

Measurement & Prediction of Phase Behaviour of Carbon Dioxide Mixtures

E. Forte¹, A. Galindo, L.G. Ruffine & J.P.M. Trusler
Department of Chemical Engineering, Imperial College, London SW7 2AZ, UK
¹e.forte-serrano07@imperial.ac.uk

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 (CO₂) 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 CO₂ in active oil-bearing formations. Indeed, miscible flooding with CO₂ 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 CO₂ used.

Motivation and aims

Framework: exploitation of the huge potential of CO₂ in EOR and development of reliable sequestration processes.

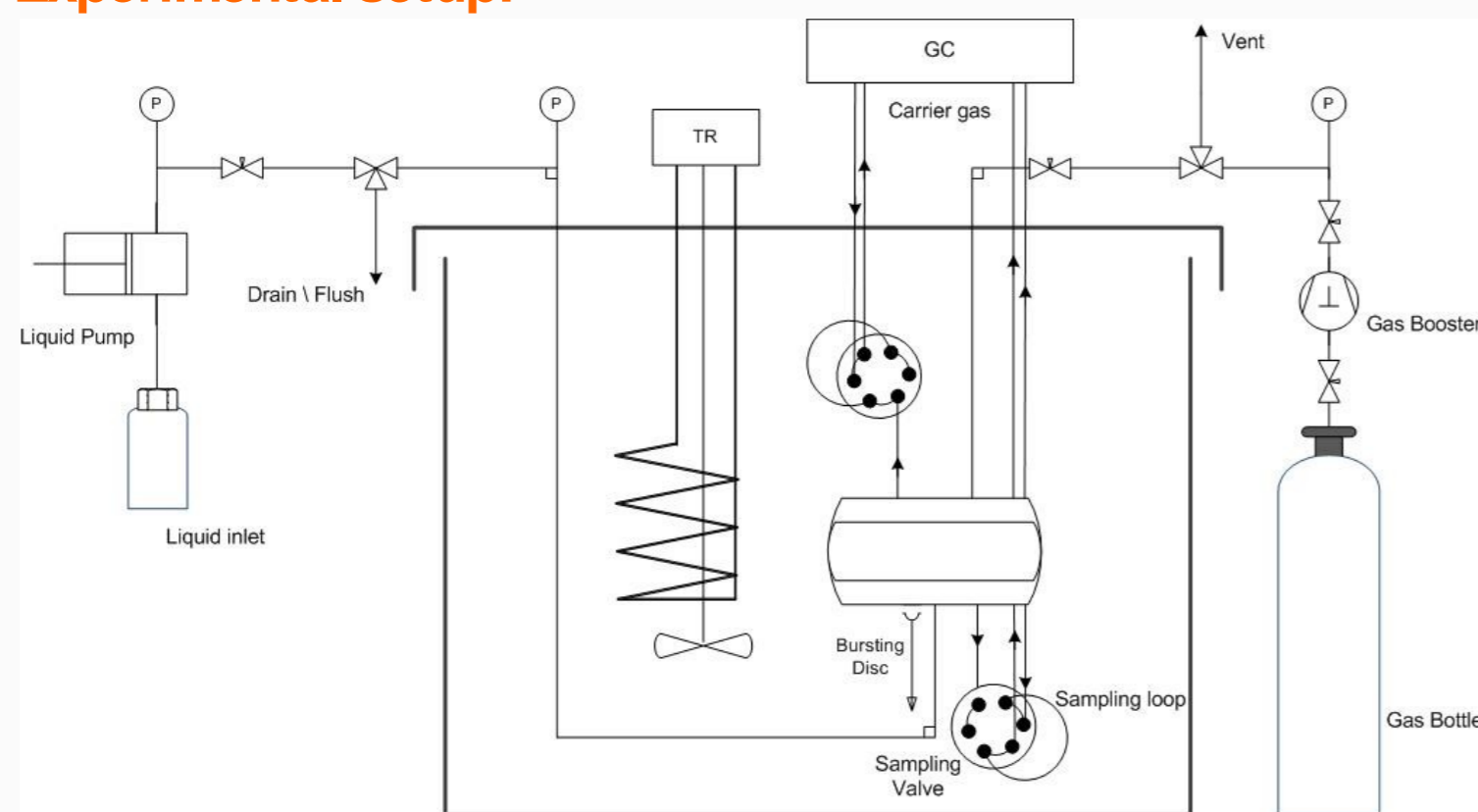
Global objective: experimental and theoretical study of the phase behaviour and phase properties of mixtures of CO₂ with hydrocarbons and brines under typical oil reservoir conditions.

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 CO₂, hydrocarbons and brines, with the purpose of optimising usage of CO₂ in oilfield processes for increasing oil production and CO₂ storage.

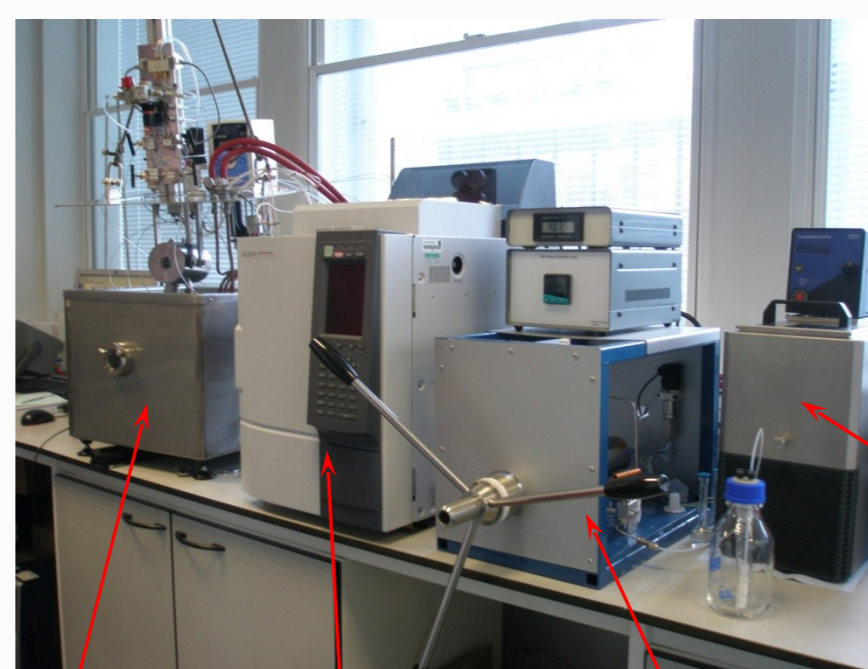
Measurement of high pressure equilibria

Experimental setup:

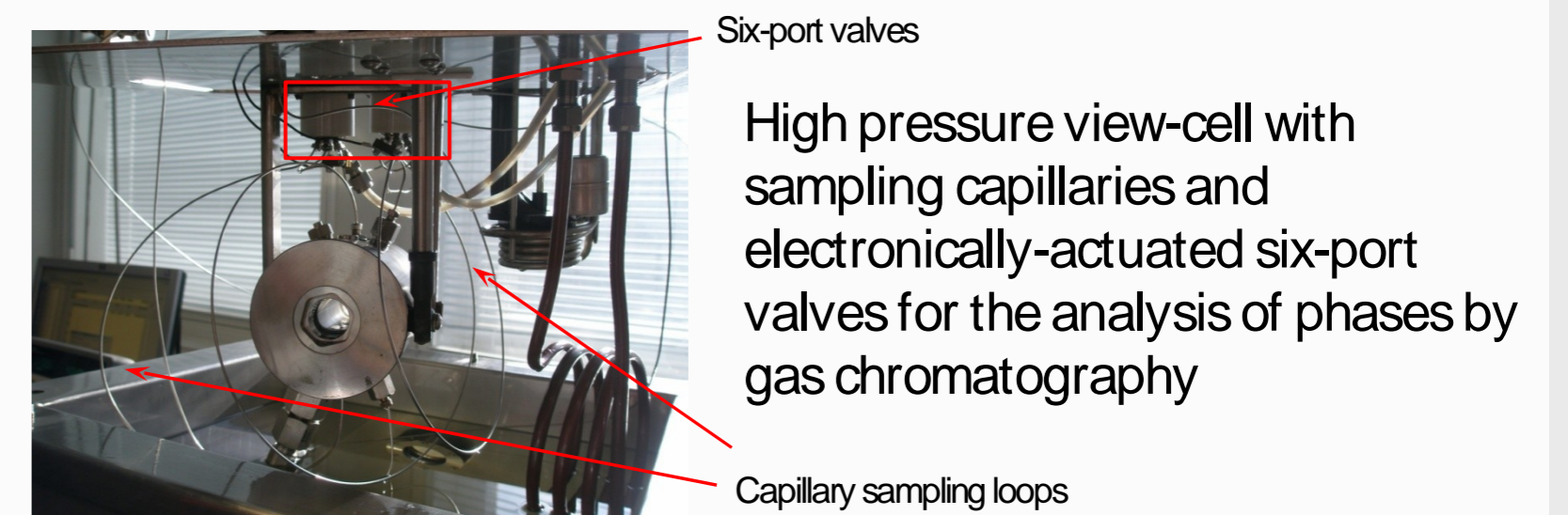


Schematic diagram of the apparatus

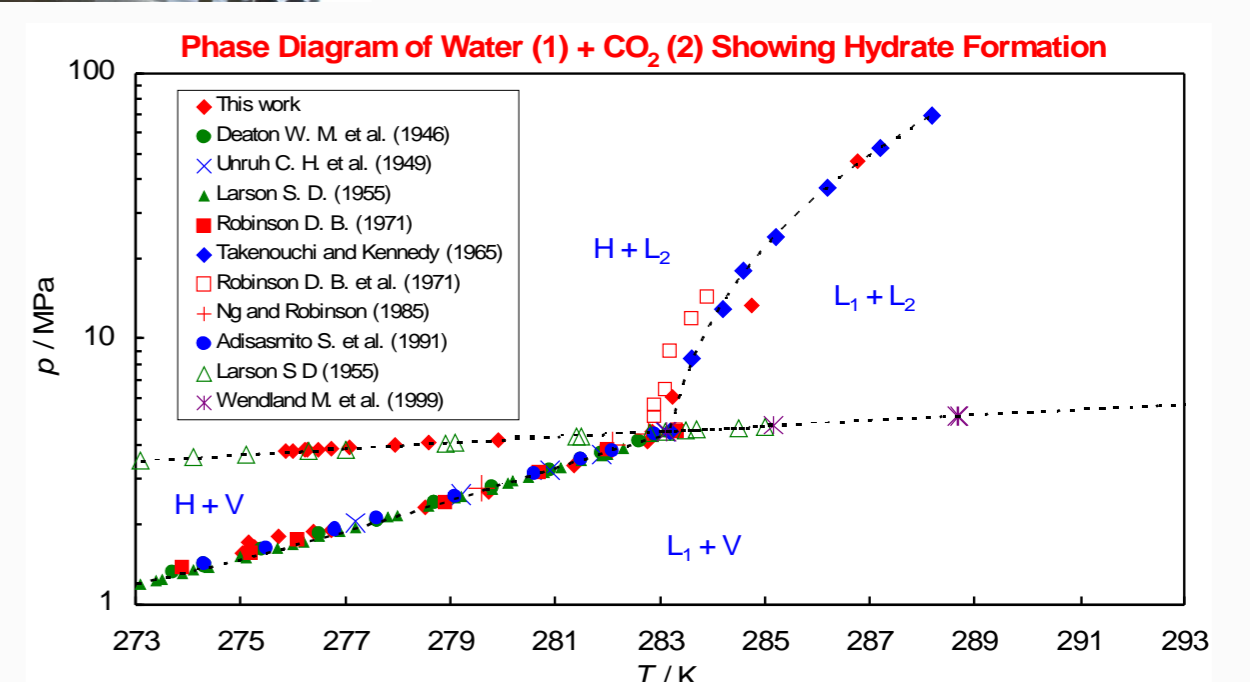
- Specifications:
- Temperature range: 253 to 423 K
 - Pressure range: 0.5 to 45 MPa



Thermal bath
Gas Chromatograph
Liquid displacement pump



Six-port valves
High pressure view-cell with sampling capillaries and electronically-actuated six-port valves for the analysis of phases by gas chromatography
Capillary sampling loops

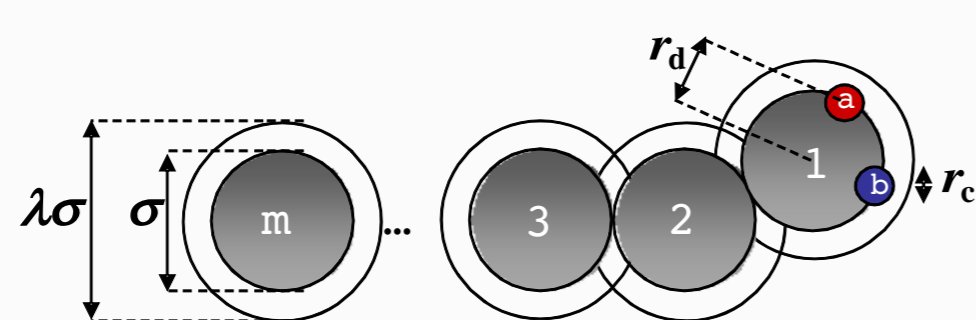


Molecular modelling

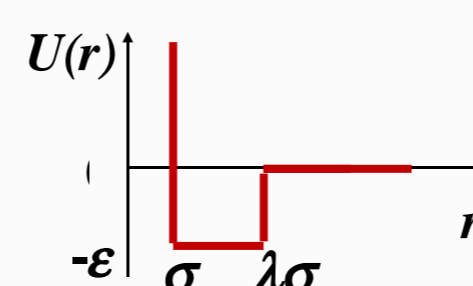
SAFT-VR (Statistical Associating Fluid Theory-Variable Range) [1-3]

Molecular based equation of state predicts bulk properties
Written in terms of free energy (A) from which all thermodynamic properties can be obtained

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



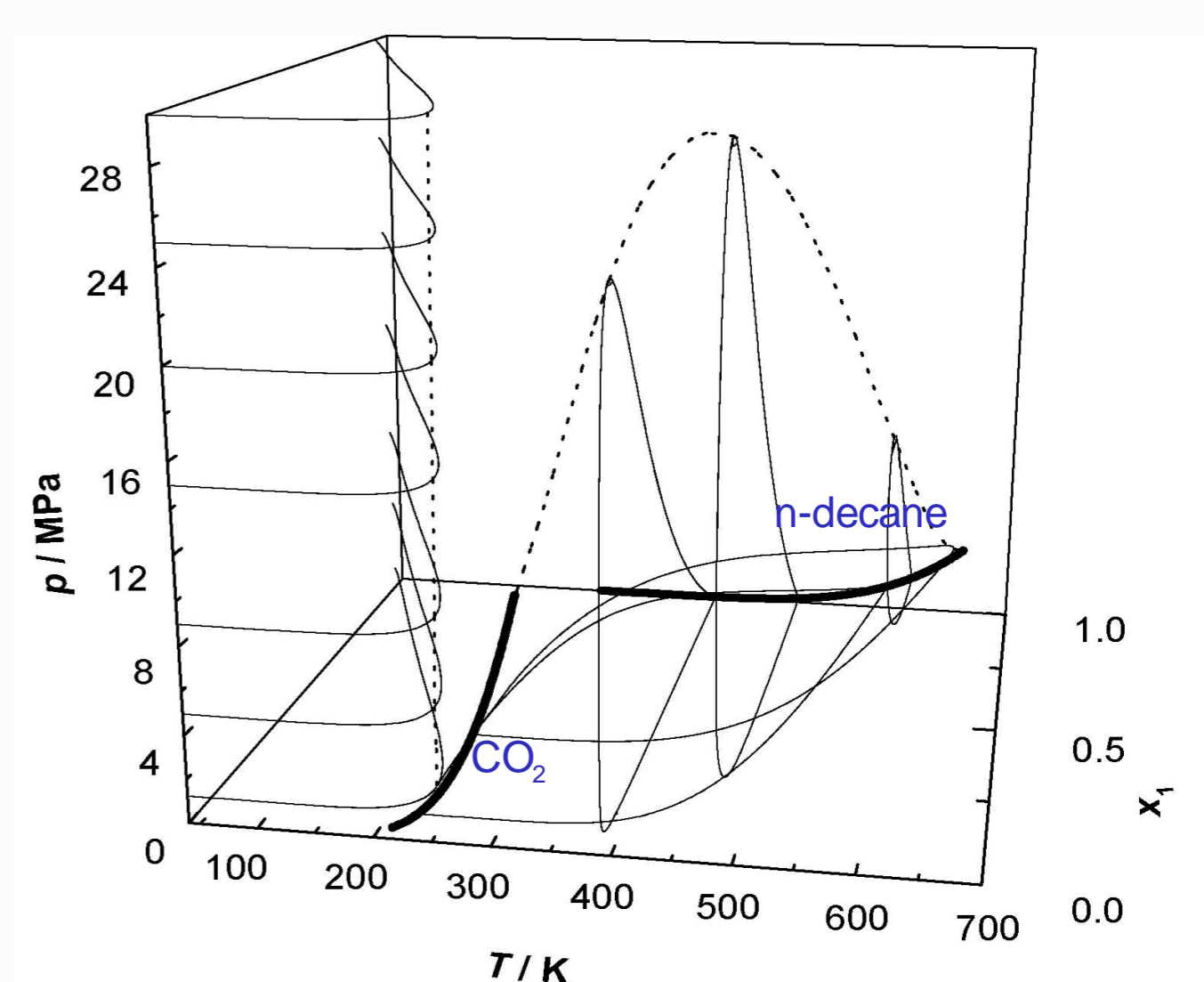
Intermolecular interactions described by means of an square-well potential



Pure components described by

$m_i, \sigma_i, \epsilon_i, \lambda_i, \epsilon_{HBijab}, r_{cijab}$ & 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) + CO₂ (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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3. Gil-Villegas, Galindo, Whitehead, Mills, Jackson, Burgess, *J. Chem. Phys.*, **106**, 4168(1997)