MefHySto

Metrology for Advanced Hydrogen Storage Solutions

WP2: Thermophysical Properties

Public Final Project Conference and Workshops | July 03.–05., 2023

David Vega-Maza, UVa. WP2 Leader

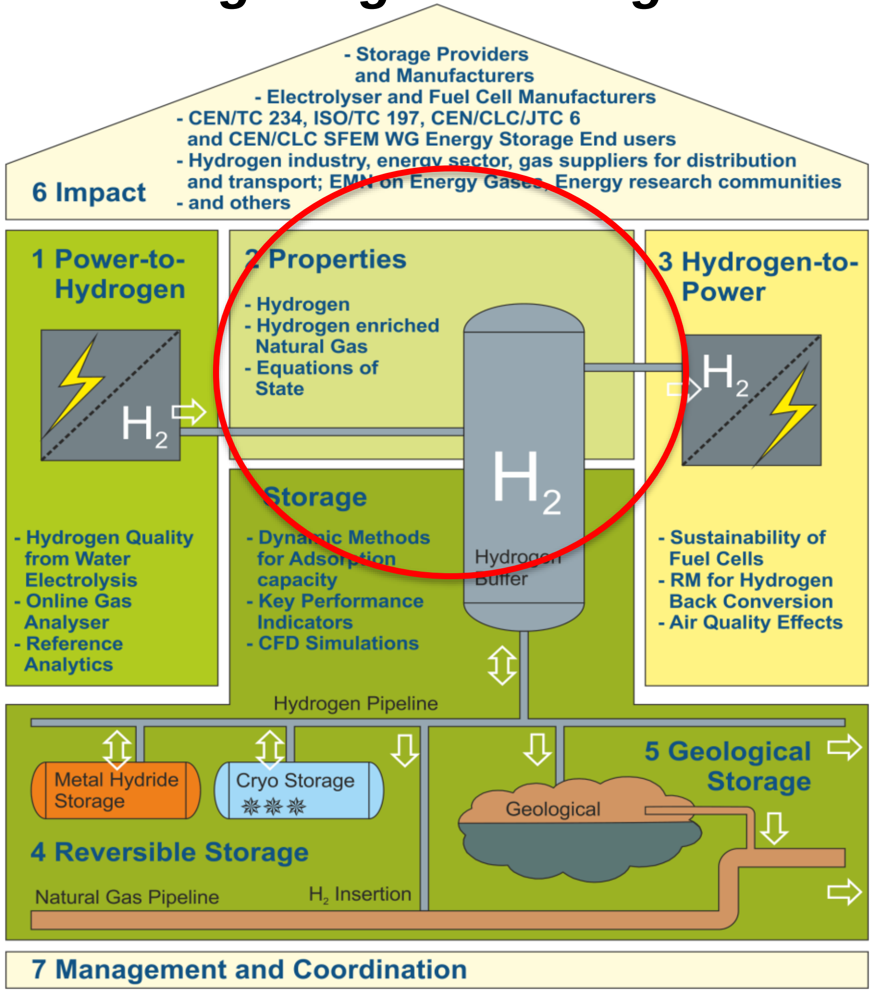
EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

WP2: Thermophysical properties of hydrogen obtained from electrolysis, hydrogen injected in the gas grids and hydrogen under geological storage conditions.

(**FUNGE-UVa**, BAM, NPL, DBI, RA)

Start M1, End M36



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Metrology for Advanced Hydrogen Storage Solutions

WP2: Thermophysical properties of hydrogen obtained from electrolysis, hydrogen injected in the gas grids and hydrogen under geological storage conditions.

Aim:

- to develop validation models for hydrogen obtained from electrolysis (power-to-gas)
- to characterize the hydrogen-enriched natural gas mixtures with a hydrogen content of up to 20 %
- to characterize hydrogen under geological storage conditions

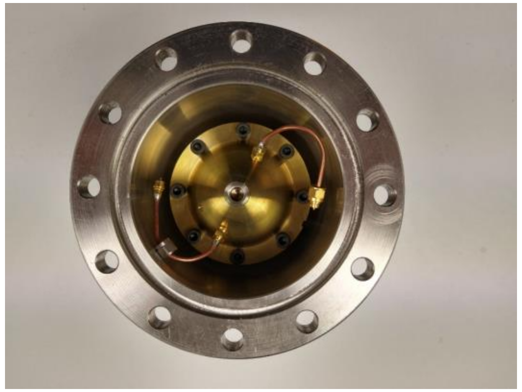
Objectives:

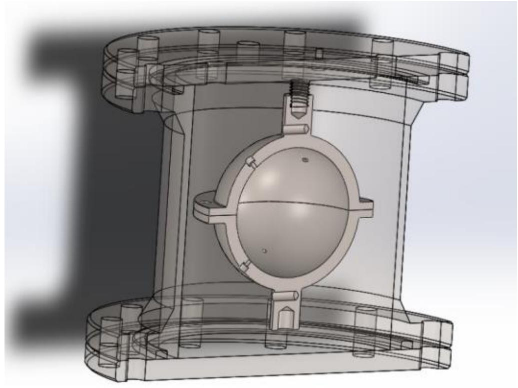
- *To improve the reference equations of state used for modelling hydrogen injection up to 20 % vol. for energy metering by providing traceable density measurements with a target uncertainty of between 0.03 % to 0.5 % as basis for accurate determination of calorific values of energy gases.*
- *To tackle metrological and thermodynamic issues in the large-scale storage of hydrogen in underground gas storages (UGS) and the conversion of existing UGS from natural gas to hydrogen.*

Task 2.1: Develop and test of experimental techniques to provide reference mixtures of humid hydrogen and humid hydrogen-enriched natural gas.

Water vapour enhancement factor in H_2

NPL multi-gas multi-pressure humidity generator





Task 2.2: Influence of the hydrogen content in the saturation curve of hydrogen-enriched natural gas mixtures

- Phase behaviour (accumulation of condensates) according to DIN EN ISO 6570 of H2-enriched natural gas (25%, 50%).
- The experimental (p, ρ, T) data of the H_2-enriched NG mixtures, at least at five different isotherms from 250 K to 375 K and at pressures up to 20 MPa

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Task 2.3: Develop reference equations of state (EOS) for hydrogen-enriched natural gas mixtures and hydrogen under geological storage conditions

- H_2 (x) + C_3H_8. x = 0.95, 0.90, 0.83 have been gravimetrically prepared
- Experimental (p, ρ, T) and speed of sound have been measured at four different isotherms from 273.15 K to 350 K and at pressures up to 20 MPa.
- H_2 (x) + CO. x = 0.90, 0.75, 0.60 have been gravimetrically prepared
- Experimental (p, ρ, T) and speed of sound of the mixtures H_2 (x) + CO. (x = 0.90, 0.75, 0.60) at four different isotherms from 273.15 K to 350 K and at pressures up to 20 MPa

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Thank you for your attention

David Vega-Maza, Uva, WP2

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Outline

- **Introduction**
- Motivation
- Water vapour enhancement factor in H_2
- Experimental (*p*, *ρ*, *T*) data of the H_2-enriched NG mixtures
- Experimental (*p*, *ρ*, *T*) data of the $H_2 + C_3H_8$ binary mixtures
- Discussion

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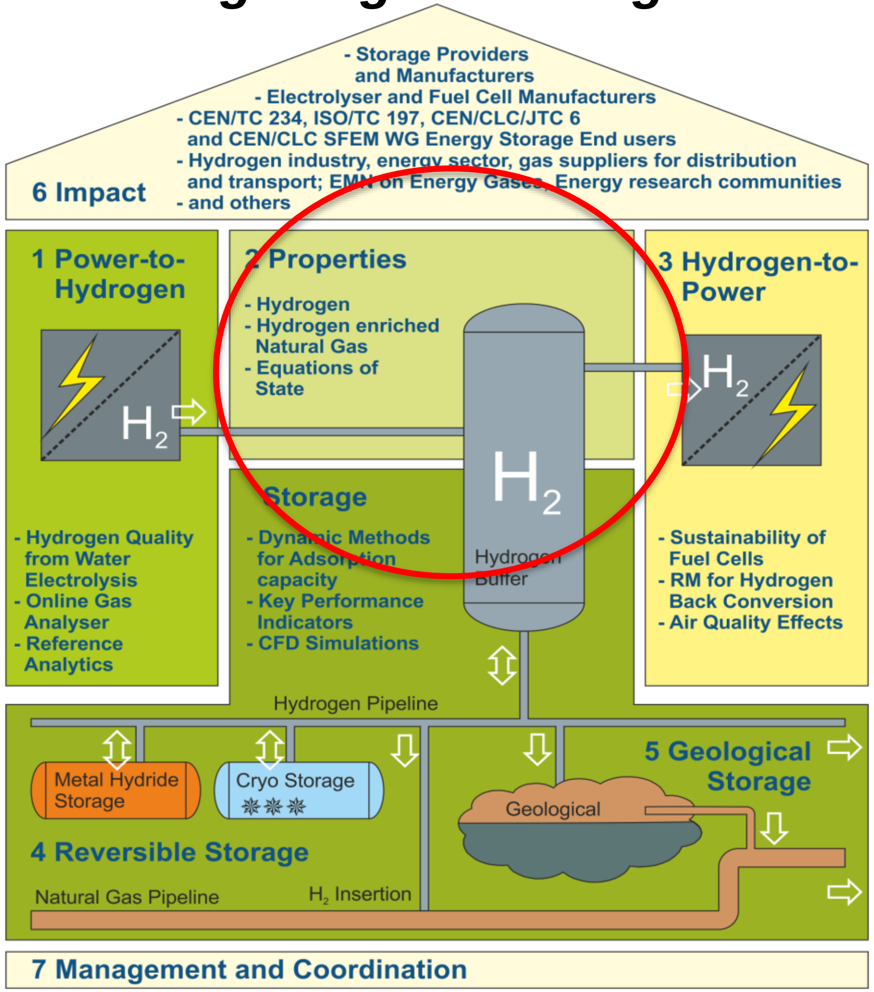

TermoCal
University of Valladolid
Thermophysics & Calibration

BAM
Bundesanstalt für Materialforschung und -prüfung

NPL
National Physical Laboratory

DBI GUT
Gas- und Umwelttechnik GmbH

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Motivation:

- All aspects of **process design**, **implementation, intensification** and safe **operation** have requirements for thermophysical property data

- These properties are best provided by **validated mathematical models** that are capable of providing reliable data in all applicable thermodynamic states

- The requirement for validation calls for **appraisal** of the available experimental data and the acquisition of **new data to fill key gaps**

Application

- Process design. Engineering
- Fiscal metering, allocation metering
- Pipeline leakage control
- Flow measurements, calibration
- Thermodynamic behaviour

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NPL progress, WP2

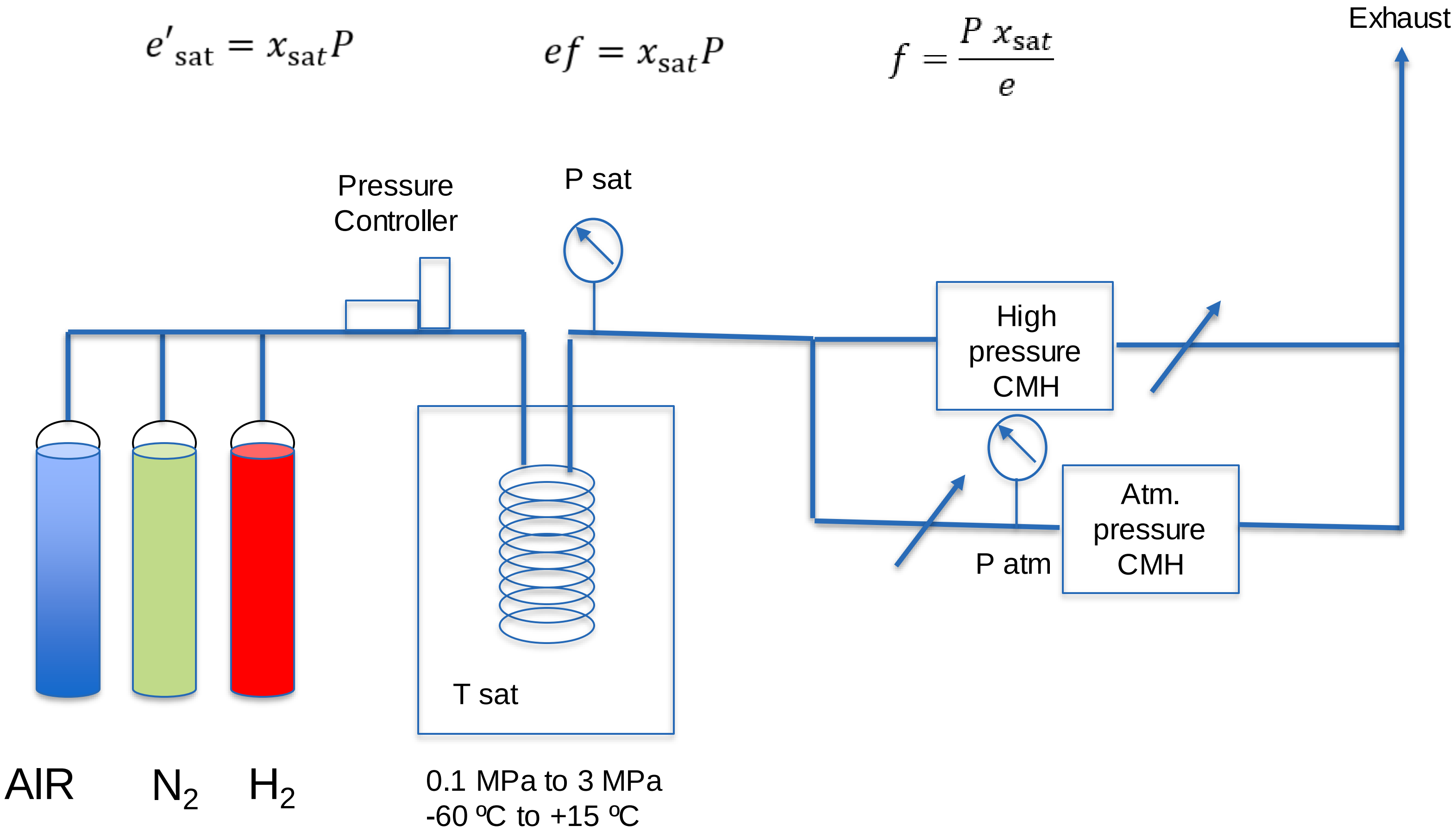
NPL National Physical Laboratory

$$e' = ef$$

$$e'_{sat} = x_{sat}P$$

$$ef = x_{sat}P$$

$$f = \frac{P\, x_{sat}}{e}$$



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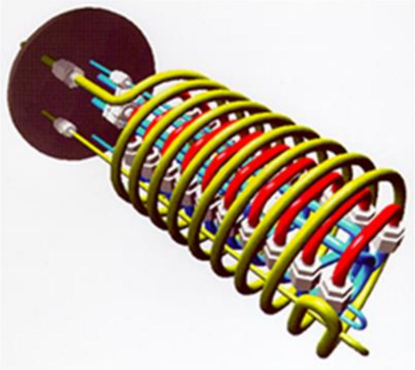
A2.1.2 Water vapour enhancement factor (WVEF) in H_2 and H_2/methane mixes.

- Evaluation measurements have been made with saturator pressures up to 3 MPa, saturator temperatures (frost points) of -40 °C and -20 °C, at a range of pressure ratios (to atmospheric pressure),
- Data is being analysed. Starting to take into account gas non-ideality of H_2 in the pressure drop ratio (thanks to suggestion by UVa).
- Initial analysis yields values of enhancement factor ratio (relative to value at atmospheric pressure).
- Enhancement factor evaluation in H_2/CH_4 mix not started yet.

NPL multi-gas multi-pressure humidity generator

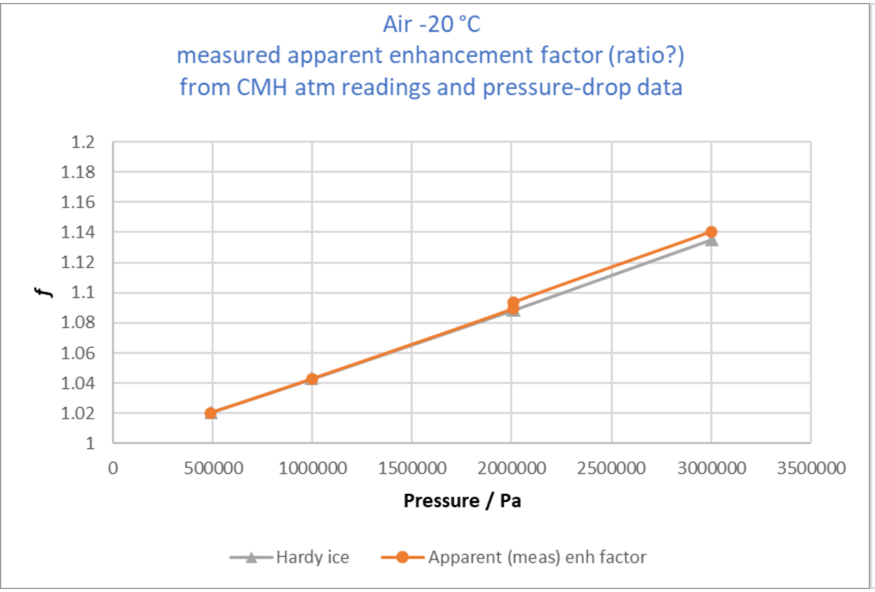
A2.1.6 Compare WVEF results with UVa and with models.

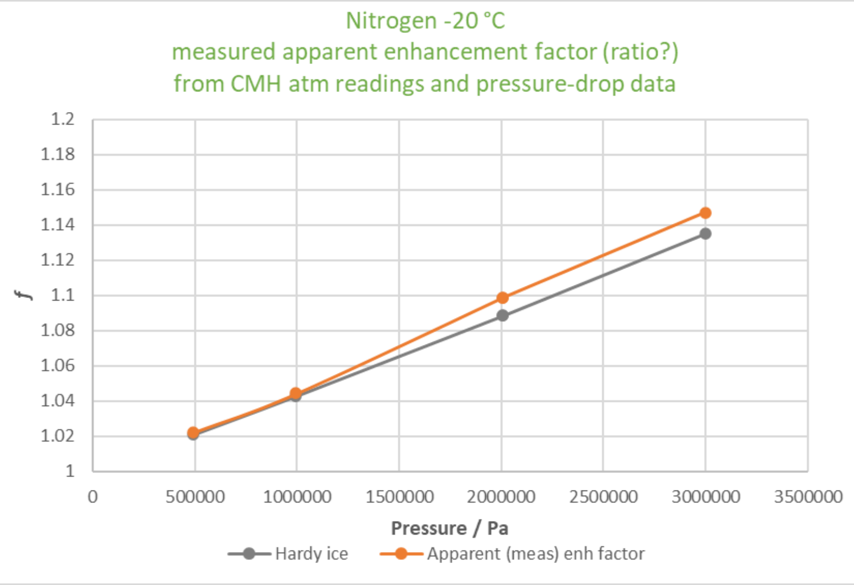
- Analysis started using GasVLE software with a variety of equations of state.

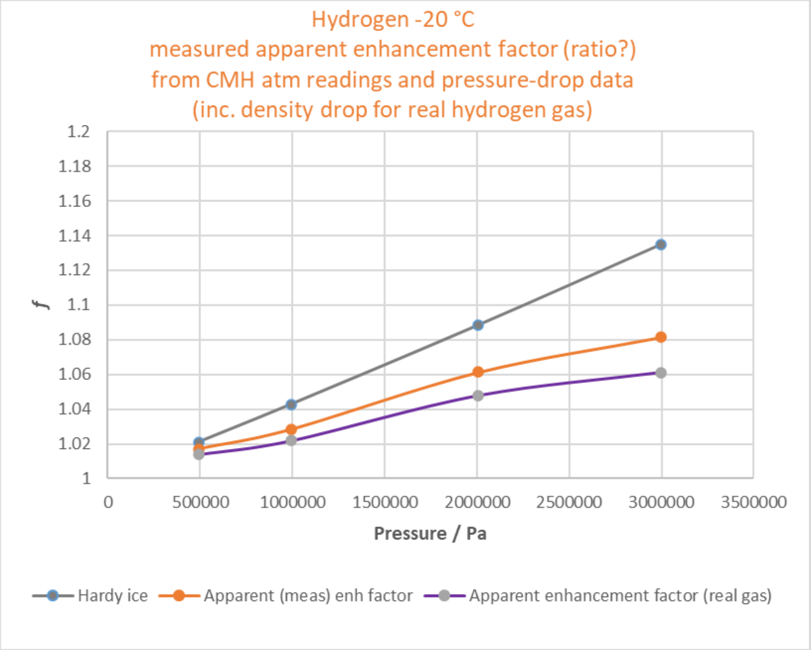


NPL progress, WP2

Provisional data, experiment to be repeated in Summer 2023 to confirm results.







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INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 48 (2023) 8645–8667

Available online at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/he

ELSEVIER

Thermodynamic characterization of the ($H_2 + C_3H_8$) system significant for the hydrogen economy: Experimental (p, ρ, T) determination and equation-of-state modelling

Check for updates

Daniel Lozano-Martín [a], Peyman Khanipour [b], Heinrich Kipphardt [b], Dirk Tuma [b], César R. Chamorro [a,]*

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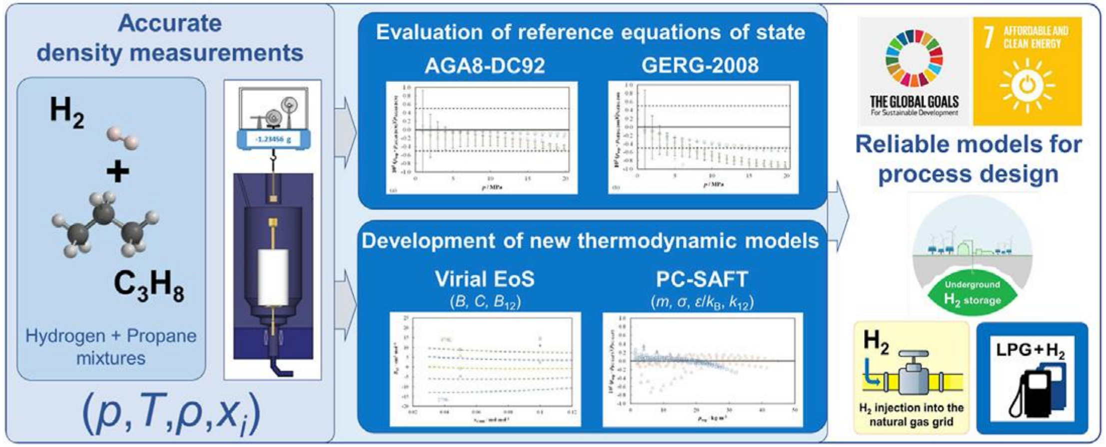
[b] *BAM Bundesanstalt für Materialforschung und -prüfung, D-12200, Berlin, Germany*



WP2: Thermophysical Properties

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BAM
Bundesanstalt für Materialforschung und -prüfung

Natural gas **G 431** without hydrogen

compound	$10^2\,x_i$ / mol mol^{-1}	$10^2\,U(x_i)$ / mol mol^{-1}
Methane	97.236138	0.002007
Nitrogen	1.400965	0.000276
Ethane	0.398705	0.000033
Carbon dioxide	0.361460	0.000113
Propane	0.201221	0.000020
N-Butane	0.100431	0.000023
Isobutane	0.100398	0.000052
Neopentane	0.050781	0.000022
N-Pentane	0.050072	0.000023
Isopentane	0.049928	0.000023
N-Hexane	0.049883	0.000018
Oxygen	*0.000012*	*0.000012*
Hydrogen	*0.000003*	*0.000003*
Carbon monoxide	*0.00000032*	*0.00000025*
Propene	*0.00000020*	*0.00000023*
Ethene	*0.00000004*	*0.00000005*
Nitrous oxide	*0.00000002*	*0.00000002*

Natural gas **G 432** without hydrogen

compound	$10^2\,x_i$ / mol mol^{-1}	$10^2\,U(x_i)$ / mol mol^{-1}
Methane	85.006261	0.002536
Nitrogen	0.950799	0.000182
Ethane	8.991769	0.000742
Carbon dioxide	1.448230	0.000161
Propane	3.002561	0.000507
N-Butane	0.200443	0.000075
Isobutane	0.199935	0.000119
Neopentane	0.050035	0.000031
N-Pentane	0.050054	0.000020
Isopentane	0.049929	0.000020
N-Hexane	0.049965	0.000016
Oxygen	*0.000012*	*0.000007*
Hydrogen	*0.000002*	*0.000001*
Carbon monoxide	*0.000001*	*0.000001*
Propene	*0.000003*	*0.000003*
Ethene	*0.000001*	*0.000001*
Nitrous oxide	*0.0000001*	*0.0000001*

BAM

Gravimetric Preparation of Gas Mixtures

— according to **ISO 6142**; **metrological traceability**

— pre-treatment of cylinders

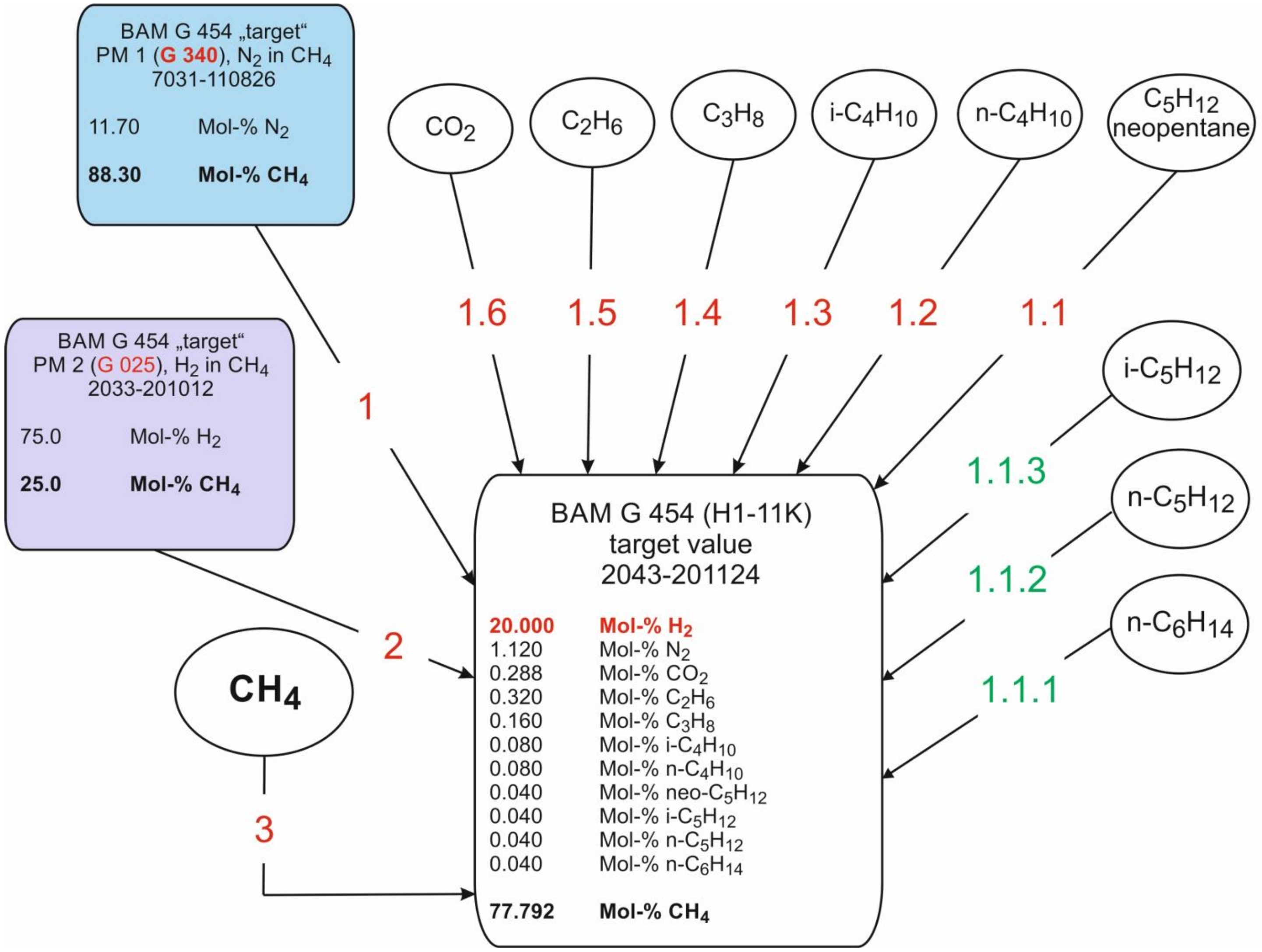
— filling station
direct gas transfer, evaporation from small cylinders, liquid injection via syringe

— use of **pre-mixtures**
considering dew points, stability, safety, and accuracy (related to the amount to be introduced)

— mechanical balance **Voland HCE 25**:
25 **kg** ± 15 **mg** (25 000.000 g ± 0.015 g)

3 syringes (1.1.1, …),
6 small cylinders (1.1, …),
2 premixtures;

3 consecutive filling steps



Consecutive filling steps and resulting pressure in the recipient cylinder

Final mixture

1.1.1.	2.32 g (3.51 ml) $n\text{-}C_6H_{14}$	
1.1.2.	1.94 g (3.07 ml) $n\text{-}C_5H_{12}$	
1.1.3.	1.94 g (3.12 ml) $i\text{-}C_5H_{12}$	
1.1.	1.95 g neo-C_5H_{12}	
1.2.	3.12 g $n\text{-}C_4H_{10}$	
1.3.	3.12 g $i\text{-}C_4H_{10}$	
1.4.	4.73 g C_3H_8	≤ 1 bar
1.5.	6.45 g C_2H_6	1 bar
1.6.	8.50 g CO_2	1 bar
1.	116.8 g PM 1 **(7031)**	16 bar
2.	98.7 g PM 2 **(2033)**	56 bar
3.	669.0 g CH_4	150 bar

Mixture Validation by *Process*-GC

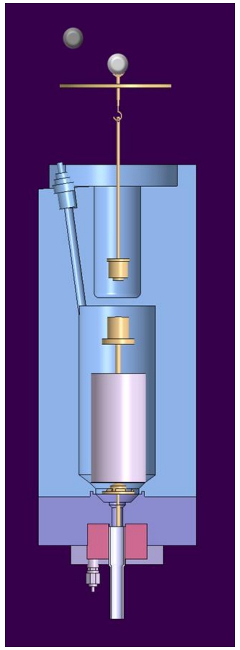
Siemens MAXUM II

- multichannel process GC, 12 TC detectors, 12 handmade packed columns;
- one single isothermal method (t = const. = 60 °C)
- bracketing method according to **ISO 12963** requires two calibration gases (usually plus and minus 5 % of the nominal sample composition)
- a complete sequence takes 4 hours only

Single Sinker Magnetic Suspension Densimeter

(250 to 400) K

20 MPa



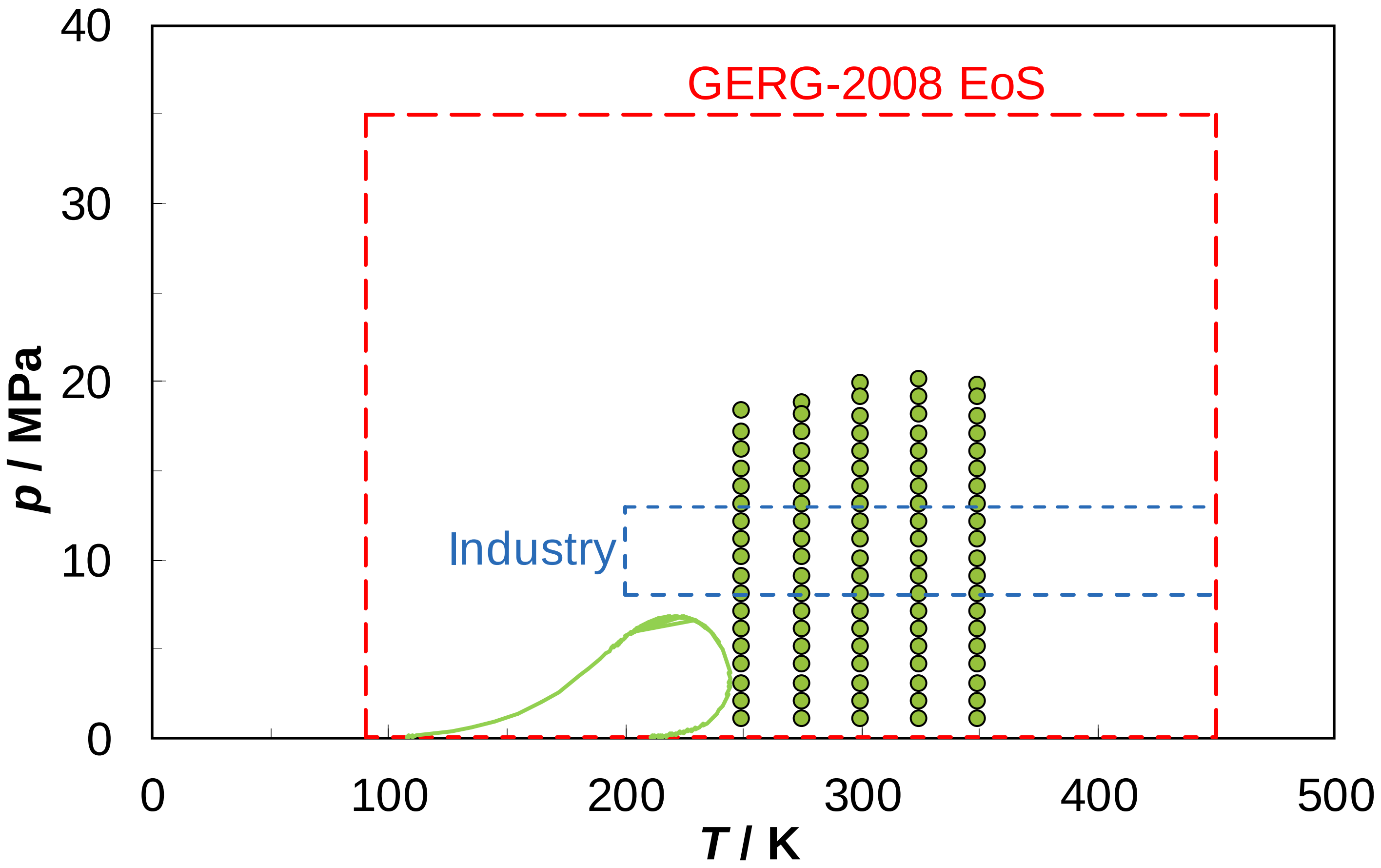
$U(T)$ (k = 2) = 4.0·10^{-3} K

(0 −3) MPa: $U(p)$/MPa (k = 2) = 60·10^{-6}·p/MPa + 1.7·10^{-3}

(3 − 20) MPa: $U(p)$/MPa (k = 2) = 75·10^{-6}·p/MPa + 3.5·10^{-3}

$U(\rho)$/kg·m^{-3} (k = 2) = 1.1·10^{-4}·ρ/kg·m^{-3} + 2.3·10^{-2}

Density Measurements: Zero-Hydrogen Mixture (BAM G 431)



G 431 "cricondentherm"

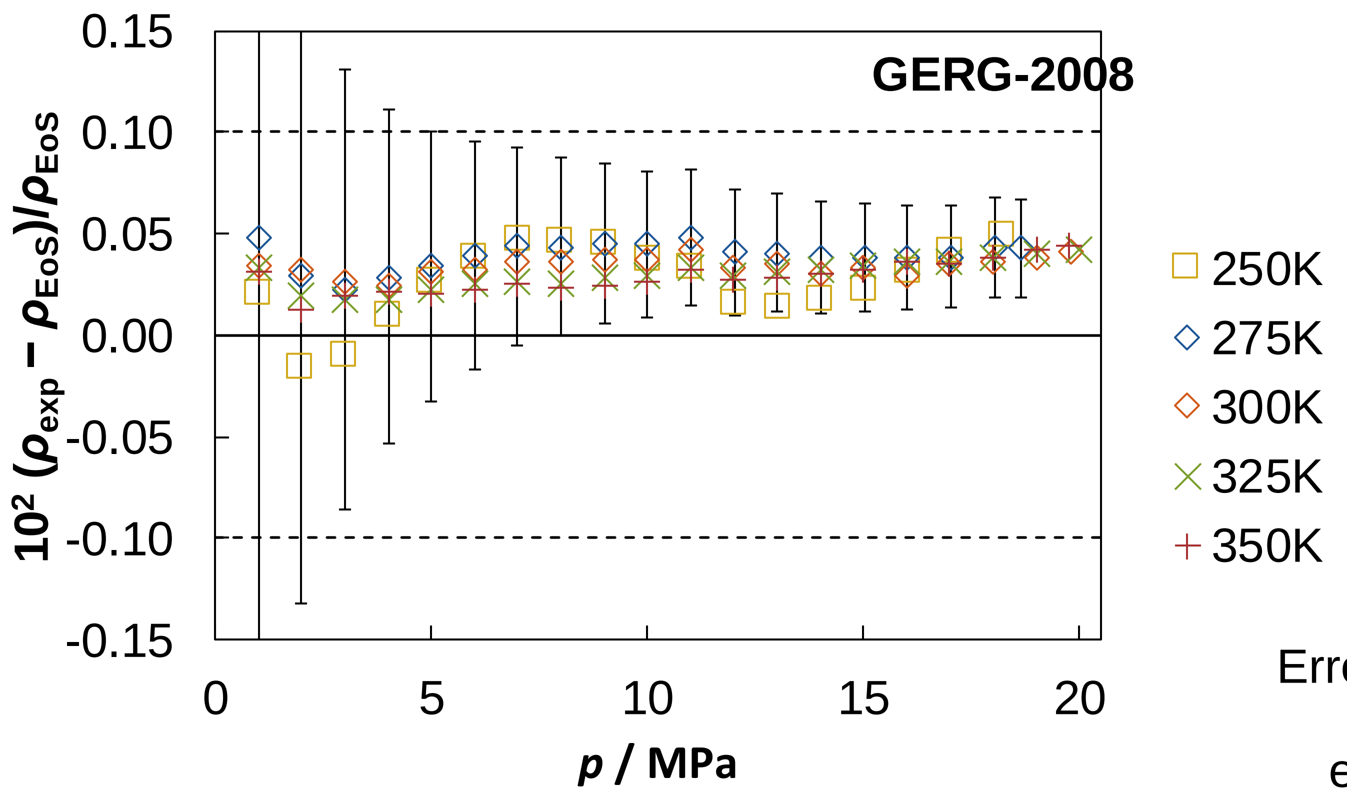
T = 242.9 K

(estimated with GERG-2008 for the target composition; neopentane added to isopentane)

p,*T* phase diagram showing the state points of the recorded data

Density Measurements: Zero-Hydrogen Mixture (BAM G 431)

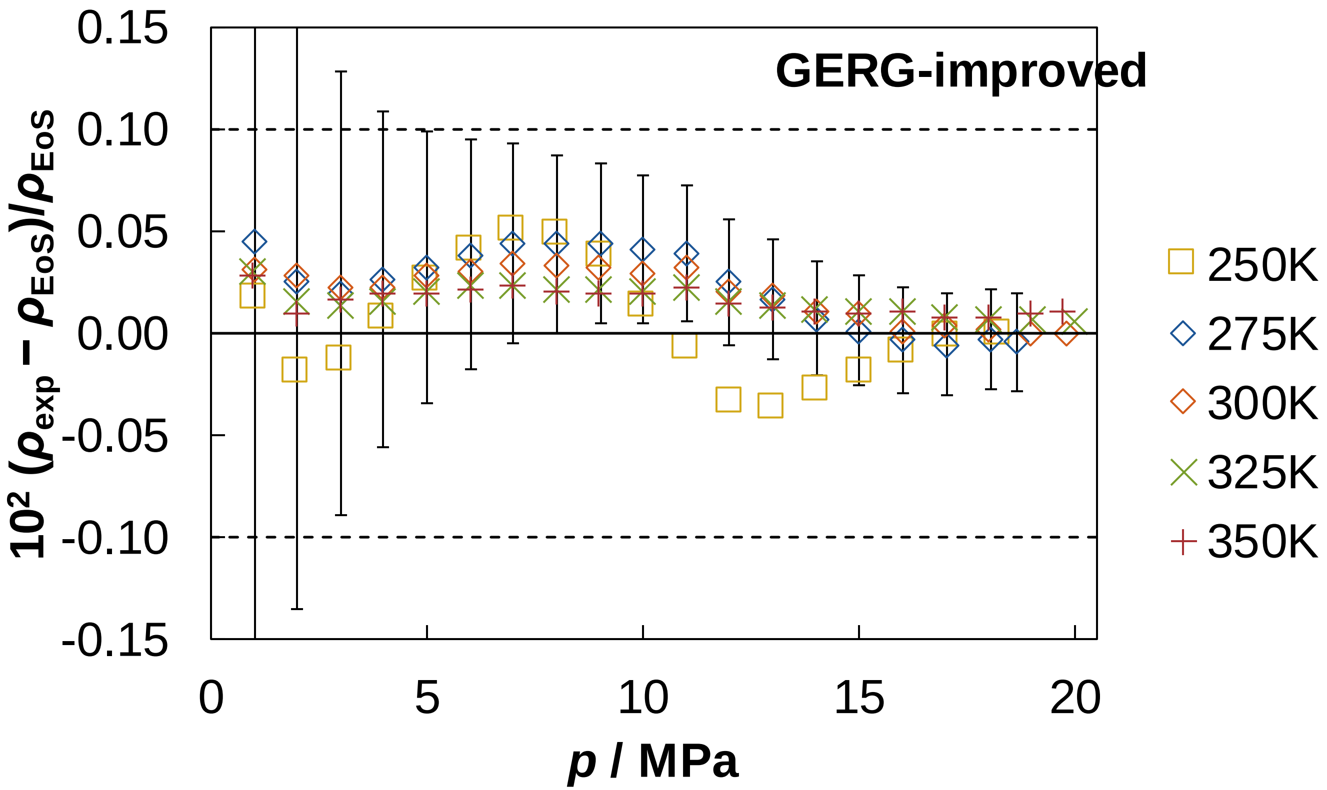
EoS model **uncertainty** of the **density** *ρ* in the **gaseous** region: **0.10 %**



Error bars: Uncertainty (k = 2) of the experimental data

Comparison between *experiment* and *GERG-2008 EoS*:
Average absolute (*value of*) relative deviation: 0.03 %; Maximum relative deviation: 0.05 %

Density Measurements: Zero-Hydrogen Mixture (BAM G 431)

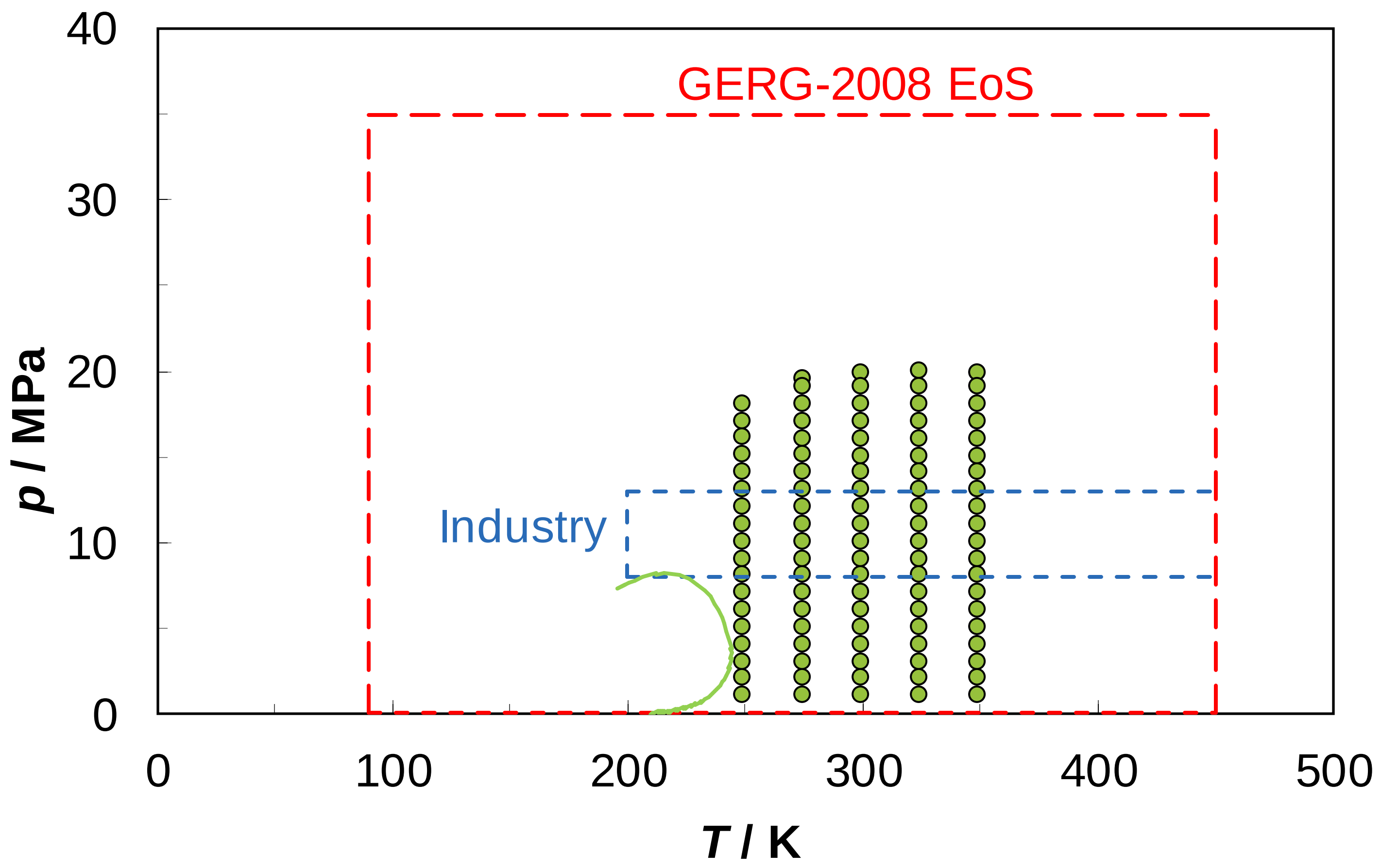


Recent improvements: new binary parameters for the reducing functions and specific departure functions of H_2 with CH_4, N_2, CO_2, and CO

Beckmüller et al., *J. Phys. Chem. Ref. Data* **50**, 013102, 2021.
Thol et al., *J. Phys. Chem. Ref. Data* **48**, 1–36, 2019
https://doi.org/10.1063/1.5093800

Comparison between *experiment* and *GERG-improved EoS*:
Average absolute relative deviation: 0.02 %; Maximum relative deviation: 0.05 %

Density Measurements: G 431 + 10 mol-% of H_2 (BAM G 453)

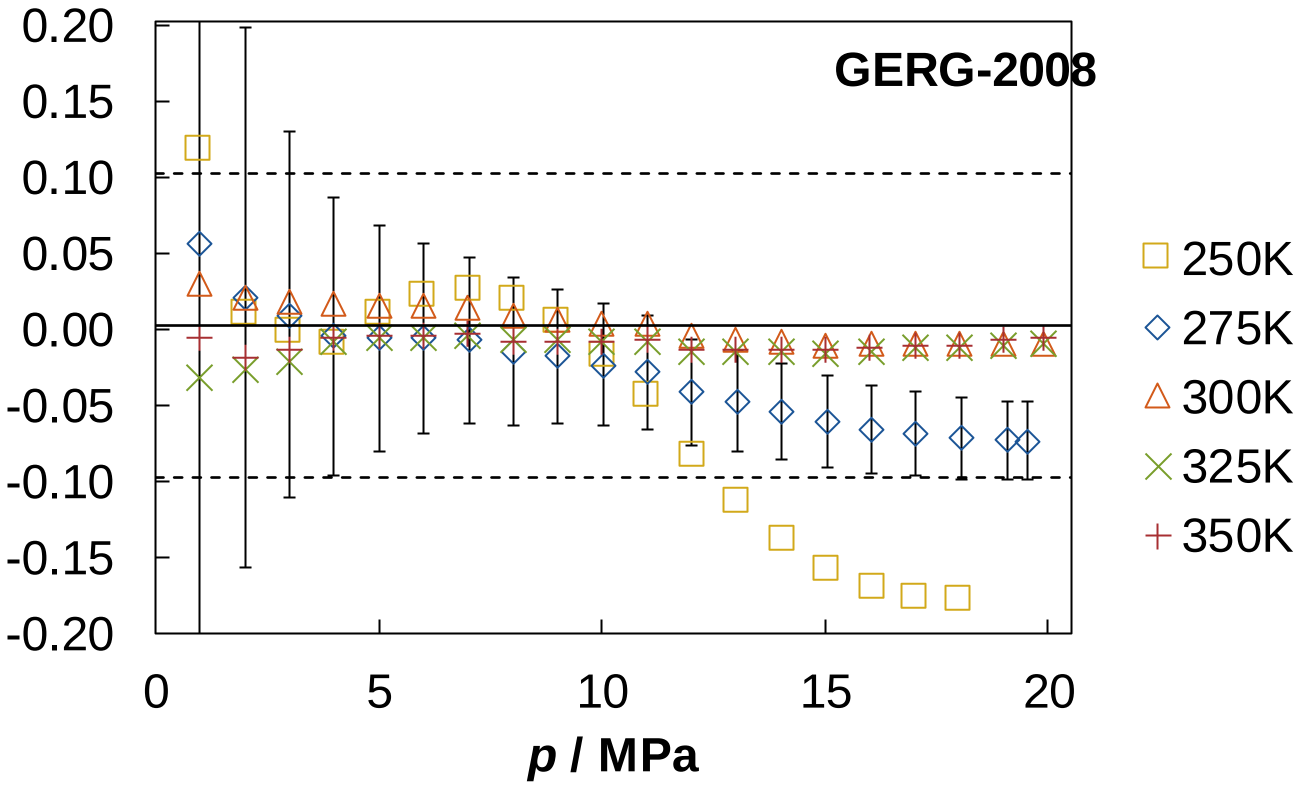


G 453 "cricondentherm"

T = 242.8 K

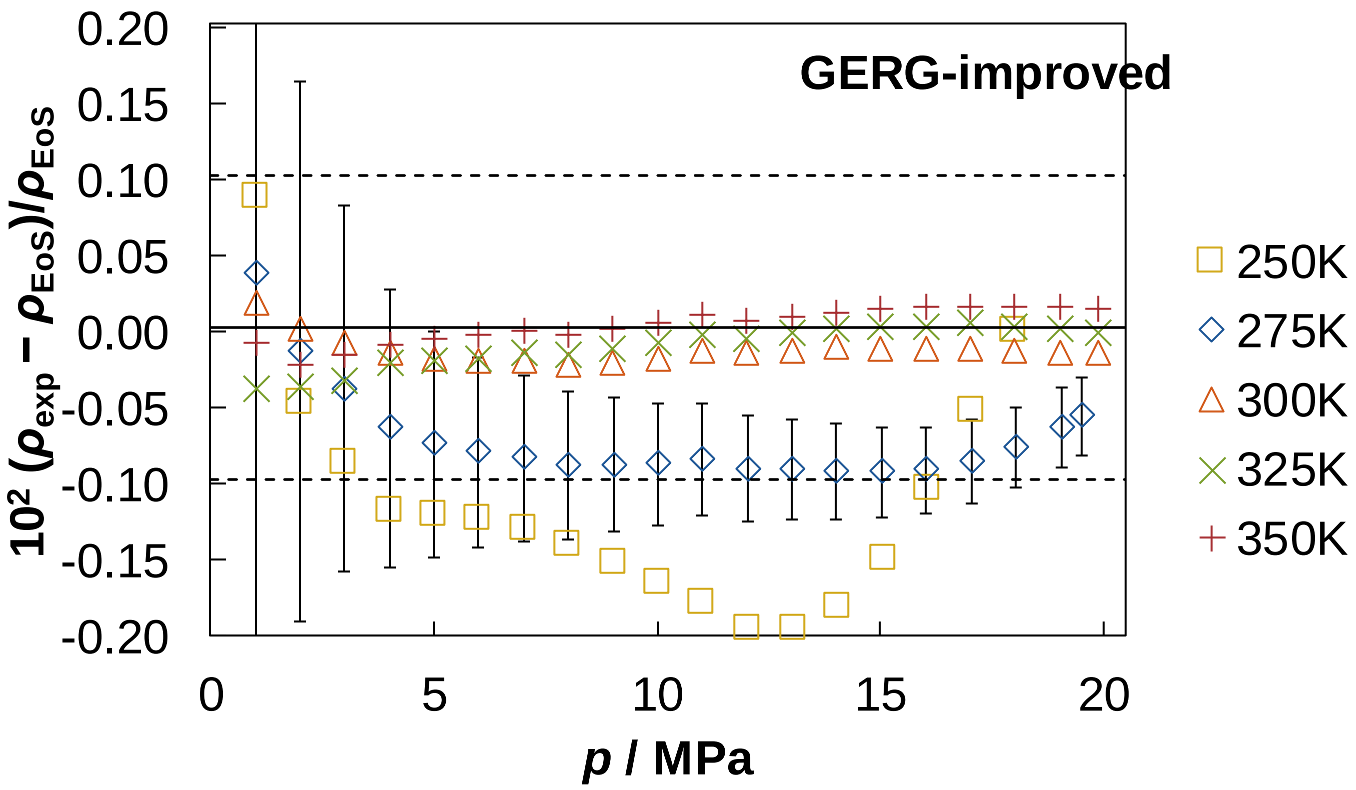
p,*T* phase diagram showing the state points of the recorded data

Density Measurements: G 431 + 10 mol-% of H_2 (BAM G 453)



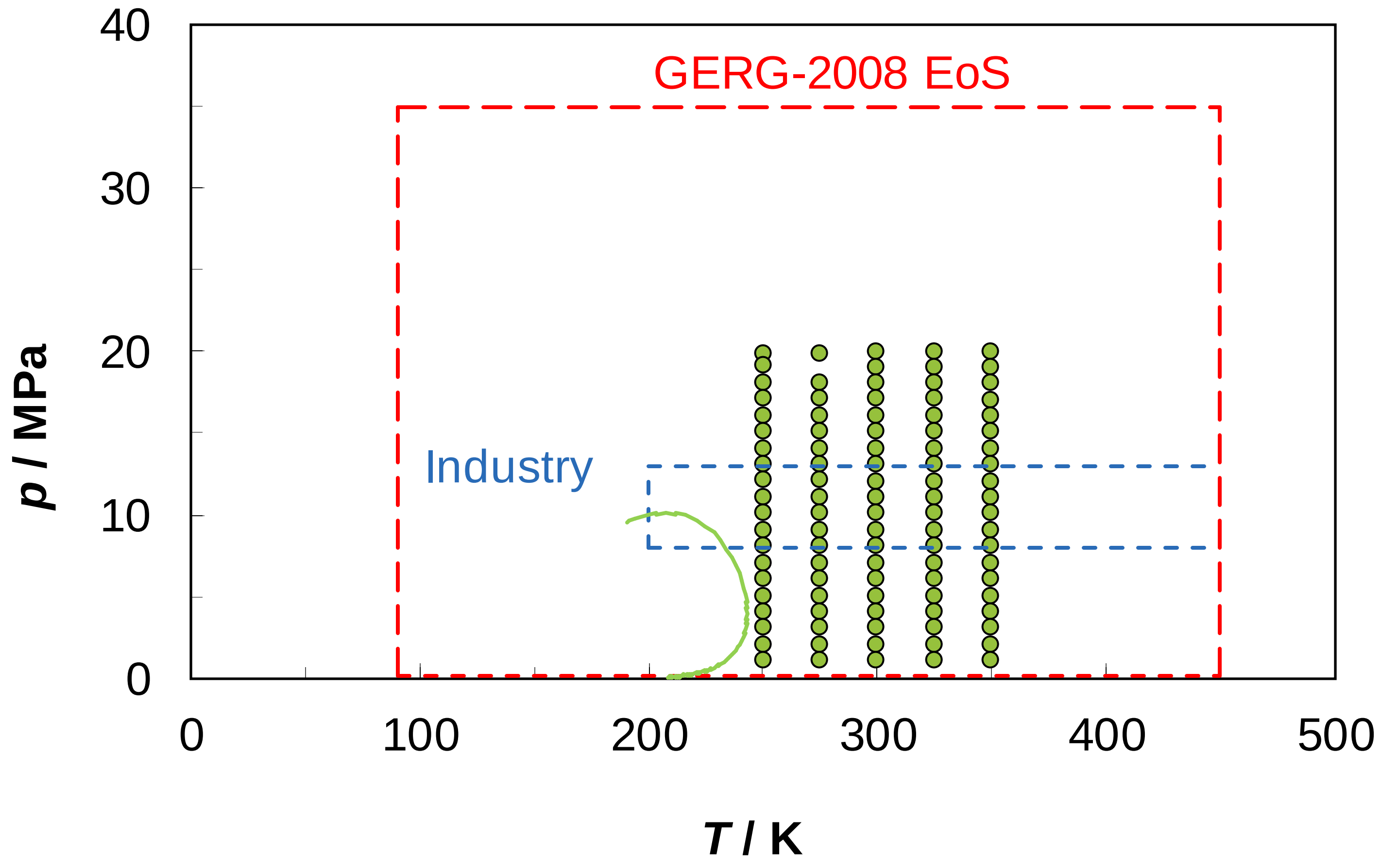
Comparison between *experiment* and *GERG-2008 EoS*:
Average absolu te relative deviation: 0.03 %; Maximum relative deviation: 0.18 %

Density Measurements: G 431 + 10 mol-% of H_2 (BAM G 453)



Comparison between *experiment* and *GERG-improved EoS*:
Average absolute relative deviation: 0.05 %; Maximum relative deviation: 0.20 %

Density Measurements: G 431 + 20 mol-% of H_2 (BAM G 454)

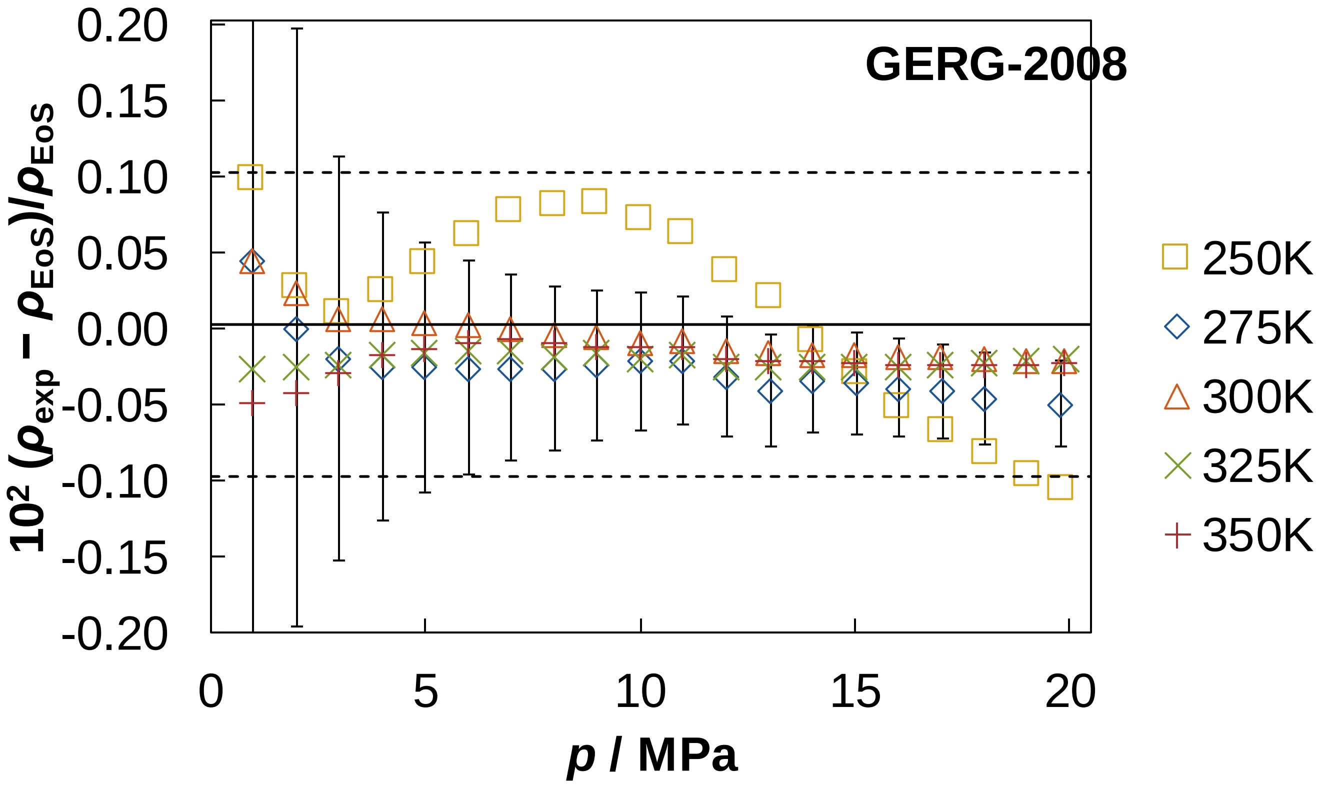


G 454
“cricondentherm”

T = 242.4 K

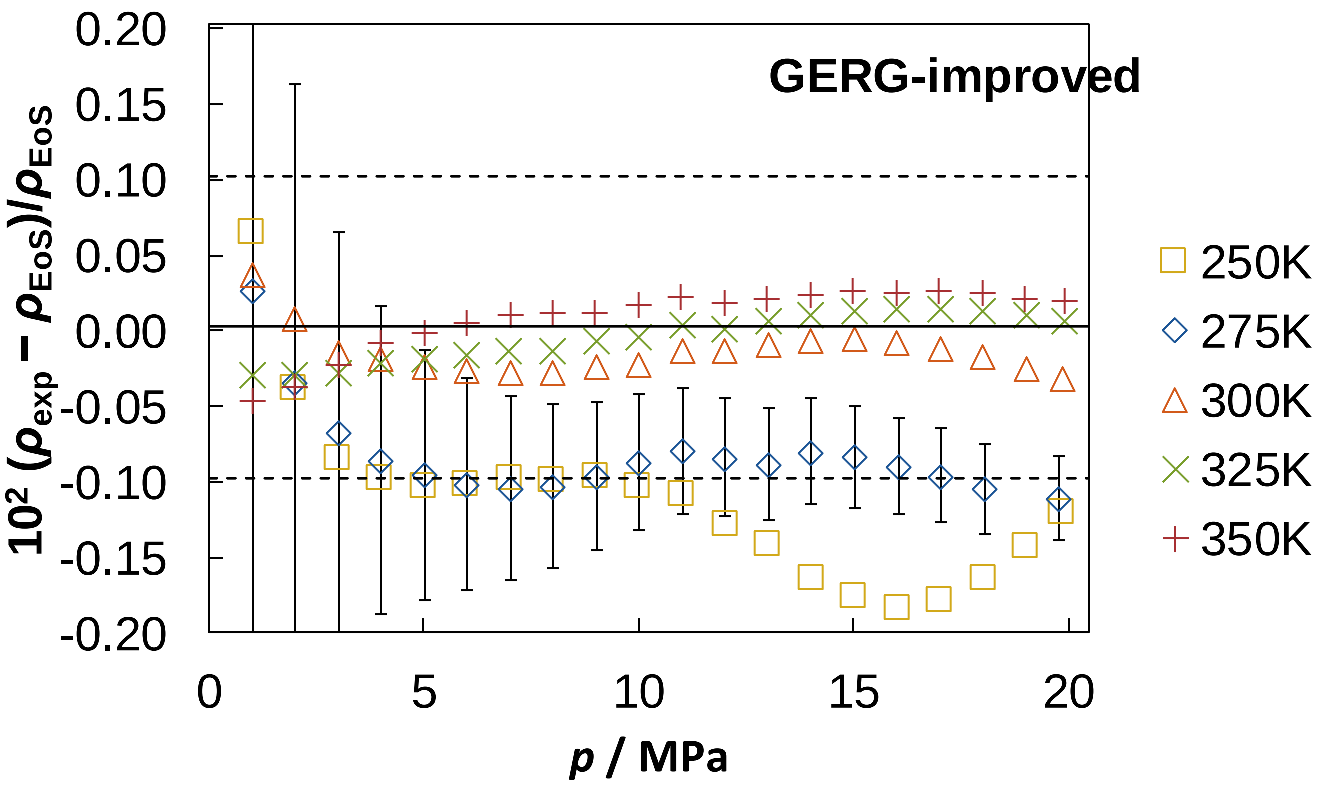
p,*T* phase diagram showing the state points of the recorded data

Density Measurements: G 431 + 20 mol-% of H_2 (BAM G 454)



Comparison between *experiment* and *GERG-2008 EoS*:
Average absolute relative deviation: 0.03 %; Maximum relative deviation: 0.11 %

Density Measurements: G 431 + 20 mol-% of H_2 (BAM G 454)



Comparison between *experiment* and *GERG-improved EoS*:
Average absolute relative deviation: 0.05 %; Maximum relative deviation: 0.19 %

Density Measurements and Model Results

- Addition of H_2 results in a larger deviation
- Most data are located within the assigned uncertainty boundary for density
- Deviations are observed for EoS model at the two temperatures close to the phase boundary (i.e., 250 and 275 K)
- Deviations of the H_2-containing mixtures from the zero line are mainly negative
- "*GERG-improved*" works better than the *classic* GERG-2008 but not for the low temperatures (250 and 275 K)

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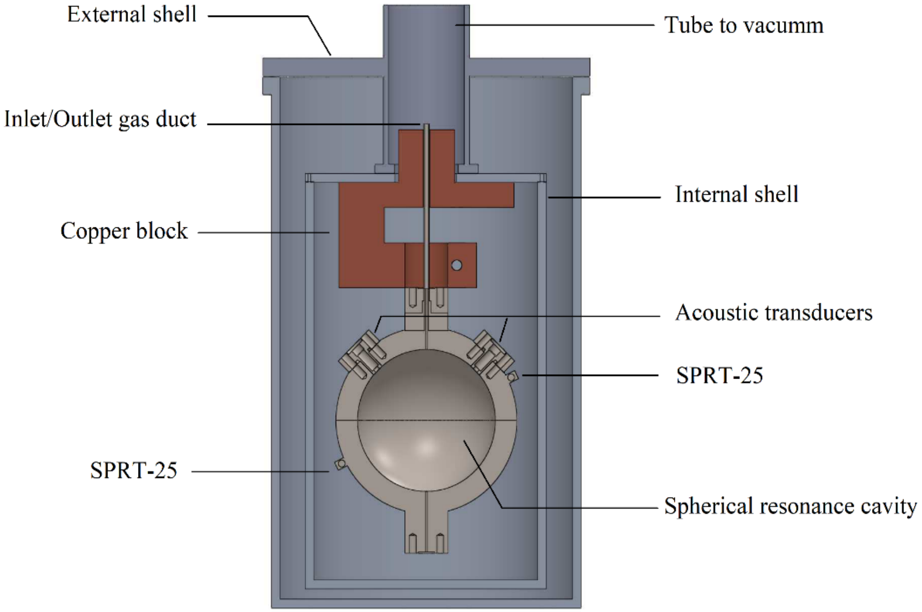
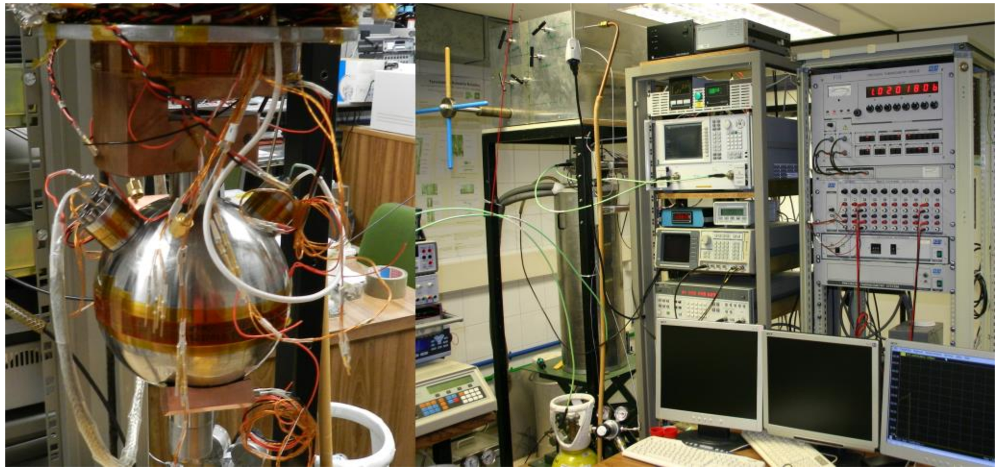
Steady-state spherical acoustic resonator





200 K < *T* < 475 K
p < 20 MPa

$U_r(p) = 0.015\%$
$U(T) = 4$ mK
$U_r(w) = 0.02\%$
$k = 2$

$$w_{0n} = 2\pi a \frac{f_{0n} - \Delta f}{z_{0n}}$$

w_{0n}: speed of sound, radial mode n
f_{0n}: resonance frequency, radial mode n
a: internal radius of the resonance cavity
z_{0n}: n-th zero of the spherical Bessel first derivative of order $l = 0$
Δf : all the frequency corrections due to the non-zero acoustic wall admittance and imperfect geometry of the cavity

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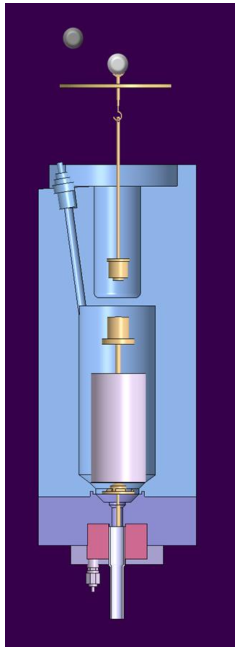
Single Sinker Magnetic Suspension Densimeter

(250 to 400) K

20 MPa



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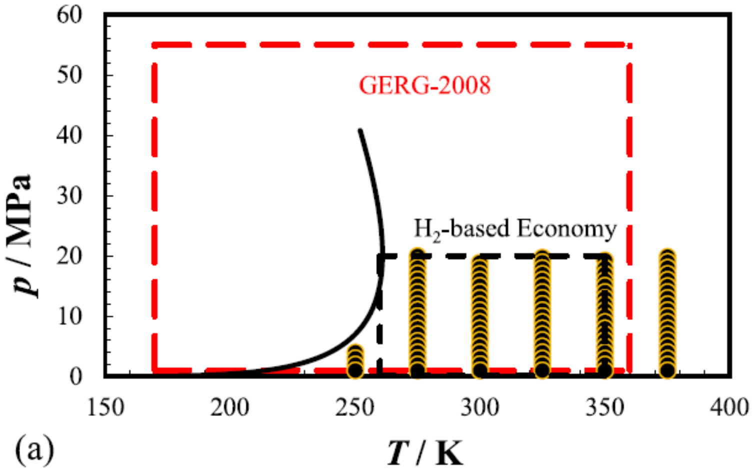
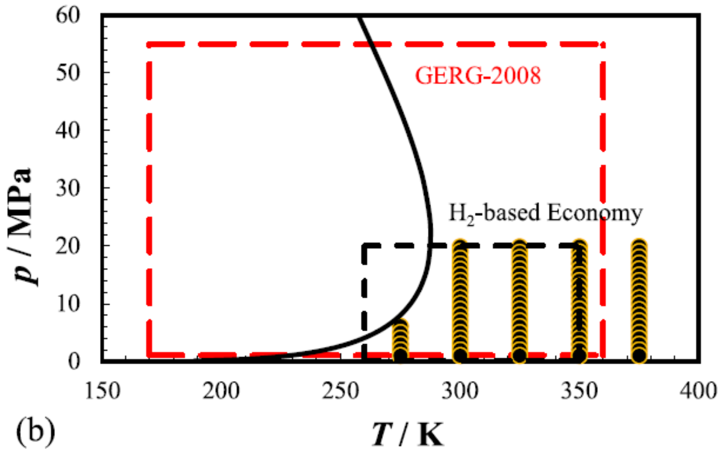
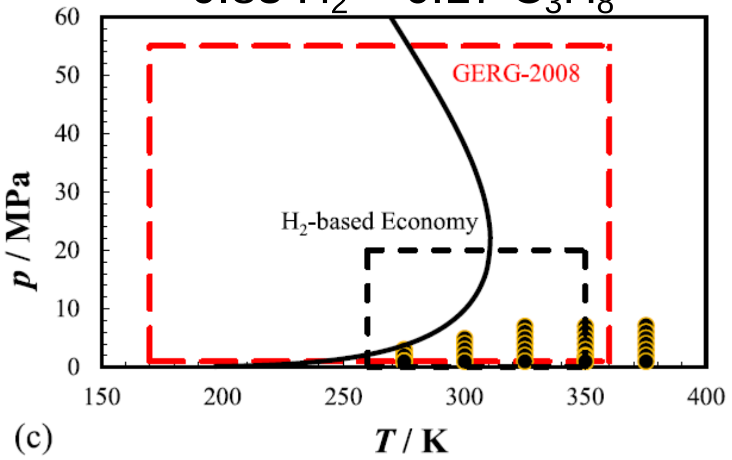


$0.90\ H_2 + 0.10\ C_3H_8$



$0.83\ H_2 + 0.17\ C_3H_8$



p,*T* phase diagrams showing the state points of the recorded data

Density Measurements and Model Results

- Addition of Propane results in a larger deviation
- Most data are located within the assigned uncertainty boundary for density for the mixture with 5% of propane
- Significant deviations are observed at lower temperatures and higher pressures

Outline

- Introduction
- Motivation
- Water vapour enhancement factor in H_2
- Experimental (p, ρ, T) data of the H_2-enriched NG mixtures
- Experimental (p, ρ, T) data of the H_2 + C_3H_8 binary mixtures
- **Discussion**

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Thank you for your attention

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States