

# Measurement & Prediction of Phase Behaviour of Carbon Dioxide Mixtures

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## Introduction

Hydrocarbon reserves play an important and continuing role as a source of both energy and feedstocks to the chemical industry. However, it is recognised that viable schemes for carbon capture and storage must be implemented to reduce emissions of carbon dioxide (CO<sub>2</sub>) and limit further accumulation of this greenhouse gas in the atmosphere.

In terms of storage, geological formations are a favourable sequestration option. Deep saline aquifers, together with depleted oil reservoirs and gas fields may be used. A significant additional benefit, in the form of enhanced oil recovery (EOR), may be achieved by sequestering CO<sub>2</sub> in active oil-bearing formations. Indeed, miscible flooding with CO<sub>2</sub> may be effective in mobilising dispersed oil droplets that remained trapped in the pore structure of the rock after secondary oil recovery. The result is increased production from the field, improving the security of energy supply while storing the anthropogenic CO<sub>2</sub> used.

## Motivation and aims

**Framework:** exploitation of the huge potential of CO<sub>2</sub> in EOR and development of reliable sequestration processes.

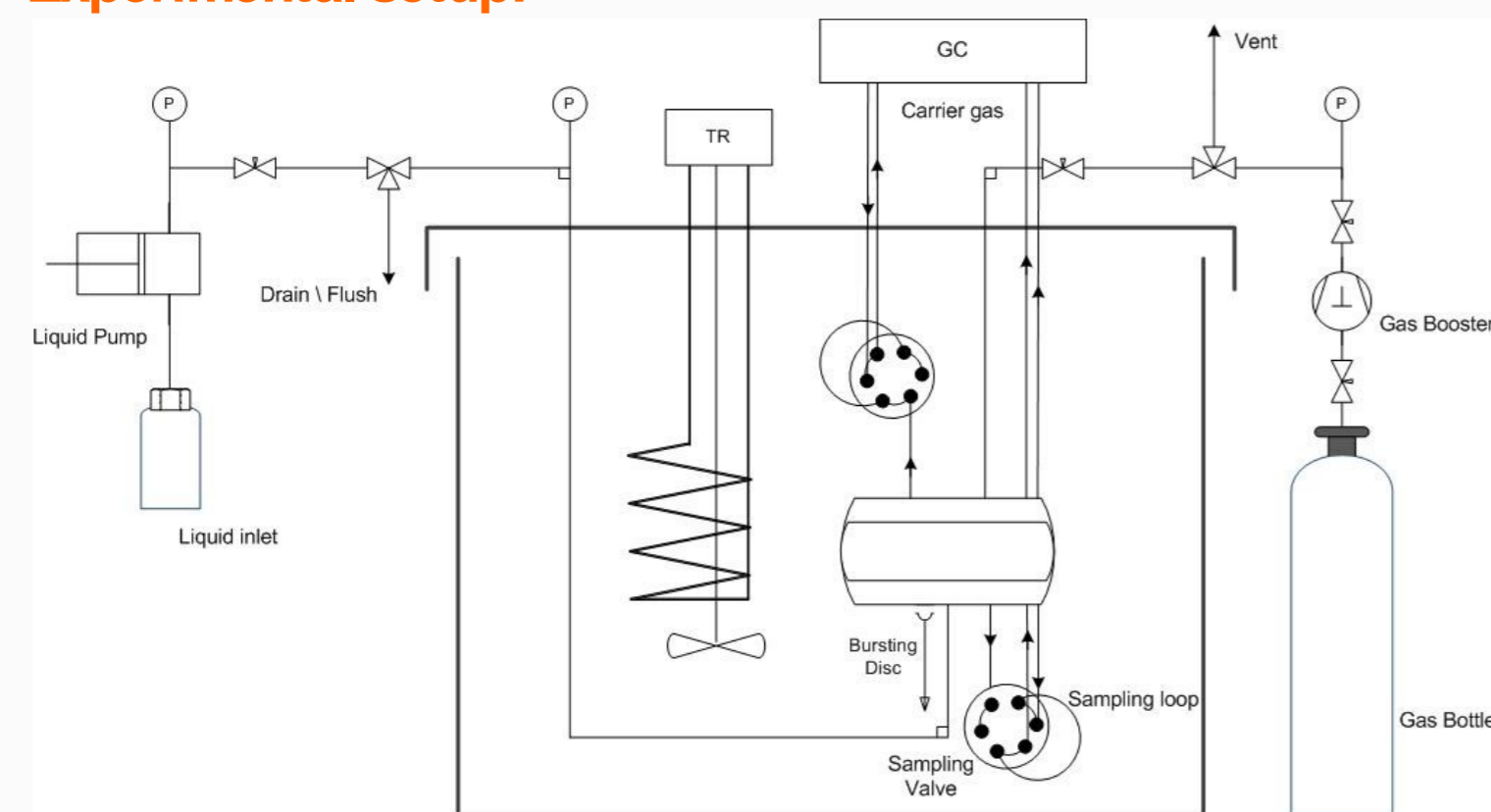
**Global objective:** experimental and theoretical study of the phase behaviour and phase properties of mixtures of CO<sub>2</sub> with hydrocarbons and brines under typical oil reservoir conditions.

**Drivers:** necessity of adequate experimental results and the absence of systematic tools for rationalising the data.

**Final aim:** developing a systematic approach to enables correlation and prediction of the phase behaviour of mixtures involving CO<sub>2</sub>, hydrocarbons and brines, with the purpose of optimising usage of CO<sub>2</sub> in oilfield processes for increasing oil production and CO<sub>2</sub> storage.

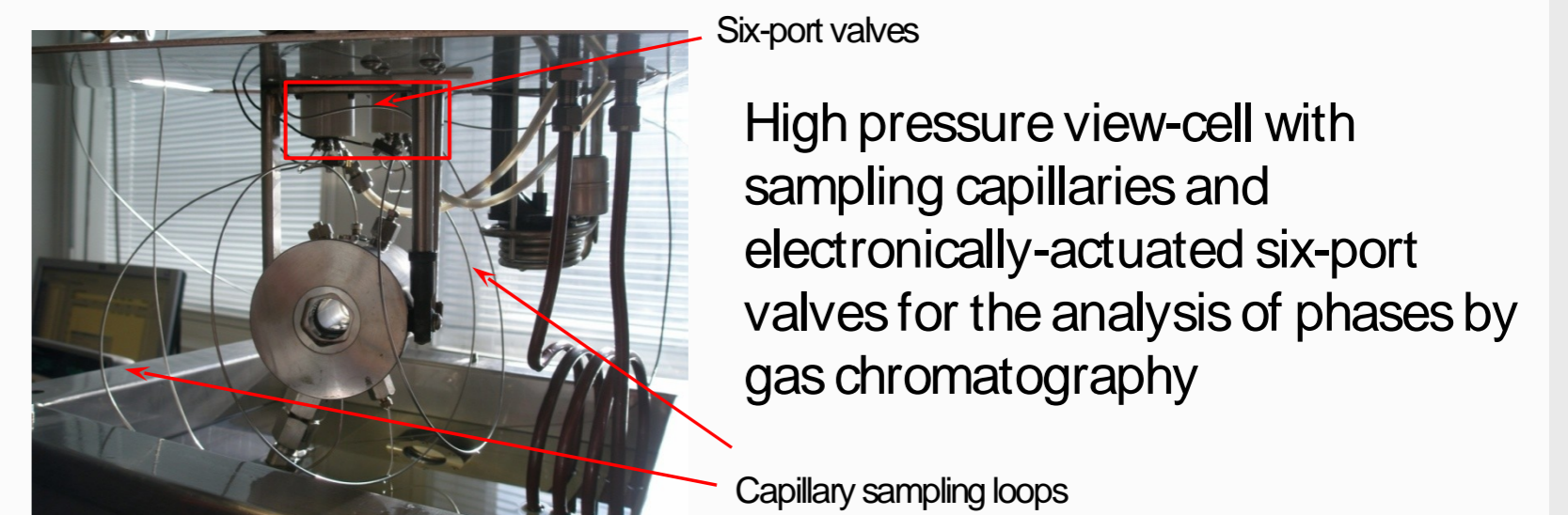
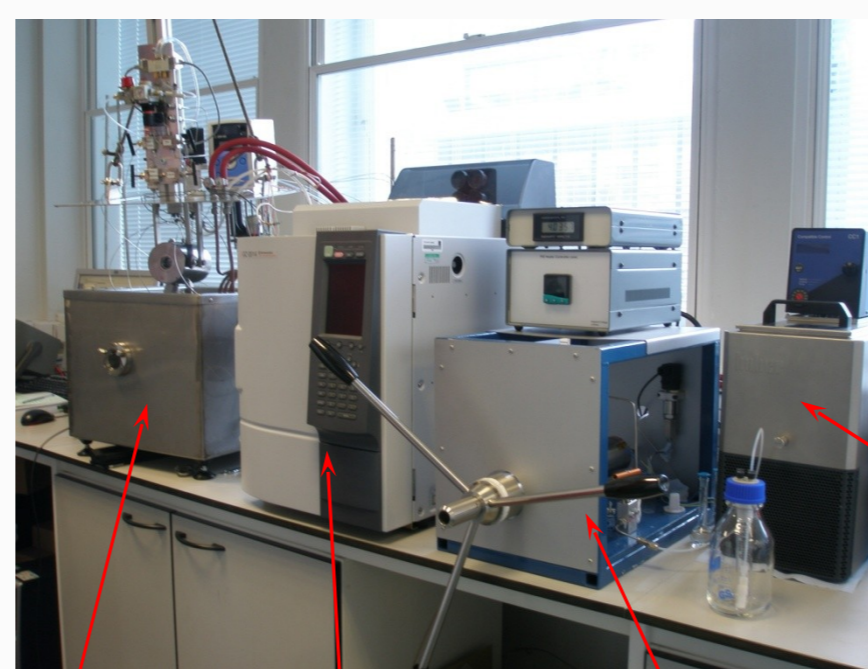
## Measurement of high pressure equilibria

### Experimental setup:



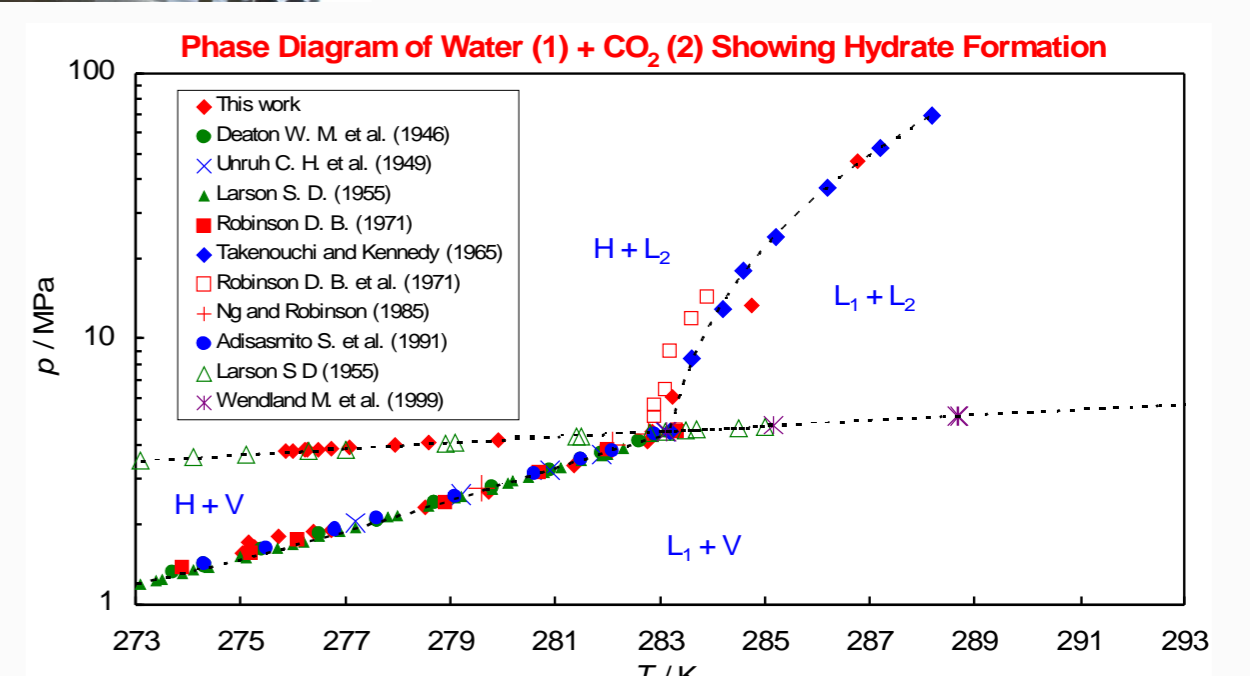
### Specifications:

- Temperature range: 253 to 423 K
- Pressure range: 0.5 to 45 MPa



Schematic diagram of the apparatus

Thermal bath  
Gas Chromatograph  
Liquid displacement pump



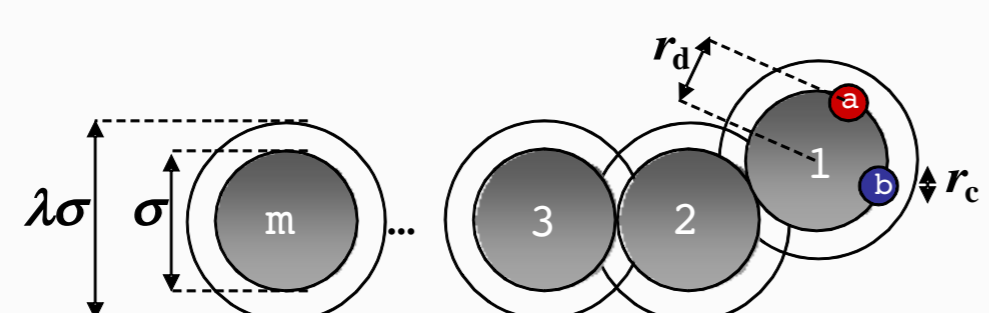
## Molecular modelling

### SAFT-VR (Statistical Associating Fluid Theory-Variable Range) [1-3]

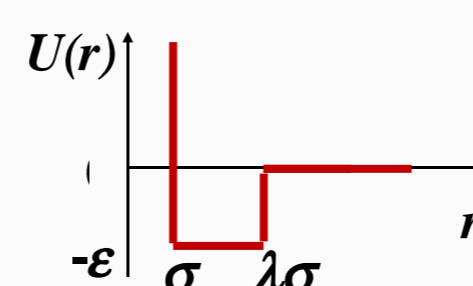
Molecular based equation of state predicts bulk properties

Written in terms of free energy ( $A$ ) from which all thermodynamic properties can be obtained

$$\frac{A}{NkT} = \frac{A^{IDEAL}}{NkT} + \frac{A^{REP}}{NkT} + \frac{A^{ATT}}{NkT} + \frac{A^{CHAIN}}{NkT} + \frac{A^{ASSOC}}{NkT}$$



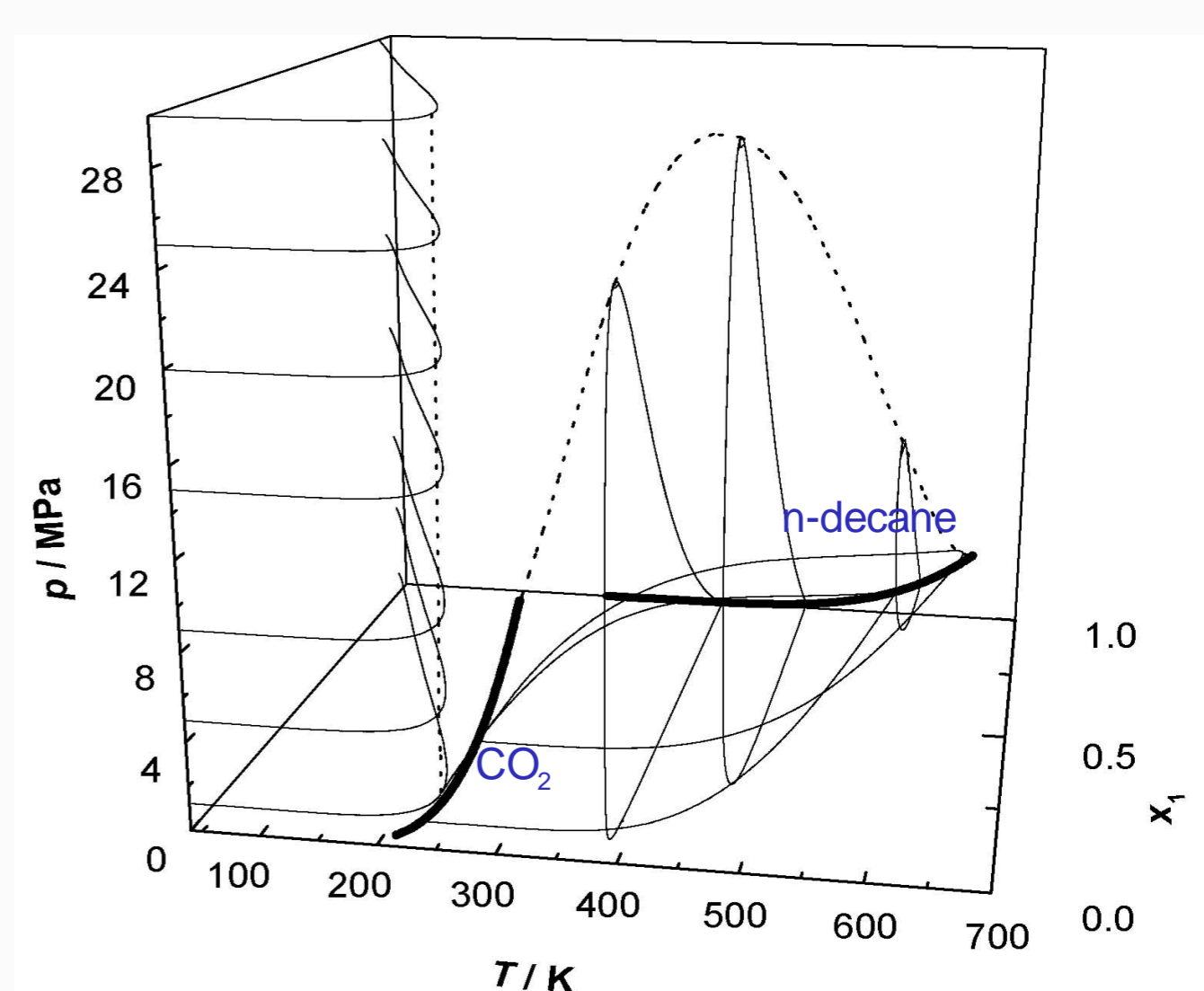
Intermolecular interactions described by means of an square-well potential



Pure components described by

$m_i, \sigma_i, \epsilon_i, \lambda_i, \epsilon_{HBi1ab}, r_{ci1ab}$  & number of sites

Mixture described by  $\sigma_{ij}, \epsilon_{ij}, \lambda_{ij}, \epsilon_{HBijab}, r_{cijab}$



SAFT-VR predictions for the phase behaviour for the mixture n-decane (1) + CO<sub>2</sub> (2)

## Summary

The experimental equipment enables:

- visual observation of phase equilibria, for example observation of hydrate dissociation
- the possibility of sampling two different phases
- on-line chromatographic analysis of the phases

The SAFT-VR approach can be used as a predictive tool to describe the phase behaviour of mixtures using only information pertaining to the pure components.

## Acknowledgements

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## References

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