Thermodynamic properties of a CO_2-rich mixture CO_2+CH_3OH in conditions of interest for CCS technology and other applications

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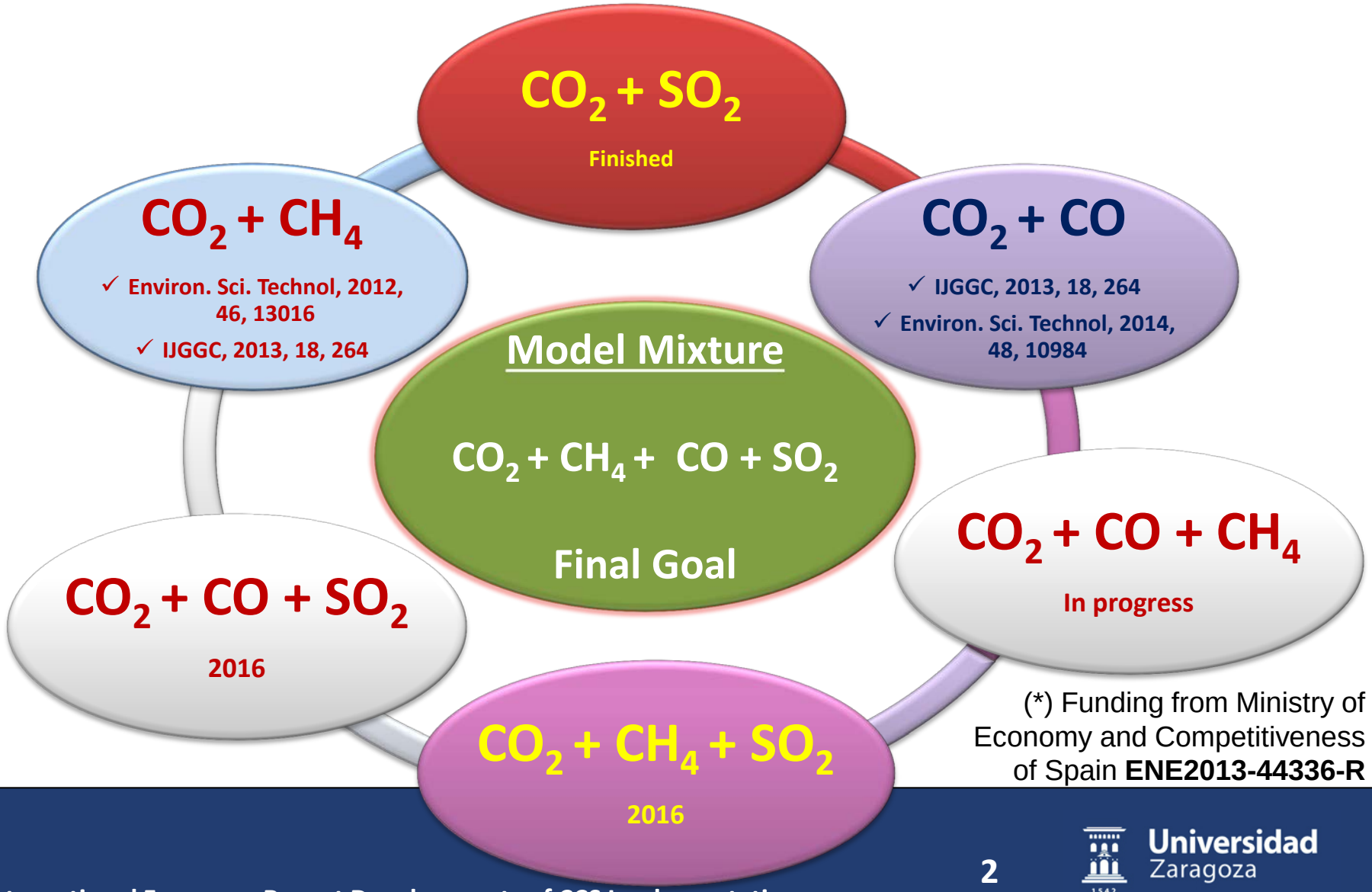
Impact of anthropogenic CO_2 quality on CCS technology; Feasibility of co-capture CO_2/SO_2*



(*) Funding from Ministry of Economy and Competitiveness of Spain **ENE2013-44336-R**

$CO_2 + SO_2$

Literature

NO DATA

$P - \rho - T - x$

$P - c - T - x$

FEW DATA

$P_{dew} - P_{bubble}$

Our Results

≈ 2000 points/isotherm

Experimental
$P - \rho - T - x$

Experimental
$P_{dew} - P_{bubble}$
$\rho_L - \rho_V$

40 isotherms

P= 0.1 – 20 or 30 MPa

x_{CO_2} = 0.8030 0.8969 0.9532 0.9699 0.9932

T = 263.15 to 373.15 K

Work Plan

Experimental
$P - c - T - x$

P < 200 MPa

- Selected Transport & Storage Parameters
- Validating EoS

ASSESSMENT OF CO_2 / SO_2 CO-CAPTURE

CO_2+SO_2 speed of sound data acquisition

Unexpected opacity of CO_2 and CO_2+SO_2 in our 5 MHz apparatus

Experimental finding: the opacity is solved by adding methanol to CO_2 or to CO_2+SO_2 mixtures

- ✓ Adaptation of our installation to mixtures containing sufficiently dense compressed gas
- ✓ Determination of the uncertainty, u_c, for CO_2+CH_3OH system

⟺

Quantification of the effect of the dopant in speed of sound values

Next presentation*

(*) C. Rivas et al. Experimental speed of sound in CO_2-rich mixtures with methanol. Extrapolation to pure CO_2.

Impurities in anthropogenic CO_2

The main impurities are:

- **N_2, H_2, O_2, Ar, S_2, H_2S+COS, NO_x, CO and water**

But methanol can be present as:

- **Hydrate inhibitor**
- **Residue from pipeline drying**

An extensive thermodynamic study of CO_2+ 3% methanol of interest for CCS technology and other applications

Methanol can be in transported and stored CO_2 but CO_2-rich mixtures CO_2+methanol are poorly studied in literature

Experimental measurements of:
- ✓ Speed of sound
- ✓ Density
- ✓ Bubble point

+ GERG c_p

Calculated values up to 195 MPa of:
- ✓ Density
- ✓ Isobaric heat capacity
- ✓ Joule-Thomson coefficient

Validation of PC-SAFT and GERG EoSs

Existing thermodynamic data on CO_2+CH_3OH

Property	Availability in the literature
$p-\rho-T$	Scarce for $x_{CO_2} > 0.75$ and $T \leq 313$ K
VLE	Widely studied
$p-c-T$	No data found
$p-c_p-T$	No data found
$p-\mu_{JT}-T$	No data found

- ✓ Stipulate the design and operation of CCS utilities
- ✓ Allow to develop and improve EoSs

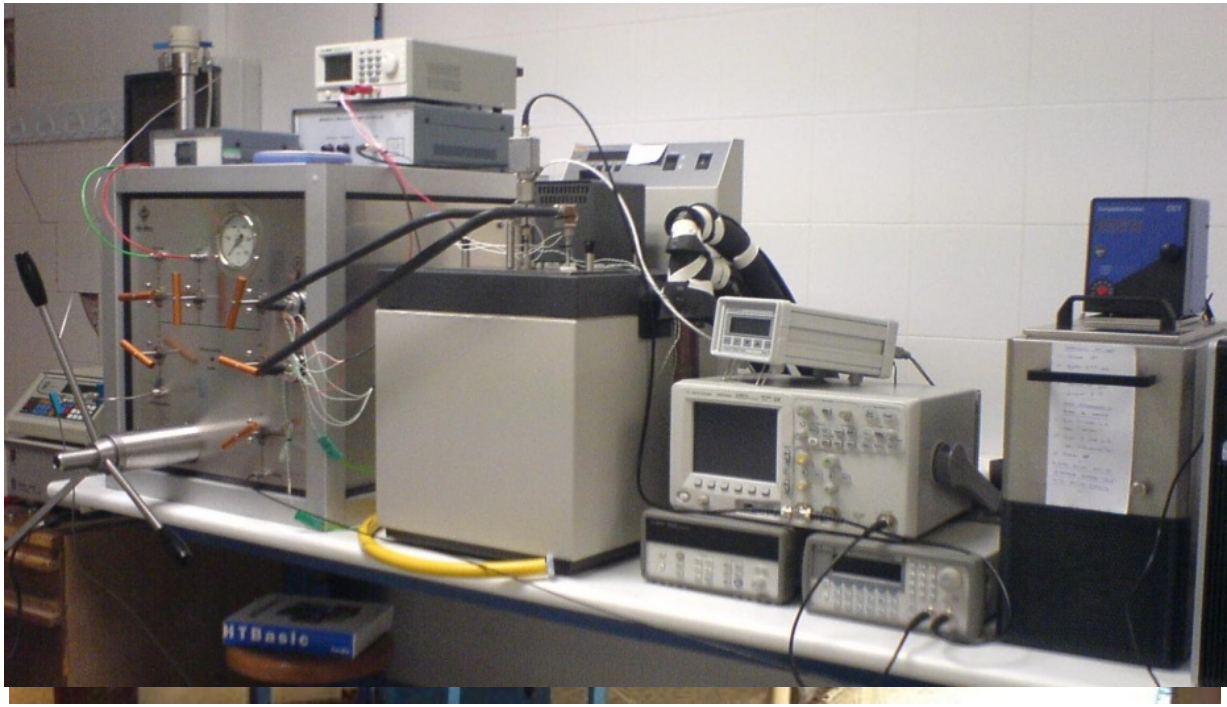
Do not cover the conditions of CCS technology

Experimental data acquisition

High Pressure Speed of Sound Laboratory, UZ, Spain

Technical specifications

- Method: 5 MHz pulsed ultrasonic system
- *T* range: 253 to 473 K
  u(*T*)= 0.015 K
- *P* range: 0.1 MPa to 200 MPa
  u(*P*)= 0.02 MPa
- *x* range: 0.0000 to 1.0000
  u(*x*)= 0.0005



Measurements of thermodynamical properties

- Liquid, compressed gases and supercritical speeds of sound

- ❑ **Evaluation of fracture propagation**
- ❑ **Calculated derivative properties from speed of sound and density**
  - Heat Capacity
  - Joule-Thomson Coefficient

$CO_2 + CH_3OH$ $P-c-T-x$ experimental results

Adaptation of our apparatus and procedure to compressed gas+liquid mixtures		Extensive thermodynamic study
x_{CO_2} = 0.7534, 0.8502, 0.9250, 0.9803	**Repeatability study:** 3 mixtures with x_{CO_2} = 0.9250	x_{CO_2} = 0.9700
T= 263.15, 298.15, 323.15 K	Each mixture 3 isotherms at T= 263.15, 298.15, 323.15 K	6 T; 263.15 <T< 313.15 K
6.00 ≤ p ≤ 190.04 MPa	6.00 ≤ p ≤ 190.04 MPa	3.28 ≤ p ≤ 194.49 MPa

u_c^*= 0.053%

$$u_c^2 = \left[(\partial c/\partial T)_p u_T\right]^2 + \left[(\partial c/\partial p)_T u_p\right]^2 + \left[(\partial c/\partial x) u_x\right]^2 + (u_c^*)^2$$

u_c= 0.059% ⇒ within the values reported in the literature for liquids and binary mixtures of compressed gases

Experimental data acquisition

Technical specifications

- **Method: vibrating tube densimeter**
- ***T* range: 263 to 473 K**
  $u(T)$= 0.006 K
- ***P* range: 0.1 MPa to 70 MPa**
  $u(P)$= 0.008 MPa
- ***x* range: 0.0000 to 1.0000**
  $u(x)$= 0.0005
- ***u* (ρ)= 0.2 – 0.4 kg/m³**

Measurements of thermodynamic properties

- Gas, liquid, critical and supercritical densities
- Vapour-liquid equilibrium

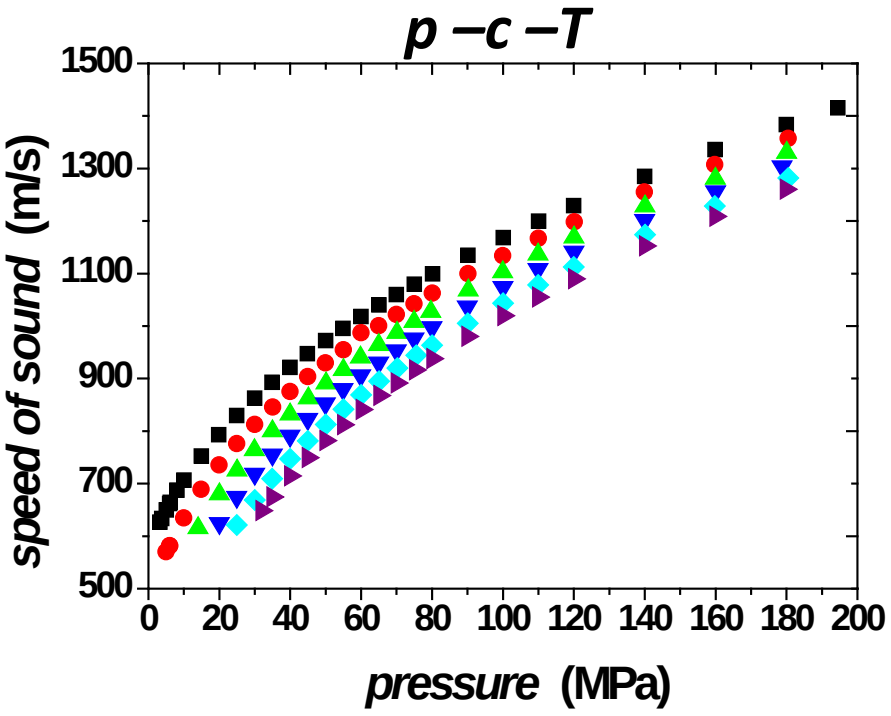
Calculated density derivative properties

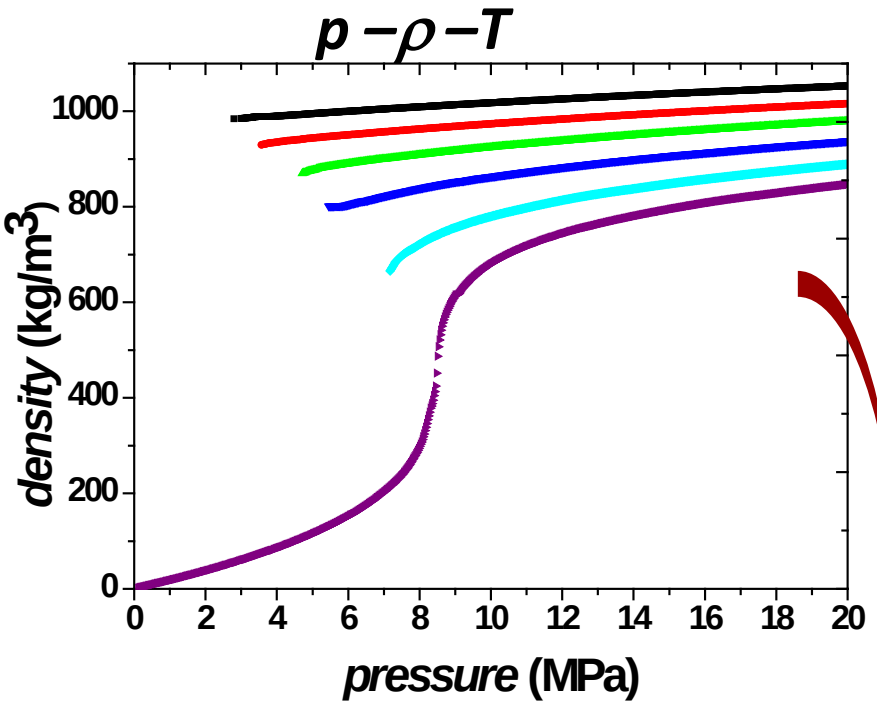
- Isothermal compressibility
- Isobaric expansivity
- Internal pressure → Solubility parameter

High pressure *P*ρ*T*- VLE laboratory, UZ, Spain

2000 points/isotherm → Quasi-continuous data along subcritical, critical, and supercritical regions of pure fluids and mixtures allow us to determine the limits of VLE, and density derivative properties

CO_2+ 3% methanol experimental results





3.28 ≤ *pressure* ≤ 194.49 MPa

***pressure* ≤ 20.00 MPa**

✓ **MRD= 1.30 % with experimental density in the literature***

(*) Berger, T.A., Deye, J.F., 1990. Analytical Chemistry, 62, 1181-1185.

Experimental study of CO_2+CH_3OH

- The repeatability and overall standard uncertainty results obtained

together with

- the agreement with the data from the literature

✓ allow us to use our experimental speed of sound, density and bubble point data to evaluate whether the PC-SAFT and the GERG EoSs predict properly the studied thermodynamic behavior for CO_2+CH_3OH

PC-SAFT EoS applied to CO_2+CH_3OH

$$\tilde{a} = \tilde{a}^{id} + \tilde{a}^{hc} + \tilde{a}^{dis} + \tilde{a}^{assoc} + \left(\tilde{a}^{QQ} + \tilde{a}^{DD} + \tilde{a}^{QD}\right)$$

- For pure compounds *m*, σ and ε calculated from the pure compounds' critical temperatures and pressures (Gil et al., 2012), and Δv_c from this work.
- The mixing parameters σ_{ij} and ε_{ij} :

$$\sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right) \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right)$$

$$k_{ij} = -0.323 + 2.88 \times 10^{-4}\ T$$

(*) Gil, L. et al., 2012. The Journal of Supercritical Fluids, 71, 26-44.

PC-SAFT EoS applied to CO_2+CH_3OH

non-self-association CO_2 ⟺ self-association compound Methanol

INDUCED ASSOCIATION*:

- The association volume, $\kappa^{A_iB_i} = \kappa^{methanol}$, and the association energy, $\varepsilon^{A_iB_i} = 0$ for **CO_2** with a 2C association scheme.
- The association volume, $\kappa^{A_iB_i}$, and the association energy, $\varepsilon^{A_iB_i}$ for **methanol** with a 2B association scheme.
- The **cross-association** parameters, $\kappa^{A_iB_j} = \kappa^{methanol}$, and $\varepsilon^{A_iB_j} = \varepsilon^{methanol}/2$.

(*) Kleiner, M., Sadowski, G., 2007. The Journal of Physical Chemistry C, 111, 15544-15553.

GERG EoS applied to CO_2+CH_3OH

$$\tilde{a} = \tilde{a}^{id} + \tilde{a}^{res} = \sum_{i=1}^{N} x_i \left[\tilde{a}_i^{id} + lnx_i\right] + \sum_{i=1}^{N} x_i \tilde{a}_i^{res} + \Delta\tilde{a}^{res}$$

- **Although methanol is not one of the 21 compounds included in the Kunz and Wagner article (Kunz and Wagner, 2012), it has been implemented in the used REFPROP 9 software. The calculations are based in the reference EoS for CO_2 (Span and Wagner, 1996) and methanol (de Reuck and Craven, 1993) together with the GERG EoS mixture model. The predicted values are slightly more accurate than those from GERG EoS as published because the pure-component EoSs are more elaborate.**

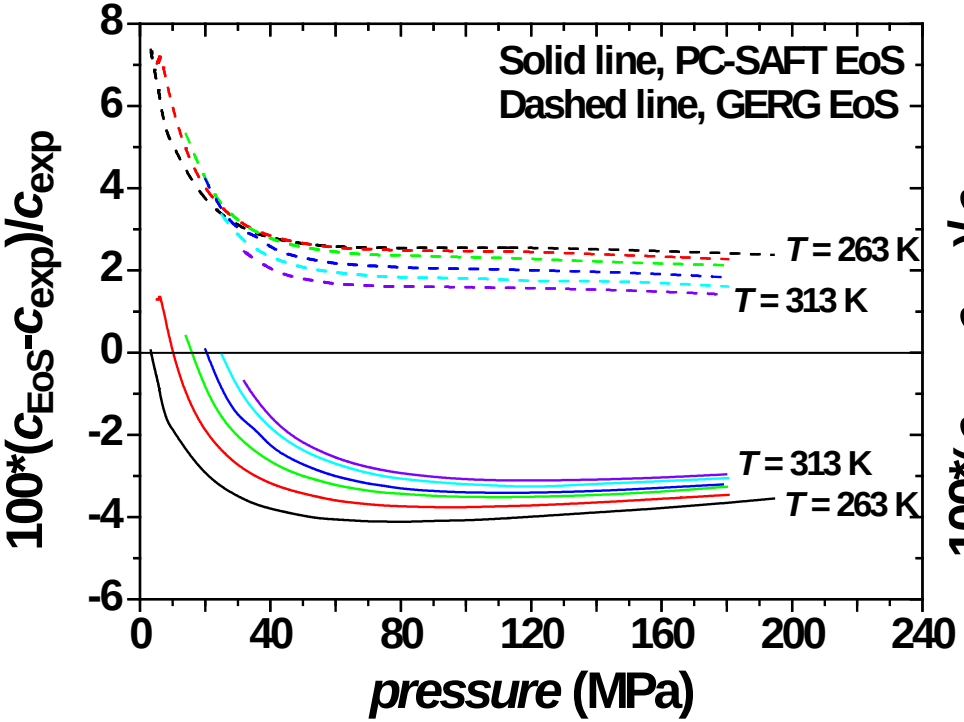
(*) Kunz, O., Wagner, W., 2012. The Journal of Chemical & Engineering Data, 57, 3032-3091.

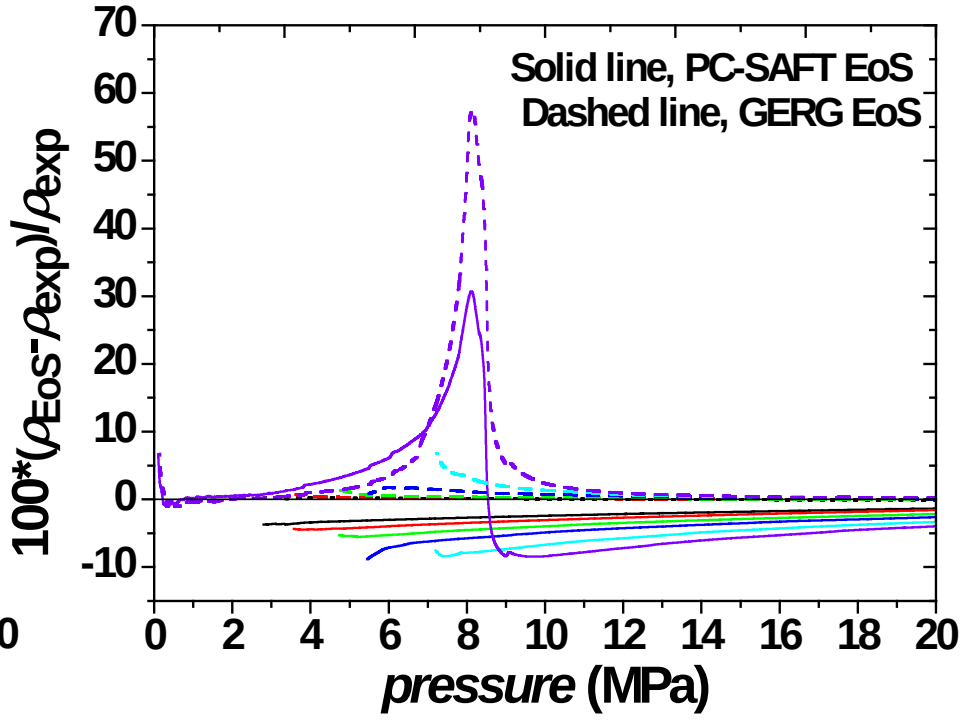
Span, R., Wagner, W., 1996. J. Phys. Chem. Ref. Data, 25(6), 1509-1596.

de Reuck, K.M., Craven, R.J.B., 1993. International Thermodynamic Tables of the Fluid State - 12, IUPAC

CO_2+ 3% methanol

PC-SAFT and GERG EoSs Validation





CO_2+ 3% methanol
PC-SAFT and GERG EoSs Validation

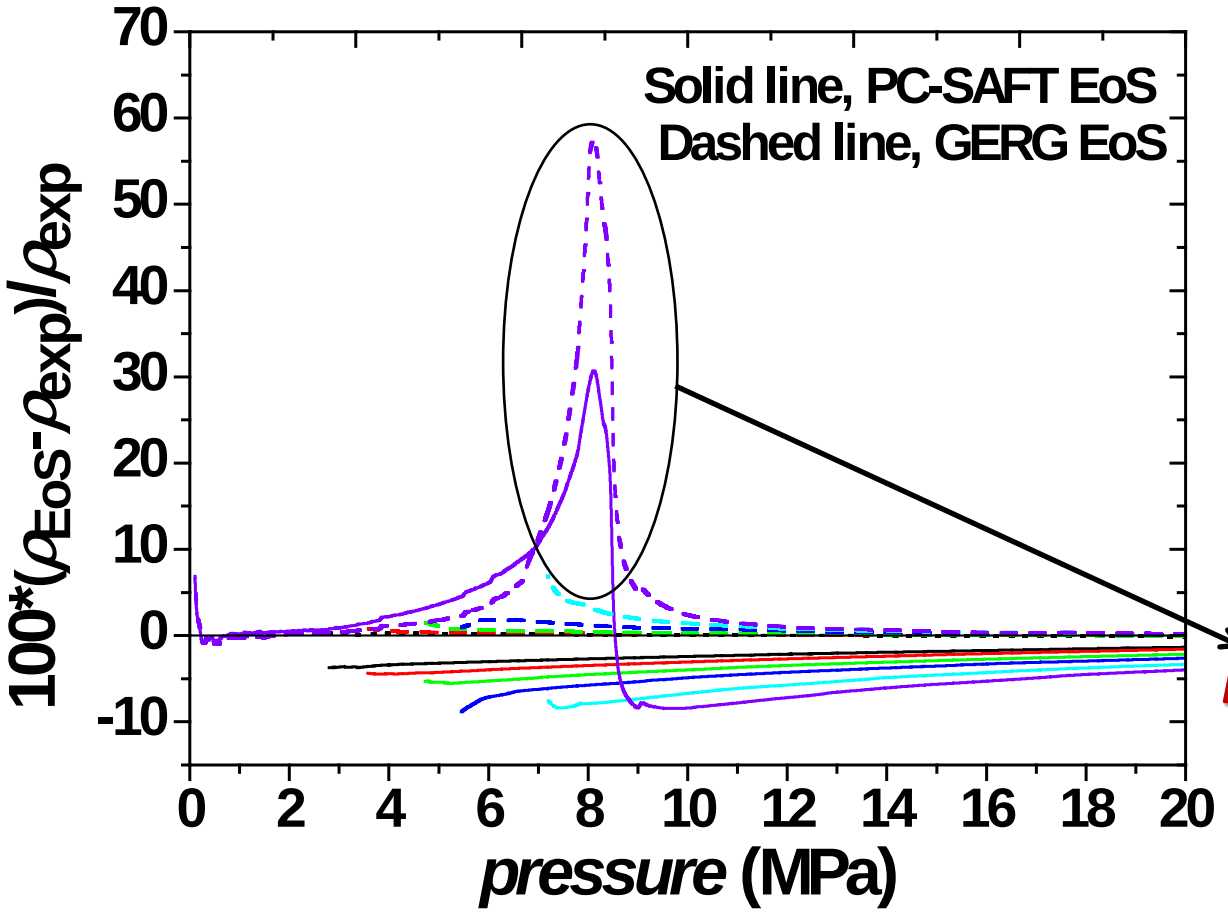
$\overline{MRD}(\%)$	PC-SAFT	GERG
Speed of sound	2.77	2.65
Density	4.07	0.64
Bubble pressure	2.23	5.67
Liquid density at VLE	6.04	1.37

$$MRD_x(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{x_{i,EoS} - x_{i,exp}}{x_{i,exp}}\right| \qquad \overline{MRD_x}(\%) = \frac{1}{N_T}\sum_{i=1}^{N_T} MRD_{x,i}(\%)$$

✓ **PC-SAFT and GERG-EoS are valid to represent the behaviour of the system under most of the studied conditions.**

***Exception*: the density near the critical point of the mixture.**

CO_2+ 3% methanol
PC-SAFT and GERG EoSs Validation



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(*) Gil, L. et al., 2012. The Journal of Supercritical Fluids, 71, 26-44.

CALCULATION METHOD OF THERMODYNAMIC PROPERTIES UP TO HIGH PRESSURES

Experimental speeds of sound at high *p* and several *T*

+

Exp. densities and GERG isobaric heat capacities at a REFERENCE *p* and several *T*

Densities and isobaric heat capacities up to high *p* and several *T*

- ❖ Equal to atmospheric pressure for liquids IN THE LITERATURE*
- ❖ Higher than atmospheric pressure for compressed gas:
  - ✓ to assure dense phase
  - ✓ depends on the mixture

FIRSTLY IN THIS WORK

(*) Dávila, M.J., Trusler, J.P.M., 2009. The Journal of Chemical Themodynamics, 41, 35-45.

CO_2 + 3% methanol Calculated properties at high pressure

Experimental speed of sound at 6 *T* and 3.28 - 194.49 MPa	Experimental density at 6 *T* and 14.0 MPa	Calculated (GERG) c_p at 6 *T* and 14.0 MPa

Calculation method of thermodynamic properties up to 195.0 MPa*:

$$c^{-2} = (\partial\rho/\partial p)_T - \left(T/\rho^2 c_p\right)(\partial\rho/\partial T)_p^2$$

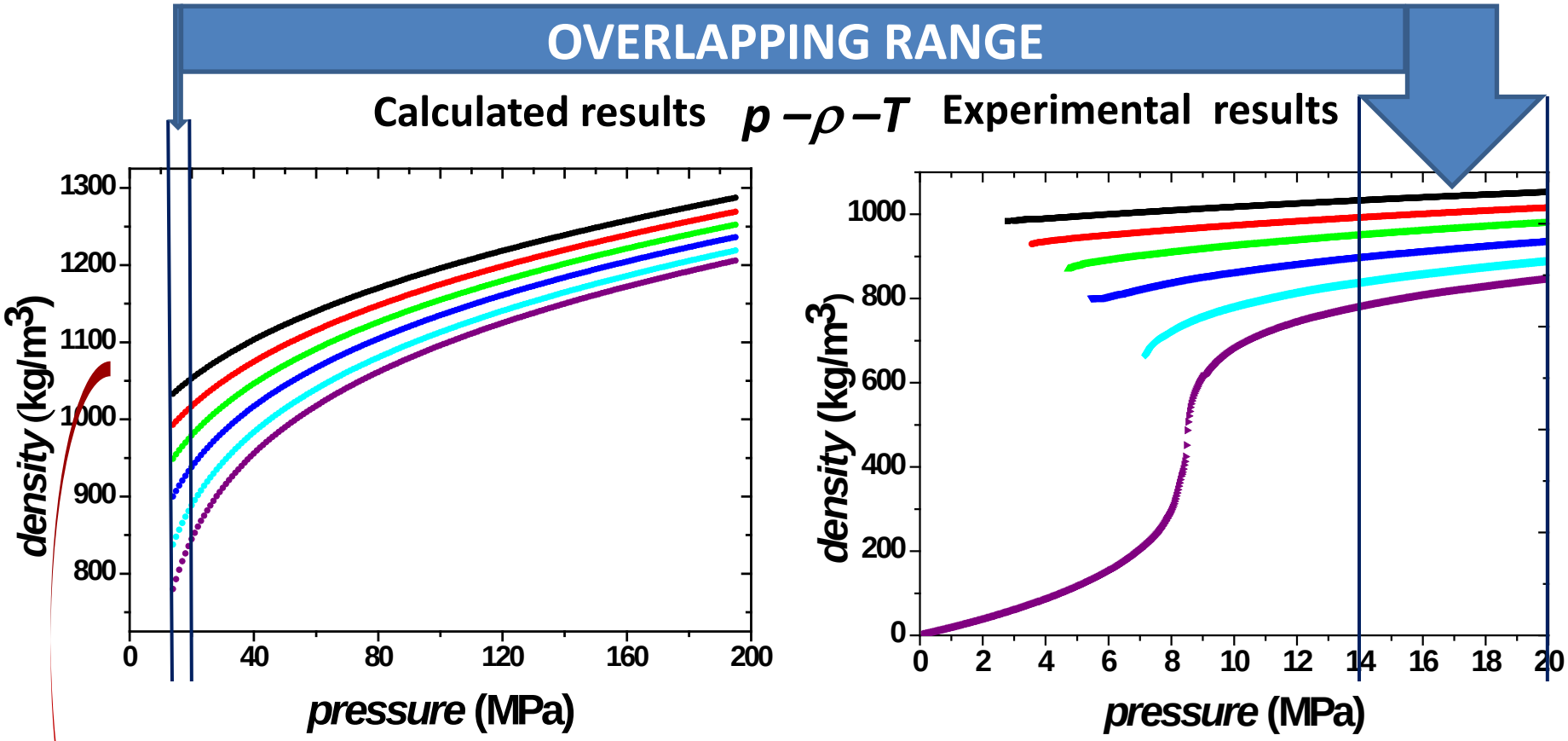
$$\left(\partial c_p/\partial p\right)_T = -\left(T/\rho^3\right)\left[2(\partial\rho/\partial T)_p^2 - \rho\left(\partial^2\rho/\partial T^2\right)_p\right]^2$$

(*) Dávila, M.J., Trusler, J.P.M., 2009. The Journal of Chemical Themodynamics, 41, 35-45.

- ✓ Density
- ✓ Isobaric heat capacity
- ✓ Joule-Thomson coefficient, $\mu_{JT} = -\frac{1}{c_p}\left[T\frac{(\partial p/\partial T)_V}{(\partial p/\partial V)_T} + V\right]$

at 6 *T*: 263.15 - 313.15 K, and 14.0 - 195.0 MPa

CO_2 + 3% methanol



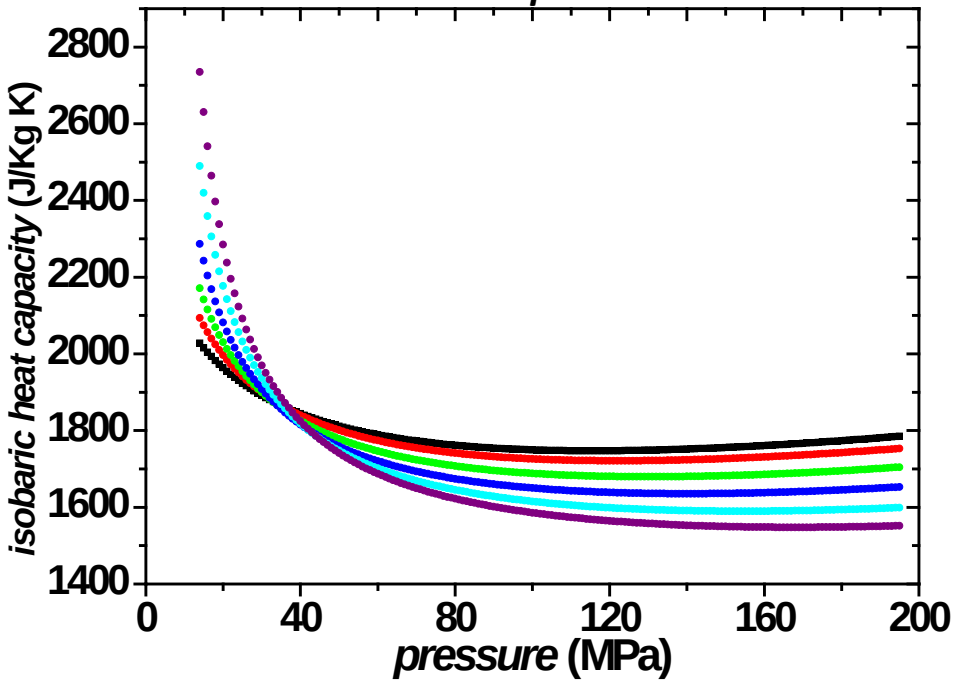
✓ Satisfactory agreement between calculated and experimental densities. MRD= 0.075 %

✓ MRD= 0.35 % with experimental density in the literature*

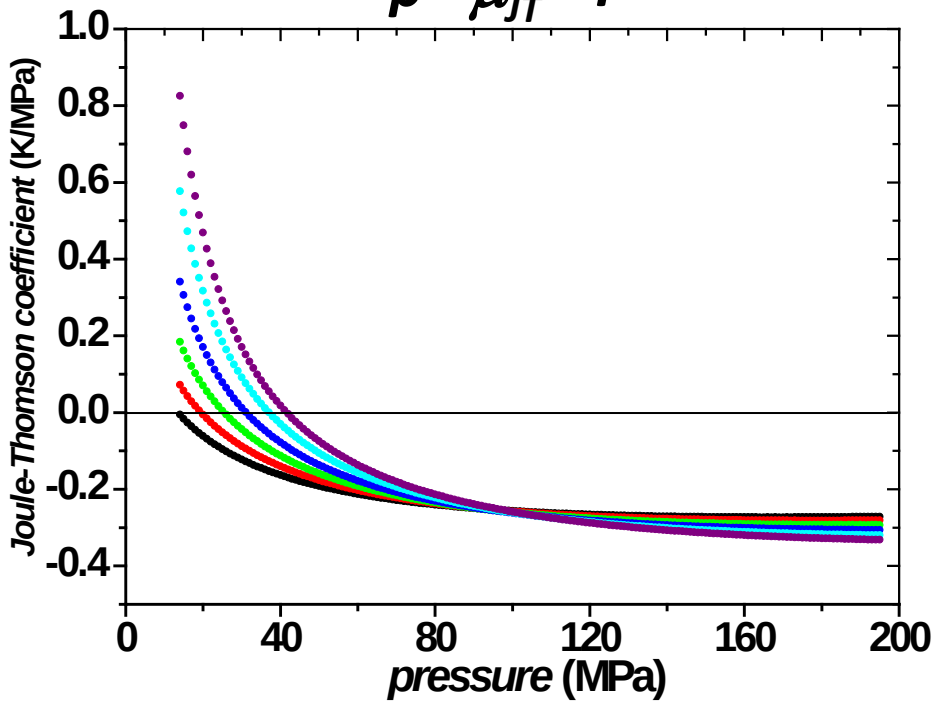
(*) Berger, T.A., Deye, J.F., 1990. Analytical Chemistry, 62, 1181-1185.

CO_2+ 3% methanol calculated results

$p - c_p - T$



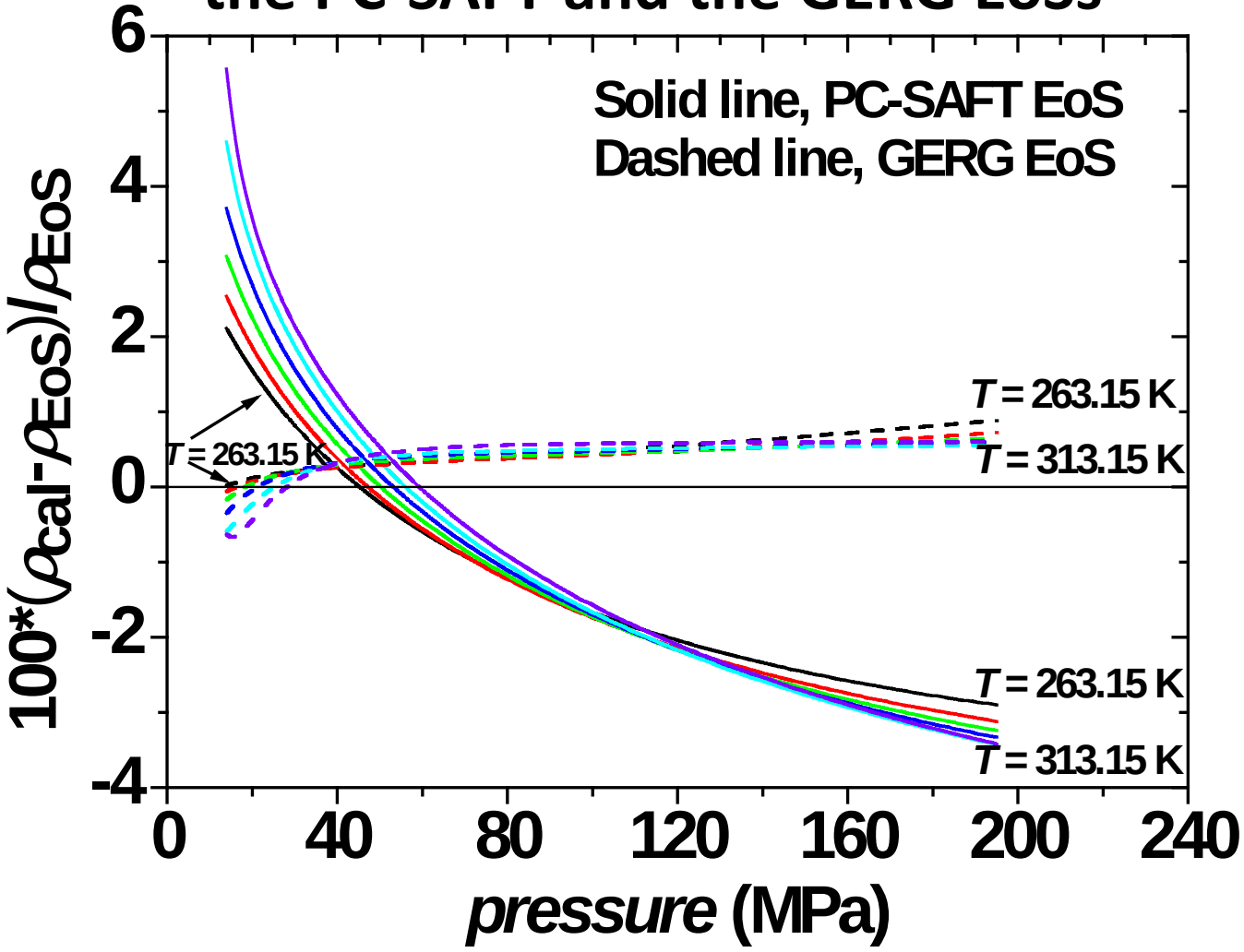
$p - \mu_{JT} - T$



14.0 ≤ *pressure* ≤ 195.0 MPa

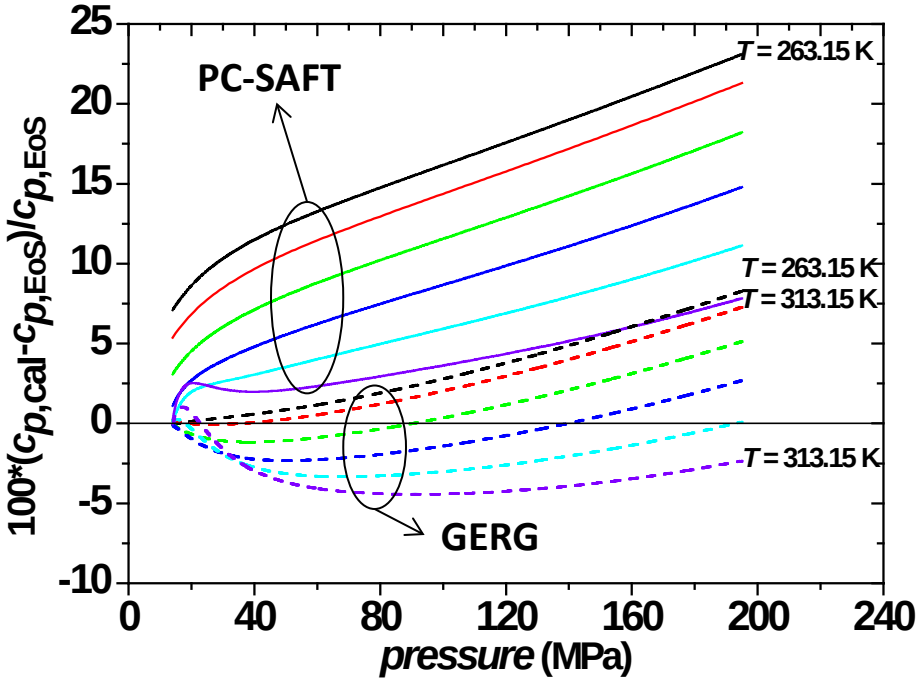
- ✓ **Crossing regions appear for the two properties**
- ✓ **μ_{JT} changes its sign for the five upper isotherms**

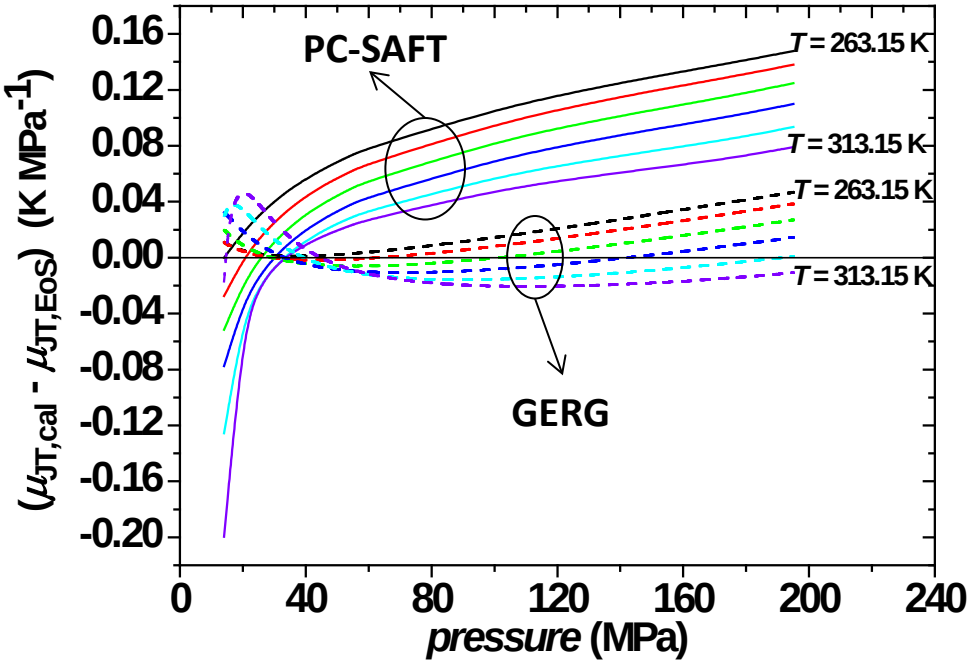
CO_2 + 3% methanol
Comparison of our calculated results with the values from the PC-SAFT and the GERG EoSs



CO_2 + 3% methanol

Comparison of our calculated results with the values from the PC-SAFT and the GERG EoSs





✓ **The calculated crossing regions agree better with predictions from GERG EoS than with those from PC-SAFT EoS.**

CO_2 + 3% methanol

Comparison of our calculated results with the values from the PC-SAFT and the GERG EoSs

$\overline{MRD}$(%)	PC-SAFT	GERG
Density	1.90	0.46
Isobaric heat capacity	10.3	2.47
$\overline{AAD}$ (K/MPa)		
Joule-Thomson coefficient	0.056	0.013

$$MRD_x(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{x_{i,cal} - x_{i,EoS}}{x_{i,EoS}}\right|$$

$$\overline{MRD_x}(\%) = \frac{1}{N_T}\sum_{i=1}^{N_T} MRD_{x,i}(\%)$$

✓ These results, together with the agreement between our calculated and experimental densities and with the literature data,

validate the calculation method

Conclusions

- Implementation of an experimental setup to measure *c* in mixtures containing compressed gases
- Presentation of accurate experimental speeds of sound (at pressures up to 194.49 MPa), densities (up to 20.00 MPa) and bubble points for the mixture $\mathbf{CO_2 + 3\% \, CH_3OH}$
- Validation of PC-SAFT and GERG EoSs for these properties, but some exceptions indicate the need to improve the models
- Calculation of ρ, c_p, and μ_{JT} up to 195.0 Mpa, *f*rom our *c* data and both our ρ and the GERG EoS c_p at a reference pressure
- Confirmation of the results from the calculation method, applied to compressed gases for the first time, via comparison with values from the PC-SAFT and GEG EoSs

ACHIEVEMENTS

- The **results of our thermodynamic study:**
  - **are a useful contribution to mitigate the lack of information in the literature on the thermodynamic behaviour of CO_2 + methanol**
  - **will allow the research community to develop and improve EoSs in the future. Neither of the two studied EoSs satisfactorily represents all the studied properties, although the GERG EoS correctly predicts the system behaviour at high pressures**

Thank you for your attention

Acknowledgment: The research leading to these results has received funding from Ministry of Economy and Competitiveness of Spain **ENE2013-44336-R** and from Government of Aragon and the European Social Fund