peter, C., Pirri, C. F., Tawil, M., Mantegazzi, A., Marzano, F., Pozzovivo, V., Verga, F., & Viberti, D. (2024). Underground Hydrogen Storage Safety: Experimental Study of Hydrogen Diffusion through Caprocks. *Energies*, *17*(2), 394. <https://doi.org/10.3390/en17020394>
- Schouten, J. (2004). Effect of H₂-injection on the thermodynamic and transportation properties of natural gas. *International Journal of Hydrogen Energy*. <https://doi.org/10.1016/j.ijhydene.2003.11.003>
- Seward, T. M., & Franck, E.U. (1981). *System hydrogen—Water up to 440/sup 0/C and 2500 bar pressure*.
- Tabak, J. (2009). *Natural Gas and Hydrogen*. Facts On File, Incorporated. <https://books.google.it/books?id=lnF9XPc3rZ4C>
- Yue, M., Lambert, H., Pahon, E., Roche, R., Jemei, S., & Hissel, D. (2021). Hydrogen energy systems: A critical review of technologies, applications, trends and challenges. *Renewable and Sustainable Energy Reviews*, *146*, 111180. <https://doi.org/10.1016/j.rser.2021.111180>