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Phase Behaviour and EoS Modelling of the Carbon Dioxide-Hydrogen System

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Acknowledgements

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$CO_2 + H_2$

$CO_2 + N_2$

Sponsors

Costain Energy & Process

Energy Technologies Institute

Background to Project

Original motivation for study: generation of VLE data to support pre-combustion decarbonisation of fuel gases.

Examples include:

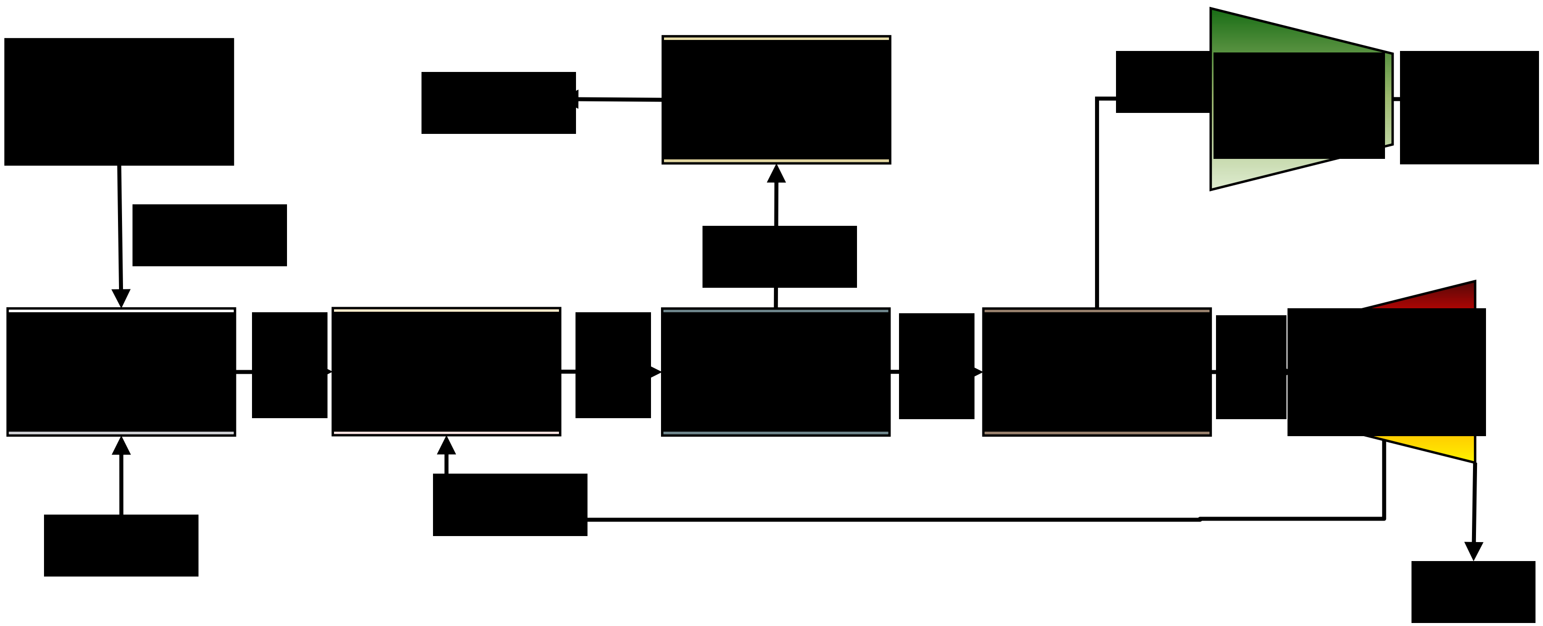
- processing of high-CO_2 natural gases
- hydrogen production from synthesis gas

Technologies include:

- traditional solvent processes (e.g. MEA process)
- membrane separations
- cryogenic flash or distillation processes
- hybrids of the above

Costain's Next Generation Capture Technology (NGCT)

- Process for electricity production from coal with 95% carbon capture
- Based on synthesis gas production and CO_2 separation to yield H_2
- Combustion/electricity production in a combined a cycle process
- NGCT achieves primary CO_2 removal by low-temperature flash processes



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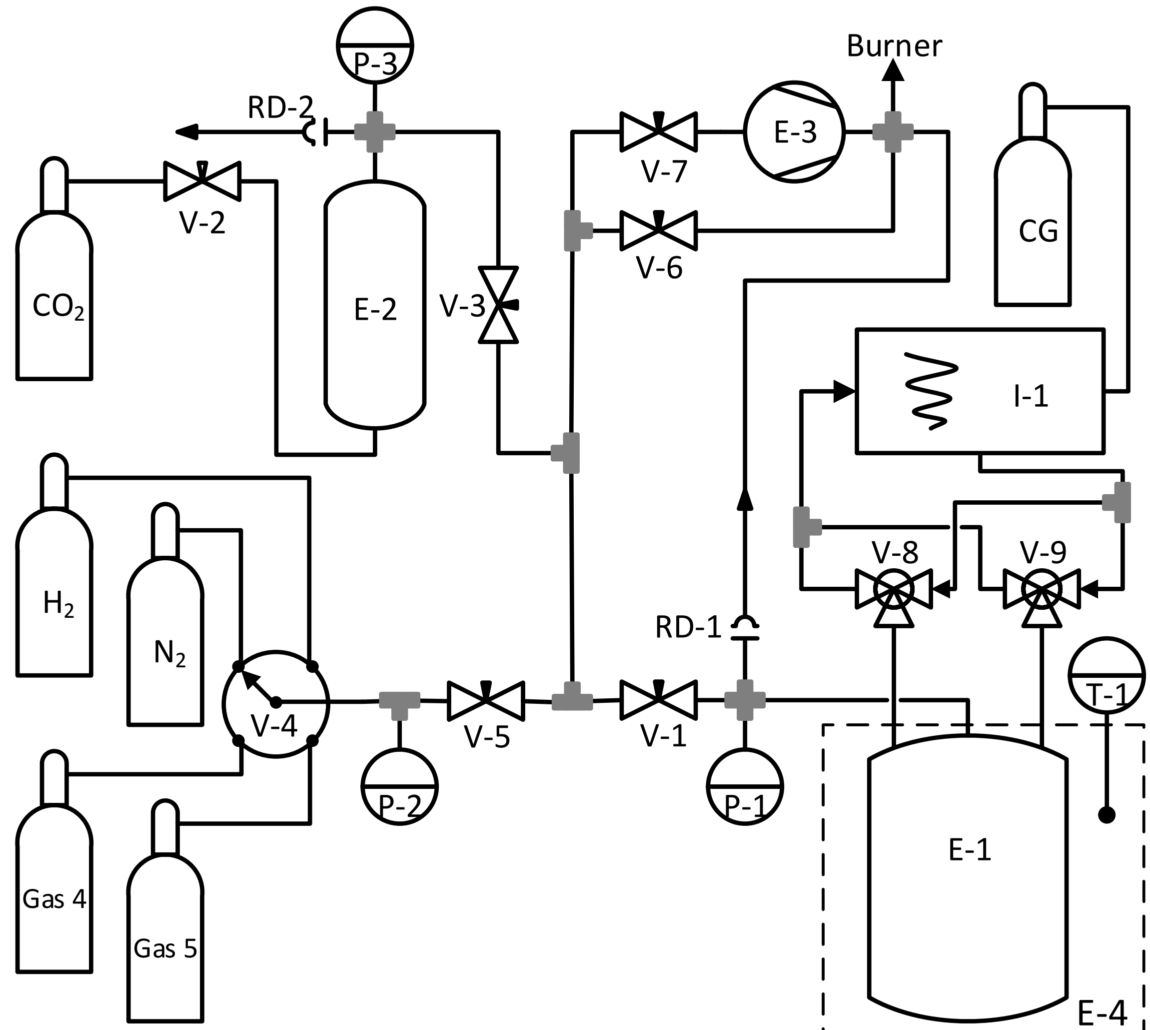
Phase Behaviour Project Plan

- Development of new VLE apparatus for studying CO_2-rich mixtures at low temperatures and high pressures
- Measurements of VLE (and also SVLE) for the CO_2 + H_2 binary system
  - Pressures up to 16 MPa
  - Temperatures approx. triple-point to critical point of CO_2
  - Fully analytical approach
- Modelling of VLE data in a form suitable for process design

- Measurement range covers two areas of interest:
  - T < 270 K (cryogenic separations)
  - T > 270 K (pipeline engineering)

Apparatus for VLE and SVLE Measurements



Emphasis on:

- uncertainty
- reliability
- automation
- safety

Working ranges:

- pressure to 20 MPa
- temperature 193 to 474 K

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Phase-Equilibrium Cell

- p_{max} = 200 bar
- V = 0.15 L
- Stainless steel
- Gold-plated, N_2-filled stainless-steel o-ring
- Magnetic stirrer
- Rolsi electro-magnetic sampling valves

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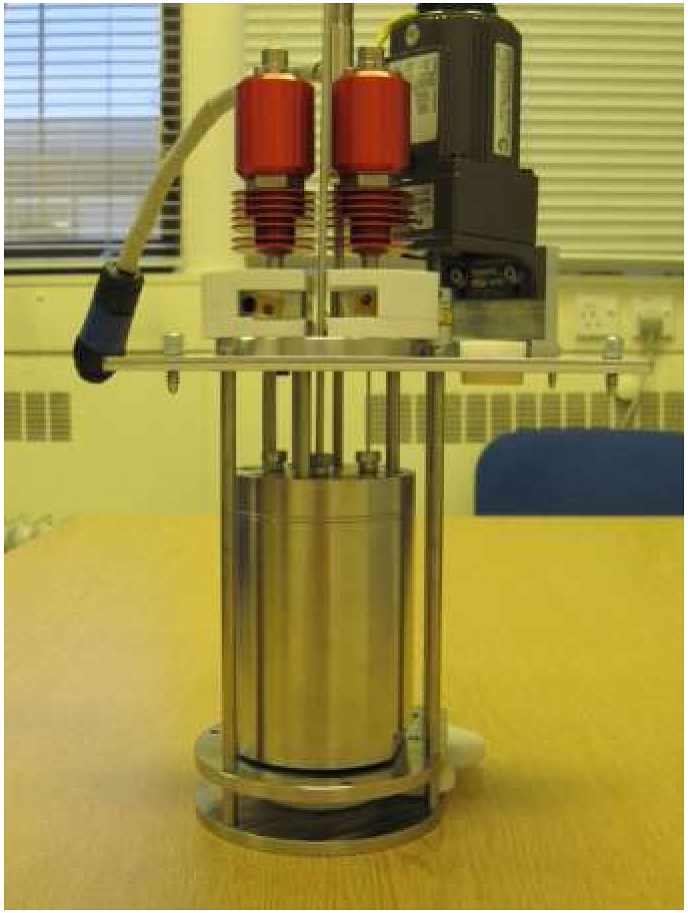
Phase-Equilibrium Cell



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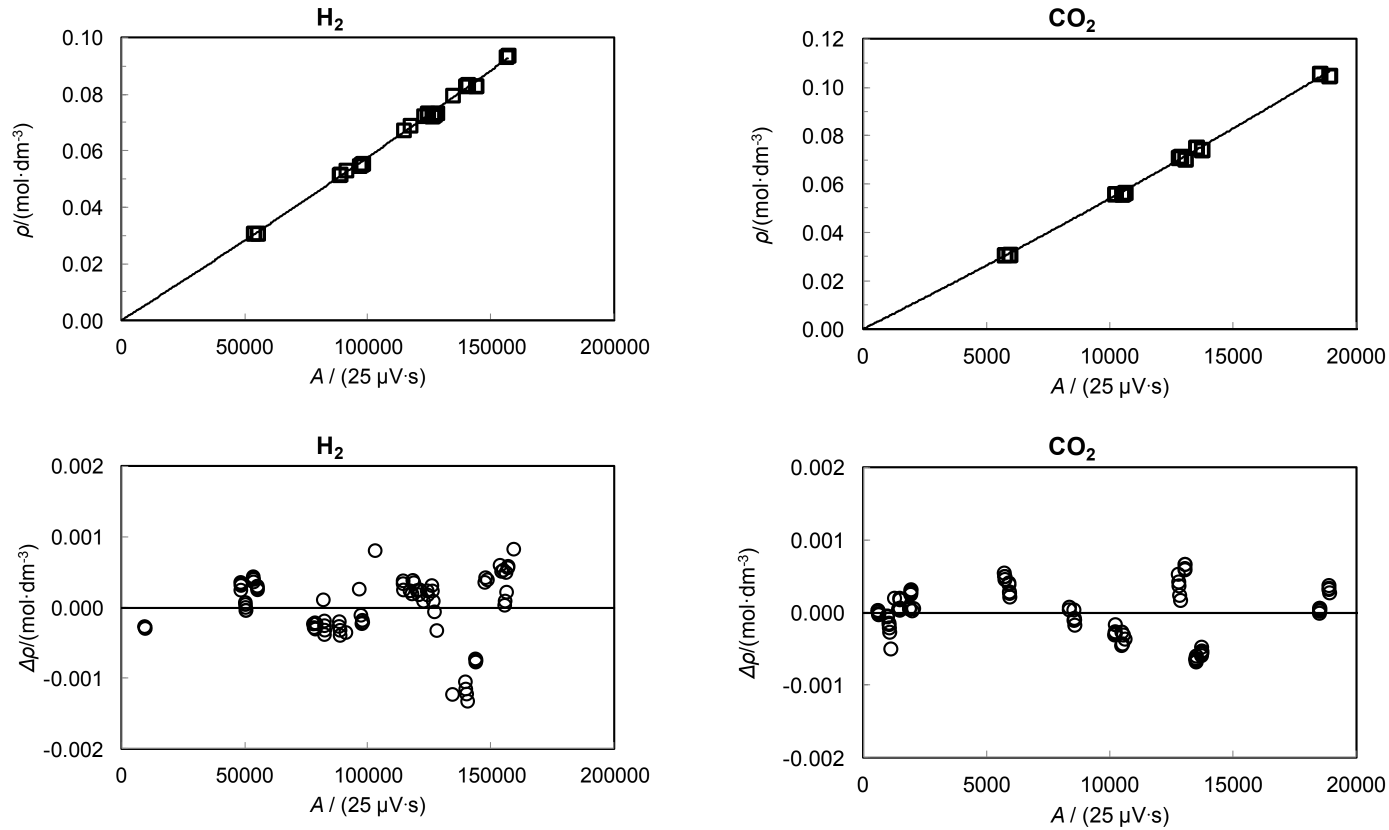
GC Calibration for H_2 and CO_2



$n_i / V = \rho_i = a_i A + b_i A^2$ Component $i = 1, 2$ Parameters: a_i and b_i for each gas

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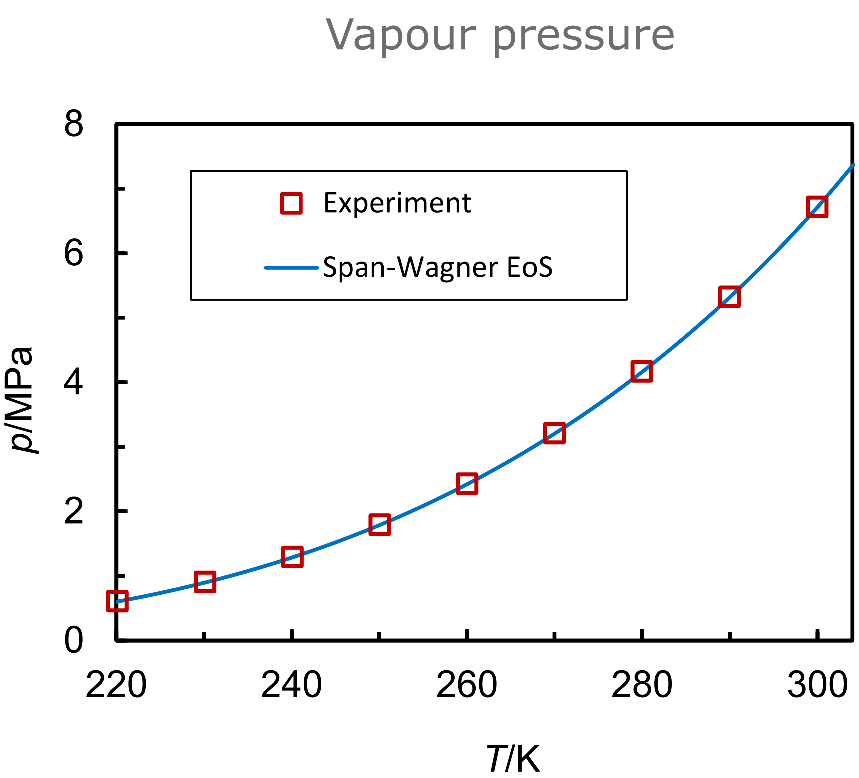
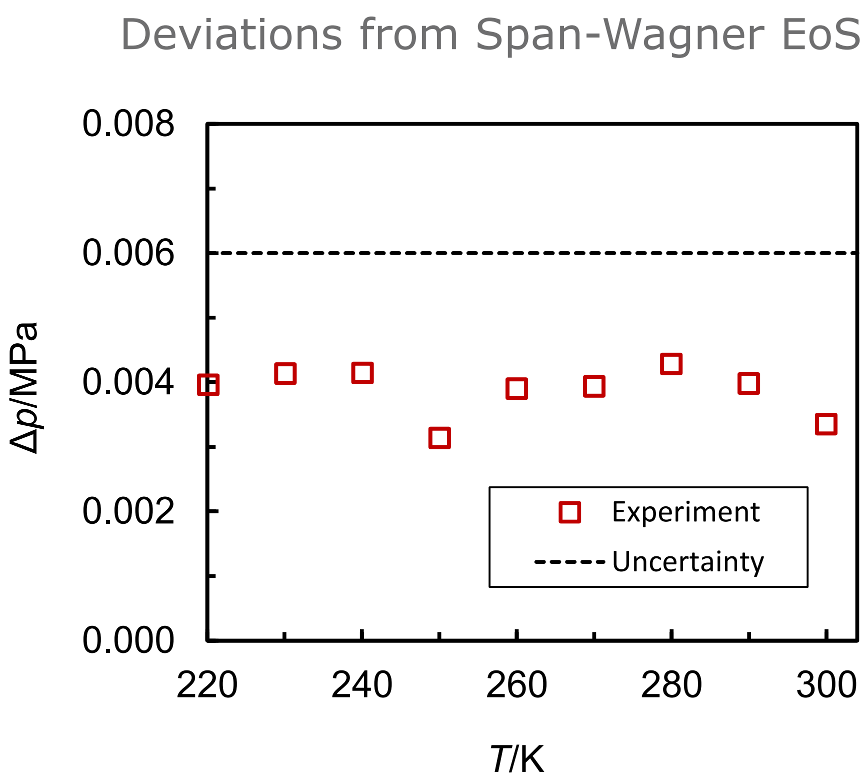
Verification: Vapour Pressure of Pure CO_2





Overall standard uncertainties:

$u(T)$ = 0.01 K; $u(p)$ = 0.003 MPa; $u(x) = 0.011x(1 - x)$; $u(y) = 0.011y(1 - y)$

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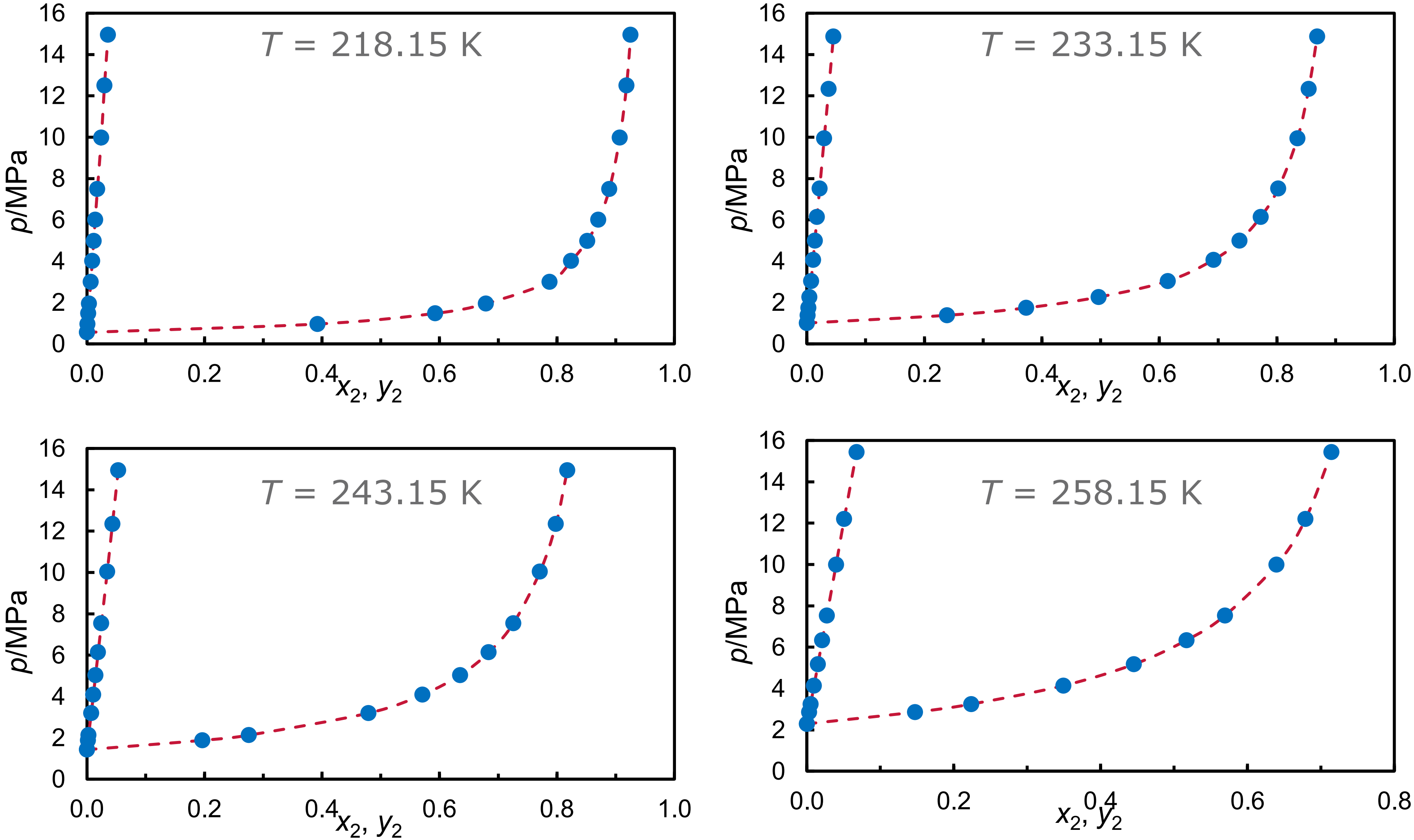
VLE Results for (CO_2 + H_2): Low Temperatures



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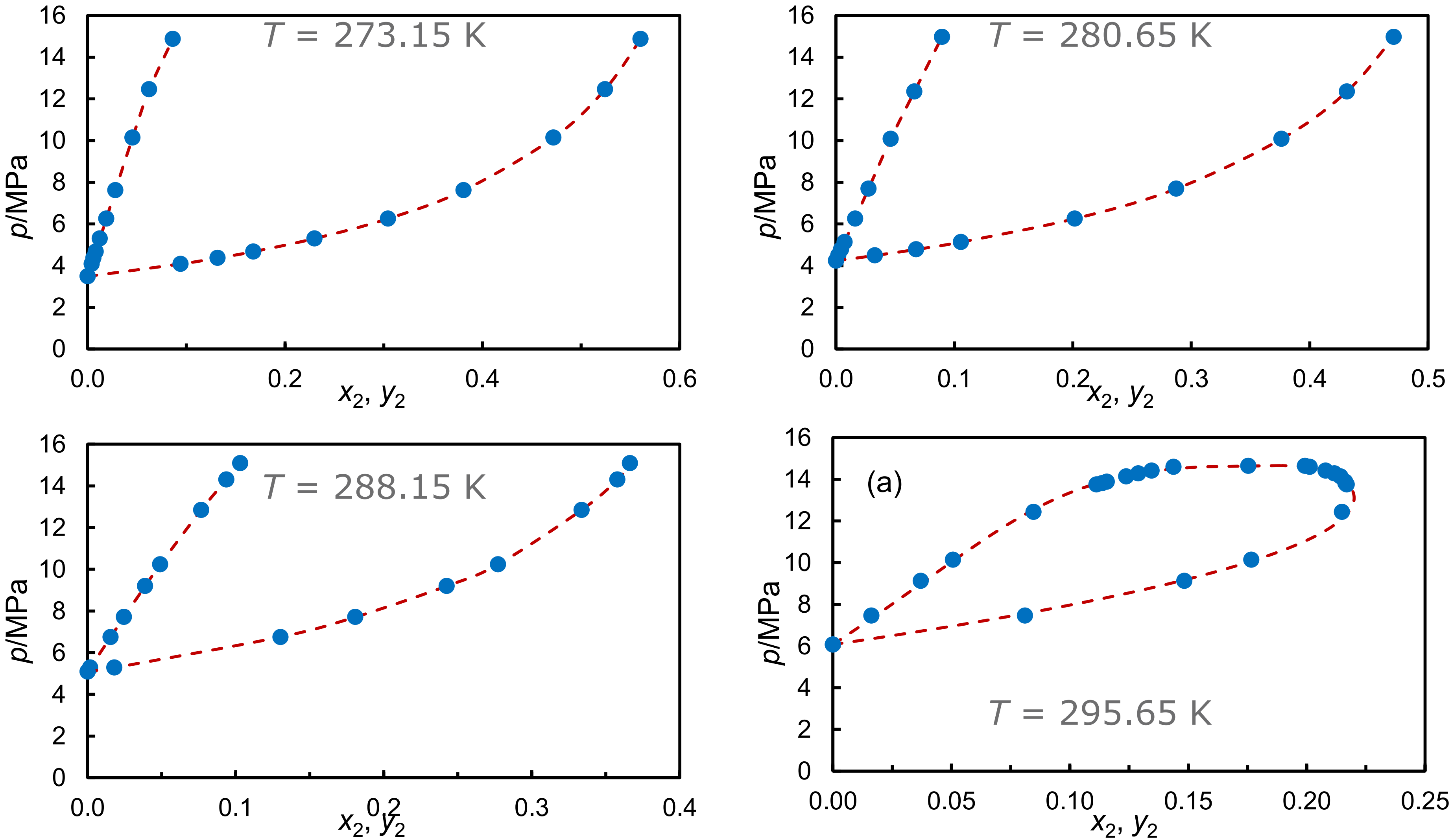
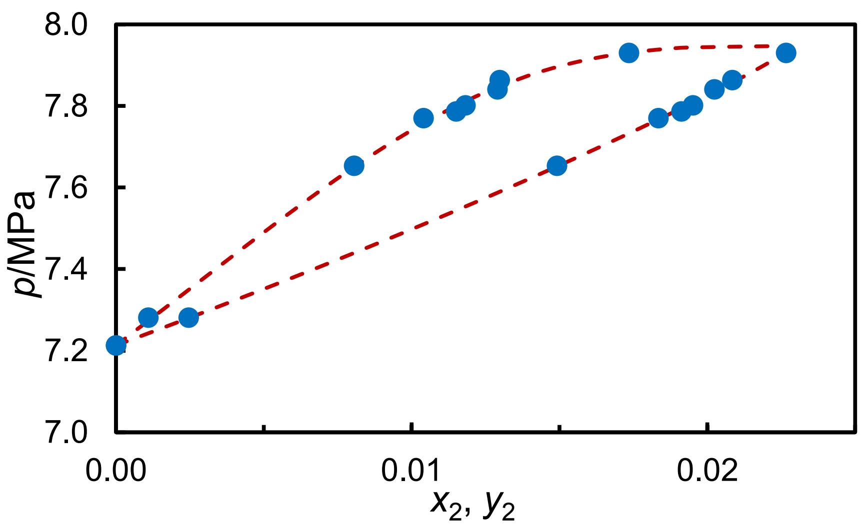
VLE Results for (CO_2 + H_2): Pipeline Regime



VLE Results for (CO_2 + H_2): … & close to CO_2 critical point



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Modelling

- Standard Peng-Robinson Equation of State
- Quadratic mixing rules for *a* and *b* parameters:

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij}) \sqrt{a_i a_j}$$

$$b = \sum_i \sum_j x_i x_j (1 - l_{ij})(b_i + b_j)/2$$

- l_{ij} = constant
- $k_{ij} = k_{ij,1} + k_{ij,2}/T$
- Up to three parameters to fit nine isotherms
- a_i, b_i from critical (or effective critical) constants and acentric factor

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Quantum Effects for H_2

- Typical equations of state (including cubic EoS and SAFT models) regress pure-component parameters against pure-component data:
  - e.g. critical constants, vapour pressure, saturated liquid density
- Hydrogen is a quantum gas with large quantum-mechanical effects below its critical temperature (T_c = 33 K)
- Quantum effects diminish at higher temperatures, so that H_2 behaves essentially classically at the present experimental temperatures
- Errors arise when EoS parameters are fitted to pure-H_2 VLE data because of the quantum effects that prevail under those conditions
- Thus for cubic EoS models (which base parameters on T_c, p_c and ω) *effective* critical constants fitted to virial coefficients are used

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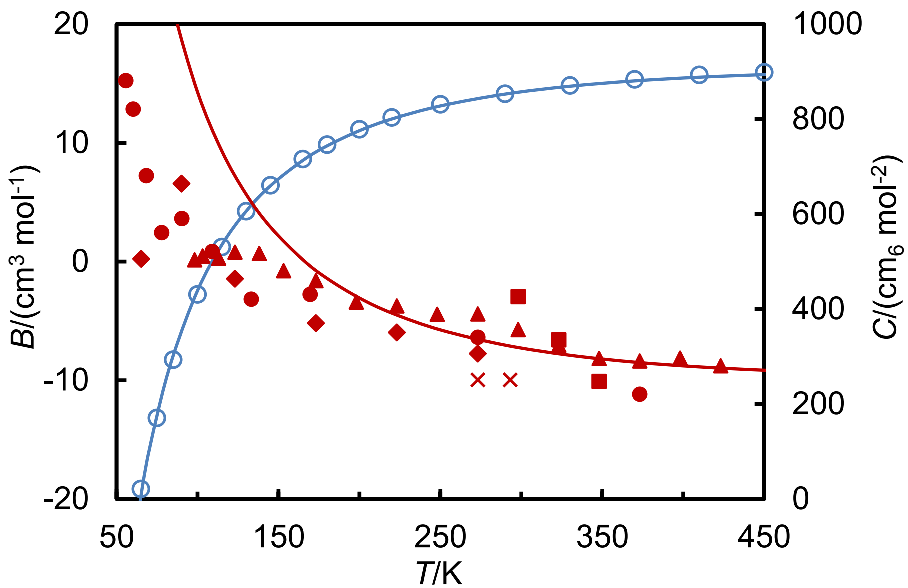
Fit for Virial Coefficients of H_2



Critical Constants of Normal Hydrogen

Parameters	T_c/K	p_c/MPa	ω
True	33.15	1.296	-0.219
Effective	31.76	1.276	-0.063

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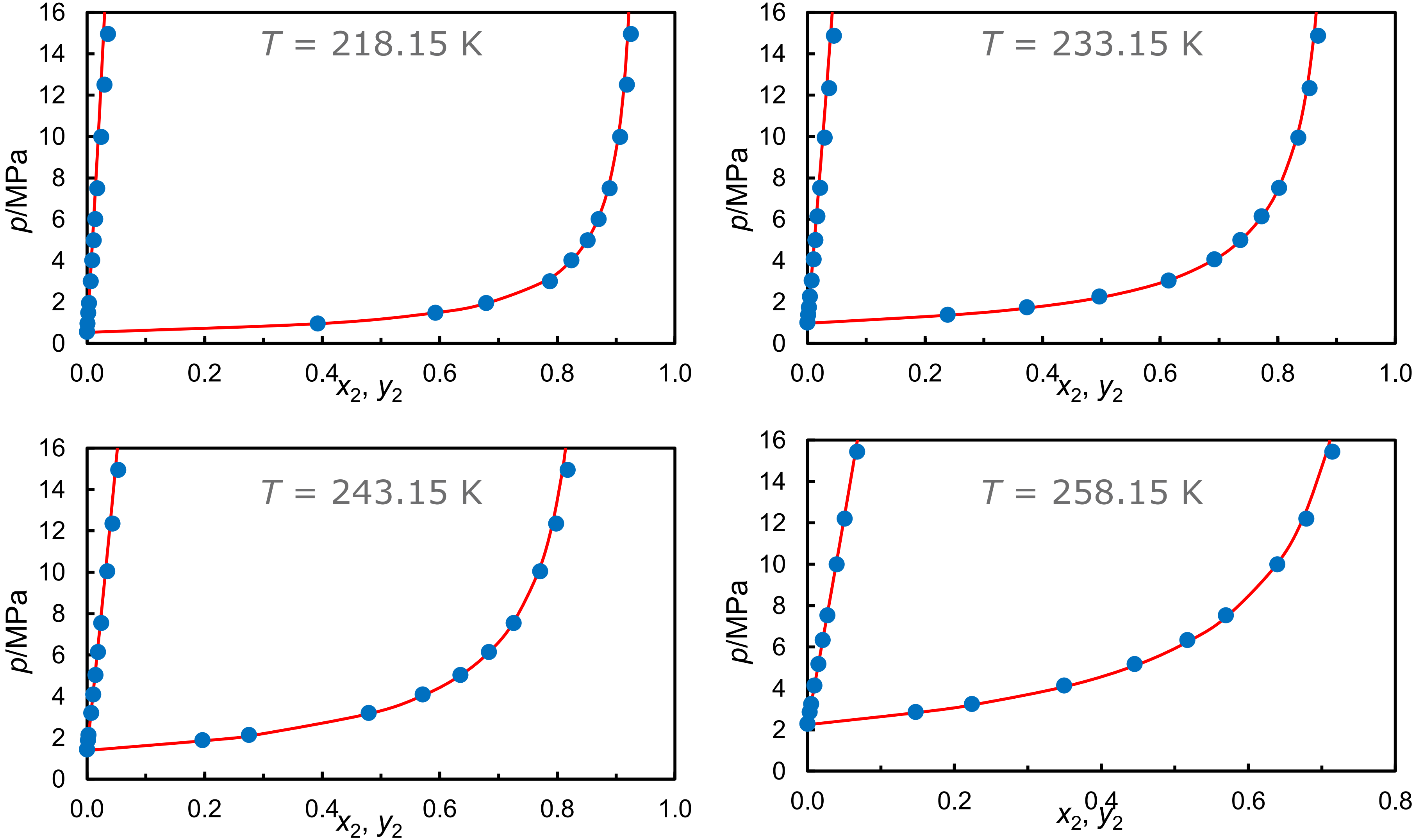
Modelling (CO_2 + H_2) with Peng-Robinson Equation

- Objective function based on composition deviations at given T and p:

$$S^2 = \frac{1}{N}\sum_{i=1}^{N}\left[(x_{2,i} - x_{2,i,\mathrm{calc}})^2 + (y_{2,i} - y_{2,i,\mathrm{calc}})^2\right]$$

- Up to three parameters: $k_{ij,1}$, $k_{ij,2}$ and l_{ij}
- Common approach is to set $l_{ij} = 0$
- ... but this leads to a relatively poor fit for CO_2 + H_2
- Fits with $l_{ij} \neq 0$ lower objective function by a factor of 4
- Global fit to all isotherms (excluding a few near-critical states): $S = 0.004$

Experiment vs Model for (CO_2 + H_2) at Low Temperatures



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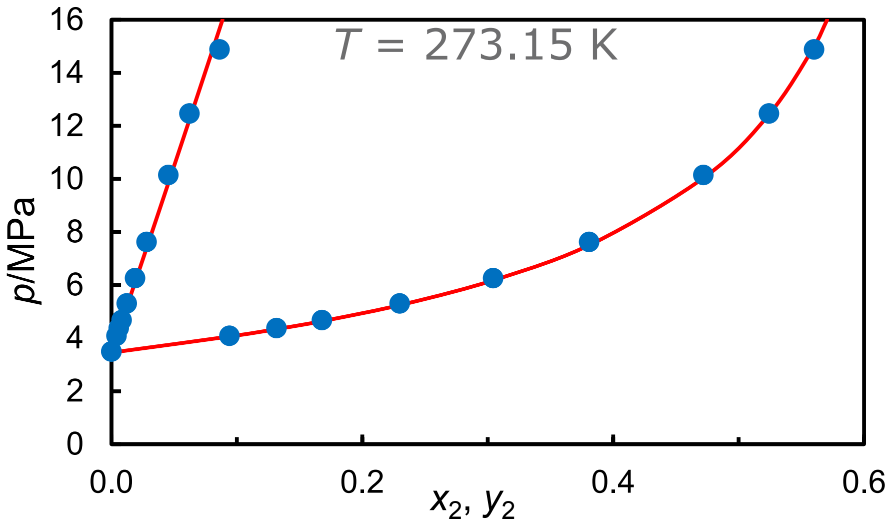
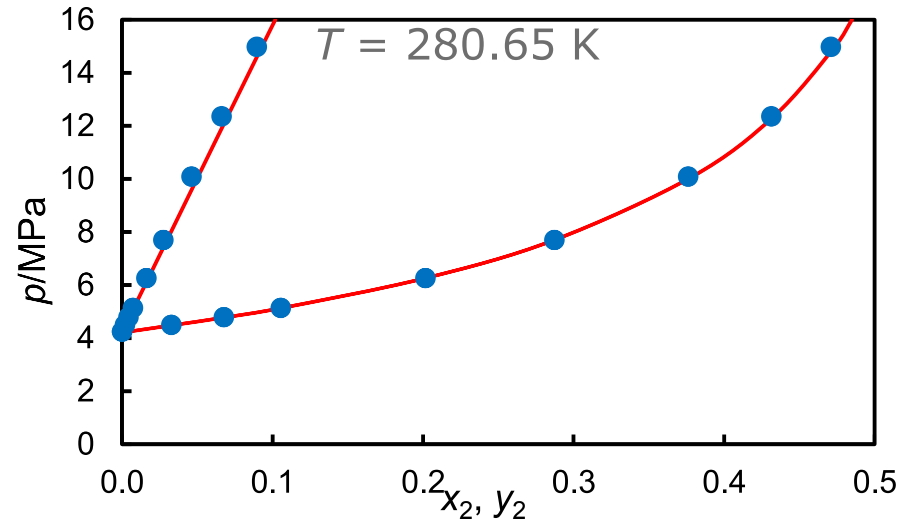
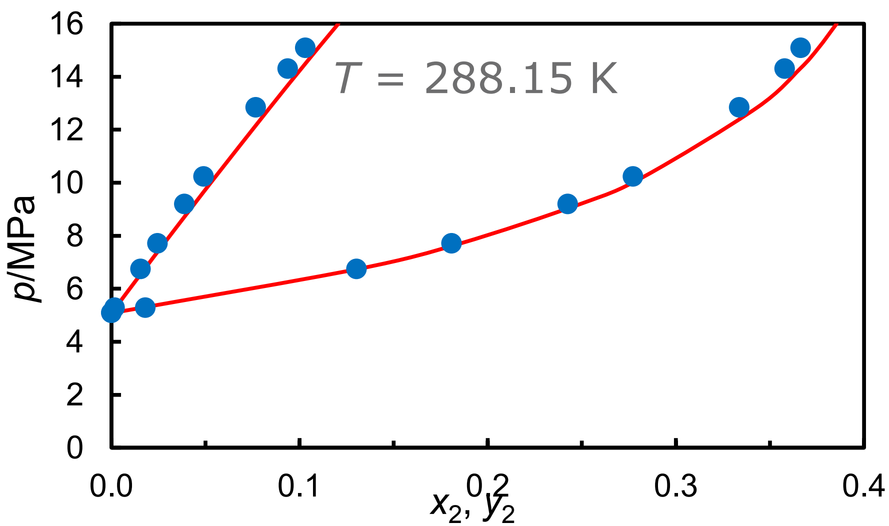
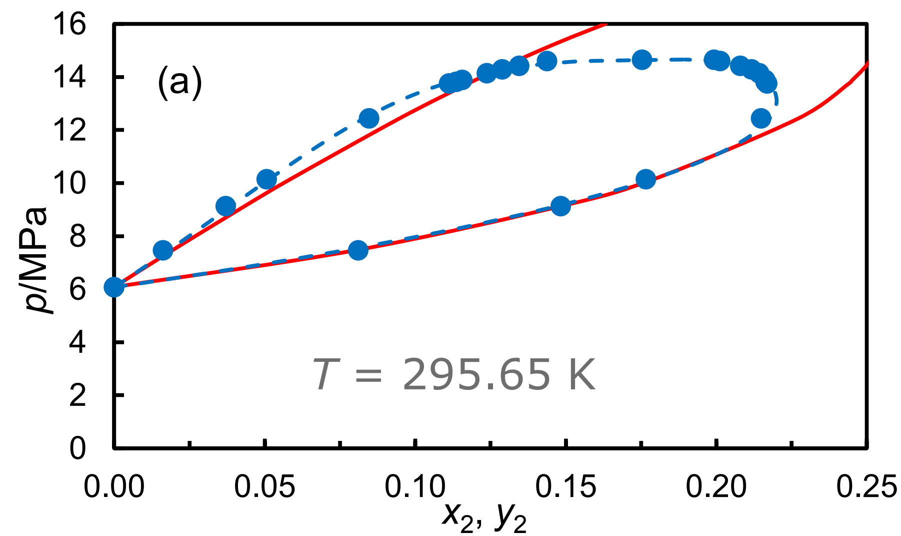
Experiment vs Model for (CO_2 + H_2) at PipelineTemperatures

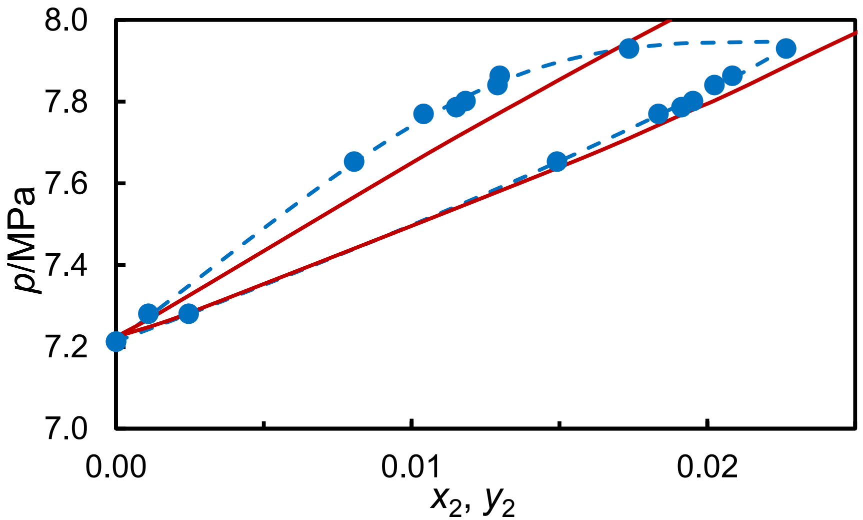








Experiment vs Model for (CO_2 + H_2)



General conclusions:

- Model with 3-parameters provides a reasonable **global fit**
- Fails near to the critical locus (as expected)
- Not within experimental uncertainty – especially bubble curves at higher temperatures
- Improved fits for restricted regions can be obtained

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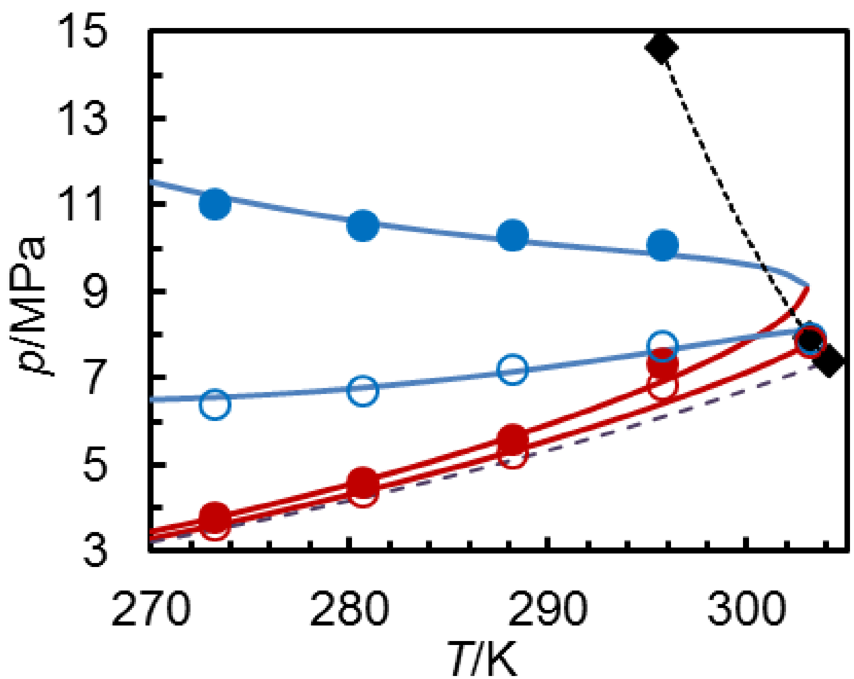
Limited Model for Pipeline Applications

- Same Peng-Robinson model but parameters fitted:
  - $T \geq 273$ K
  - $x_{H2} \leq 0.06$ with coexisting values of y_{H2}
- Much improved representation with S = 0.002



Phase Envelopes

($0.95\ CO_2 + 0.05\ H_2$): ●, ●

($0.98\ CO_2 + 0.02\ H_2$): ○, ○

PR model:

Critical locus:

CO_2 VP curve:

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Summary

Experiment:

- New equipment constructed and validated
- High-quality calibrations and low overall uncertainties
- (CO_2 + H_2) measured at temperatures between the triple point and critical points of CO_2

Modelling:

- 'Standard' Peng-Robinson equation used
- 'Effective' critical constants for H_2
- Quadratic mixing rules for both *a* and *b* parameters
- Provides a fair global fit
- Local fit for pipeline regime gives a good representation of the data

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PE EoS

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)}$$

Single substance:

$$a = 0.457235\,(RT_c)^2 \alpha(T) / p_c$$

$$b = 0.077796\,RT_c / p_c$$

$$\alpha(T) = \left[1 + \left(0.37464 + 1.54226\,\omega - 0.26992\,\omega^2\right)\left(1 - \sqrt{T/T_c}\right)\right]^2$$

Mixture:

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij}) \sqrt{a_i a_j}$$

$$b = \sum_i \sum_j x_i x_j (1 - l_{ij})(b_i + b_j)/2$$