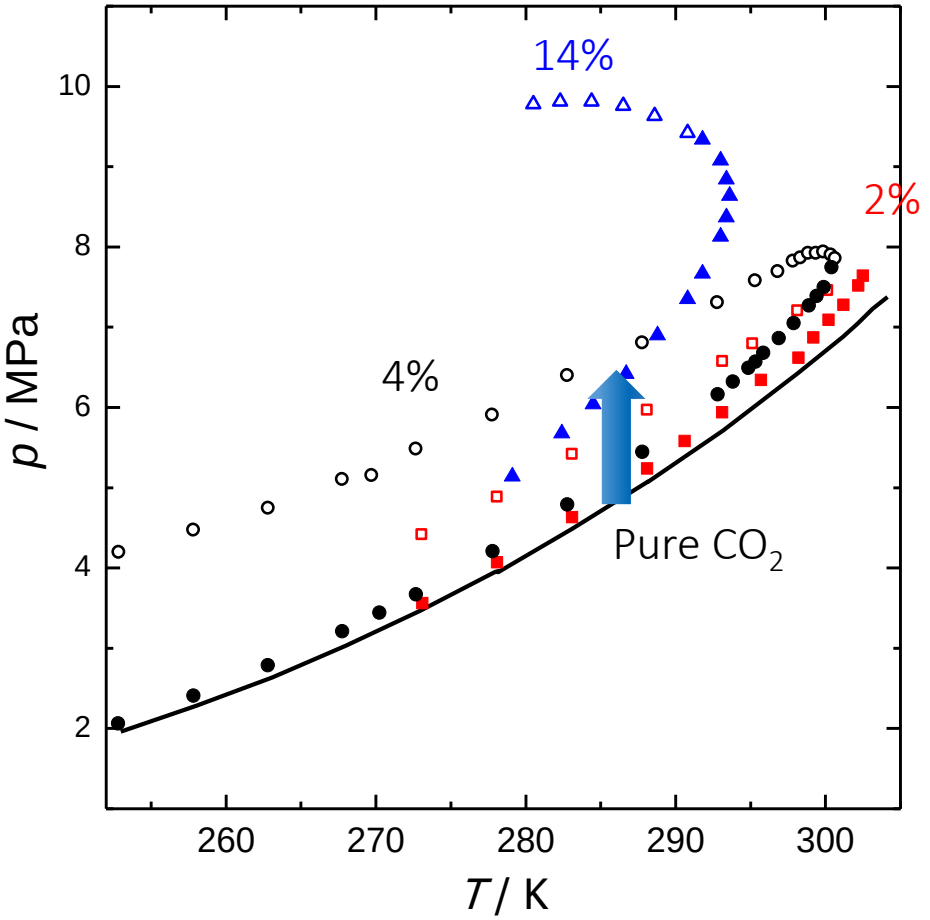
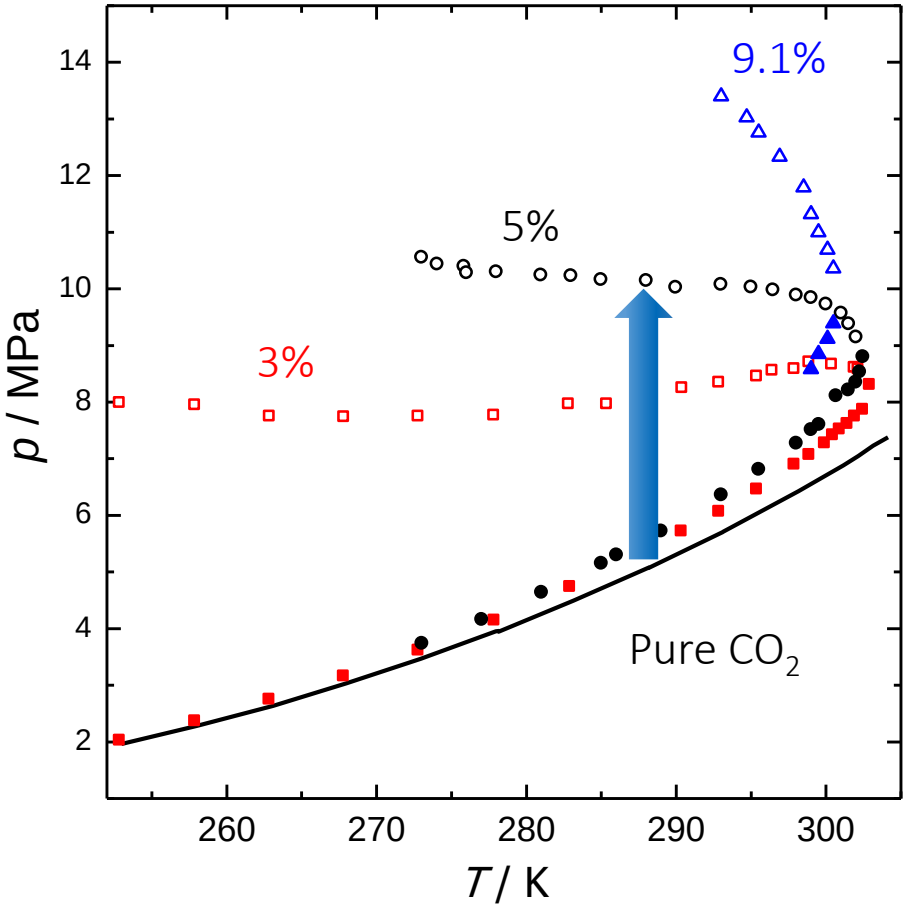
$p - T$ phase boundary of $CO_2 + N_2$ and $CO_2 + H_2$

$CO_2 + N_2$

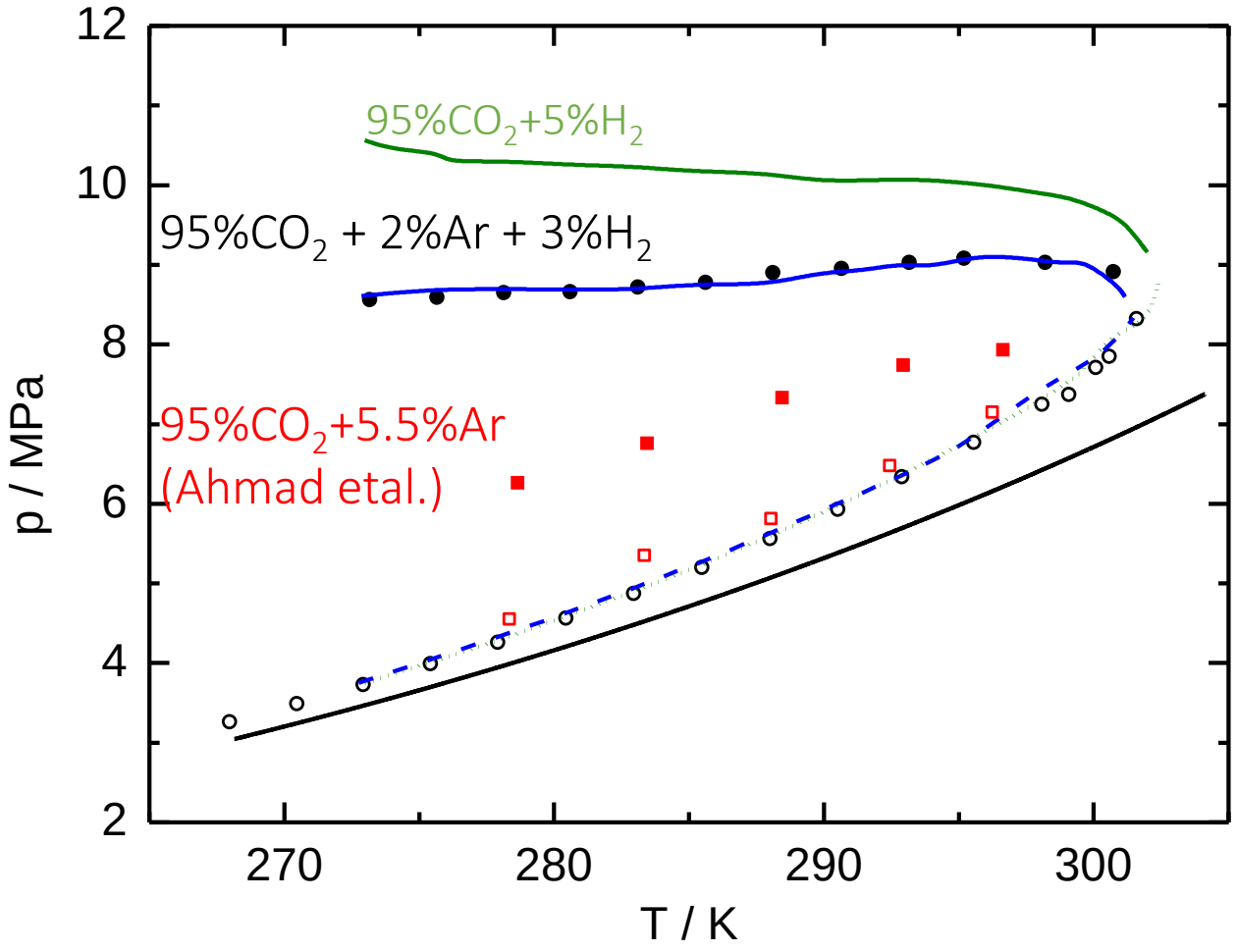


$CO_2 + H_2$



p – *T* phase boundary of CO_2 + Ar + H_2

Total mole fraction of impurities = ~5%



— 95%CO_2+2%N_2+3%H_2

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Which equation of state is the most suited to model thermodynamic properties for the CCS processes?

The Peng-Robinson Equation of State

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$$

- Requires binary interaction parameters (k_{ij}) to describe mixtures.
- Temperature independent k_{ij}
- Temperature dependent k_{ij} (linear fit and Boltzmann fit for the H_2-CO_2 pair)

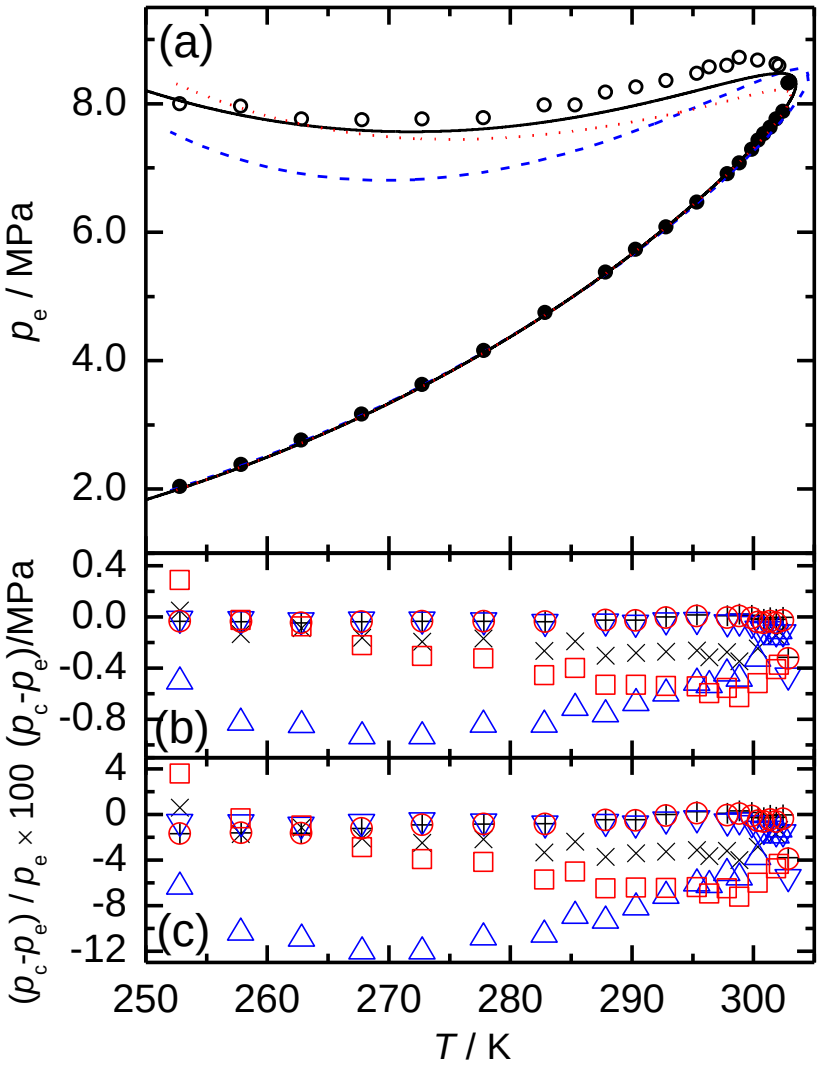
The GERG-2004/GERG-2008/EOS-CG Equation of State

$$\alpha(\delta,\tau,\bar{x}) = \alpha^o(\rho,T,\bar{x}) + \sum_{i=1}^{N} x_i \alpha_{oi}^r(\delta,\tau) + \Delta\alpha^r(\delta,\tau,\bar{x})$$

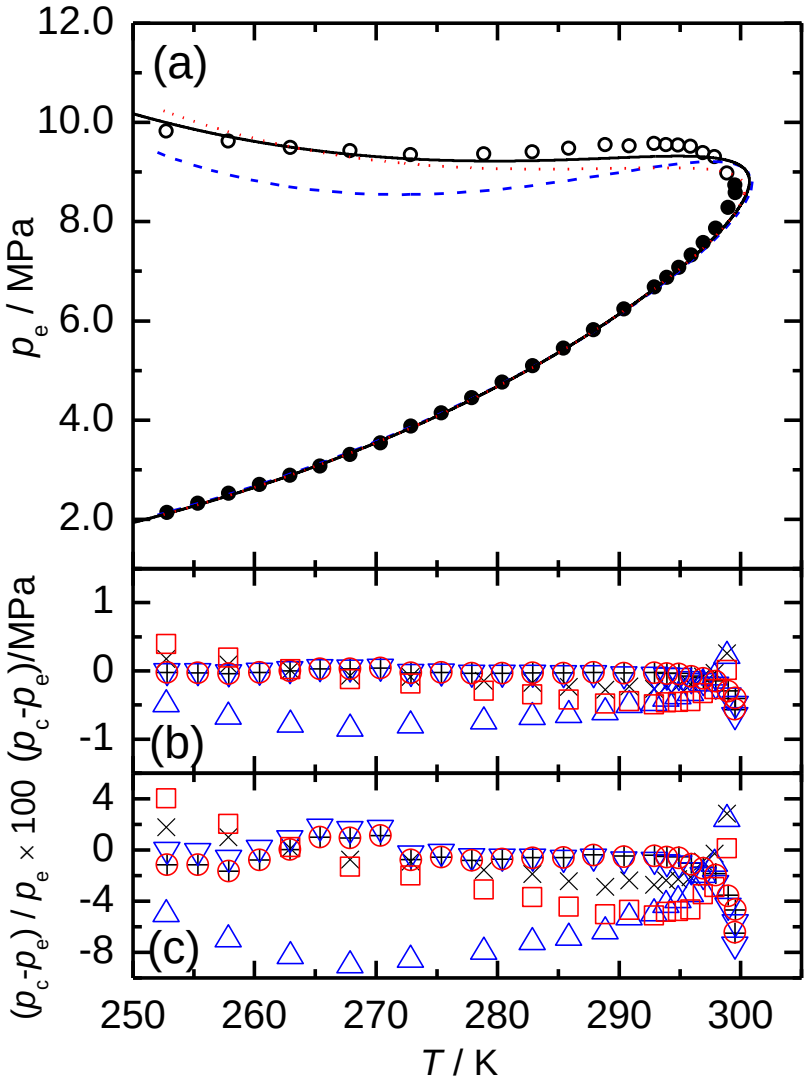
- For each binary pair, 4 adjustable parameters are required to calculate δ and τ.
- The departure functions need more adjustable parameters , e.g. The Da^r of the CO_2-N_2 pair uses 34 adjustable parameters.
- EOS-CG new binary parameters for CO_2-Ar and N_2-Ar and new specific departure function for CO_2-Ar

gSAFT (https://www.psenterprise.com/products/gsaft)

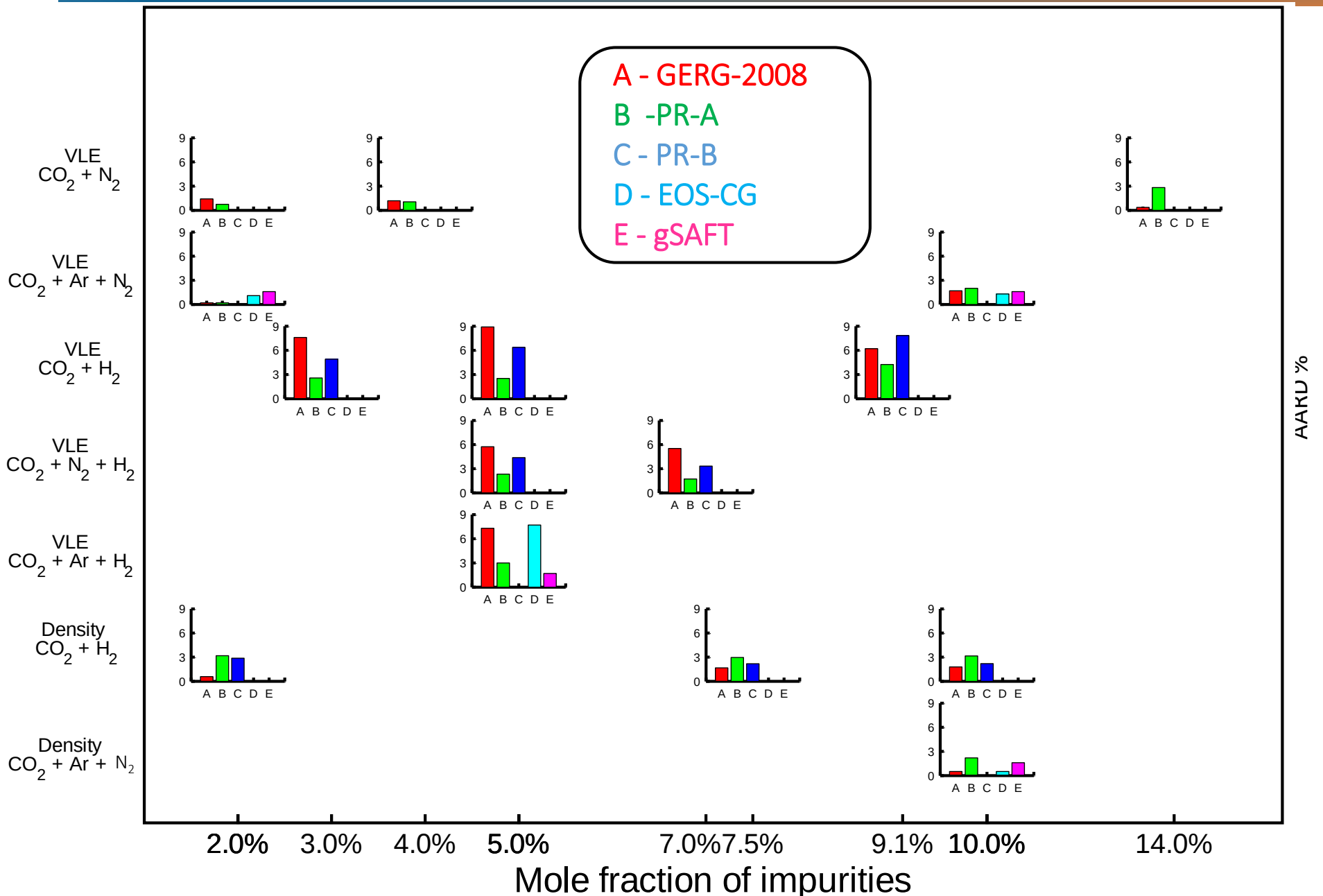
97%CO_2+3%H_2



93%CO_2 + 4%N_2 + 3%H_2



Evaluation of equations of state



Conclusions

- H_2 and H_2O are the key components in terms of understanding the thermodynamic properties of CO_2 mixtures relevant to CO_2 compression and transport.
- The presence of H_2 significantly increases the pressures required to form a homogeneous phase of impure CO_2.
- Permeant gases (e.g. N_2 and H_2) decrease the solubility of H_2O in CO_2 under liquid or supercritical conditions.
- **Currently, no single EoS is better than the others for both VLE and density predictions.**
- We recommend GERG-2008/EOS-CG for density calculation and the cubic EoS for VLE calculations of the mixtures with H_2

Future possibilities
Monitoring the composition of CO_2 streams

Needs to be fast, quantitative & inexpensive of monitoring composition and phase

Composition

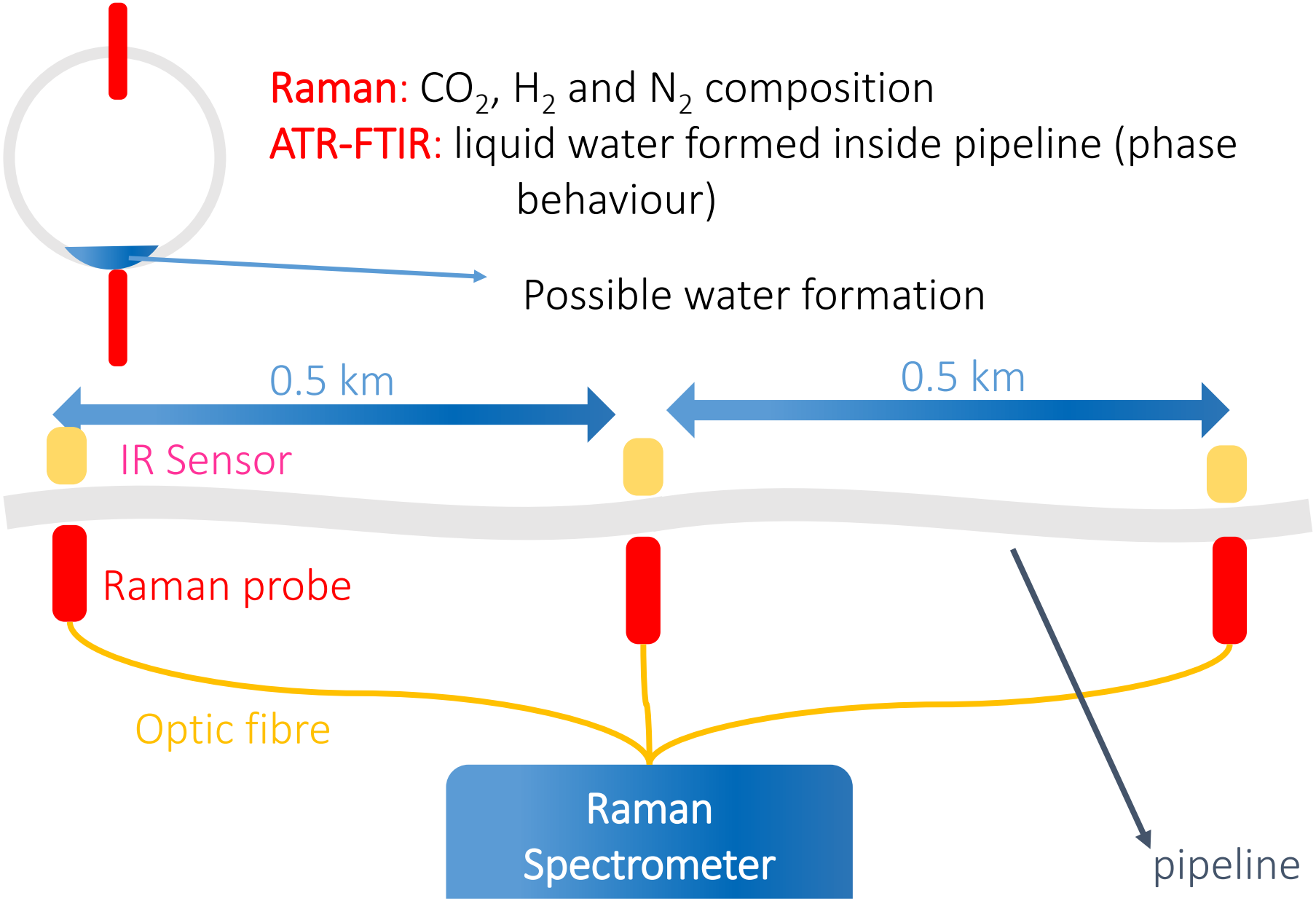
Flow rate

Capture plant + pump station to pipe interface

Raman: CO_2, H_2 and N_2 composition

FTIR: water concentration in CO_2

Future possibilities
Quality control along hundred mile long pipelines



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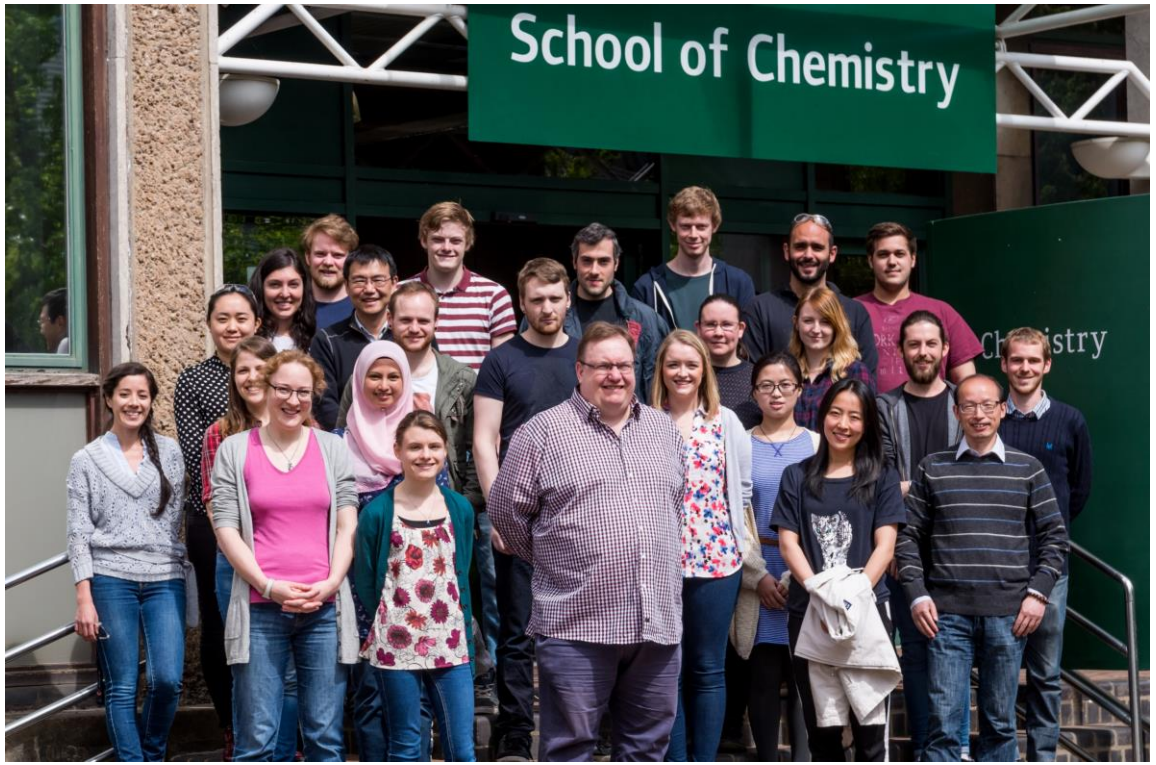
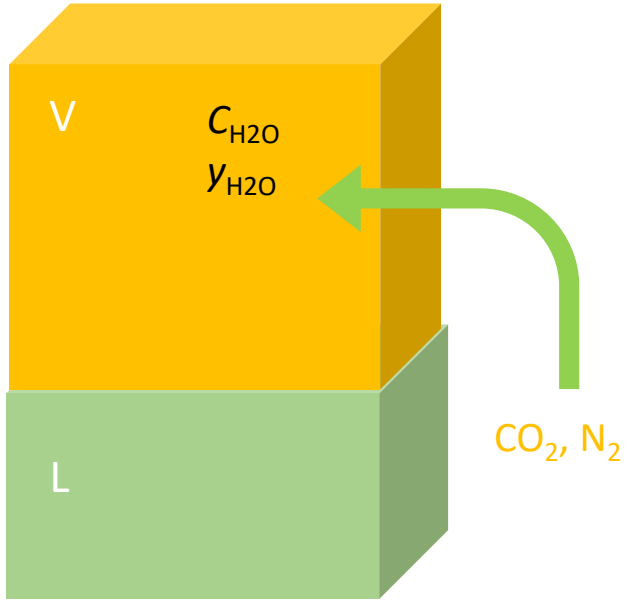


	Tc/K	Pc/bar
CO2	304	73.8
N2	126	33.9
H2	33	13.0
Ar	151	48.7

Solubility of H_2O in $CO_2 + N_2$

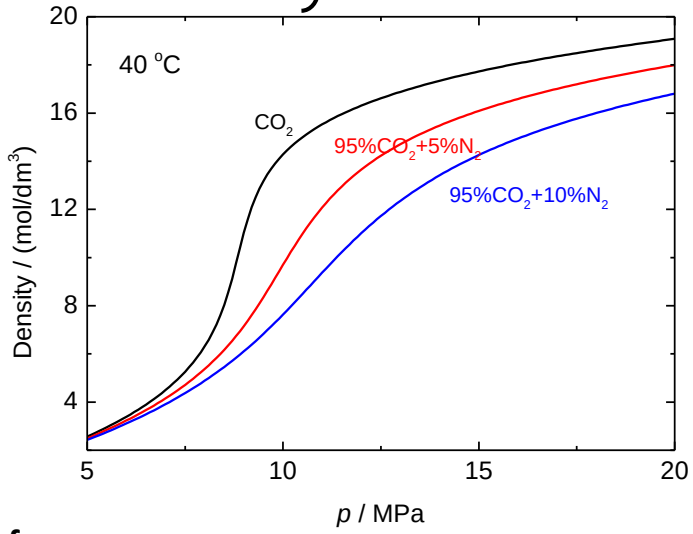
Equilibrium state



$$C_{H2O} = b_0 + b_1\rho + b_2\rho^2 \quad (m)$$

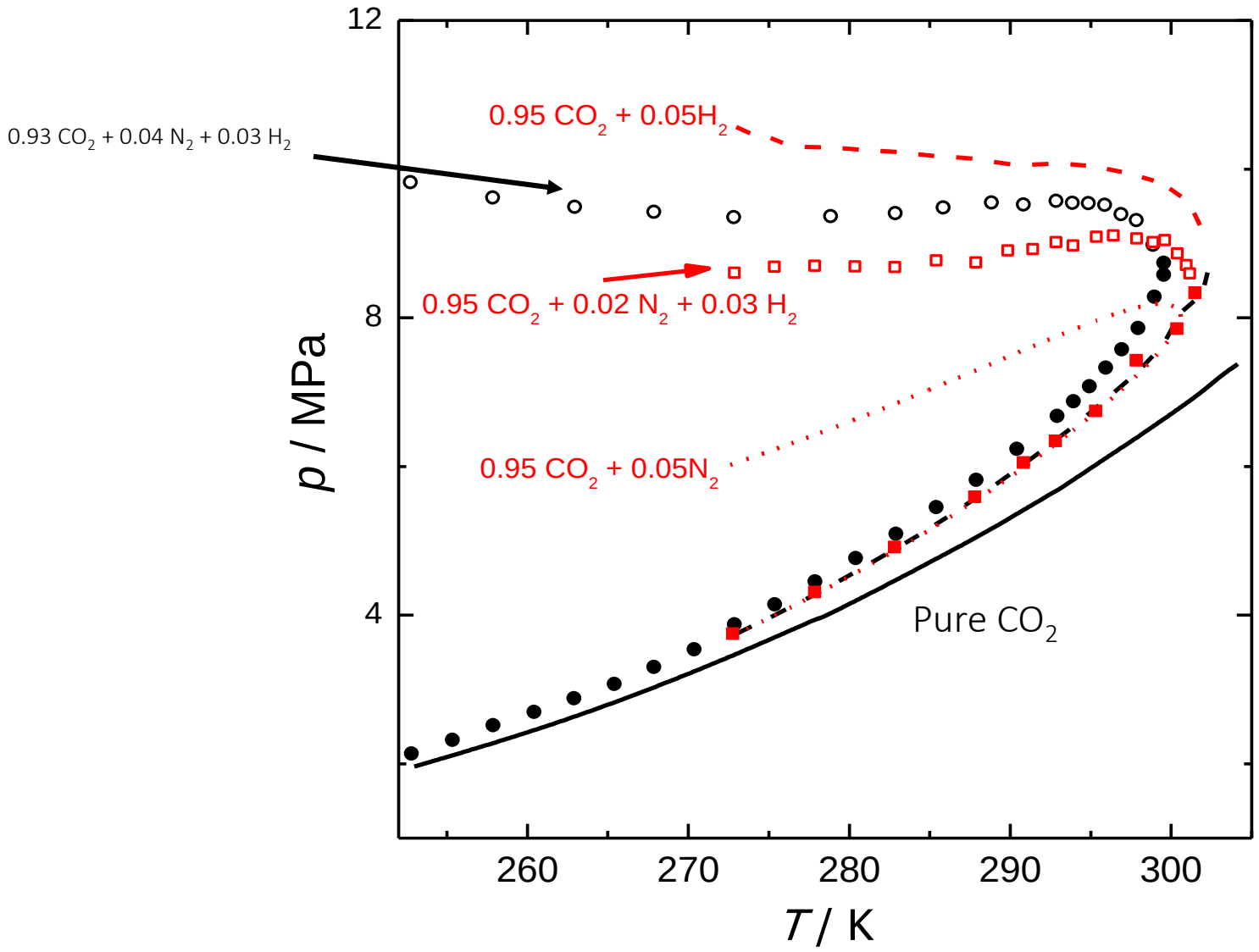
$$\rho_m = f(T,P,x_i)$$

y_{H2O}



Average of absolute relative deviations of y_{H2O}

	N	25 °C	N	40 °C
CO2	4	1.4%	5	4.9%
95%CO2 + 5% N2	4	3.2%	7	3.9%
90% CO2 + 10% N2	3	4.2%	7	4.5%
All	11	2.8%	19	4.4%

Dilute $CO_2 + N_2$ mixtures (y_{N2}<0.1)

$p - T$ phase boundary of the ternary system of $CO_2 + N_2 + H_2$