

APM 2013

The Advanced Process Modelling Forum

17-18 April 2013, London

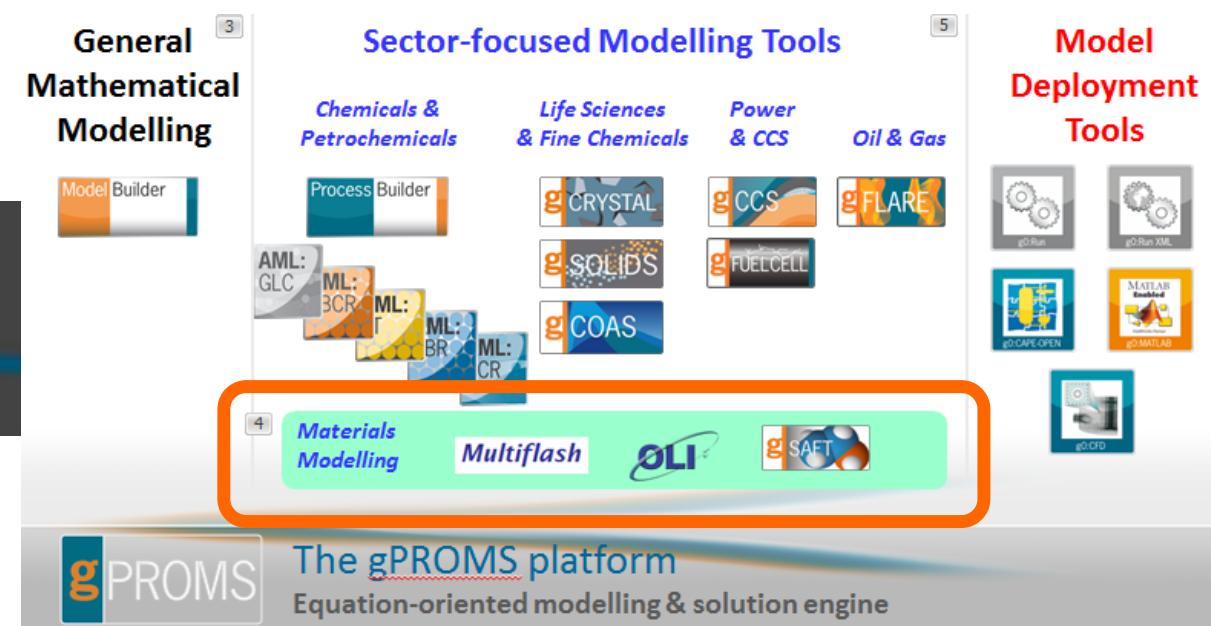


gSAFT Advanced Thermodynamics From theory to industrial application

Javier Rodriguez – Consultant, Power & CCS

- Physical properties in gPROMS
- SAFT- γ Mie Equation of State
- gSAFT technology
- Application: Compression/transmission in gCCS
- Ongoing work

Physical properties in gPROMS



■ gPROMS Properties

- based on Multiflash®+ DIPPR®
- used within most gPROMS-family products

■ OLI®

- aqueous and mixed solvent electrolytic systems

■ CAPE-OPEN thermo physical property interface

- allows access to Aspen Properties® and other CAPE-OPEN compliant physical property systems



■ Next-generation physical properties technology

■ Based on SAFT- γ Mie equation of state

– Theory developed by Molecular Systems Engineering group at Imperial College London

Objective: Unified & consistent physical properties across gPROMS-family products



Multiple phases...



Gas
Liquid



Gas
Liquid



Gas
Liquid
(Solid)



Gas
Liquid
Hydrate



Solid
(Liquid)
(Gas)



Liquid
Solid



Liquid
Solid
Micelle

Complex materials & challenging behaviour...

*strongly-associating
compounds*

*near-critical
point behaviour*

*acids
& bases*

*oligomers
& polymers*

*complex gas/liquid
phase envelopes*

*salts &
salt hydrates*

ions

Objective: Unified & consistent physical properties across gPROMS-family products



Process Lifecycle

Fundamental Process R&D

Optimal selection of “auxiliary” process materials (solvents, entrainers, etc.)

Process Development

Good predictive capability with little or no experimental data

Plant Design

Accurate calculation of physical properties over wide ranges of conditions

Plant Operations

Accurate calculation of physical properties over wide ranges of conditions

Requirement:
Fundamental basis on molecular interactions

Requirement:
**Information (e.g. parameter values)
transferable from one compound to another**



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SAFT- γ Mie Equation of State

SAFT: Chapman, Gubbins, Jackson, Radosz, *Ind. Eng. Chem. Res.*, 29, 1709 (1990)

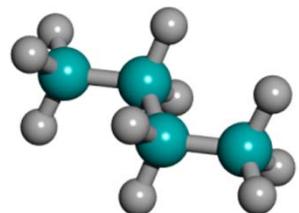
SAFT-VR: Gil-Villegas, Galindo, Whitehead, Mills, Jackson, Burgess, *J. Chem. Phys.*, 106, 4168 (1997)

SAFT- γ : Lymeriadis, Adjiman, Jackson, Galindo, *Fluid Phase Equilib.*, 274, 85 (2008)

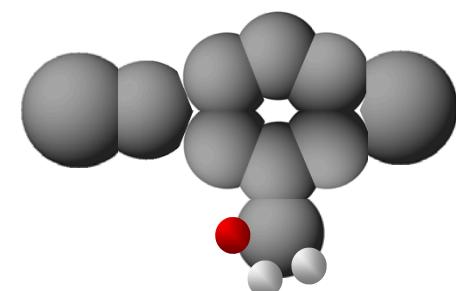
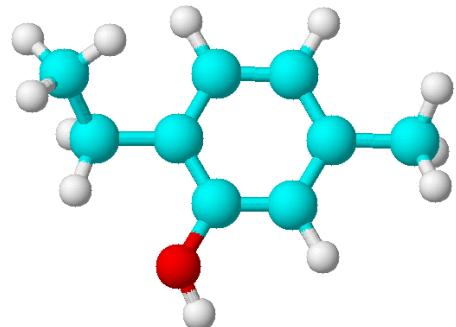
SAFT- γ Mie: Papaioannou, Lafitte, Avendaño, Adjiman, Jackson, Muller, Galindo, *in preparation* (2013)

- Each molecule comprises one or more (generally non-identical) functional groups

n-butane

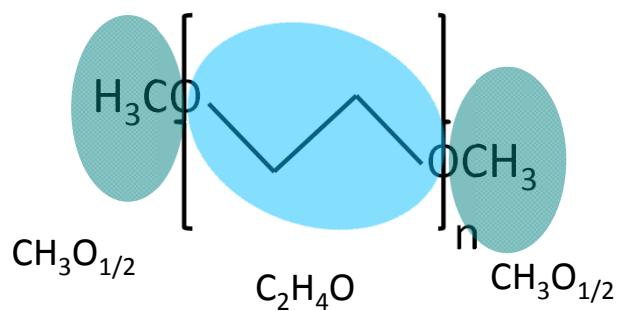


2-ethyl-5-methylphenol



polyethylene glycol

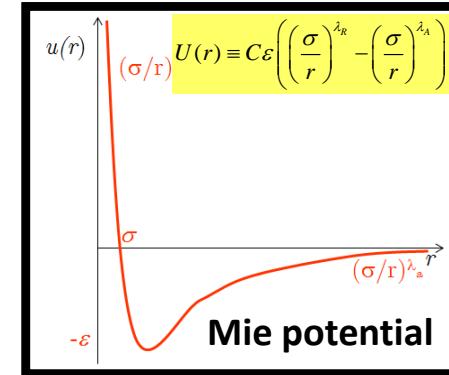
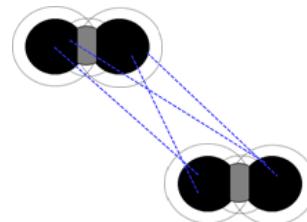
dimethyl ether (PEGDME)



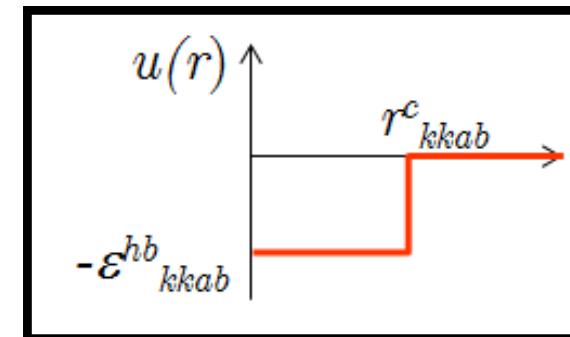
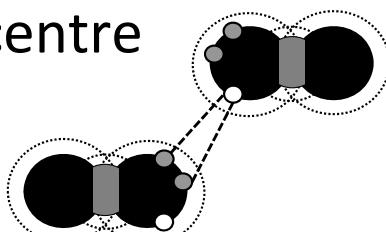
- Each group comprises one or more identical segments

- Interactions

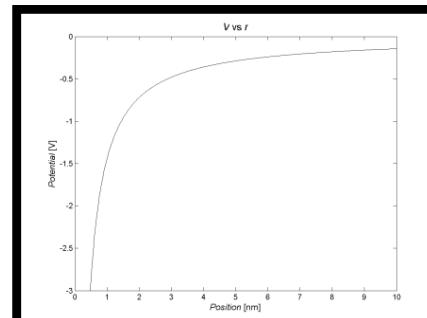
- dispersion/repulsion (van der Waals) forces between segments



- hydrogen bonding via off-centre electron donor/acceptor (“association”) sites

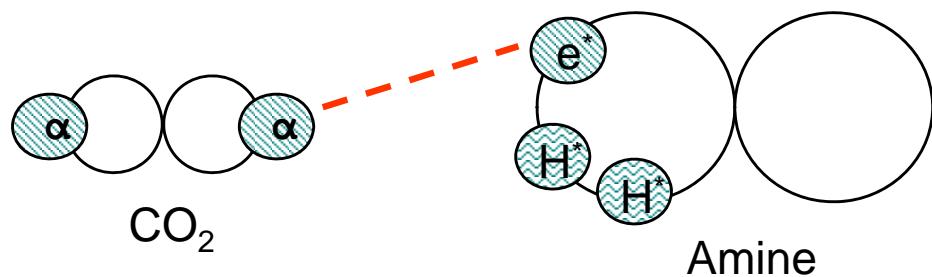


- ionic (coulombic) forces



- Association is central to SAFT theory
 - represents hydrogen bonding via electron donor/acceptors

- Reactions mediated through association sites
 - new species formed do not need to be considered explicitly
 - reaction products are modelled as aggregates of reactants



The values of the group/group interaction parameters
are assumed to be constant across
different molecules and mixtures
in different phases
under different temperatures, pressures and compositions

An approximation

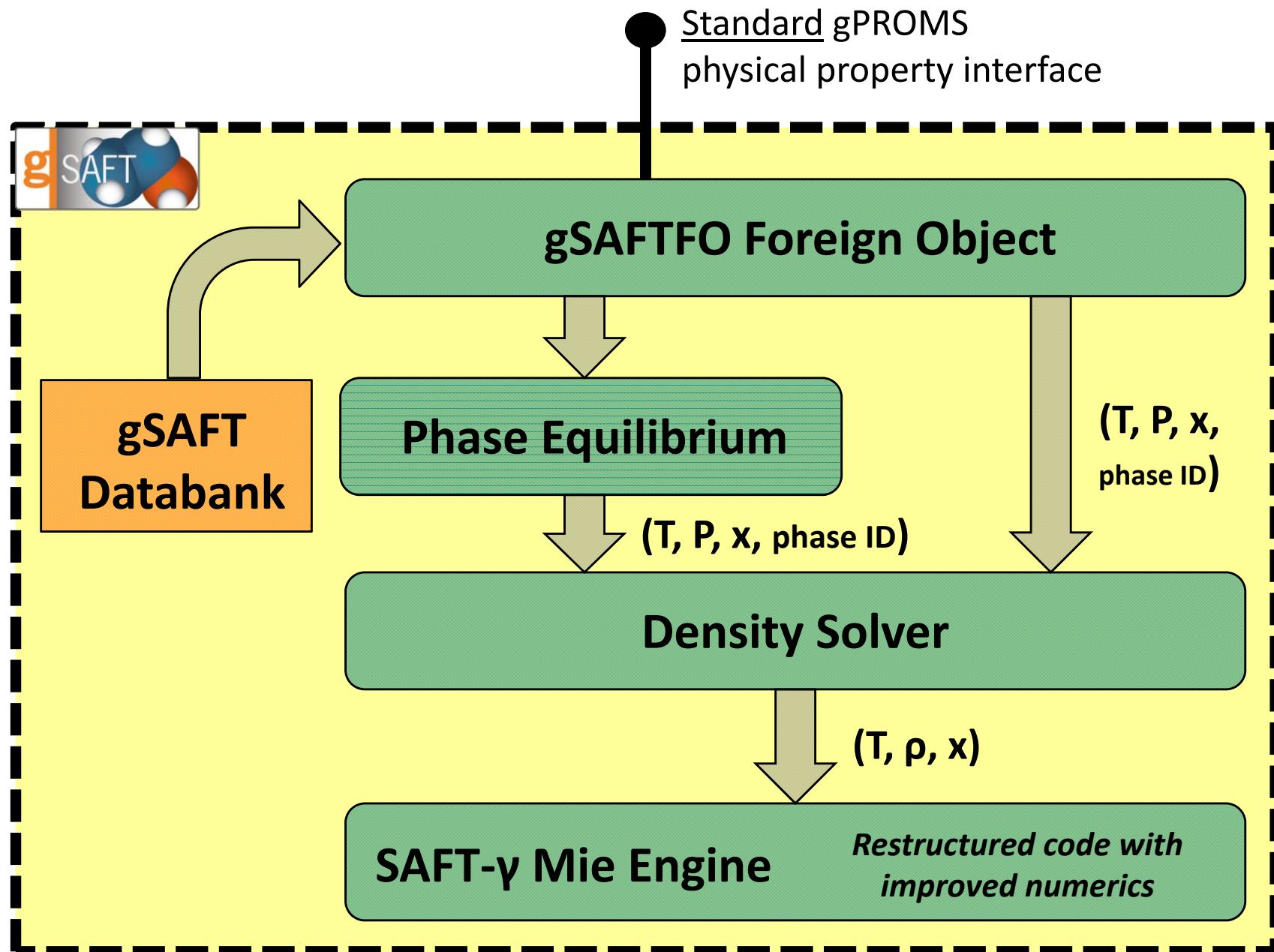
- based on SAFT- γ Mie's fundamental molecular basis
- supported by practical evidence

gSAFT technology

SAFT- γ -Mie in gPROMS

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gSAFT implementation



The gSAFT Databank

Structure



GROUPS

- Shape factor
- Number of segments
- Segment size
- Mie potential parameters
 - interaction energy
 - attractive & repulsive exponents
- Zero or more types of association sites, each characterised by
 - number of sites
 - association energy
 - association range
- Electrostatic charge, q

UNLIKE GROUP PAIRS

- Mie potential parameters
 - Cross- interaction energy
 - attractive & repulsive exponents
- Association sites
 - association energy
 - association range

N.B. Any missing parameters are approximated via combining rules

COMPOUNDS

- Numbers of groups of each type

The gSAFT Databank

Implementation: xml file



```
 TEXT FILE CO2_H2.xml (Mixture_Estimation_CO2_H2_official_FO_xml)
1 <gsaft>
2 <compounds>
3   <compound name = "CO2">
4     <group multiplicity = '1'>CO2</group>
5   </compound>
6   <compound name = "H2">
7     <group multiplicity = '1'>H2</group>
8   </compound>
9 </compounds>
10 <groups>
11 <group name = 'CO2'>
12   <mw>44.0095</mw>
13   <heatCapacity type = 'polynomial'>
14     <a>19.80</a>
15     <b>7.344e-2</b>
16     <c>-5.602e-5</c>
17     <d>1.715e-8</d>
18   </heatCapacity>
19   <numberOfSegments>2</numberOfSegments>
20   <shapeFactor>0.847</shapeFactor>
21   <groupInteraction>
22     <lambdaRepulsive>26.408</lambdaRepulsive>
23     <lambdaAttractive>5.055</lambdaAttractive>
24     <sigma>3.05E-10</sigma>
25     <epsilon>207.89</epsilon>
26   </groupInteraction>
27 </group>
28 <group name = 'H2'>
29   <mw>2.01588</mw>
30   <heatCapacity type = 'polynomial'>
31     <a>27.14302</a>
32     <b>-0.009274</b>
33     <c>-1.4e-5</c>
34     <d>7.65e-9</d>
35   </heatCapacity>
```

Standard databank
provided
as part of gSAFT

The gSAFT Databank

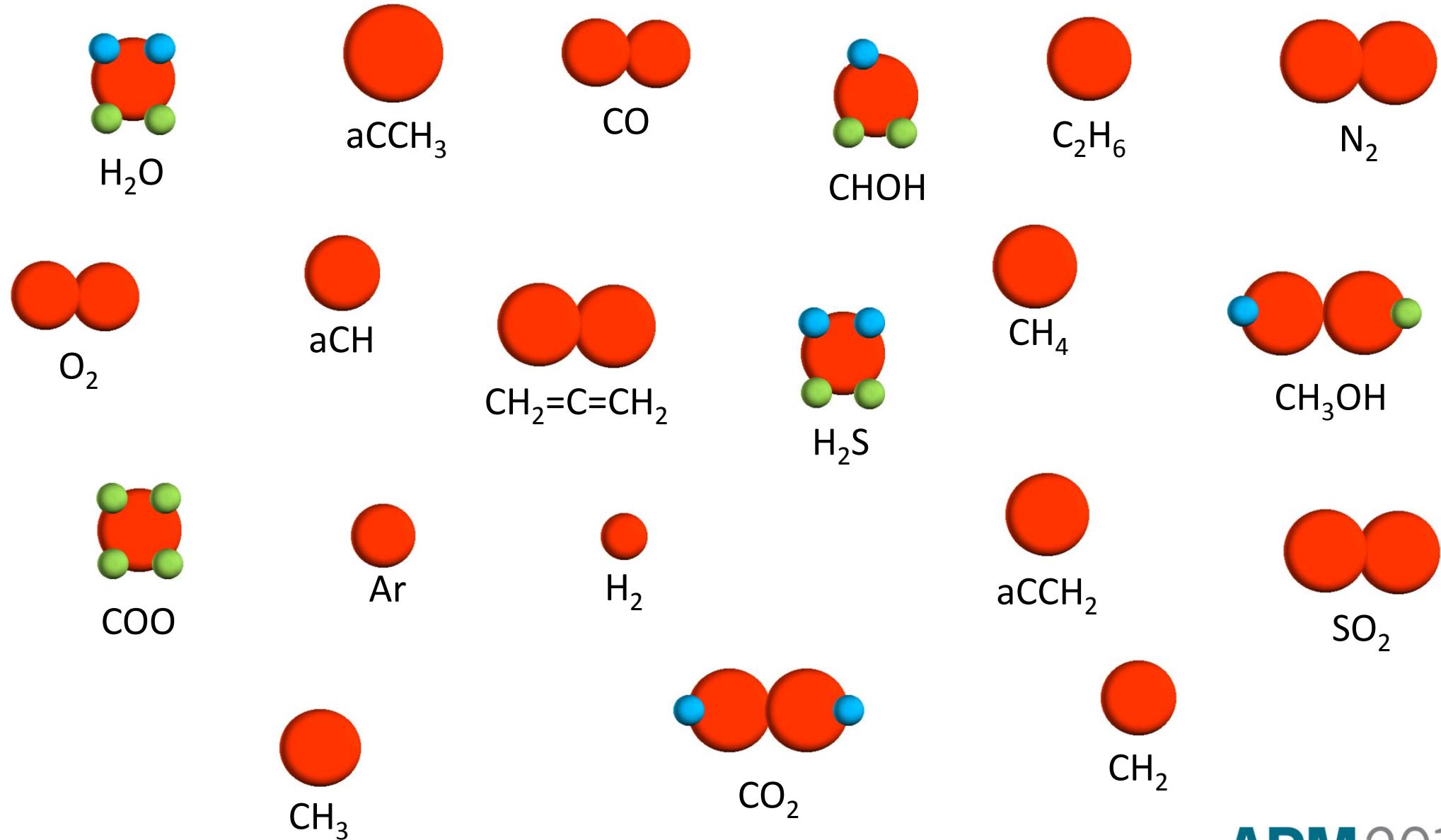
Parameter estimation



- Group parameters preferably estimated from pure component experimental data
 - vapour pressure and saturated liquid densities
 - typically: 30%-90% of the experimental critical temperature
- Both “like” and “unlike” group interaction parameters may be obtained from pure component data
 - e.g. data for n-alkanes may be used to obtain parameters for CH₃ group, CH₂ group and CH₃/CH₂ cross-interactions
- Binary mixture data (e.g. phase envelopes) also used to obtain
 - “unlike” group/group interaction parameters that cannot be obtained from pure component data
 - e.g. because no data are available for a molecule that contains both groups
 - “like” group/group interactions for groups which do not appear in molecules for which suitable pure component data are available, e.g.
 - H₂ parameters from data for H₂/CO₂ mixtures
 - Na⁺ and Cl⁻ parameters from data for aqueous NaCl solutions

The gSAFT Databank

Current contents

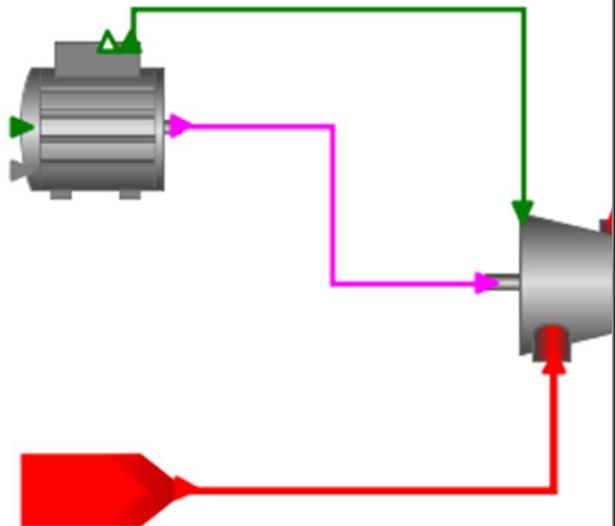


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gSAFT technology Use within gPROMS



ElectricDrive



SourceCO₂

MODEL CompressorSection (aCCS CO₂ Compression-Liquefaction)

1 PARAMETER

2 PUBLIC co

3 PRIVATE ph

4 Ns

5 NP

6

7 # Foreign O

8 # interpolat

9 # interpolat

10 # interpolat

11 # interpolat

12 # interpolat

13 # interpolat

14 #####

15 co

16 #####

17 # Interpolat

18 PRIVATE la

19 PRIVATE la

20

21 # Scale fact

22 PRIVATE ph

23 PRIVATE ps

24 PRIVATE he

25

26 # Non prop

27 PRIVATE ph

28 PRIVATE d_

29 PRIVATE d_

30 PRIVATE v_

31

32 # Non prop

33 num

34 p_

35 p_

36 F_

37 T_

38 w_

39 w_

40

CO₂

CO₂Source_1 (SourceCO₂)

Cumulative flow Don't track cumulative flow

Property calculation Gas

Composition specification Molar basis

Specify... Both pressure and flowrate

Flowrate basis Mass flowrate

Specify

Physical properties "gSAFTFO::mass:CO₂_compression_liquefaction.MFL"

Temperature 268.15 K

Mole fraction

Uniform for entire array Per element

Components	mol/mol
H ₂	.0004
CO ₂	.9977
H ₂ O	.0017
N ₂	0
O ₂	0
CO	.0001
H ₂ S	.0002
SO ₂	0
METHANE	0
AR	0

Pressure 1.2e5 Pa

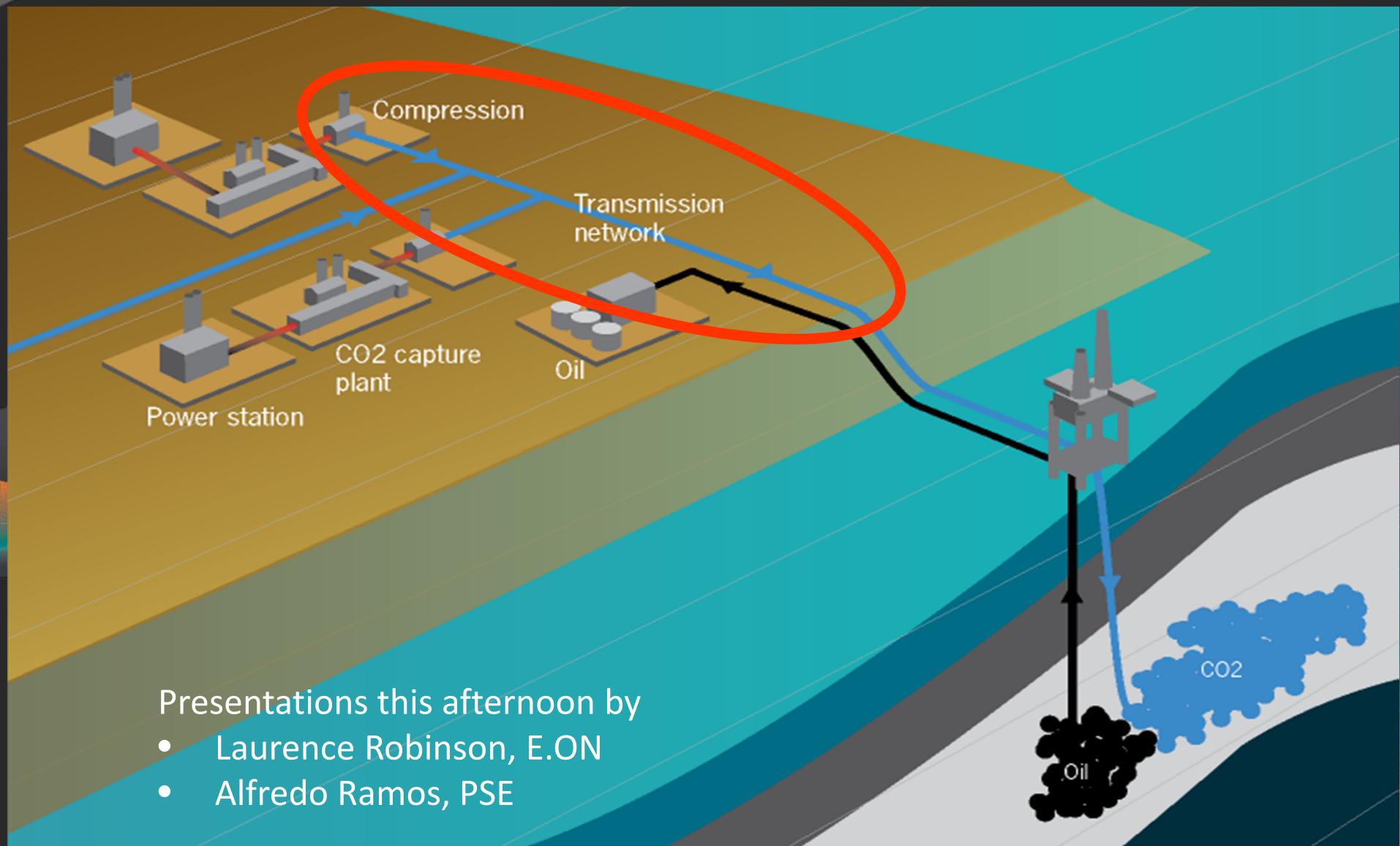
Mass flowrate 208775/3600 kg/s

OK Cancel Reset All Help

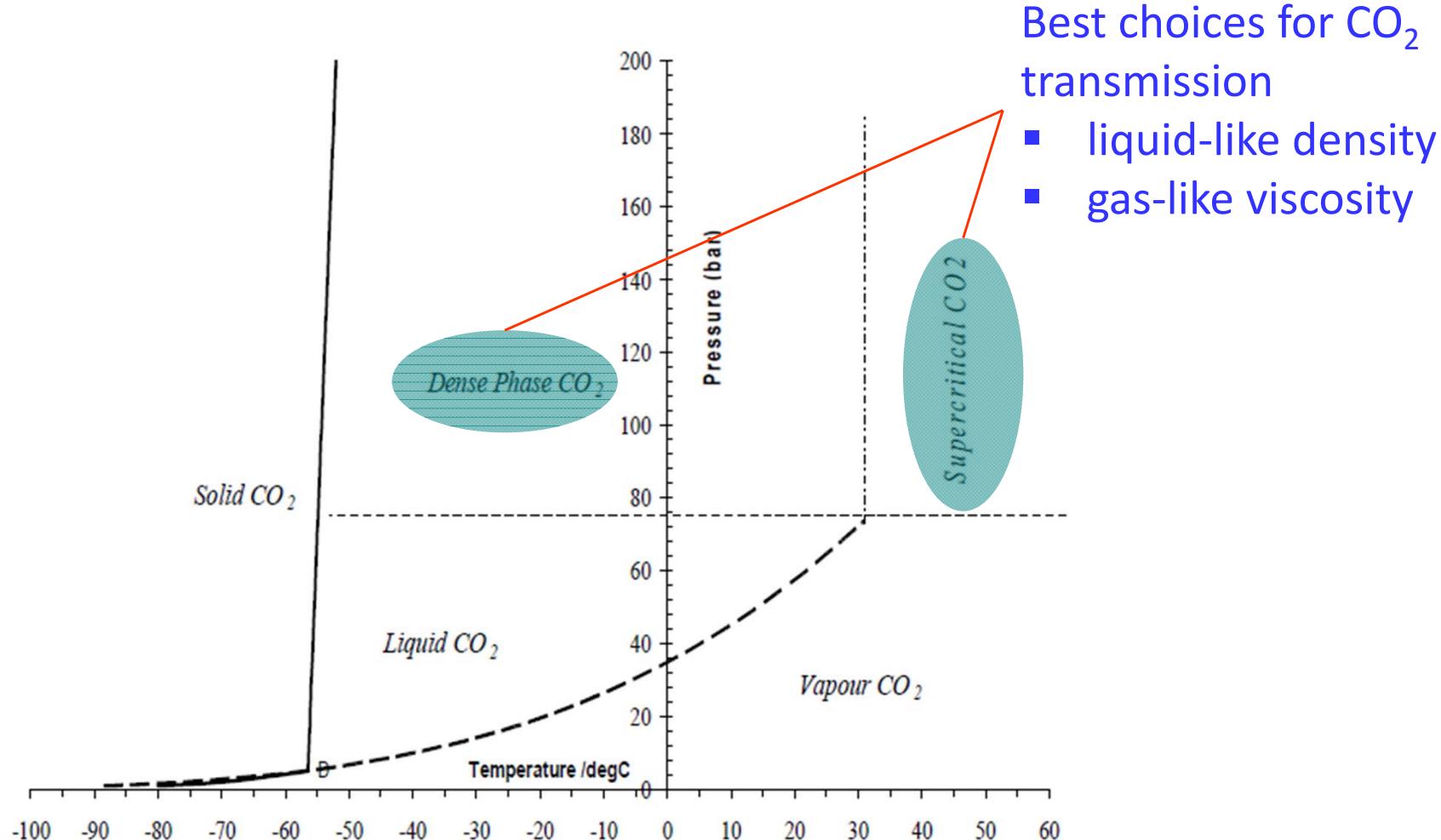
gSAFT for compression/transmission in gCCS

An application example

The gCCS project



Physical properties for compression/transmission in CCS CO₂ phase diagram



Physical properties for pure CO₂ predicted very accurately by Span & Wagner EoS
Span, Wagner. "A new equation of state for carbon dioxide covering the fluid region from the triple-point
temperature to 1100 K at pressures up to 800 MPa."
Journal of physical and chemical reference data 25 (1996): 1509.

Physical properties for compression/transmission in CCS

Challenges I: Impurities



From post-combustion (dry basis):

CO₂ (>99%), N₂ (<0.17%), O₂ (<0.01%), SOx (10 ppmv), traces of Ar

From pre-combustion (dry basis):

CO₂ (>95.6%), H₂S (<3.4%), H₂ (<3%), N₂ (<0.6%), CO (<0.4%), Ar (<0.05%), CH₄ (350 ppmv)

From oxyfuel (dry basis):

CO₂ (>74.66%), N₂ (<15%), Ar (<2.5%), O₂ (<6.15%), SOx (<2.5%), NOx (<0.25%), traces of CO

...plus H₂O

The presence of impurities significantly affects physical properties (densities, phase envelope, critical temperature and pressure,...)

→ impact on compressor/pump power, pipeline capacity, potential for hydrate formation & two phase flow, distance between booster stations...

Physical properties for compression/transmission in CCS

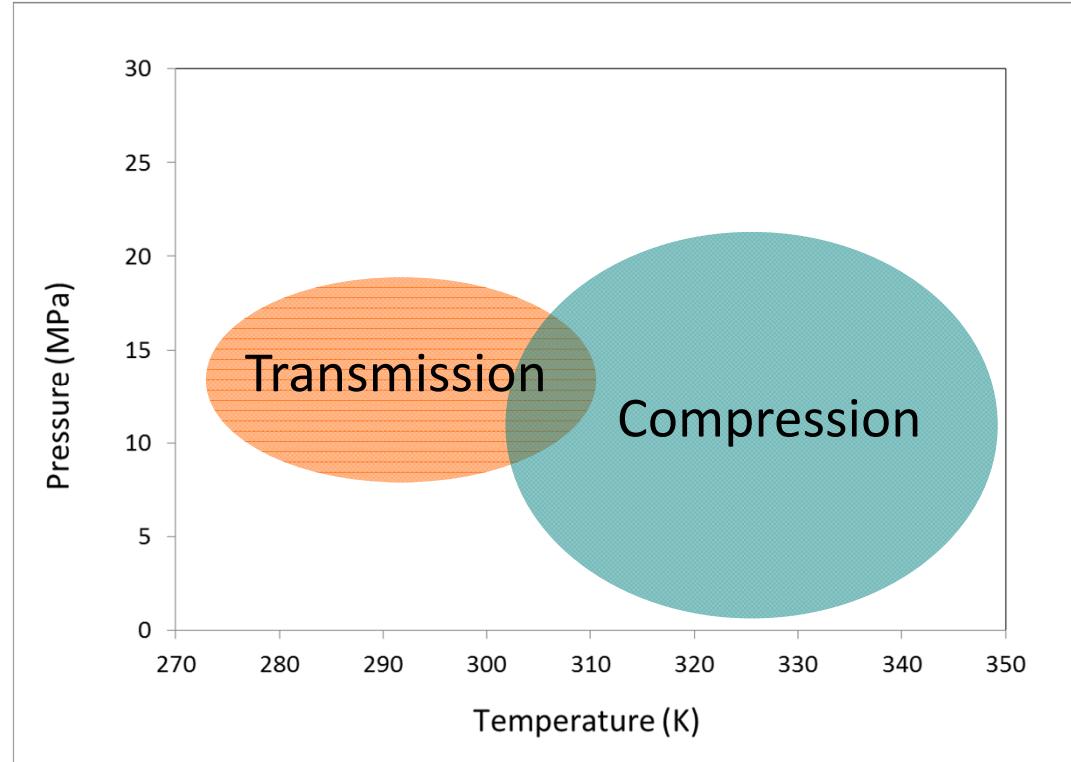
Challenges II: Wide range of conditions

■ Compression subsystem

- Pressures
 - Inlet 0.5 to 5 bara
 - Outlet 10 to 200 bara
- Temperatures
 - Inlet 20-41 °C
 - Outlet 40-130 °C

■ Transmission subsystem

- Pressures
 - 50-200 bara
- Temperatures
 - -5-40 °C



■ Recent literature review of experimental data

- Li, Hailong, et al.
"PVTxy properties of CO₂ mixtures relevant for CO₂ capture, transport and storage: Review of available experimental data and theoretical models."
Applied Energy 88.11 (2011): 3567-3579.

■ Limited range of conditions

■ Gaps for several binary mixtures

- some mixtures (e.g. CO₂-SO₂) are very corrosive
→ experimentation problematic

■ Very scarce data for ternaries and beyond

- useful for validation purposes

- Impurities

- Wide range of conditions

- Limited experimental data



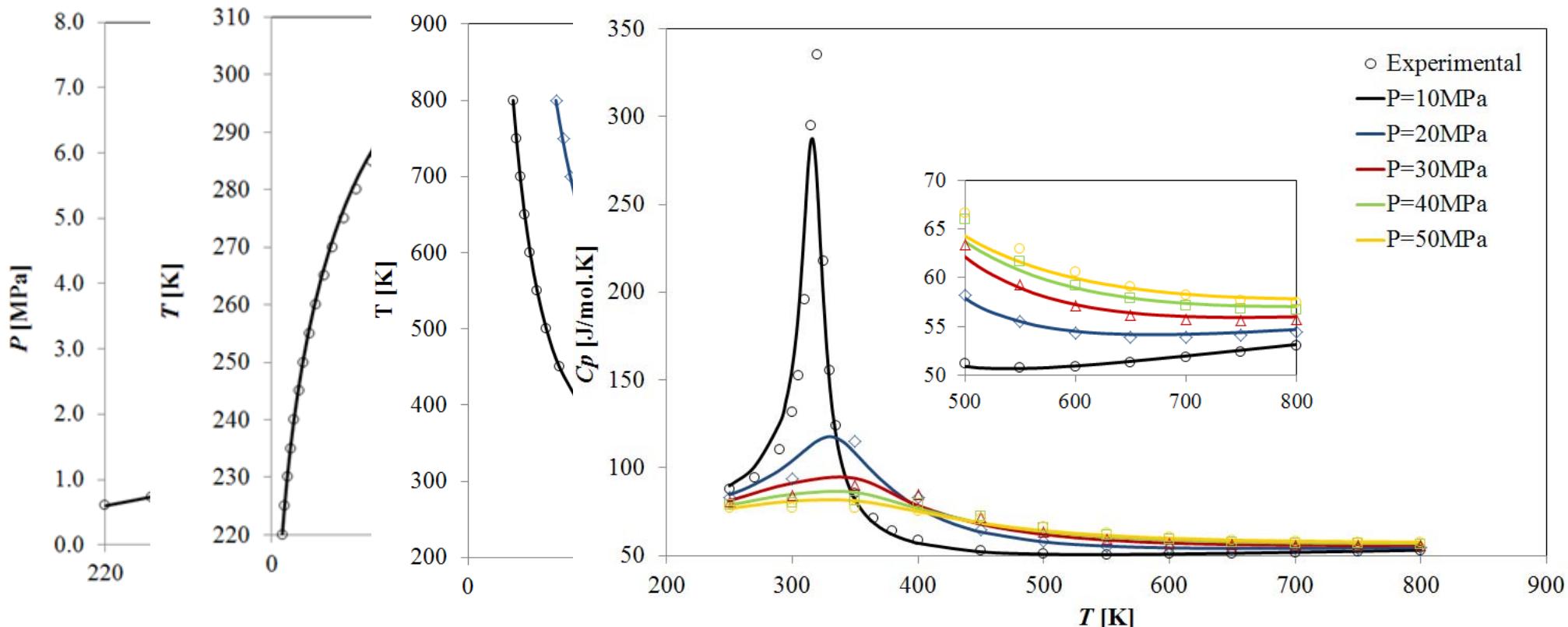
A predictive equation of state is required

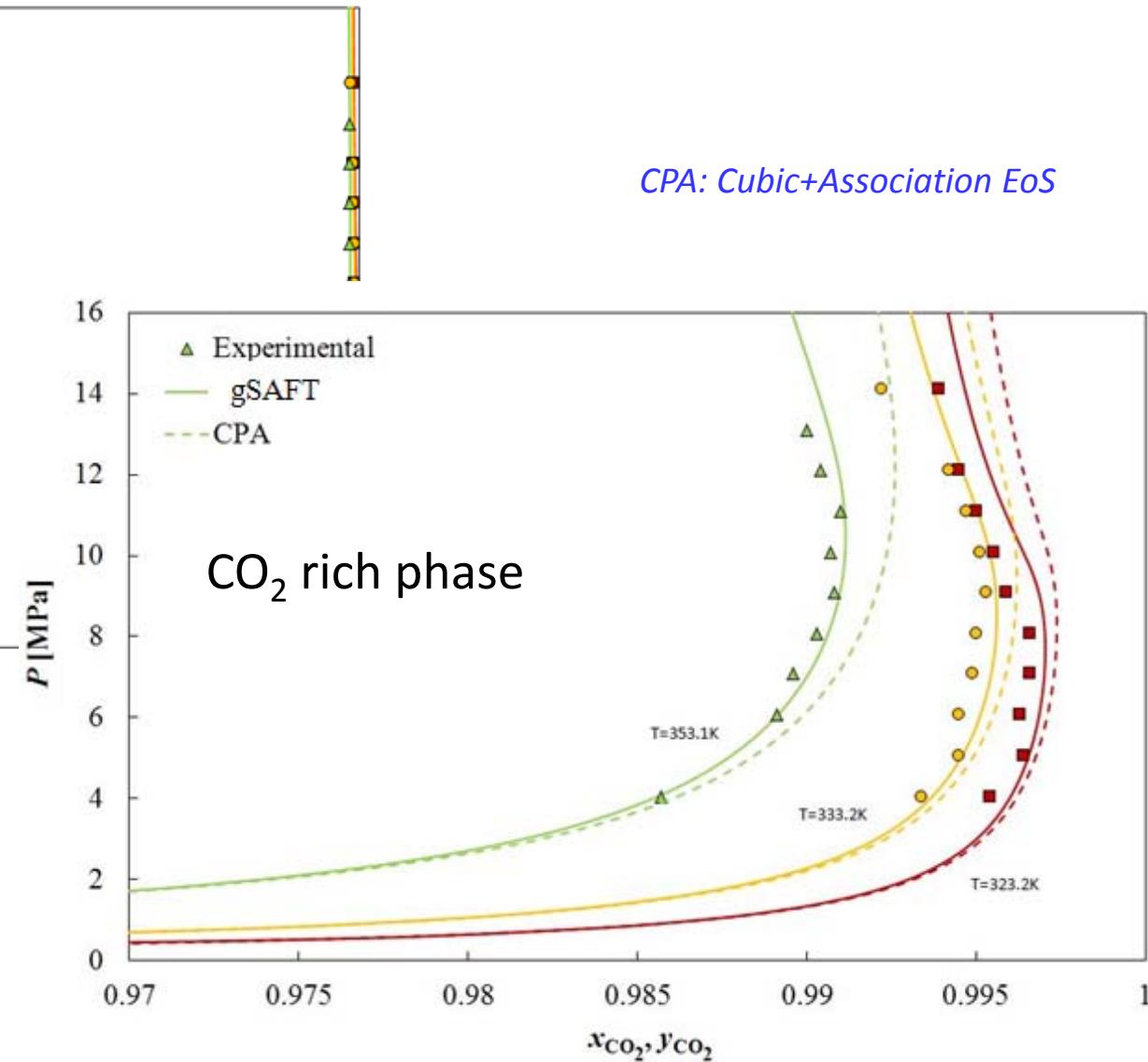
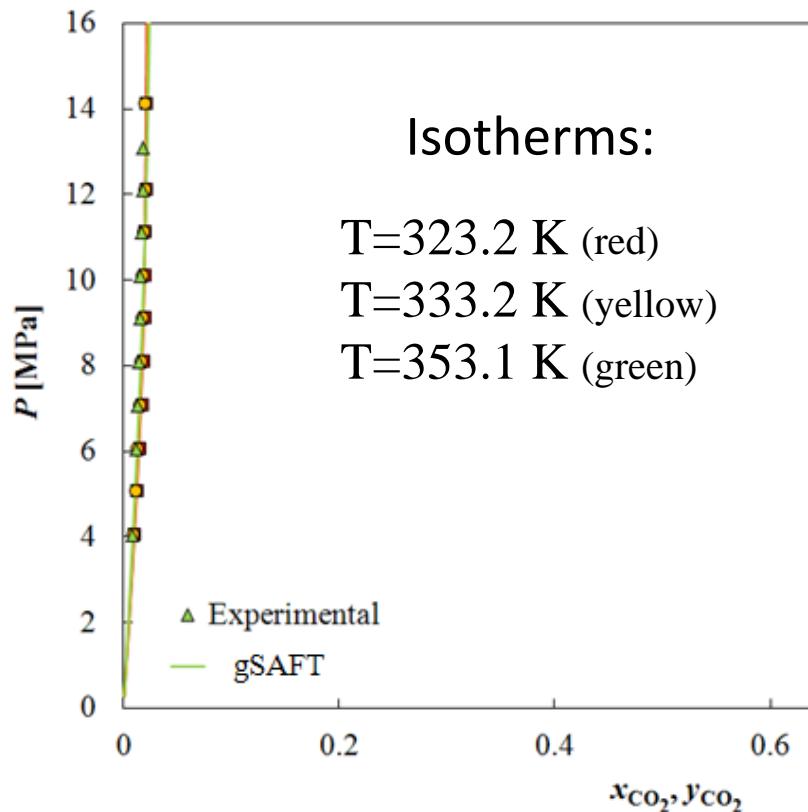


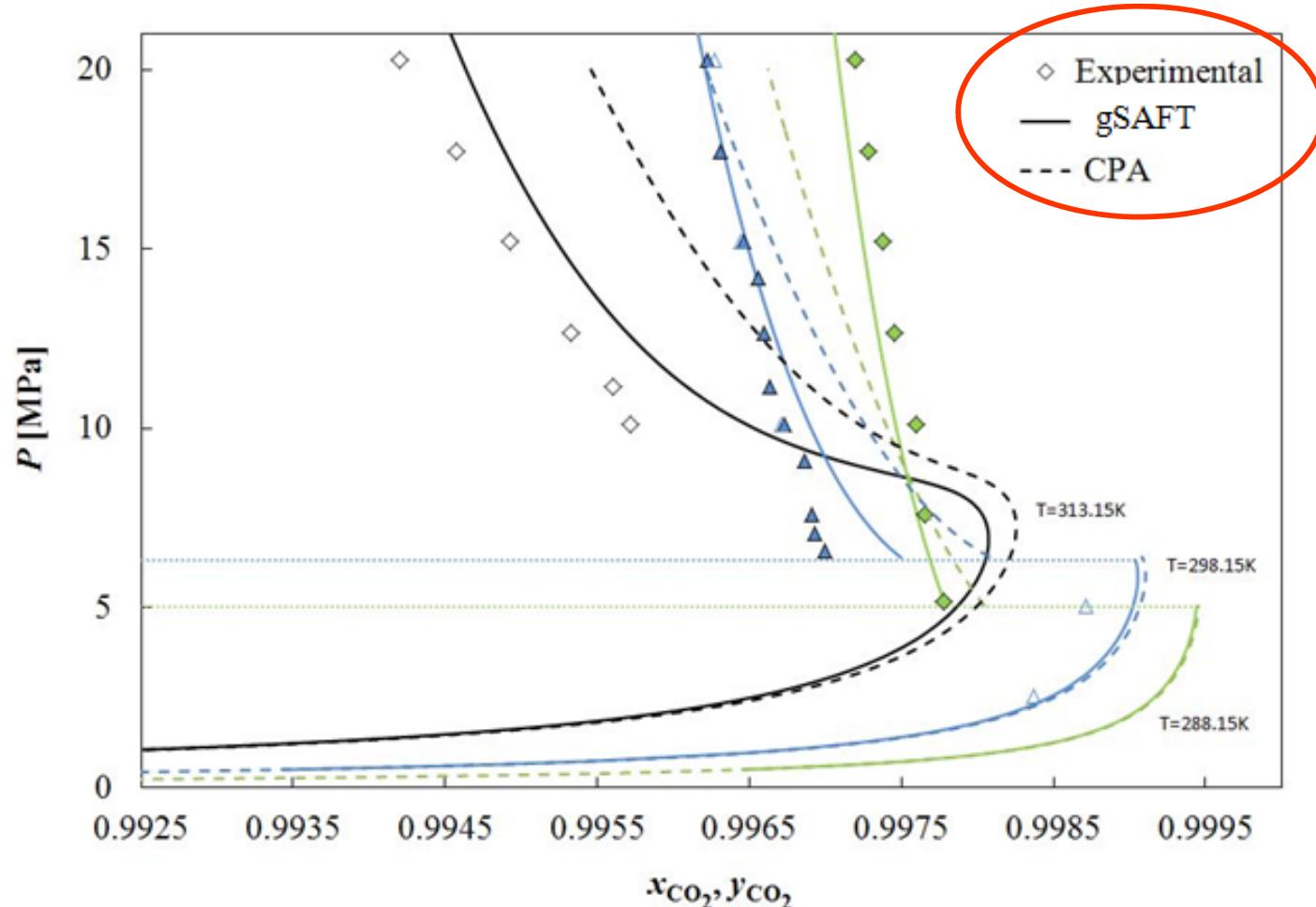
- applied to mixtures of CO₂, CO, H₂O, Ar.....
- small molecules → single group each

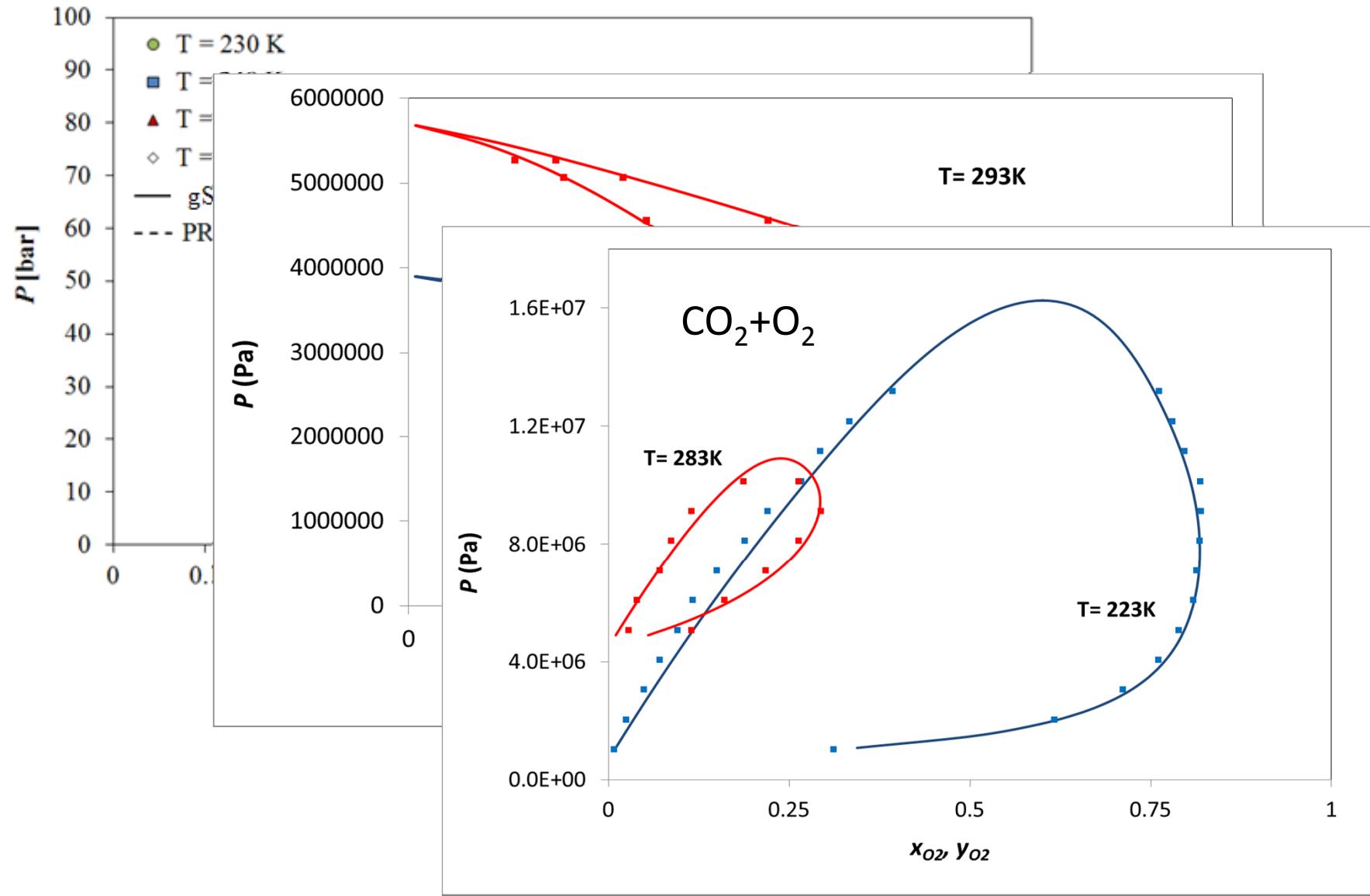
Comparisons: Pure CO₂

Physical property	AAD (%)	Trange [K]	No Data Points
Vapour pressure [MPa]	0.07	220.0 – 300.0	17
Saturated liquid density [kg/m ³]	0.41	220.0 – 300.0	17
Density [kg/m ³]	2.52	250.0 – 800.0	71
Isobaric Heat Capacity [J/mol.K]	3.73	250.0 – 800.0	71

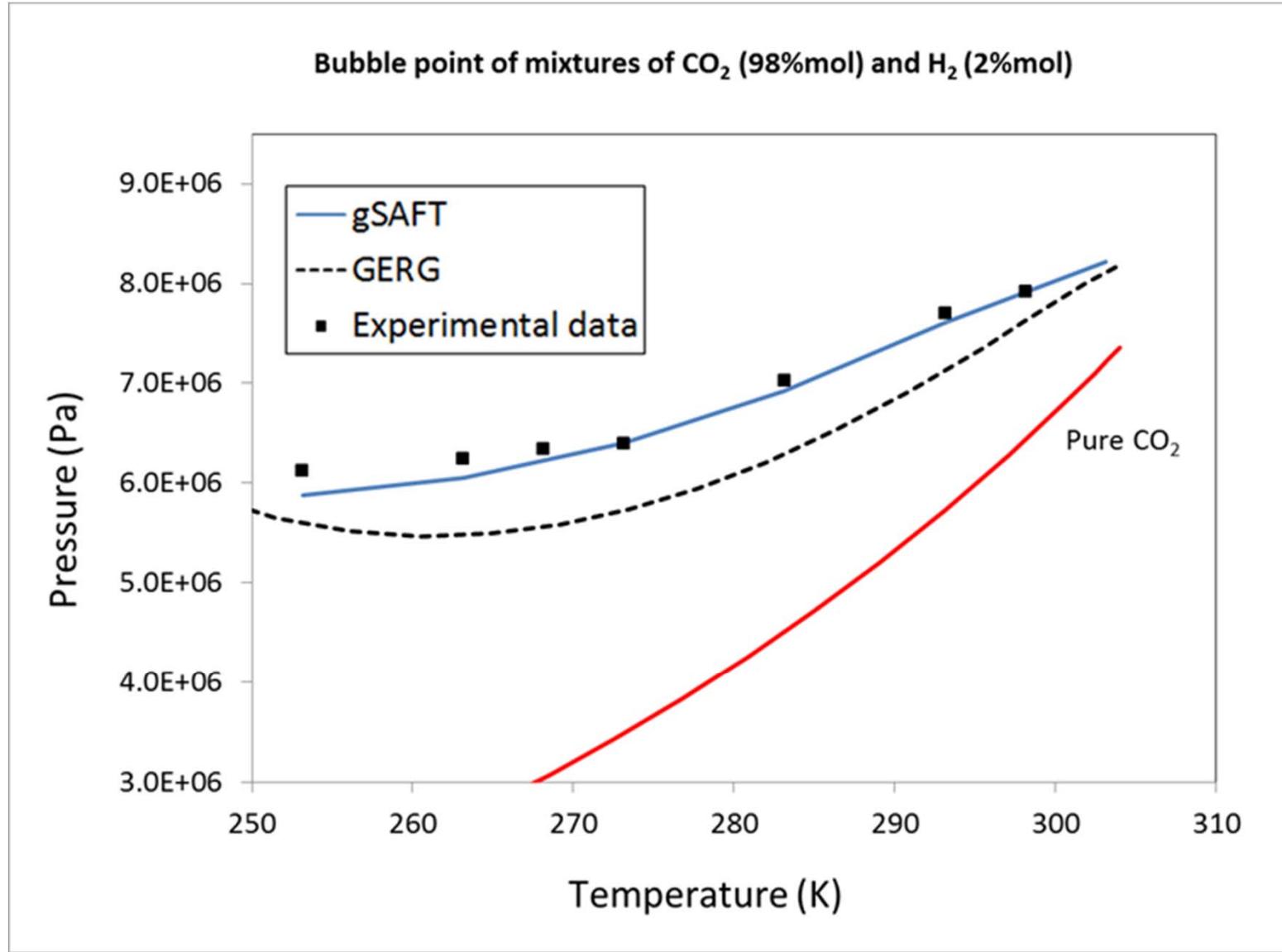


Comparisons: Binary mixture $\text{H}_2\text{O} + \text{CO}_2$ 

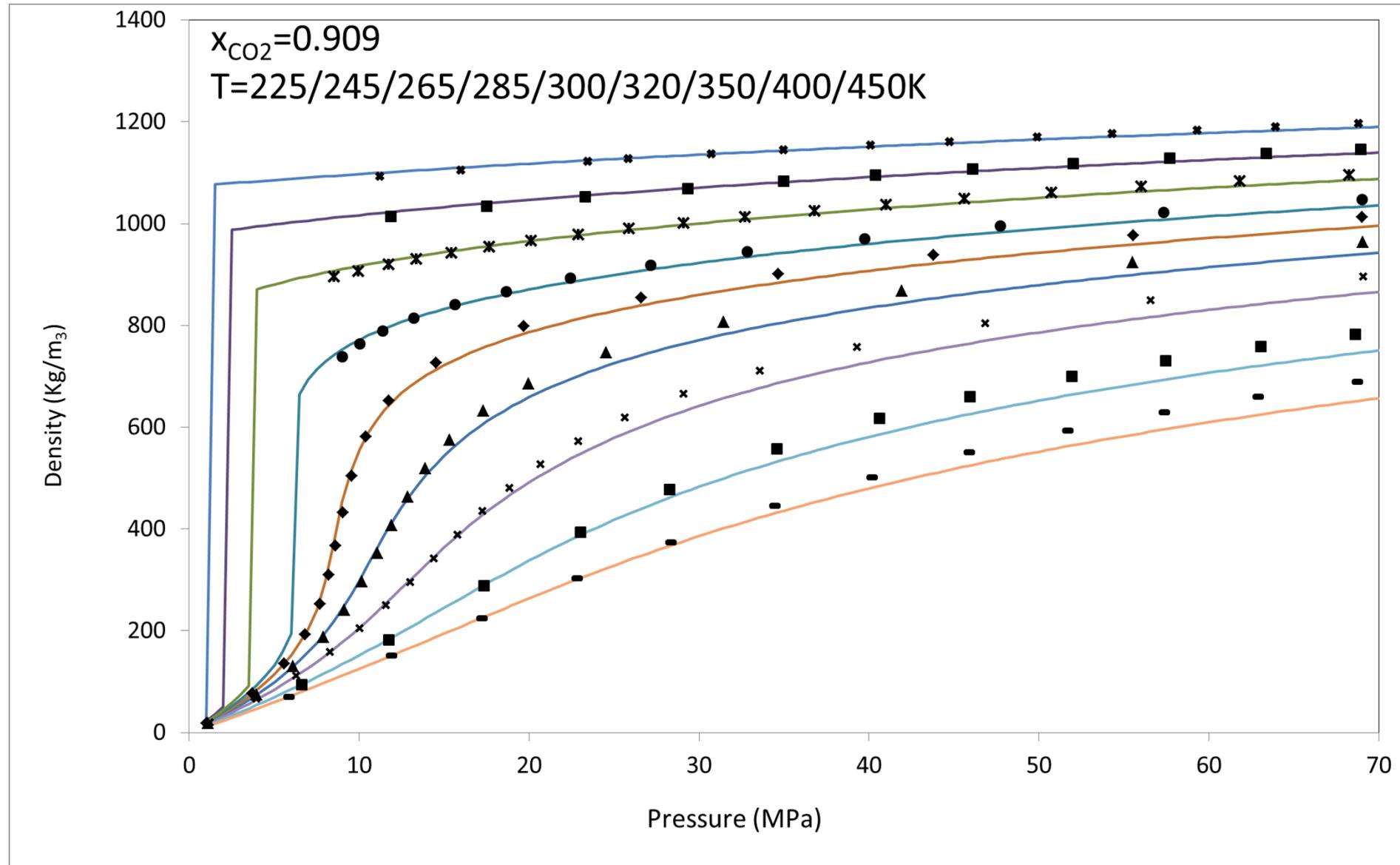
■ CO_2 rich phase – low temperatures

Comparisons: Binary mixtures CO₂+impurities

Predictions for near-pure CO₂: Bubble point of CO₂+H₂



Predictions for near-pure CO₂: CO₂+N₂ densities

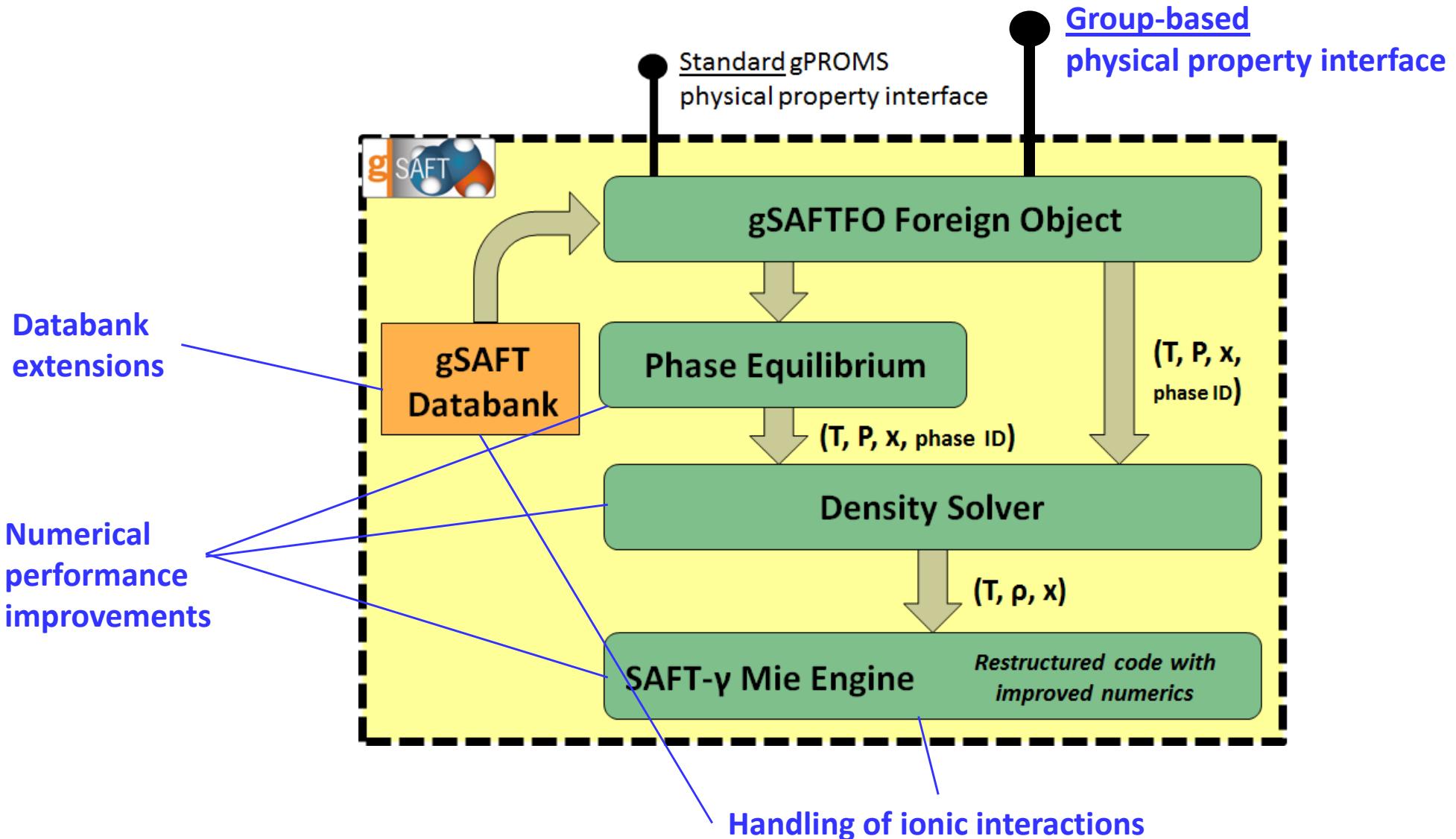




gSAFT: ongoing work

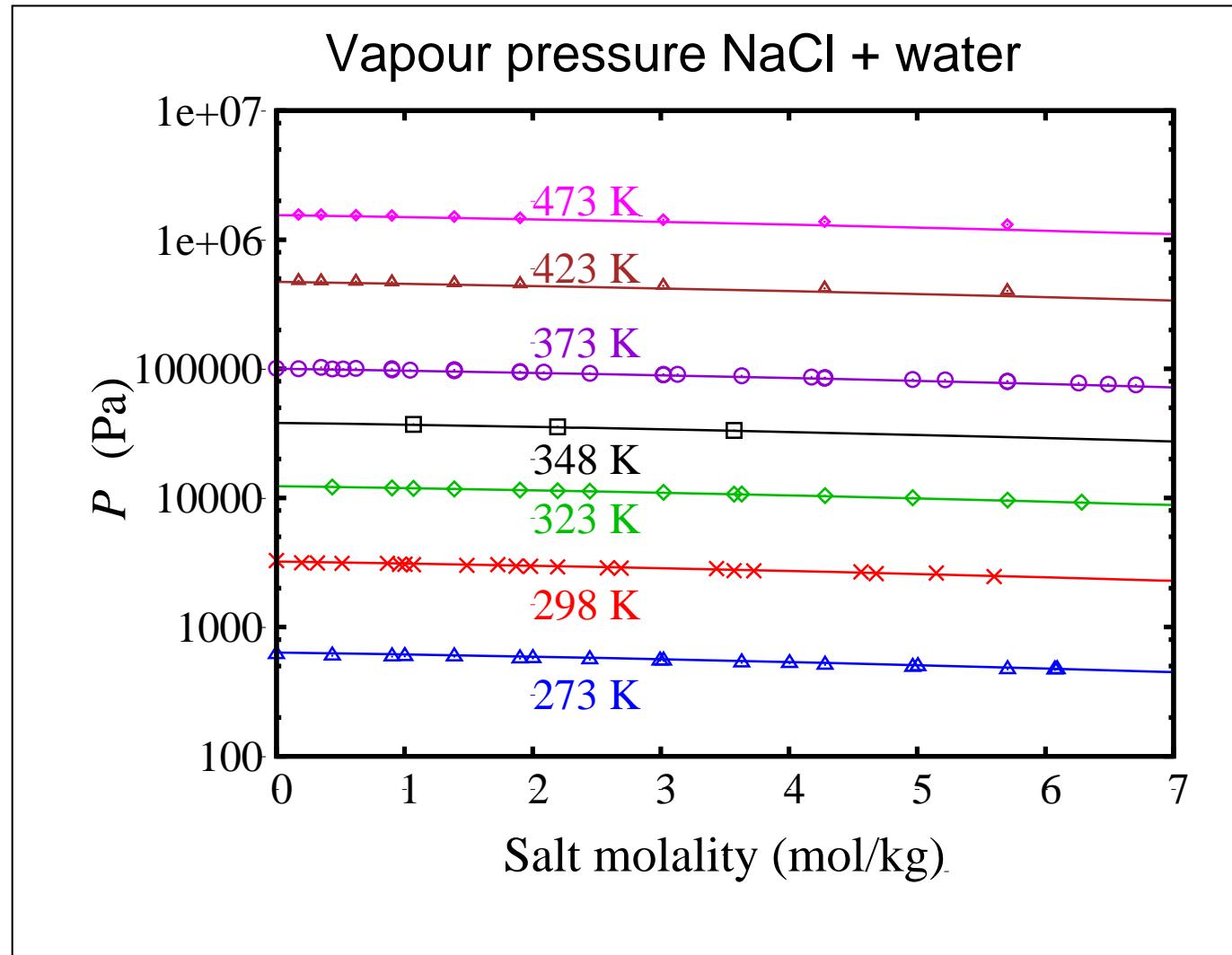
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gSAFT: ongoing work



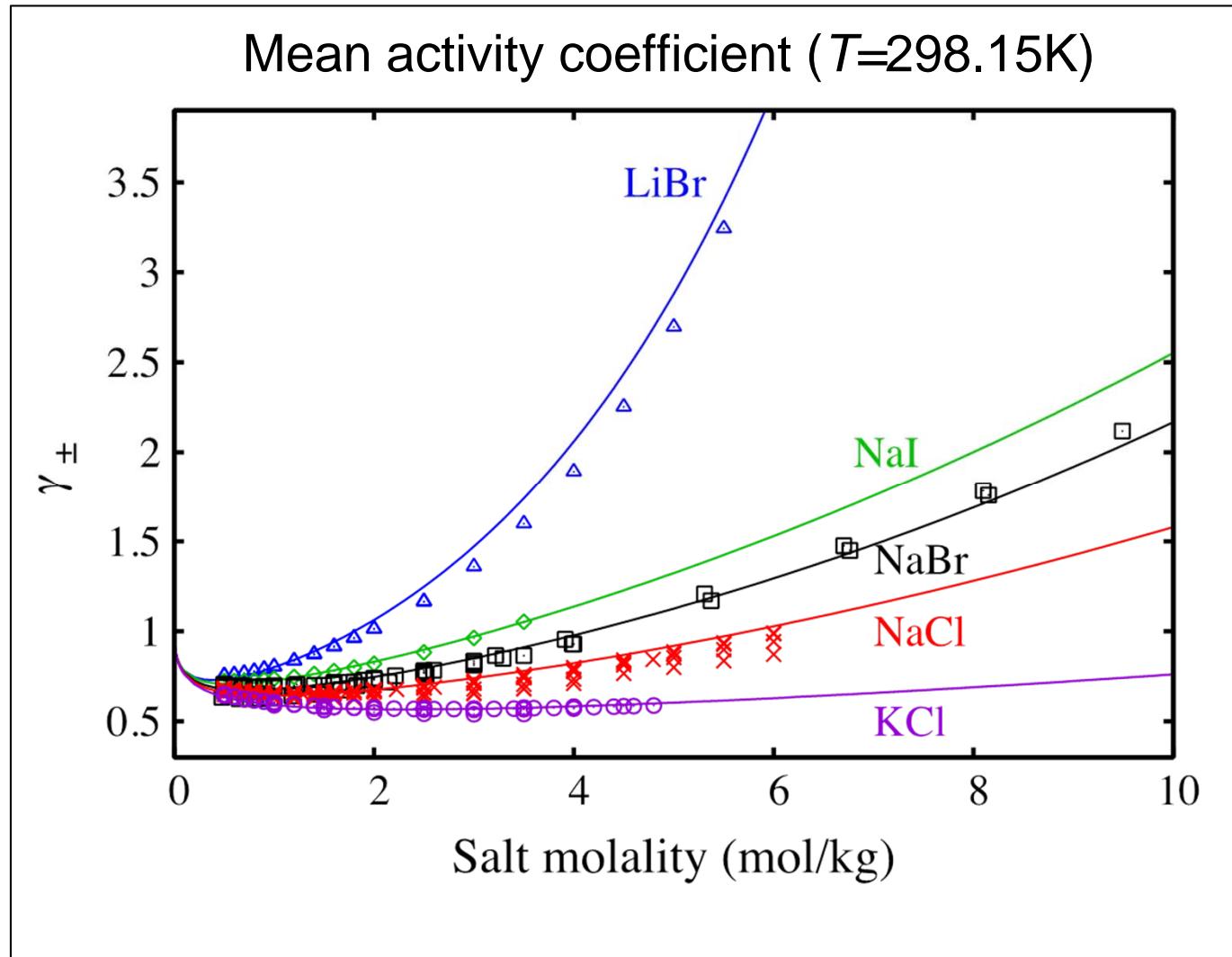
Electrolytes in the SAFT framework

Eriksen, Dufal, Haslam, Adjiman, Galindo, Jackson, "Modelling electrolyte solutions with the SAFT-VRE approach", Internal presentation Imperial College London, 2013



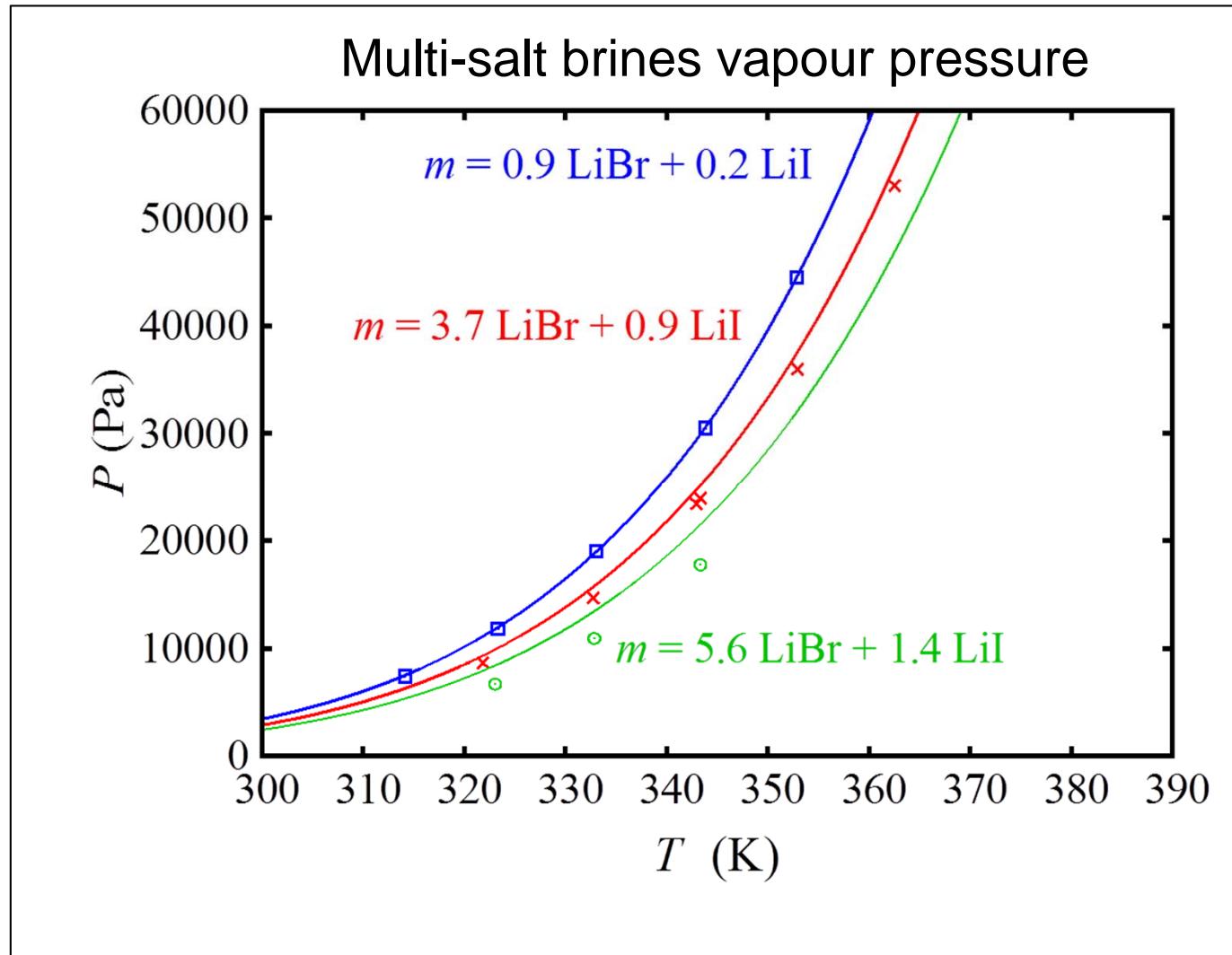
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Thank you!

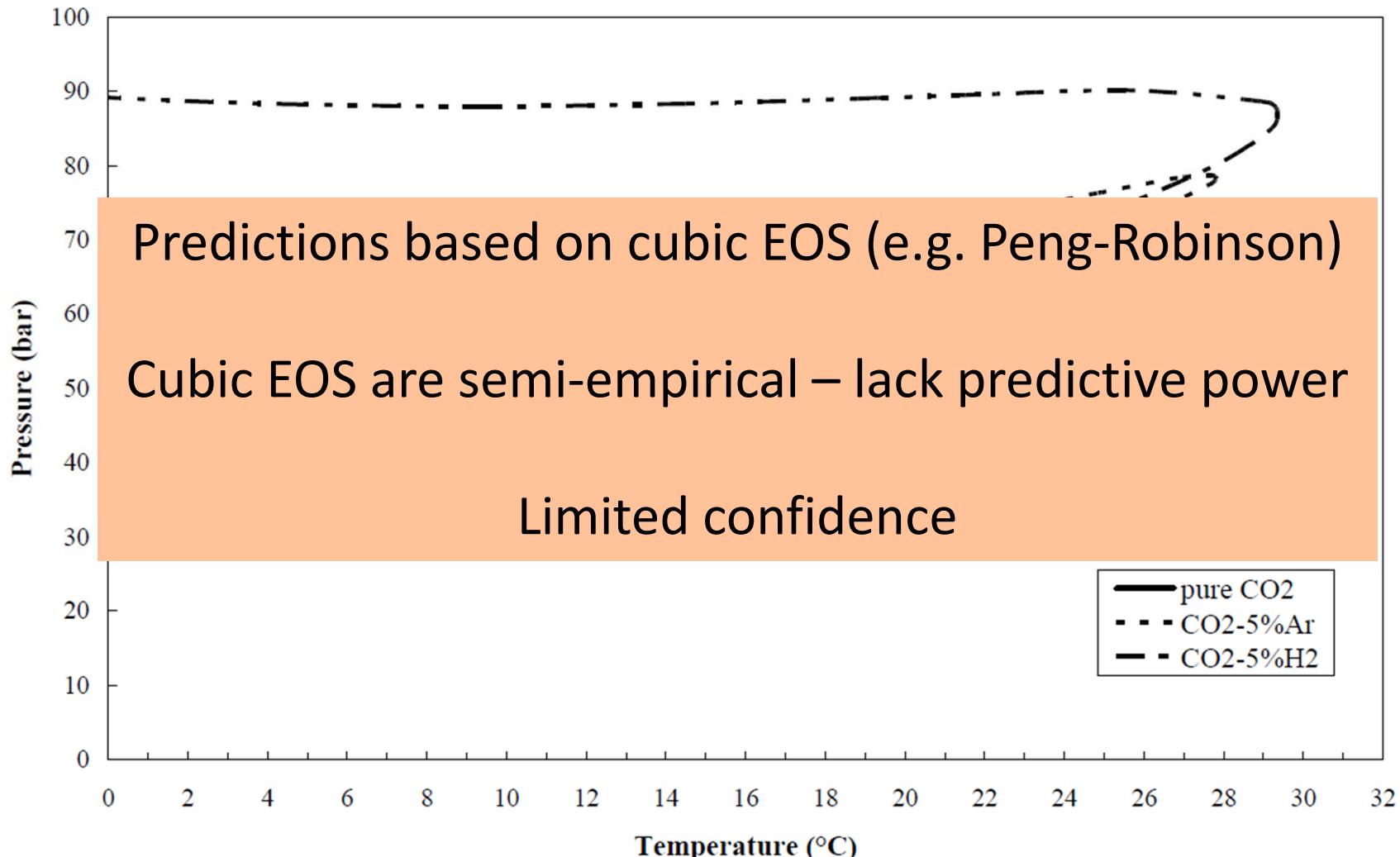


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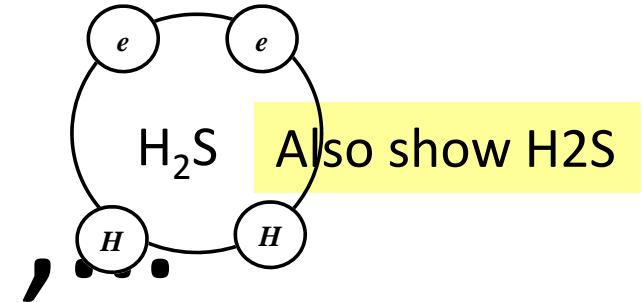
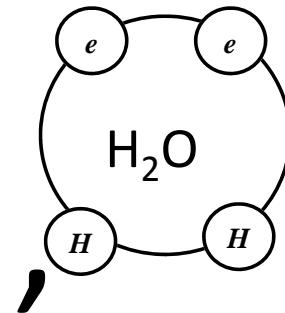
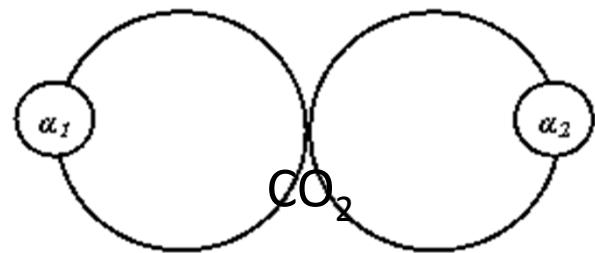
The Advanced Process Modelling Forum

Physical properties for compression/transmission in CCS

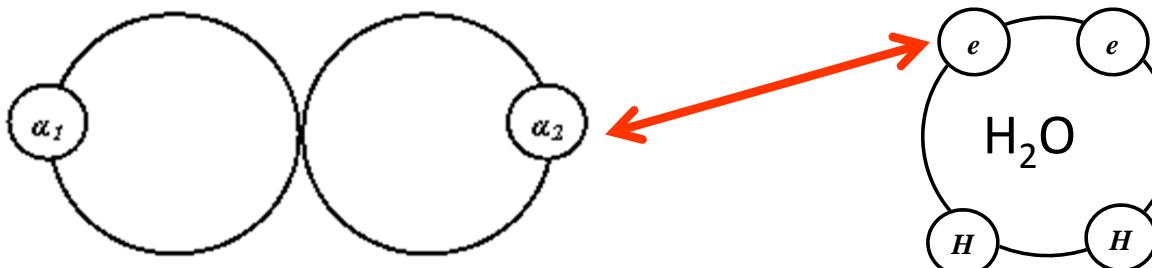
Challenges I: Impurities



Race, J. M., Seevam, P. N., and Downie, M. J. "Challenges for offshore transport of anthropogenic carbon dioxide." ASME, 2007.



- Molecular parameters are adjusted to pure component and saturated liquid density experimental data (from NIST)
- H₂ is fitted to vapour liquid equilibrium data from the CO₂+H₂ system
- H₂S and H₂O are self-associating compounds
- Binary interactions:



Compression Train System – Component models

