RUHR-UNIVERSITÄT BOCHUM

Experimental Work at RUB and Tsinghua and a New Model Describing Thermodynamic Properties of CO_2-rich Mixtures

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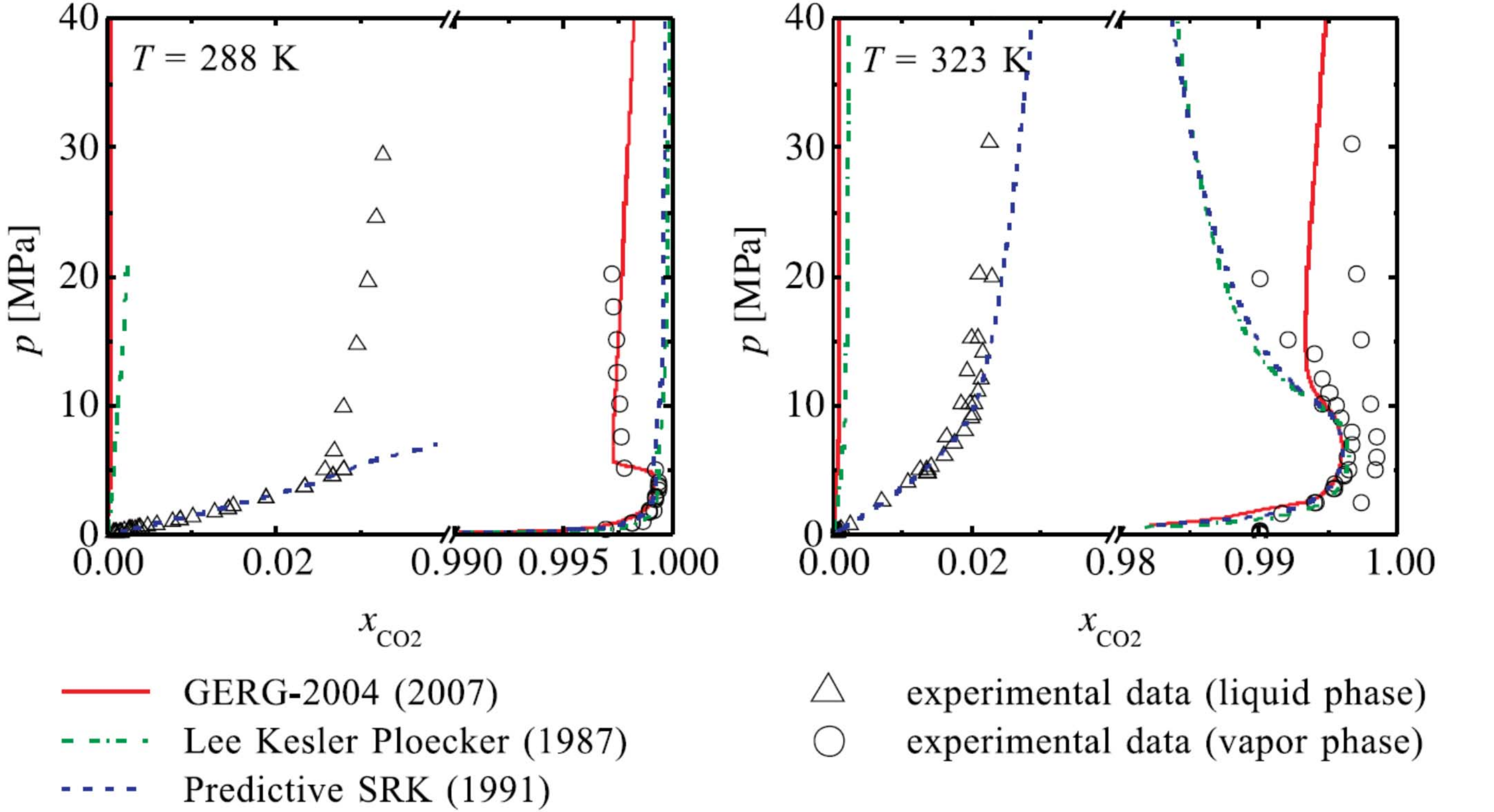
The GERG-2008 Model by Kunz and Wagner

- Helmholtz-model for mixtures (fundamental equation of state!)
- Introduced independently by Lemmon & Tillner-Roth in mid 90's
  - Pure fluid equations of state (EOS)
  - Mixing rules for reduced input parameters δ_m and τ_m

$$\alpha(\delta,\tau,\bar{x}) = \sum_{i=1}^{N} x_i \left[\alpha_{oi}^{0}(\rho,T) + \ln x_i\right] + \sum_{i=1}^{N} x_i \alpha_{oi}^{\mathrm{r}}(\delta_{\mathrm{m}},\tau_{\mathrm{m}}) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha_{ij}^{\mathrm{r}}(\delta_{\mathrm{m}},\tau_{\mathrm{m}})$$

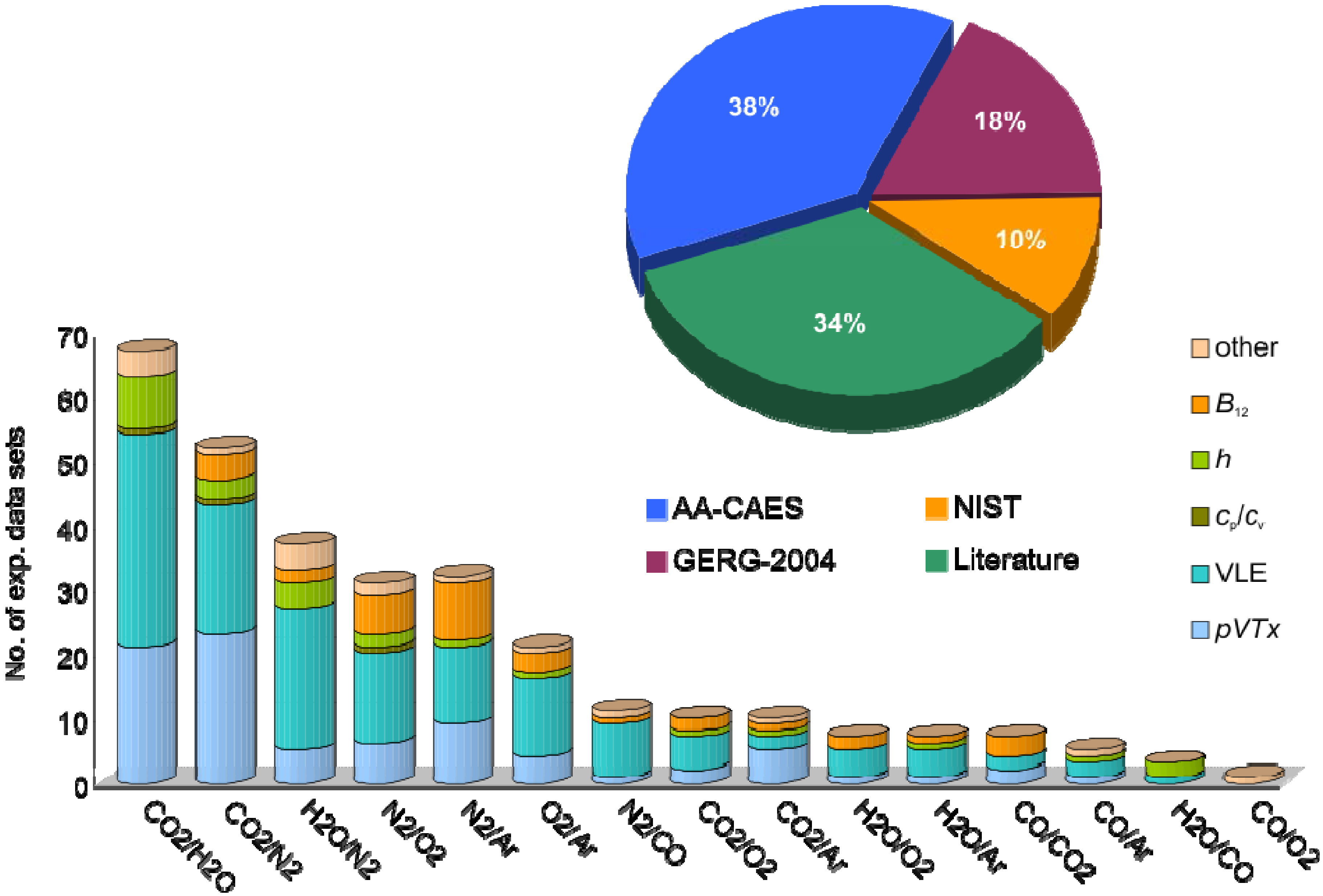
Methane (CH_4)	n-Pentane (n-C_5H_{12})	Hydrogen (H_2)
Nitrogen (N_2)	Isopentan (i-C_5H_{12})	**Carbon monoxide (CO)**
Carbon dioxide (CO_2)	n-Hexane (n-C_6H_{14})	Hydrogen sulphide (H_2S)
Ethane (C_2H_6)	n-Heptane (n-C_7H_{16})	**Water (H_2O)**
Propane (C_3H_8)	n-Octane (n-C_8H_{18})	**Oxygen (O_2)**
n-Butane (n-C_4H_{10})	n-Nonane (n-C_9H_{20})	**Argon (Ar)**
Isobutane (i-C_4H_{10})	n-Decane (n-$C_{10}H_{22}$)	Helium (He)

The GERG-2008 Model by Kunz and Wagner



- Developed with focus on natural-gas (like) mixtures, not for CCS

EOS-CG – Improving GERG-2008 for CO_2-Rich Mixtures



Thermophysical Properties in IMPACTS

Tsinghua: Density Measurements (single sinker, medium to high density)	**RUB: Density Measurements** (dual sinker, low to medium density)	**SINTEF: Accurate VLE Measurements**
RUB: Relative Permittivity Measurements (dew points)	**RUB: Mixture Models** (fluid phase, improved or new comp.)	
SINTEF: Recommen. for Transport-Property Models		

Thermophysical Properties – the Broader View

IMPACTS

CO2MIX / BIGCCS

Tsinghua: Density Measurements (single sinker, medium to high density)	**RUB: Density Measurements** (dual sinker, low to medium density)	**SINTEF: Accurate VLE Measurements**	**RUB: Density Measurements** (single sinker, medium to high density)
RUB: Relative Permittivity Measurements (dew points)	**RUB: Mixture Models** (fluid phase, improved or new comp.)	**RUB: Phase Equilibrium Algorithms** (VLE, LLE, SLE, HLE, …) E.ON	**RUB: Speed of Sound Meas.** (pulse / echo, high density)
SINTEF: Recommen. for Transport-Property Models	**RUB: Liquid Density Measurements** (cryo. temp., LNG + related) EMRP, GERG	**RUB: Solid Phase Models** (ice, dry ice, hydrates) DFG	**SINTEF: Mixture Models** (mostly engineering models)

Experimental Equipment Involved

IMPACTS

relative permittivity
apparatus at RUB

dual-sinker densimeter
at RUB

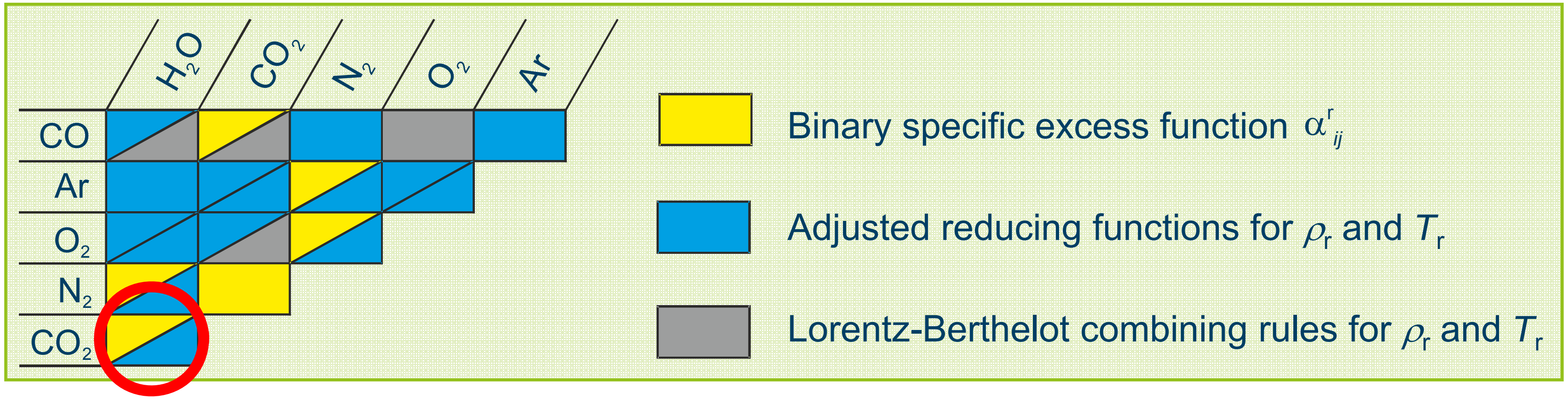
VLE apparatus
at SINTEF

single-sinker densimeter
at Tsinghua

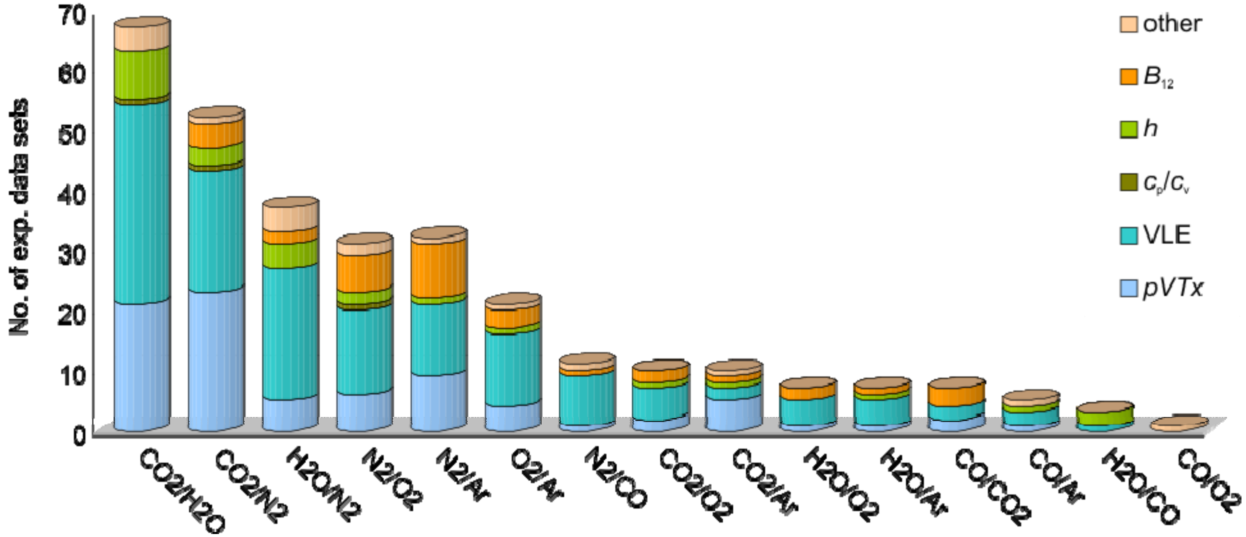
single-sinker densimeter
& speech of sound at RUB

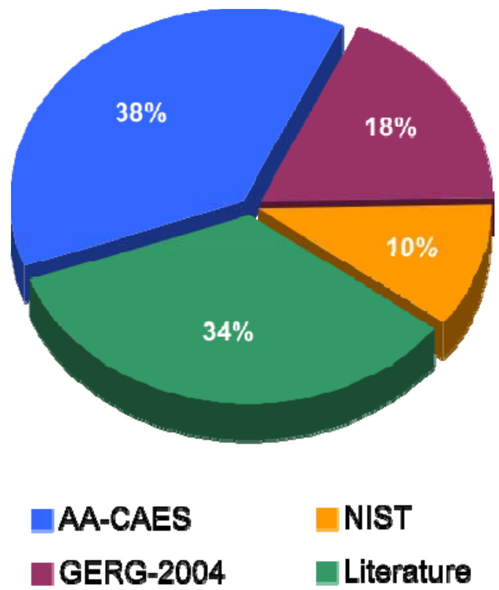
cryogenic-liquid
densimeter at RUB

EOS-CG – Improving GERG-2008 for CO_2-Rich Mixtures



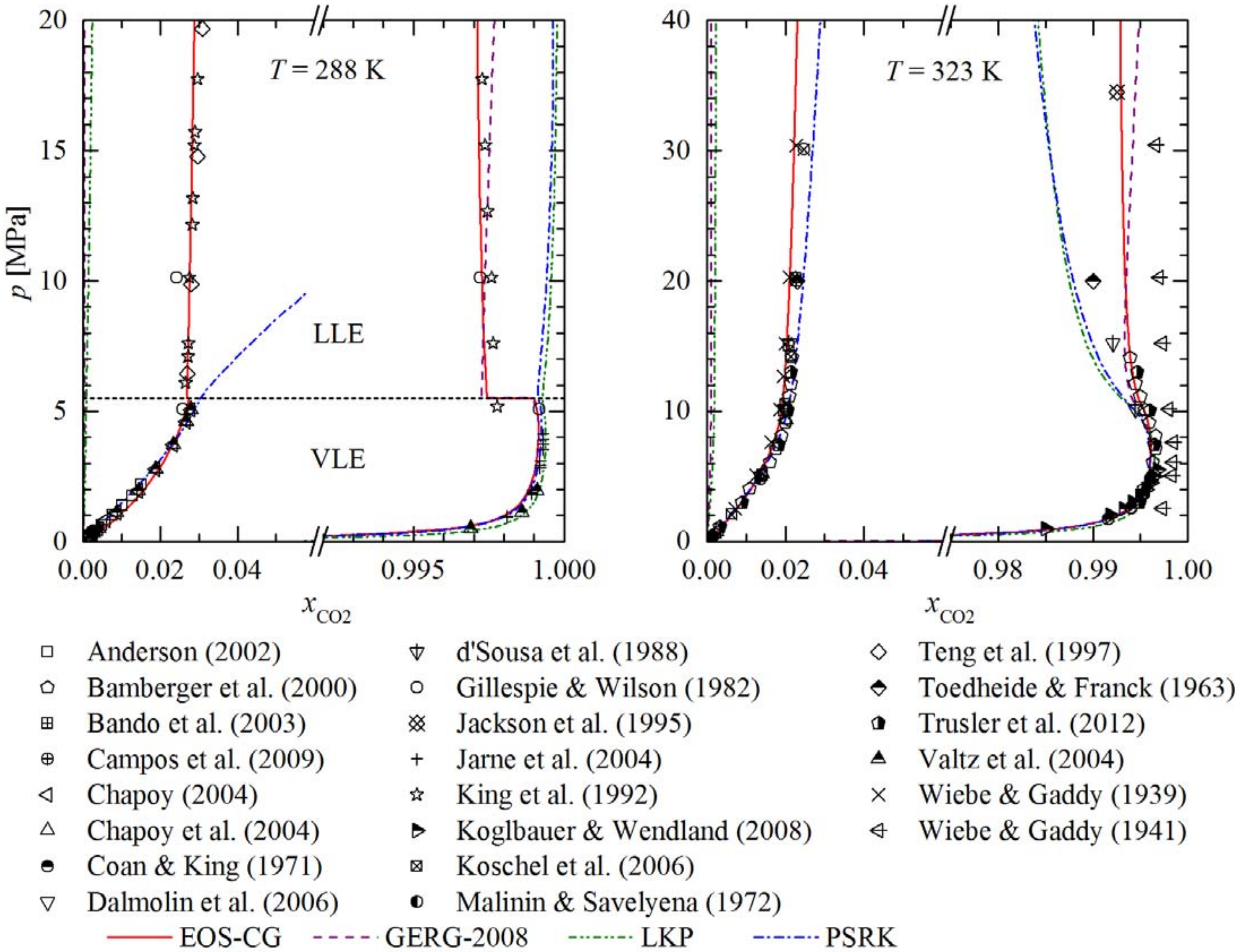
- **5 mixtures:** new excess functions
- **5 mixtures:** new reducing parameters





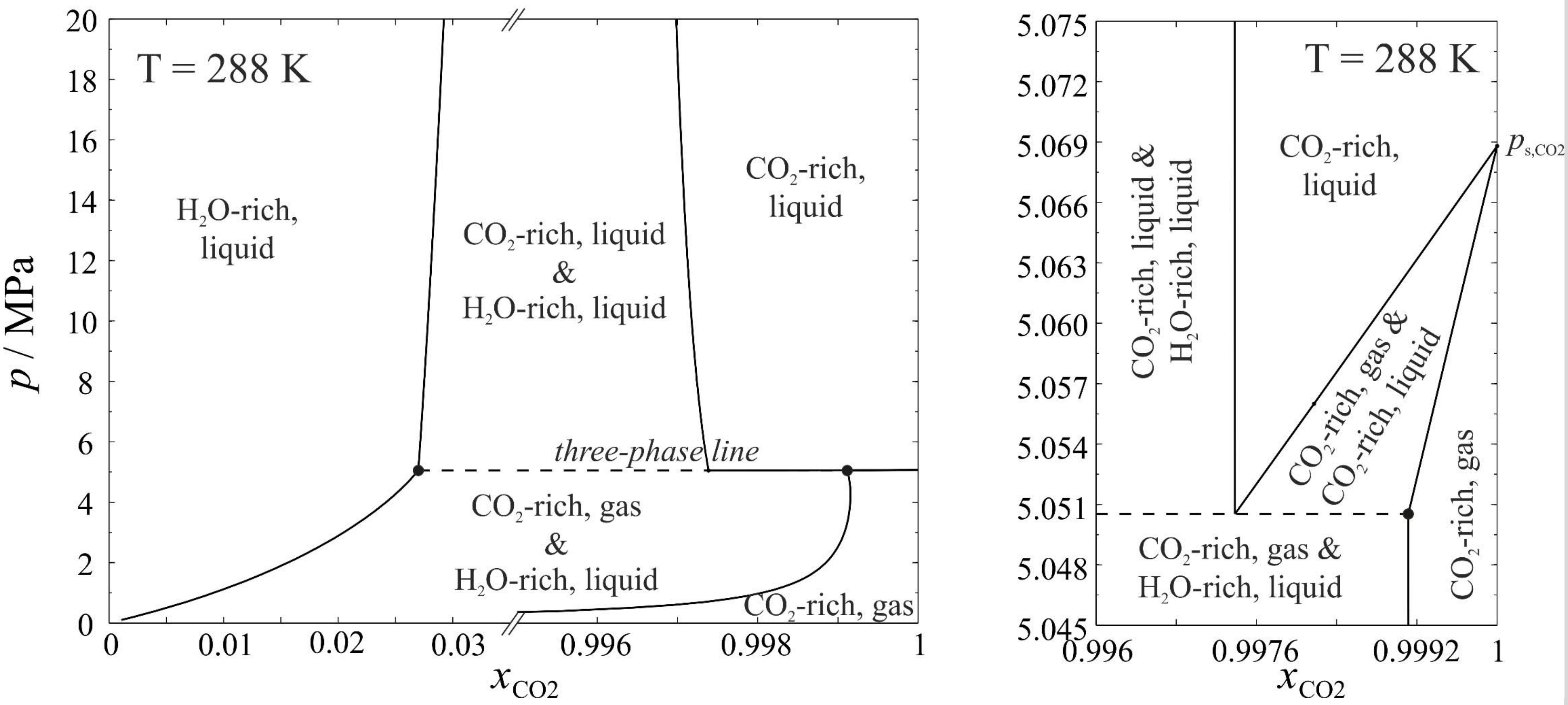
EOS-CG – Improving GERG-2008 for CO_2-Rich Mixtures

- **Example H_2O – CO_2:** Phase Boundaries



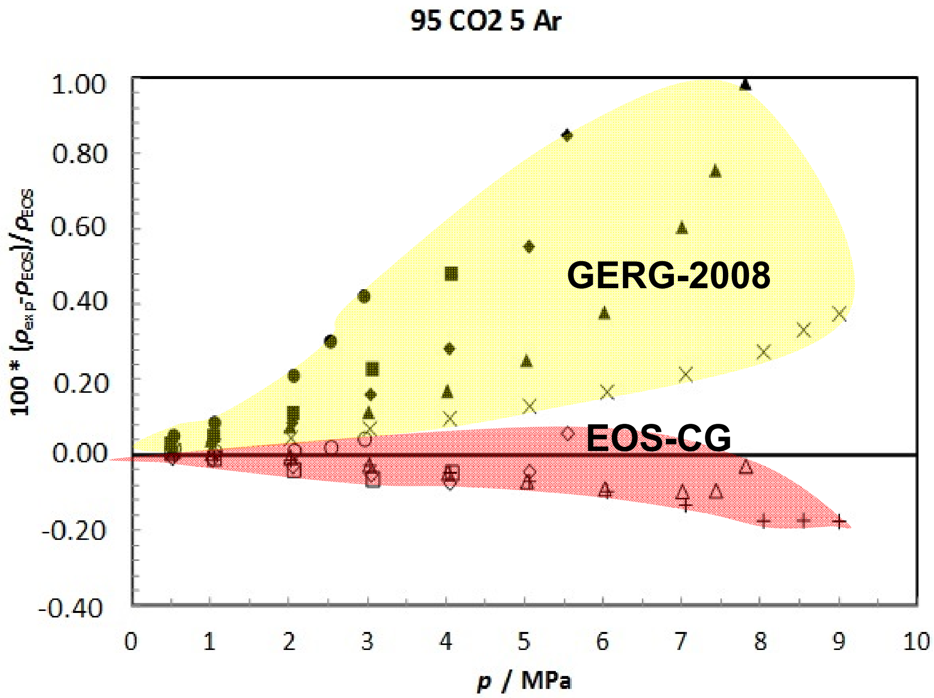
EOS-CG – Improving GERG-2008 for CO_2-Rich Mixtures

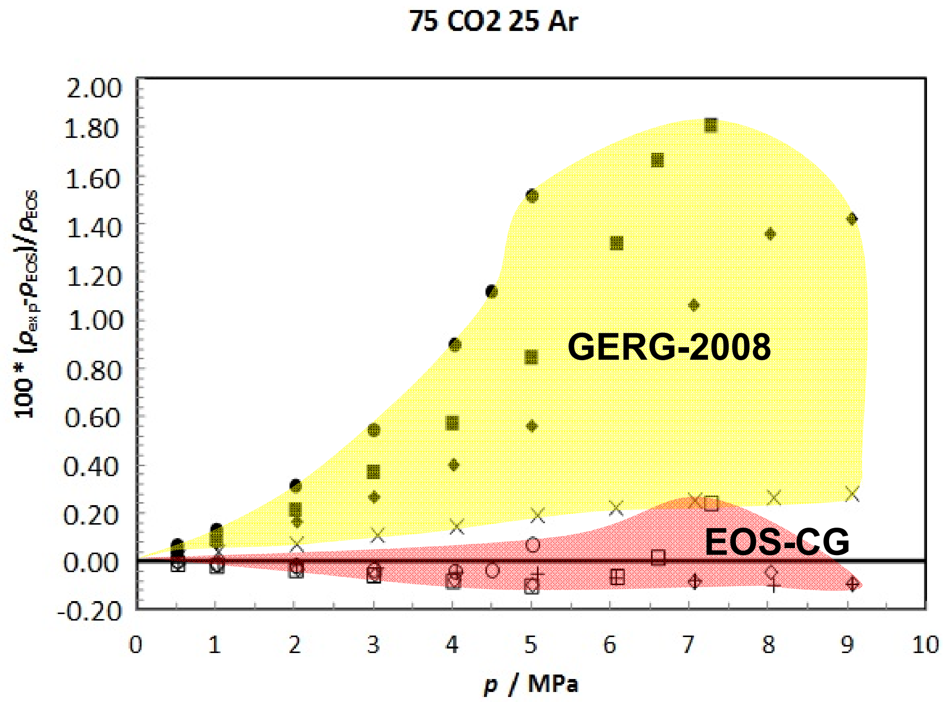
- Numerically stable (phase-equilibrium) algorithms available



Validating EOS-CG with IMPACTS Data

- **Example CO_2 – Ar:** Homogeneous Density Data

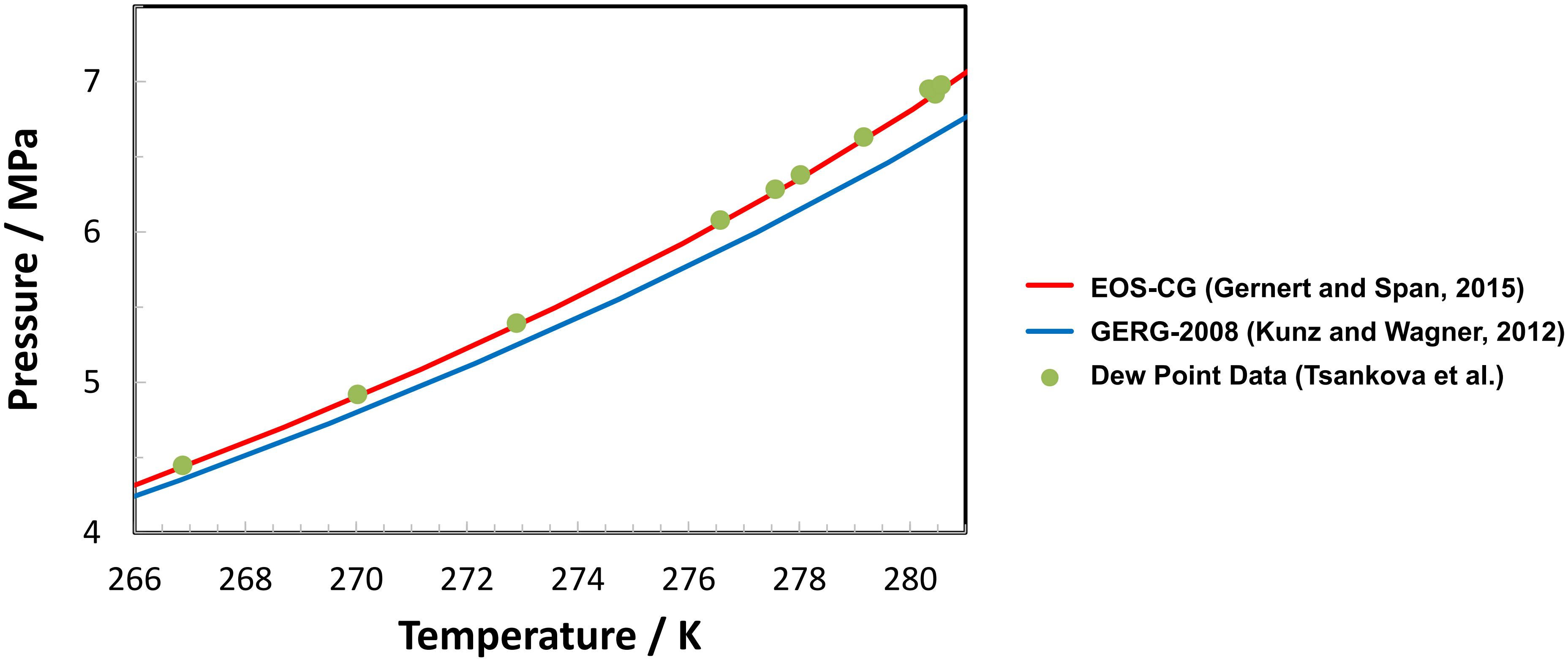




- Recent measurements within IMPACTS confirm superiority of EOS-CG for CO_2-rich mixtures
- Still larger deviations close to the critical points of the mixtures, further improvements for main components seem possible (but maybe not mandatory)

Validating EOS-CG with IMPACTS Data

- **Example CO_2 – Ar:** Dew Point Data (75% CO_2, 25% Ar)



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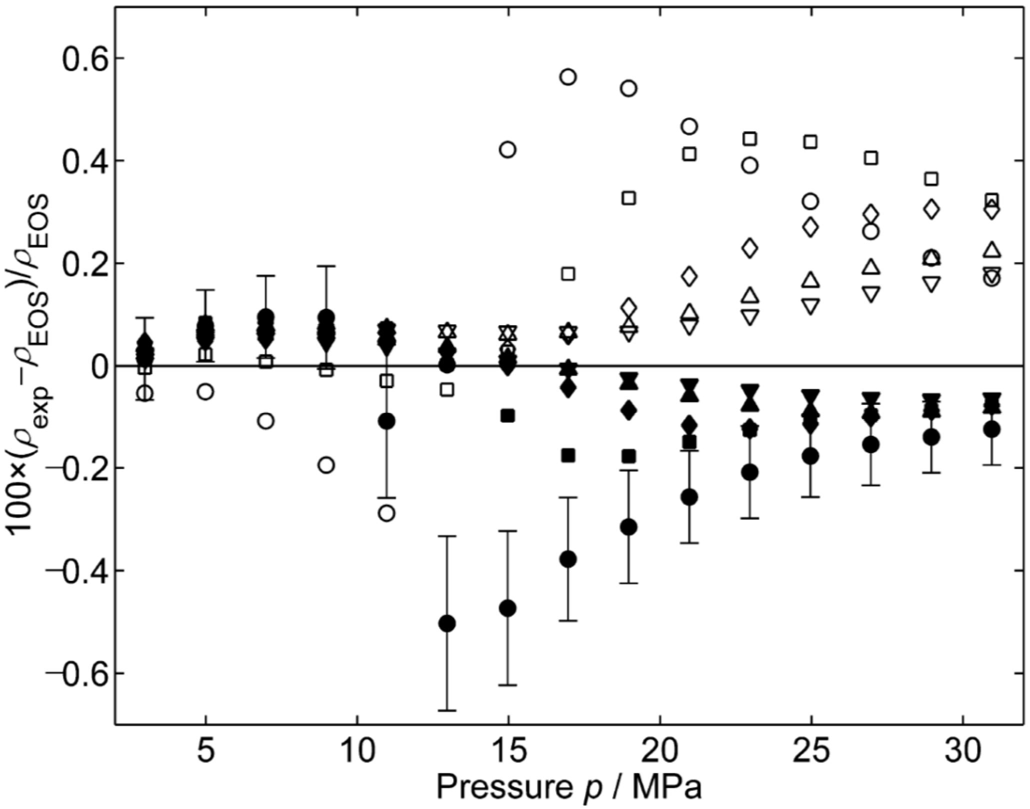
Validating EOS-CG with IMPACTS Data

- **Example CO_2 – N_2 – Ar:** Homogeneous Density Data (90% / 5% / 5%)



Open Symbols: EOS-CG (Gernert and Span, 2015)

Full Symbols: GERG-2008 (Kunz and Wagner, 2012)

Experimental Data by Yang et al. (2015)

- Recent measurements within IMPACTS confirm superiority of EOS-CG for CO_2-rich mixtures
- Still larger deviations close to the critical points of the mixtures, further improvements for main components seem possible (but maybe not mandatory)

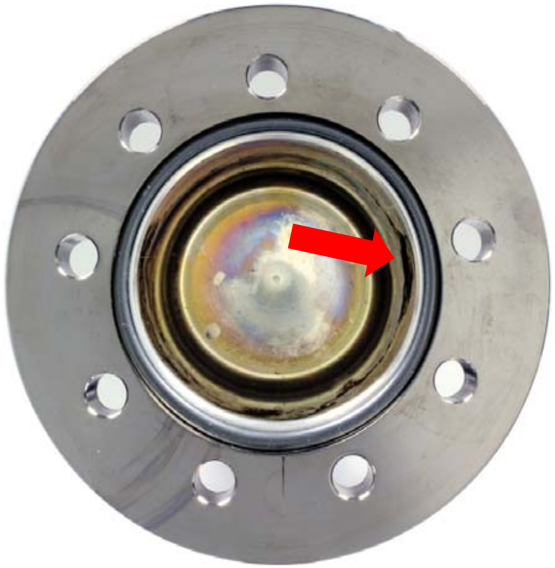
Experimental Results from RUB and Tsinghua

Data measured within IMPACTS close some important gaps in the data set available for "main components":

- **CO_2 – N_2:** Homogeneous density data
- **CO_2 – Ar:** Homogeneous density / dew point data
- **CO_2 – H_2:** Homogeneous density data (not yet completed)
- **CO_2 – CH_4:** Homogeneous density data close to the critical point
- **CO_2 – N_2 – Ar:** Homogeneous density data close to the critical point

A number of serious drawbacks in experimental work:

- Problems with experimental setups
- **CH_4 – O_2:** Mixtures could not be prepared with sufficient pressure even outside of the explosive range (explosive mixtures during filling)
- **CH_4 – CO:** Solid C formation triggered by some kind of catalytic reaction with cell material



Consideration of Minor Components in IMPACTS

		Chlorine	Hydrogen Chloride	Diethanolamine	Monoethanolamine	Methanol	Ammonia	Sulphur Trioxide	Sulphur Dioxide	Nitrogen Dioxide	Nitrogen Oxide	Hydrogen Sulfide	Methane	Hydrogen	Carbon Monoxide	Argon	Oxygen	Nitrogen	Water
Major Components	Carbon Dioxide	x	x	o	o	x	x		x	x	x	x	x	x					
	Water	o	x	x	x	x	x	x	x	o	o	x	x	x					
	Nitrogen	o	o	o	o	x	x		x	o	x	x	x	x					
	Oxygen	o	o	o	o	x	o		x	o	o	o	x	x					
	Argon	o	o	o	o	x	x		x	o	o	o	x	x					
	Carbon Monoxide	o	o	o	o	x	x		o	o	o	x	x	x					
	Hydrogen	o	o	o	x	x	x		x	o	o	x	x						
	Methane	o	o	o	o	x	x		x	o	o	x							
Minor Components	Hydrogen Sulfide	o	o	o	o	x	o		o	o	o								
	Nitrogen Oxide	o	o	o	o	o	o		o	o									
	Nitrogen Dioxide	o	o	o	o	o	o		o										
	Sulphur Dioxide	x	x	x	o	x	o	x											
	Sulphur Trioxide																		
	Ammonia	o	o	o	x	x													
	Methanol	o	x	x	x														
	Monoethanolamine	o	o	x															
	Diethanolamine	o	o																
	Hydrogen Chloride	x																	
	Chlorine																		

Covered by EOS-CG

Covered by GERG-2008 / Tillner-Roth & Friend for Ammonia

Covered by new upcoming models from University of Washington and NIST

No dedicated mixture-model available

x Data available (DDB and/or TRC)

o No data in DDB and TRC

Sulphur Trioxide should be rejected; database not sufficient to fit the pure fluid

Pure Fluid Equations under development

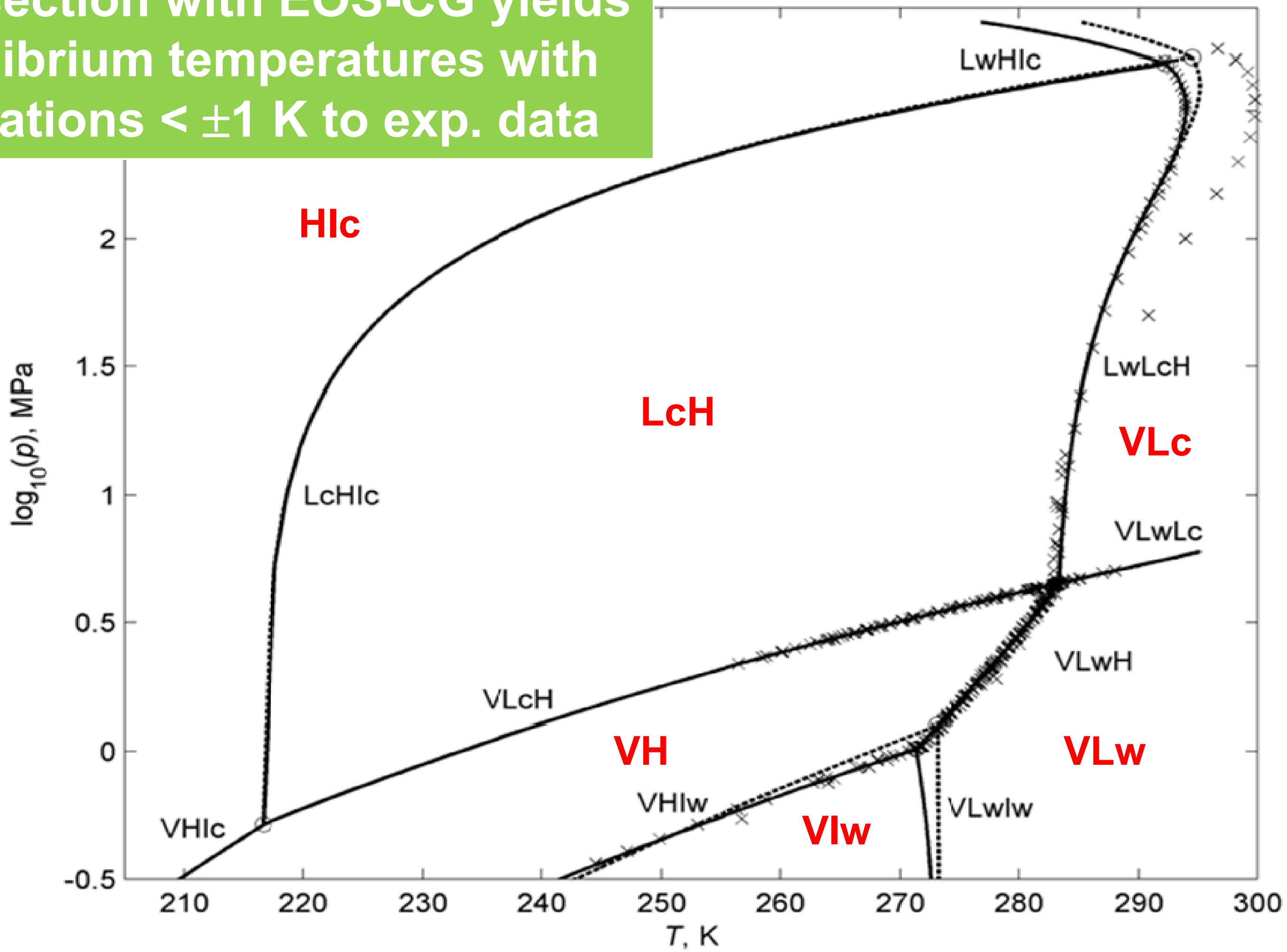
Consideration of Minor Components in IMPACTS

		chlorine	hydrogen chloride	diethanolamine	monoethanolamine	sulphur dioxide	hydrogen sulfide	methane	hydrogen	carbon monoxide	argon	oxygen	nitrogen	water
major components	carbon dioxide	LB	LB	lin	lin	red								
	water	LB	lin	red	red	red								
	nitrogen	lin	LB	lin	lin	red								
	oxygen	lin	lin	LB	LB	red								
	argon	lin	lin	lin	lin	lin								
	carbon monoxide	lin	LB	lin	lin	lin								
	hydrogen	lin	lin	lin	red	lin								
	methane	lin	LB	lin	lin	red								
minor components	hydrogen sulfide	LB	LB	lin	lin	LB								
	sulphur dioxide	red	LB	red	LB									
	monoethanolamine	lin	lin	red										
	diethanolamine	lin	lin											
	hydrogen chloride	red												
	chlorine													

- EOS-CG model of *Gernert and Span (2015)*
- GERG-2008 model of *Kunz and Wagner (2012)*
- red – New model, reducing parameters fitted
- lin – New model, linear combination rule
- LB – New model, Lorentz-Berthelot combination rule

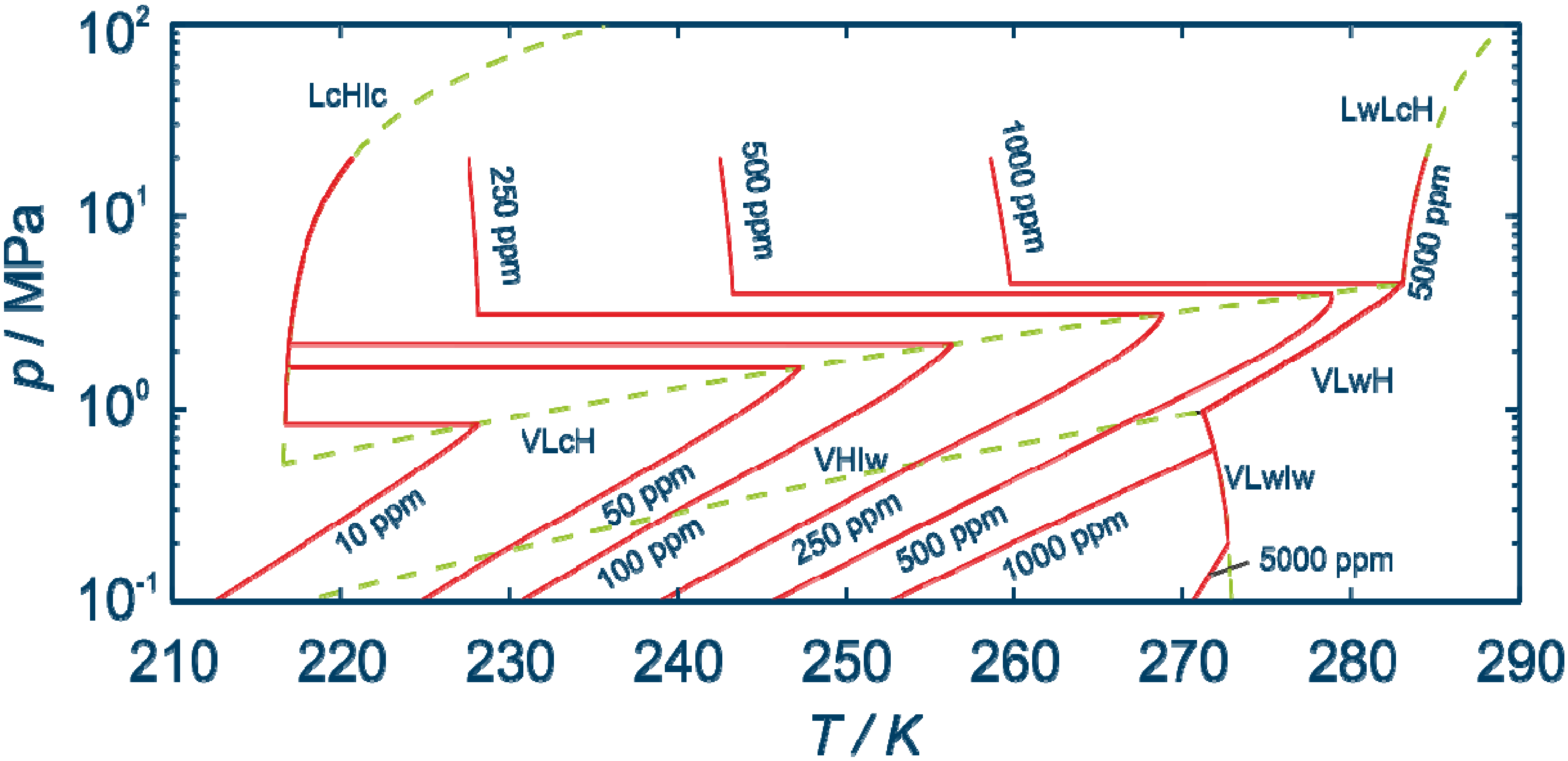
Phase Equilibria with Solid Phases – Hydrates

Intersection with EOS-CG yields equilibrium temperatures with deviations < ±1 K to exp. data



- Accurate description of CO_2 / H_2O hydrate formation
- Consistent to accurate VLE / LLE / homogeneous phase model

Allowable Water Content in CO_2

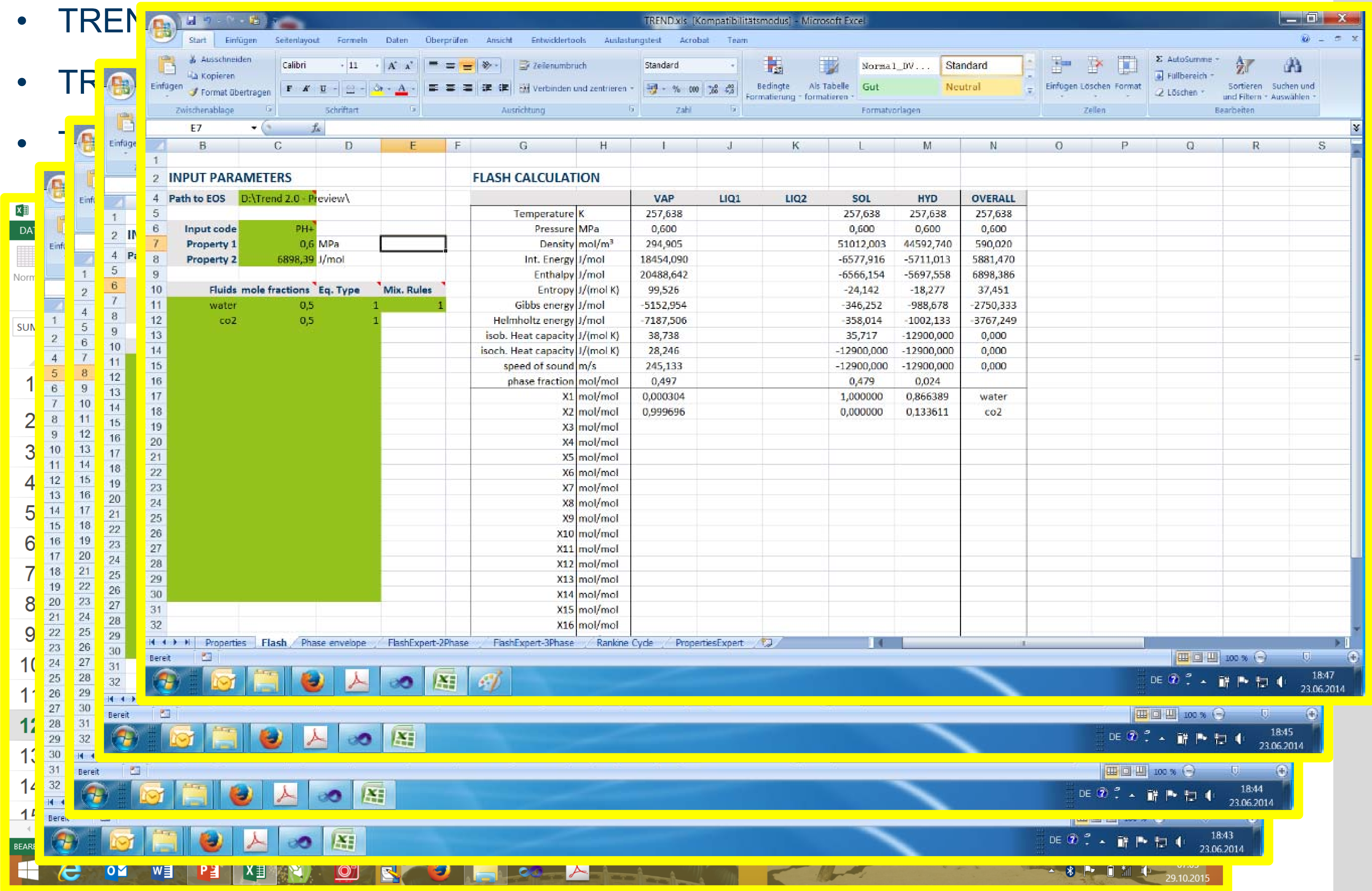


- - Three phase lines in the binary system CO_2 + H_2O

— Temperatures at which solid phase emerges for different H_2O contents in the binary system CO_2 + H_2O

TREND – A Contribution to the "Tool Box"

- TREN
- TR
- -



Thank You For Your Attention!

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