THERMODYNAMIK

RUHR-UNIVERSITÄT BOCHUM

50 Jahre

RUB

Thermodynamic Property Models for Transport and Storage of CO_2

Roland Span

UKCCS Research Centre Meeting, York 2014

Options for CCS

Category	Fuel	O_2 Supply	CO_2 Separation
Pre-Combustion Process (IGCC / NGRCC)	Lignite	Cryogenic	Physical Absorpt.
	Hard Coal	OTM / ITM	Chemical Absorpt.
	Natural Gas		H_2 Membrane
			CO_2 Membrane
Integrated Process (Oxy-Fuel)	Lignite	Cryogenic	Condensation
	Hard Coal	OTM / ITM	
	Natural Gas	Chemical Looping	
Post-Combustion Process (exhaust gas cleaning)	Lignite		Chemical Absorpt.
	Hard Coal		Chilled Ammonia
	Natural Gas		Solid Adsorbents
			Membrane Reactor

Conditioning | Compression, Transport | and Storage of CO_2

Multi-Disciplinary Property Research

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Property models typical for chemical engineering

Conditioning | Compression, Transport | and Storage of CO_2

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Property models typical for geology / geo sciences

Conditioning | Compression, Transport | and Storage of CO_2

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Property models typical for energy technologies

Conditioning | Compression, Transport | and Storage of CO2

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Oxyflame – DFG Collaborative Research Centre
RUB with RWTH Aachen and TU Darmstadt

Conditioning | Compression, Transport | and Storage of CO2

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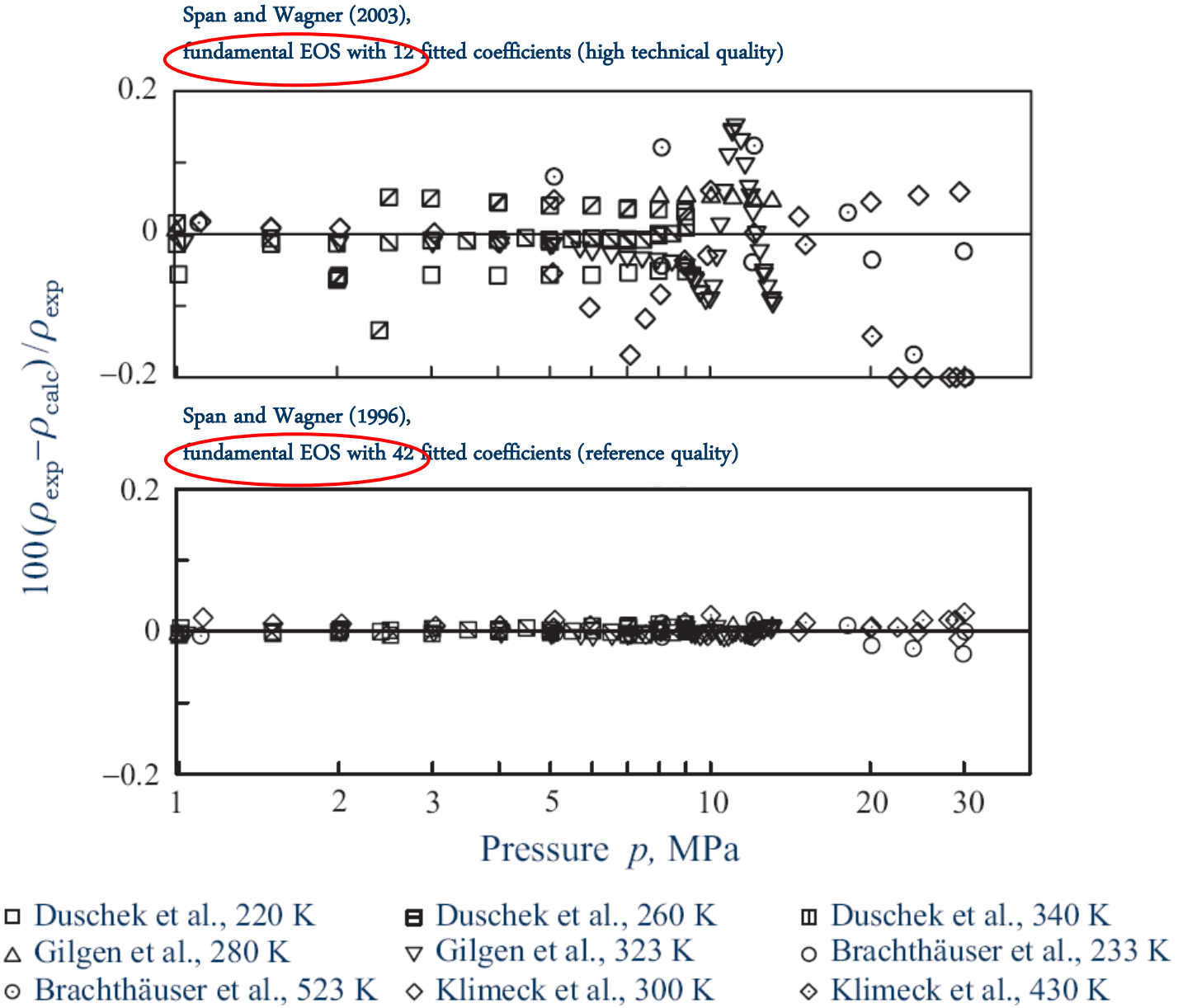
Develop a model / a set of models which …

- **describes homogeneous states with high (reference) accuracy**
- **consistently describes VLE / LLE equilibria**
- **consistently describes equilibria with solid phases (ice, dry ice, hydrates)**

Conditioning | Compression, Transport | and Storage of CO2

Thermodynamic Properties of Pure CO_2



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

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

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- Two options:
  - Mixing rules with four adjustable, binary specific parameters

$$\tau_m = \frac{T_r(\mathbf{x})}{T} \quad \text{with} \quad T_r(\mathbf{x}) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \beta_{T,ij}\gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \left(T_{c,i} T_{c,j}\right)^{0.5}$$

$$\delta_m = \frac{\rho}{\rho_r(\mathbf{x})} \quad \text{with} \quad \frac{1}{\rho_r(\mathbf{x})} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \beta_{\rho,ij}\gamma_{\rho,ij} \frac{x_i + x_j}{\beta_{\rho,ij}^2 x_i + x_j} \frac{1}{8}\left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}}\right)^3$$

  - Combination rules

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  - Binary excess functions

$$\alpha_{ij}(\delta_m,\tau_m) = \sum_{k=1}^{K_{Pol,ij}} n_k \delta_m^{d_k} \tau_m^{t_k} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_k \delta_m^{d_k} \tau_m^{t_k} \exp\left[-\eta_k (\delta_m - \varepsilon_k)^2 - \beta_k (\delta_m - \gamma_k)\right]$$

- Two options:
  - Binary specific excess function – $F_{ij} = 1$, parameter in α_{ij} fitted
  - Generalized excess function – F_{ij} fitted, parameter in α_{ij} generalized

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- Four levels of accuracy, depending on available experimental data and relevance of the binary subsystem
  - Only combination rules for T_r, ρ_r
  - Mixing rules with four adjustable parameters for T_r, ρ_r
  - Adjusted mixing rules & generalized excess function
  - Adjusted mixing rules & binary specific excess function

UNIQUE!

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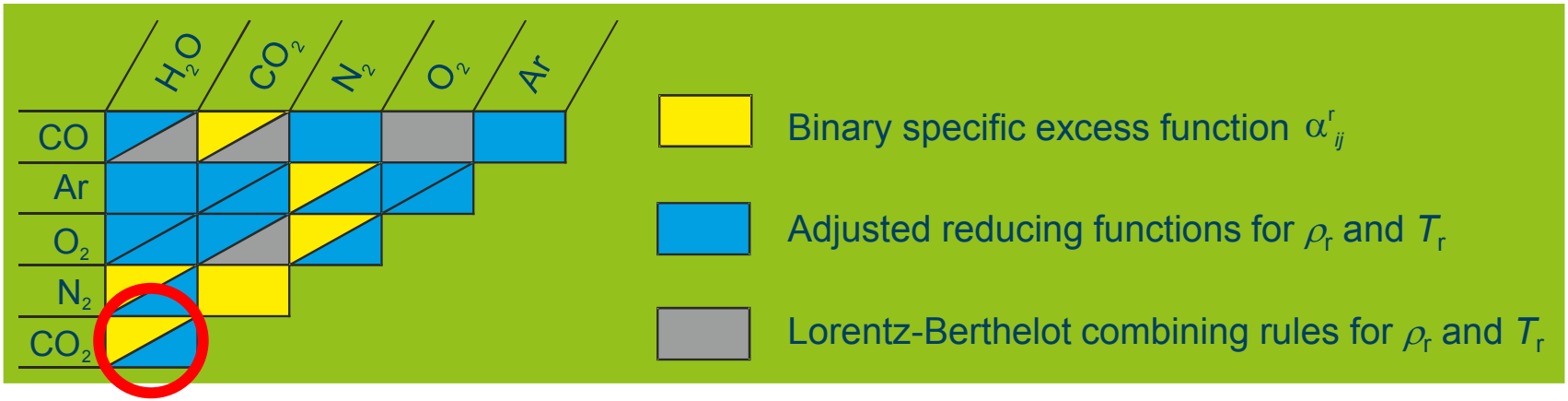
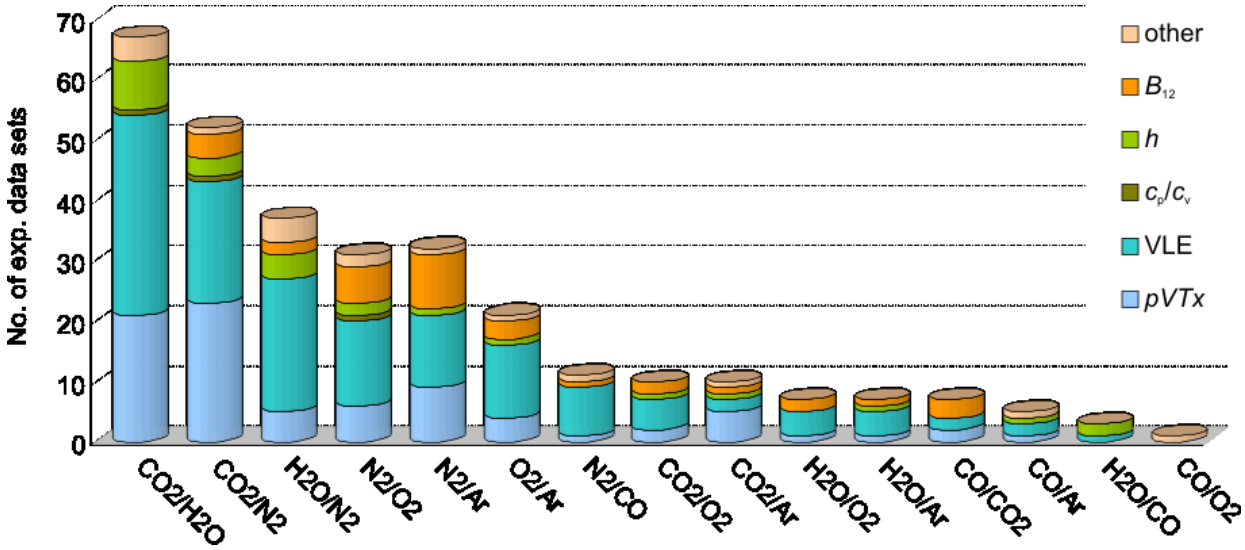
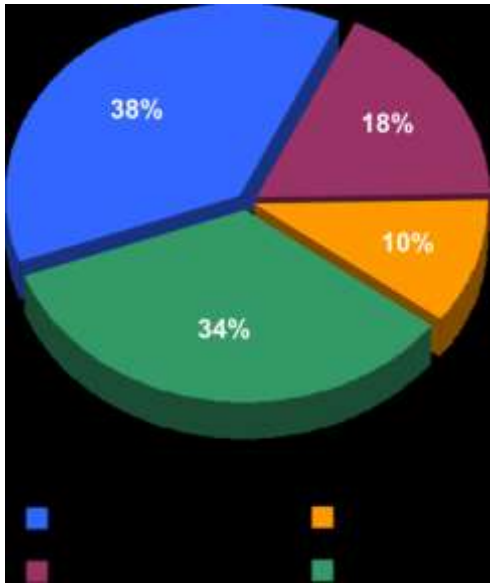
Methane (CH_4)	n-Pentane (n-C_5H_{12})	Hydrogen (H_2)
Nitrogen (N_2)	Isopentan (i-C_5H_{12})	**Carbon monoxide (CO)**
Carbon dioxide (CO_2)	n-Hexane (n-C_6H_{14})	Hydrogen sulphide (H_2S)
Ethane (C_2H_6)	n-Heptane (n-C_7H_{16})	**Water (H_2O)**
Propane (C_3H_8)	n-Octane (n-C_8H_{18})	**Oxygen (O_2)**
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)

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



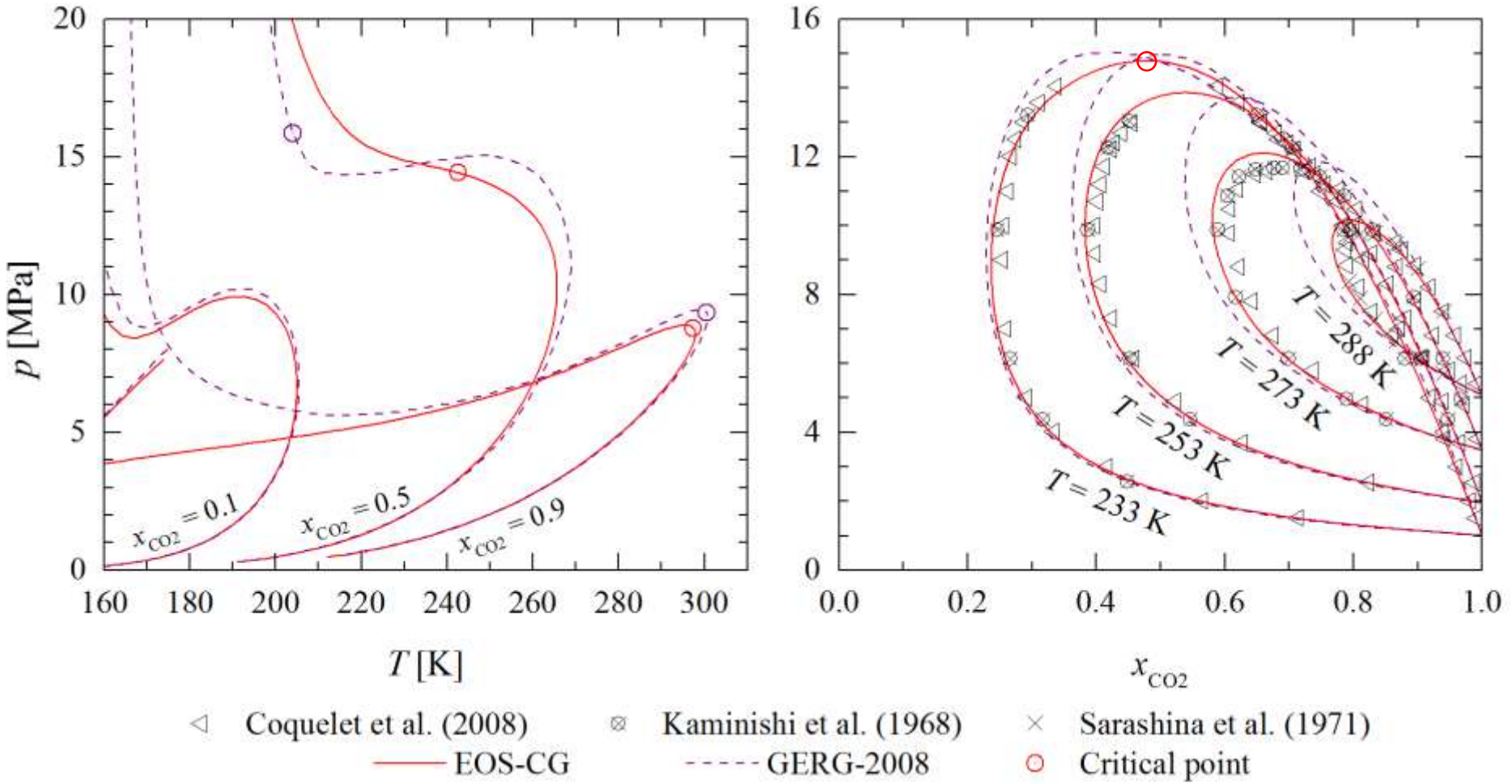
- **5 mixtures:** new excess functions
- **5 mixtures:** new reducing parameters





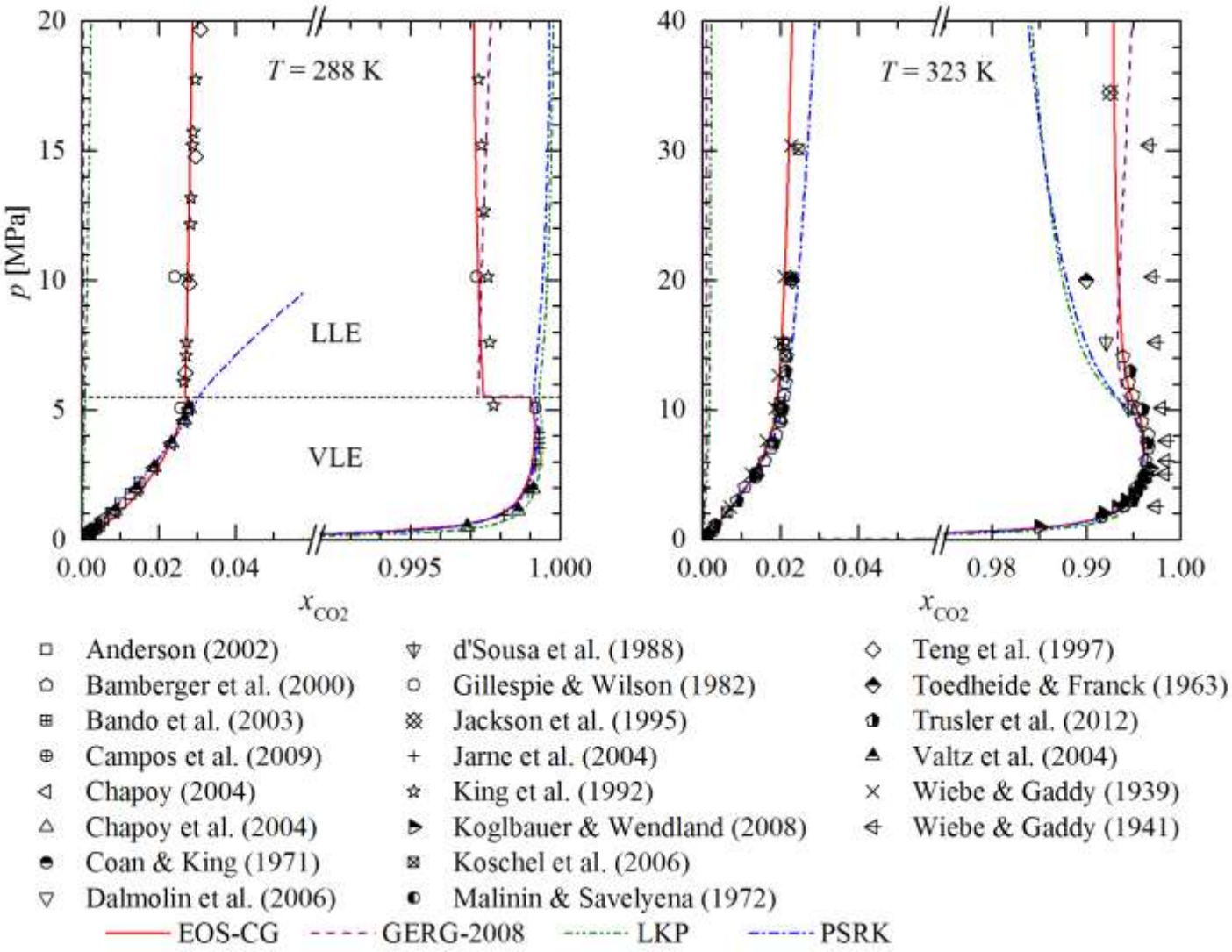
Property Models for CO_2-Rich Mixtures – EOS-CG

- **Example CO_2 – Ar:** Phase boundaries
  - Improvements compared to GERG-2008 at high pressure



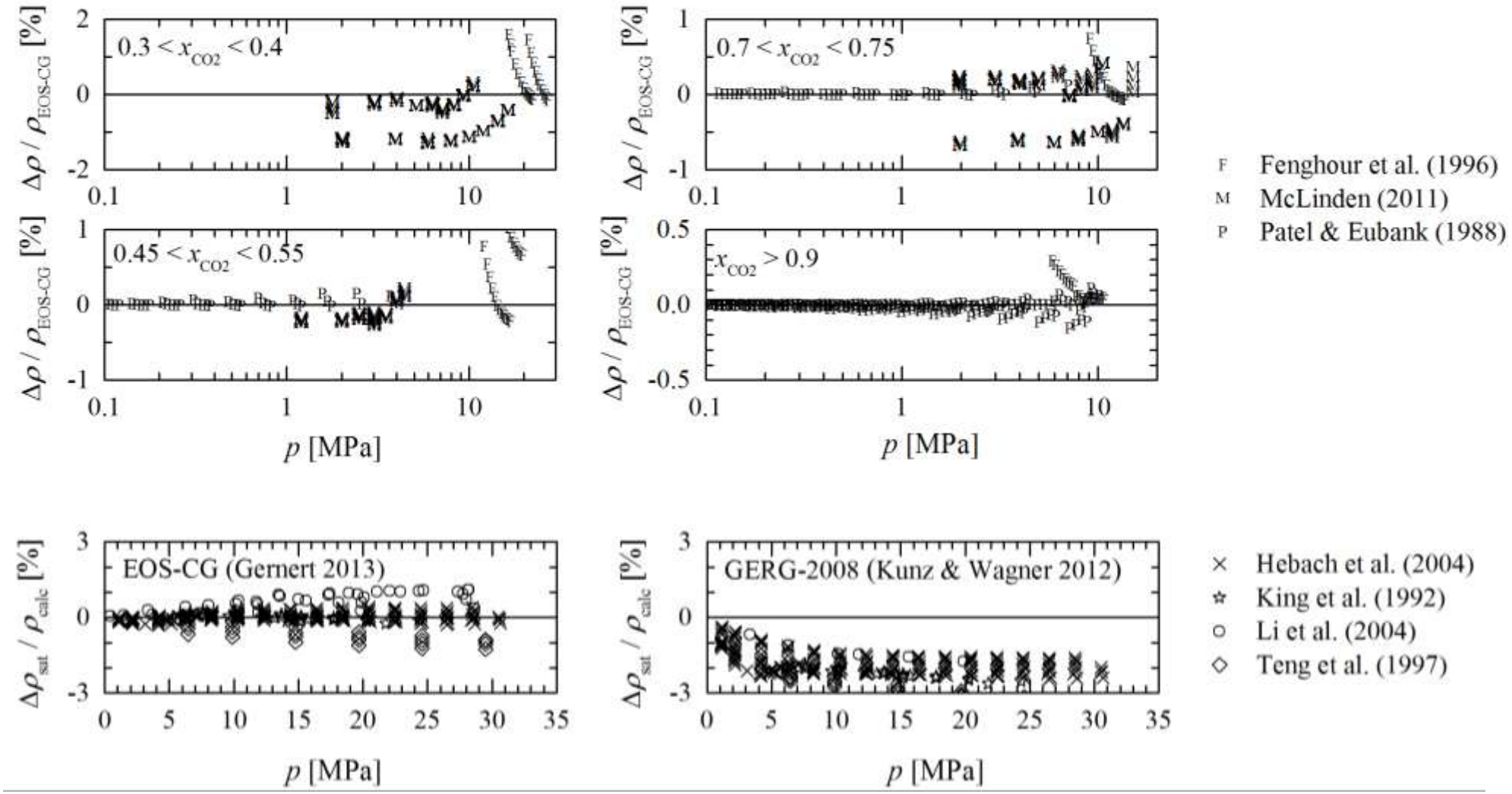
Property Models for CO_2-Rich Mixtures – EOS-CG

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



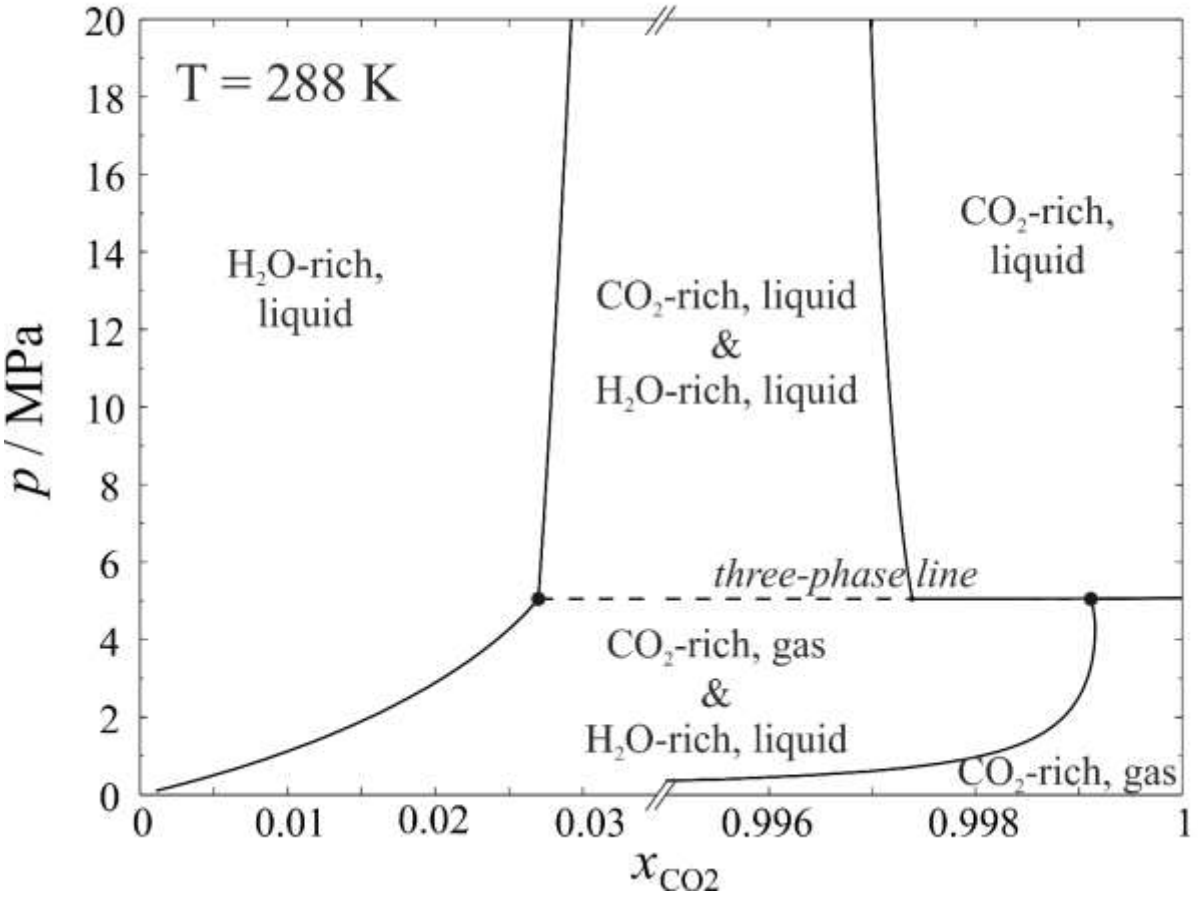
Property Models for CO_2-Rich Mixtures – EOS-CG

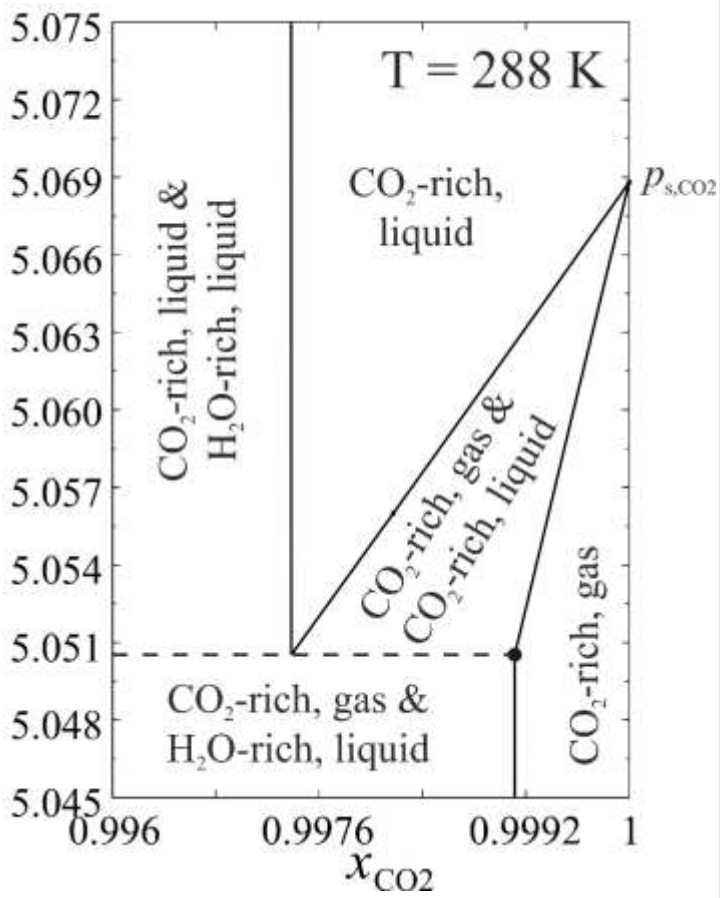
- **Example H_2O – CO_2:** Densities



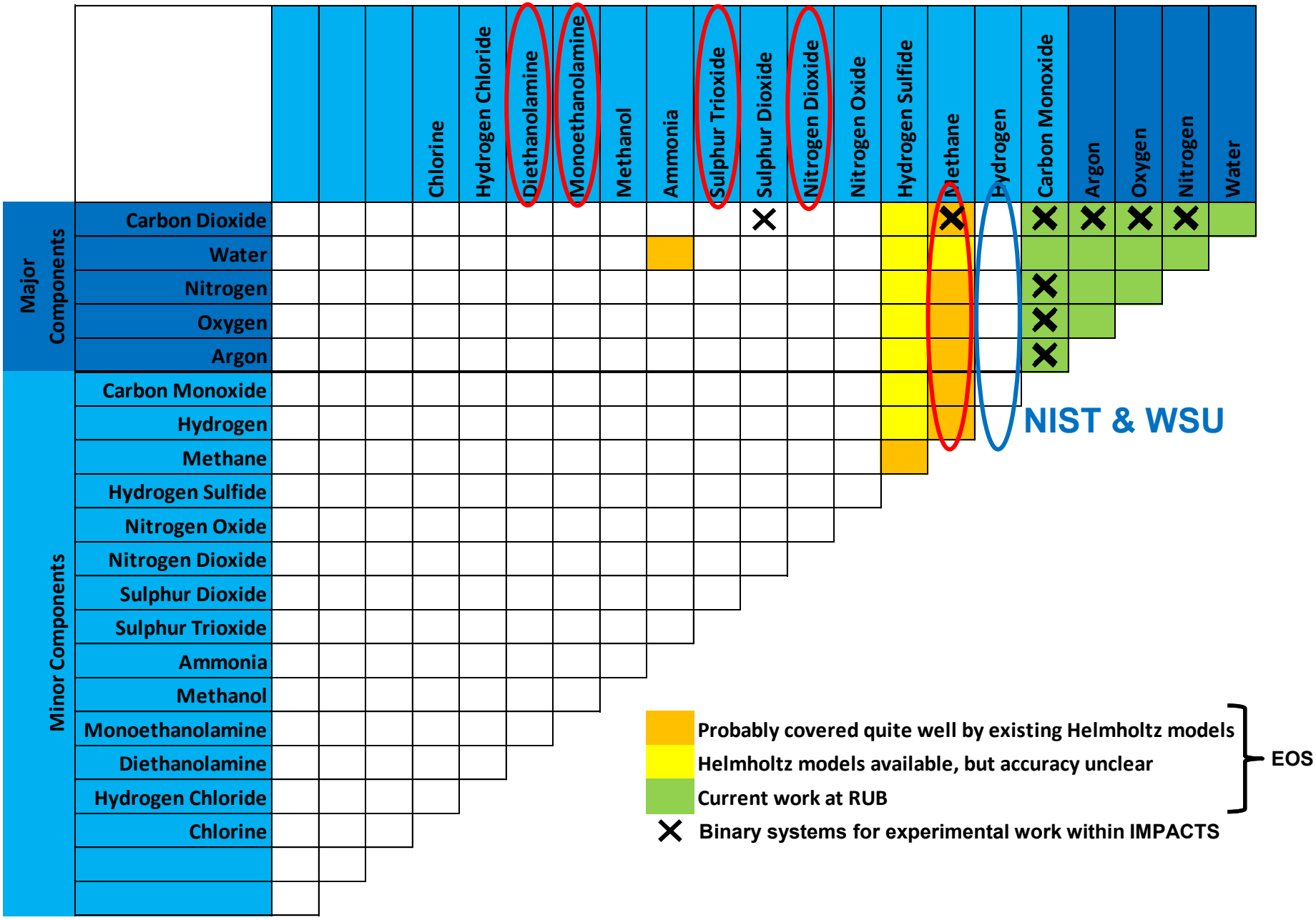
Property Models for CO_2-Rich Mixtures – EOS-CG

- Numerically stable (phase-equilibrium) algorithms available

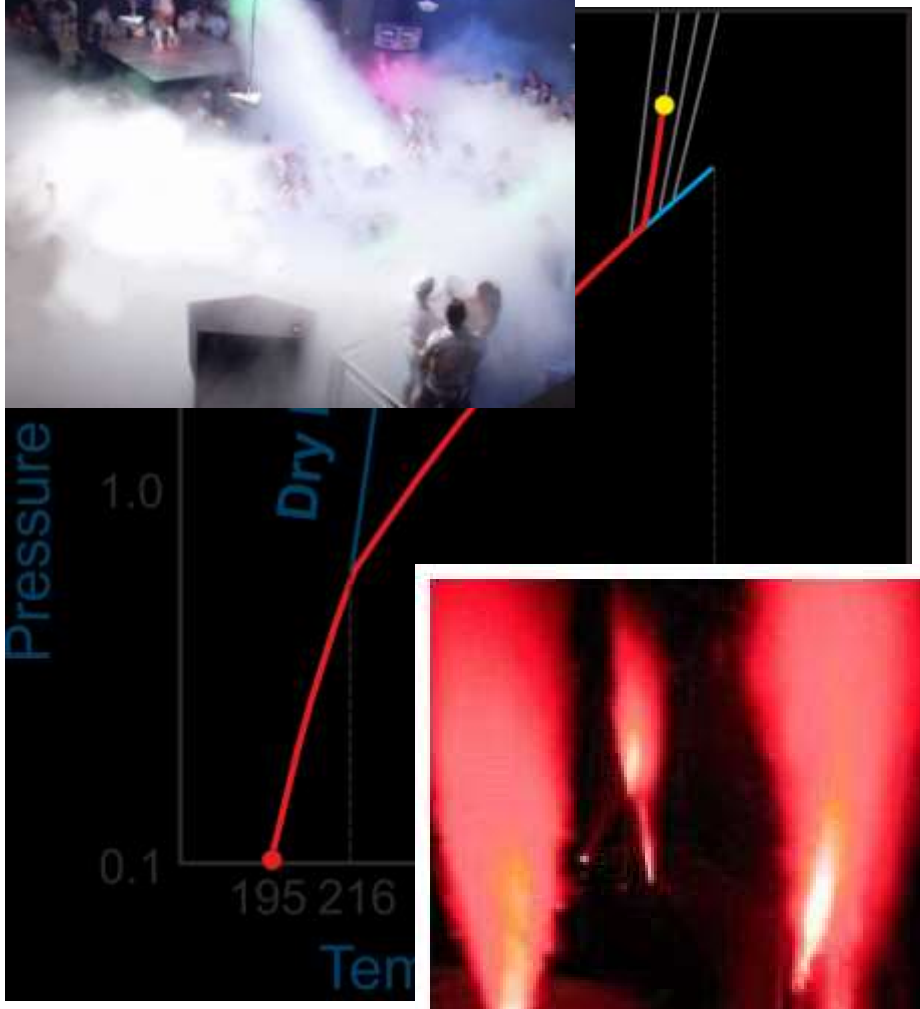




Much Room for Improvement: IMPACTS



Low-Temperature Phase Equilibria for CO_2



- CO_2 in pipelines is liquid
- Pressure loss (leaks or flooding of evacuated pipeline segments) results in liquid / vapor system
- Further expansion leads to formation of a dry ice / vapor system at about 195 K
- For a description of the process (enthalpy) flash calculation with solid phase
- Similar effects for low tempera-ture transport / capture

⇨ Consistent fundamental equation for dry ice required!

Phase Equilibria with Solid Phases – Dry Ice

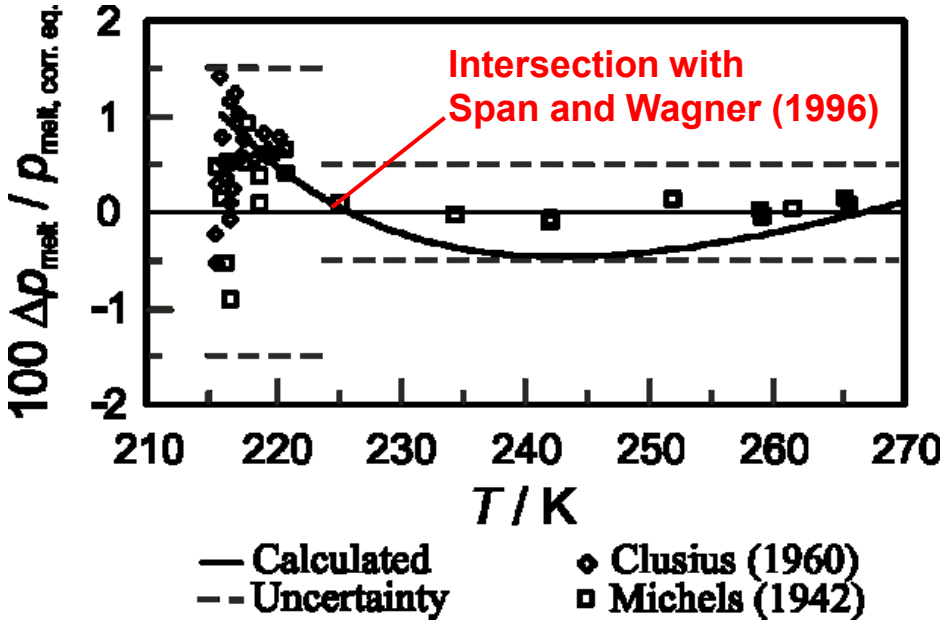
- Fundamental equations for solid CO_2 (dry ice) developed
- *Jäger and Span (2010, 2012):* Gibbs enthalpy as a function of pressure and temperature
- Approach by Tillner-Roth (1998) adapted
- Fitted only to data for solid CO_2

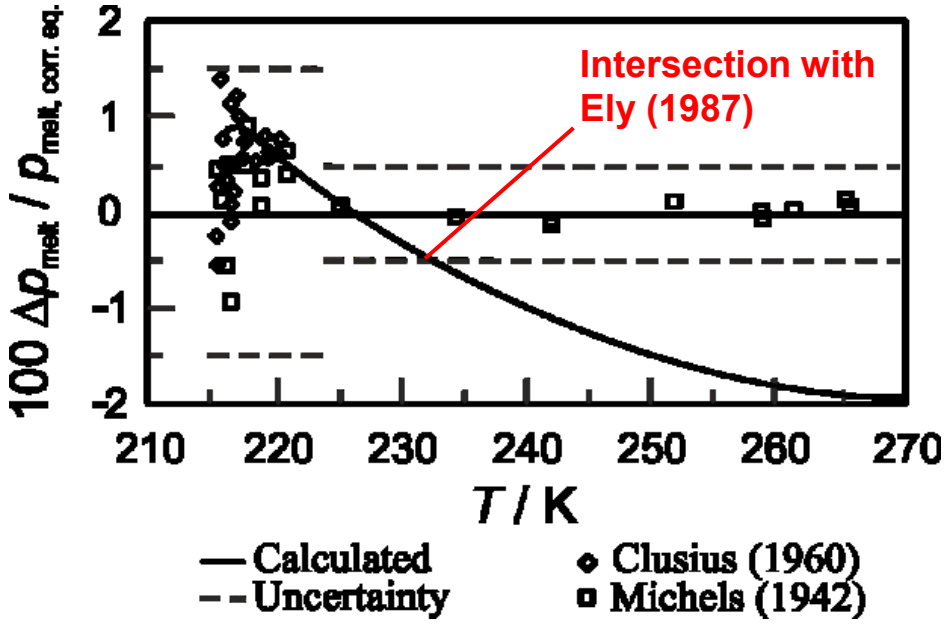
$$g(p,T) = h_0 - Ts_0 + \int_{T_0}^{T} c_p(T,p_0)\mathrm{d}T - T\int_{T_0}^{T} \frac{c_p(T,p_0)}{T}\mathrm{d}T + \int_{p_0}^{p} v(p,T)\mathrm{d}p$$

- *Trusler (2011):* Helmholtz energy as a function of molare volume and temperature
- Fitted also phase equilibrium with adjacent fluid-phase

Phase Equilibria with Solid Phases – Dry Ice

- Intersection with Gibbs enthalpies from EOS for fluid states yields **consistent** SVE / SLE data (sublimation / melting pressure)
- Allows for flash calculations into the melting / sublimation region



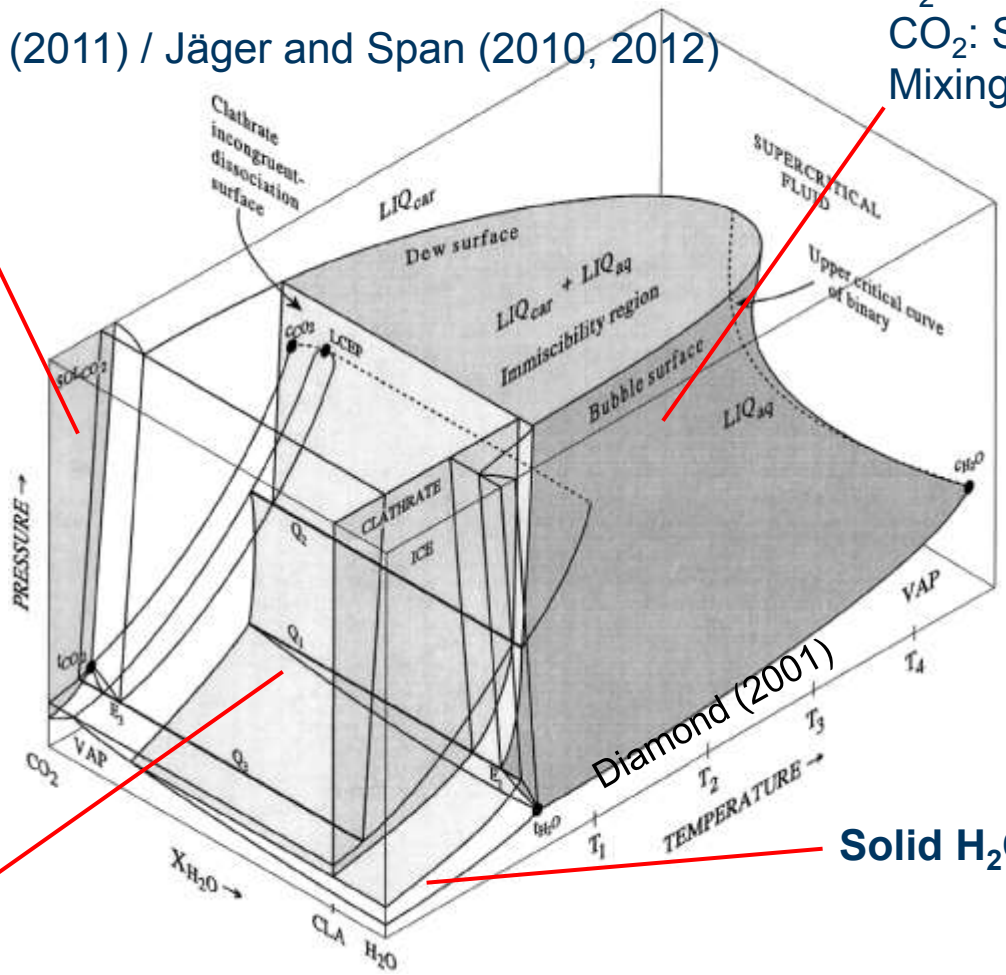


- The property model used for the fluid phases has a significant impact!

Phase Equilibria in the System CO_2 / H_2O

Fluid region:
H_2O: Wagner and Pruss (2002)
CO_2: Span and Wagner (1996)
Mixing rules: Gernert and Span (2013)

Solid CO_2: Trusler (2011) / Jäger and Span (2010, 2012)



Solid H_2O: Feistel and Wagner (2006)

Hydrates: Jäger, Vinš, Hrubý, and Span, R. (2013)

Phase Equilibria with Solid Phases – Hydrates

- The model of Ballard und Sloan (2002) was chosen and slightly modified:

$$\mu_w^H\left(T,p,f_J\right)=g_w^\beta\left(T,p\right)-RT\sum_i v_i \ln\left[1+\sum_J C_{i,J}\left(T,p\right)f_J\right]$$

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- Adjustable parameters of the model:

σ, ε

Potential-parameters

↳ fitted but almost unchanged

κ_1, κ_2

Pressure dependence of the molar volume

↳ **fitted** to $\mu(T,p)$-data generated from experimental data & fluid model

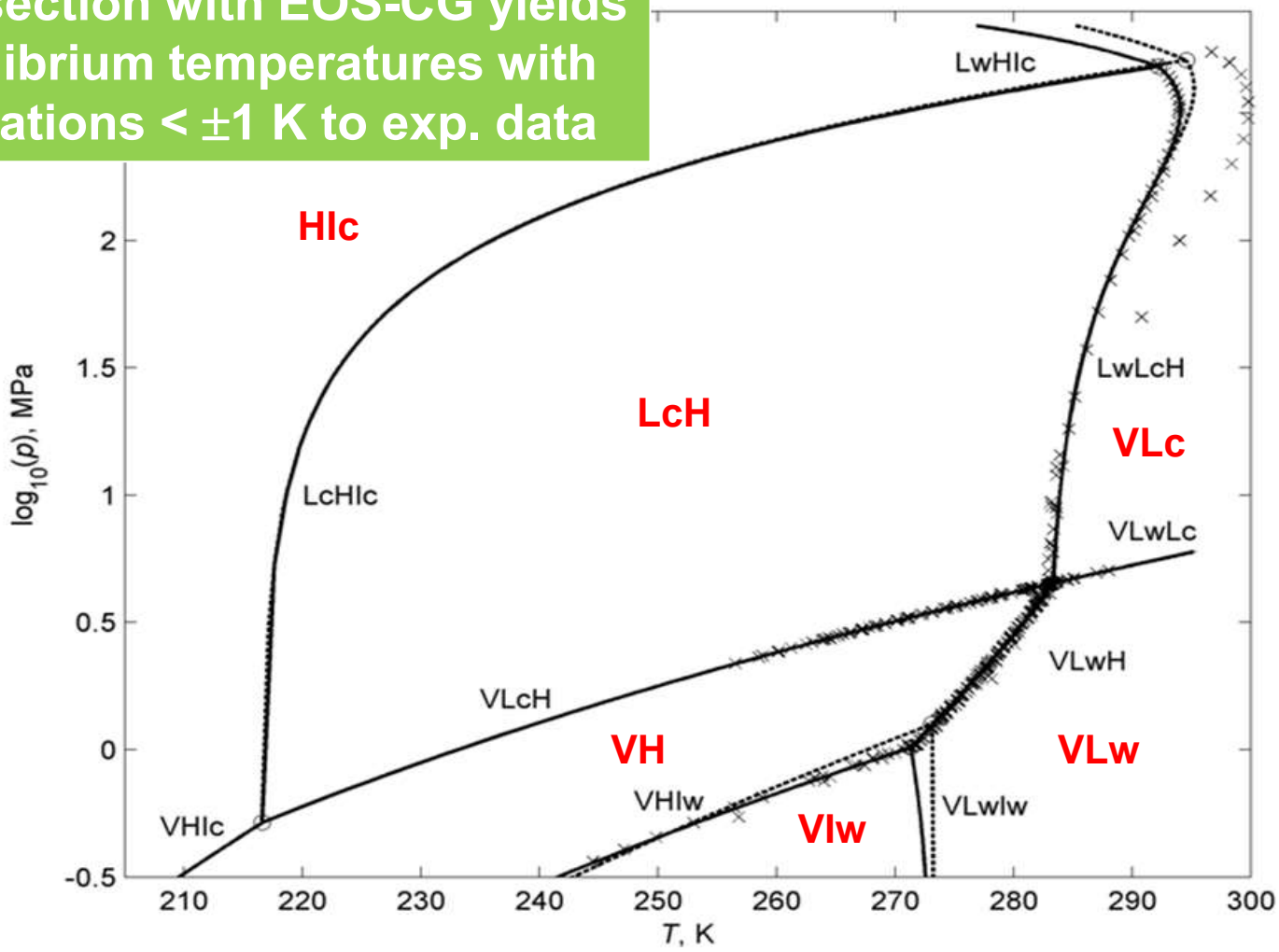
$g_w^{\beta,0}, h_w^{\beta,0}$

Reference state

↳ consistency to reference state of fluid model

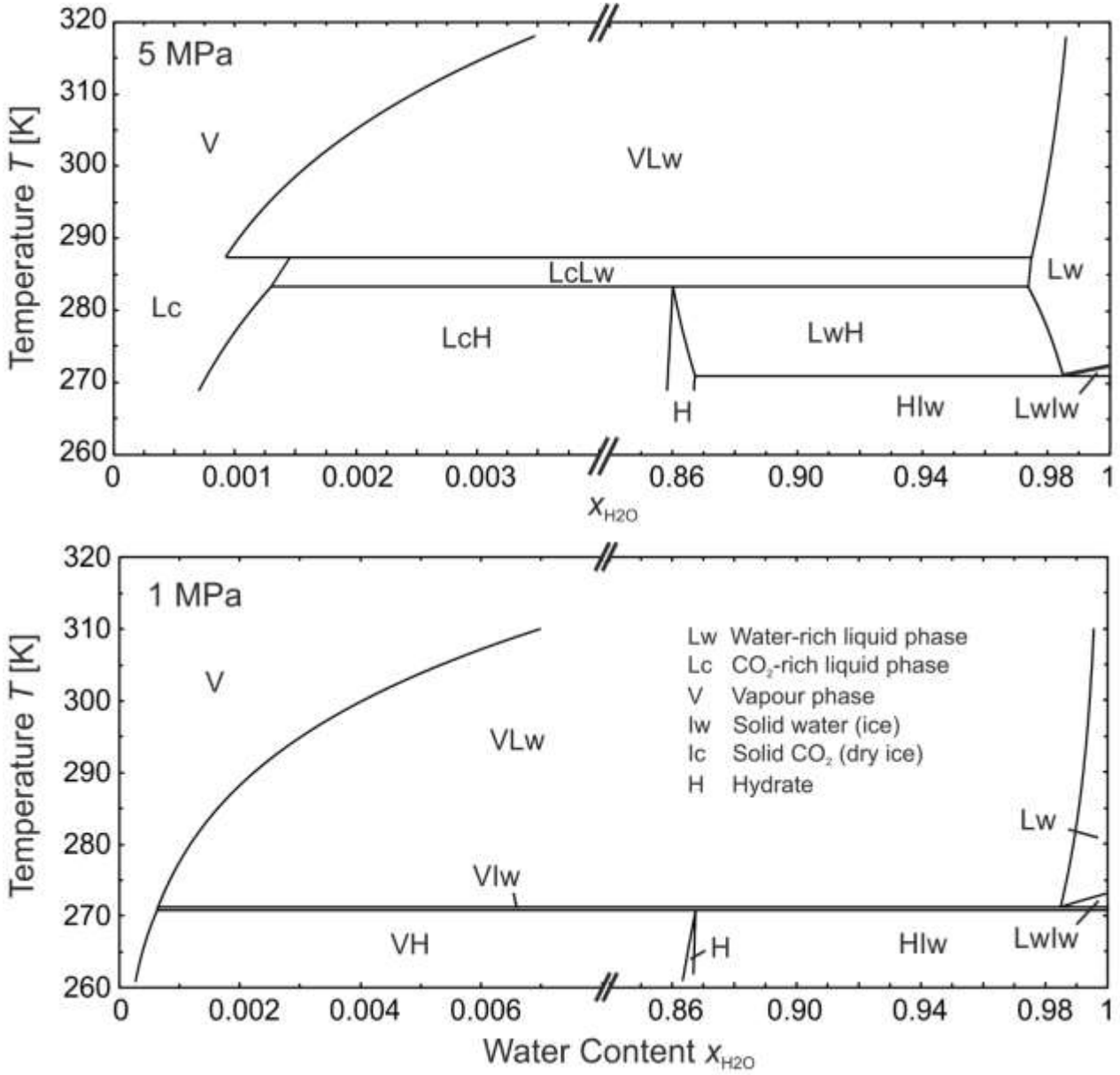
Phase Equilibria with Solid Phases – Hydrates

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



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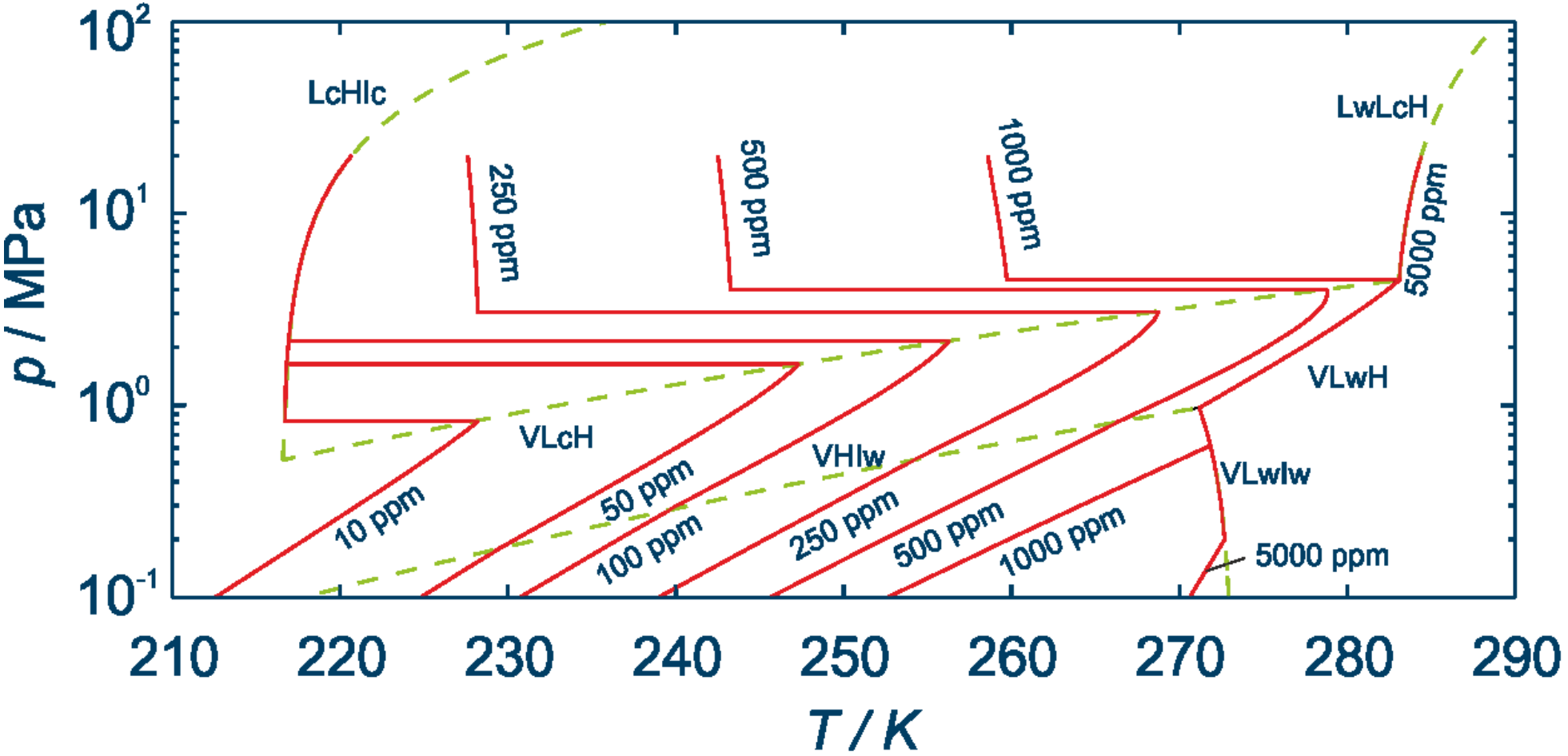
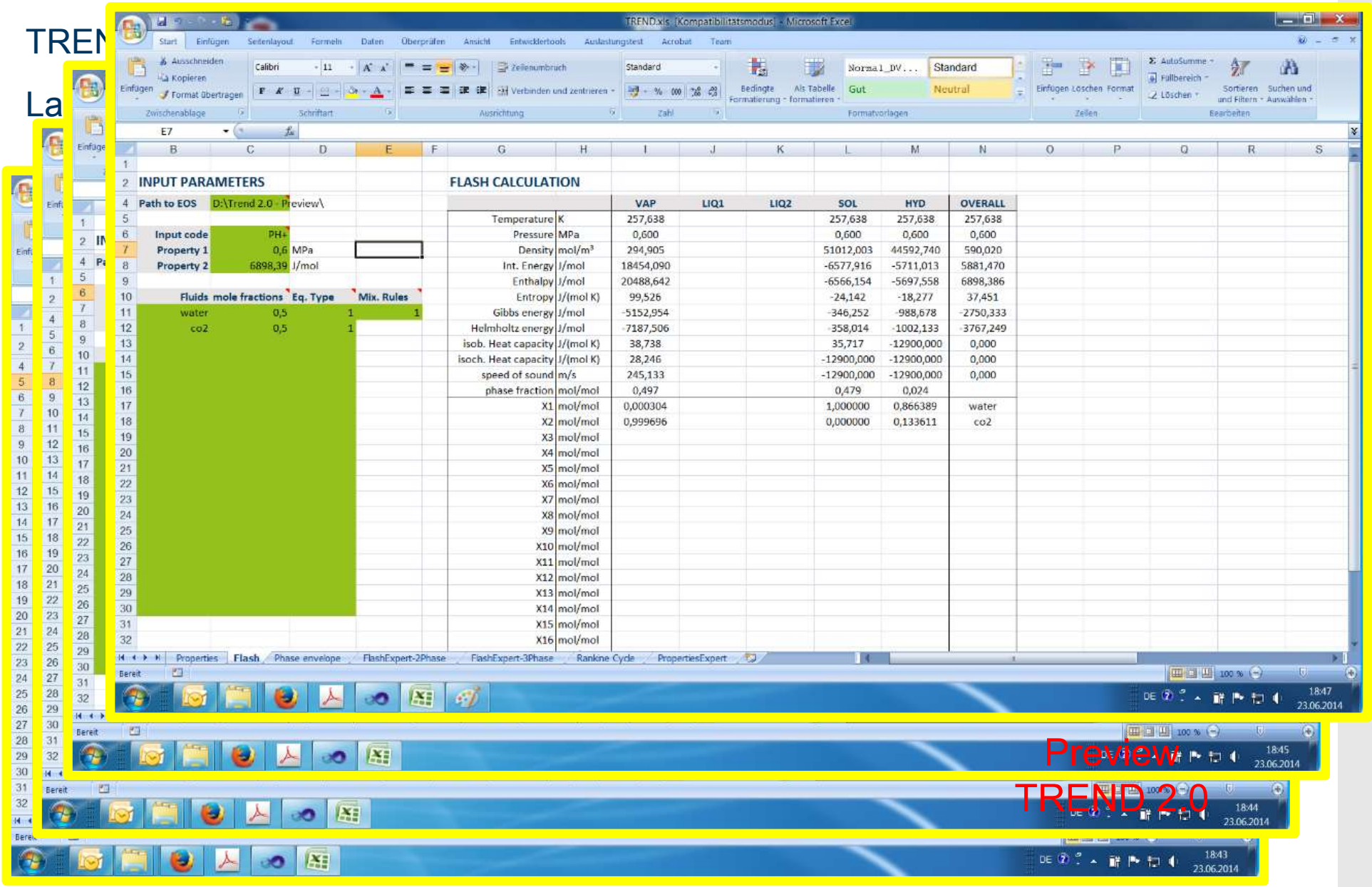


– – Three phase lines in the binary system CO_2 + H_2O

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

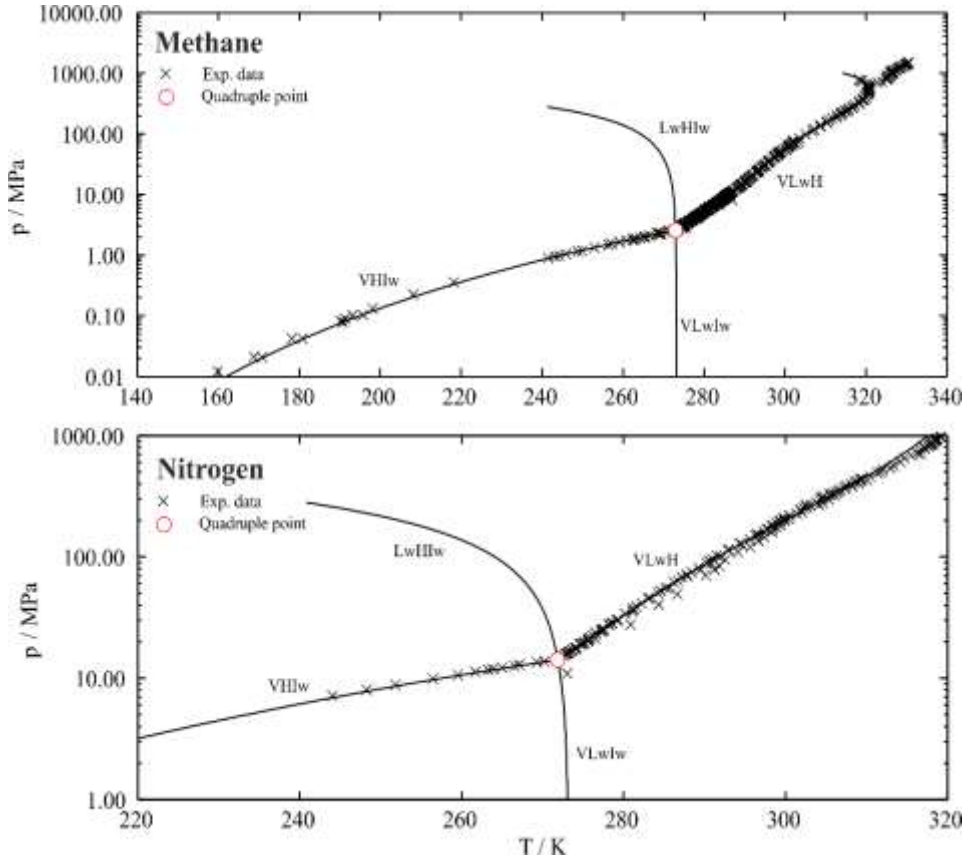
TREND – Software Made Available

- TREN
- La



Other Hydrates

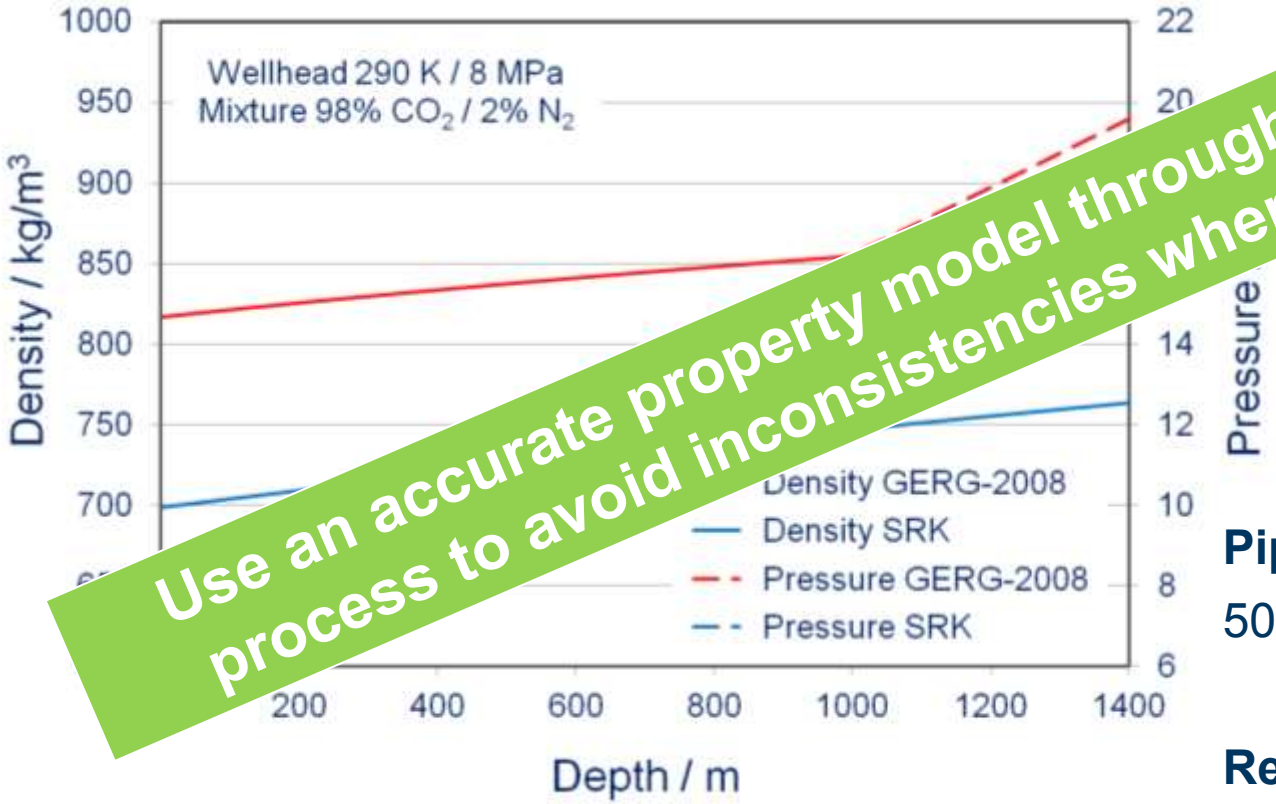
- Hydrate models (consistent to accurate multiparam. mixture models for fluid phase) will soon be published for water with
  - Nitrogen
  - Oxygen
  - Argon
  - Carbon monoxide
  - Methane
  - Ethane
  - Propane



- **A corresponding model for mixed hydrates is still pending**

Avoiding Inconsistencies – Injection of CO_2

- Engineers working on pipelining of CO_2 use GERG-2008 / EOS-CG
- Reservoir engineers use cubic EOS (+ hydrate / electrolyte models)
- Severe inconsistencies, e.g., for injection of CO_2 (-rich mixtur



Use an accurate property model throughout the whole process to avoid inconsistencies wherever possible!

Pipeline engineer delivers
500 to/h ⇨ 577 m^3/h at 19.6 MPa

Reservoir engineer receives
577 m^3/h at 18.1 MPa ⇨ 440 to/h

Avoiding Inconsistencies

- CO_2 in geological storage
  - Mixtures with brines instead of water
- CO_2 capture from natural gas / two phase gas pipelines
  - Mixed hydrates
  - Mixtures with hydrate inhibitors
- CO_2 scrubbing from flue gas / natural gas
  - Systems containing scrubbing agents
- CO_2 ….

In the long run the main challenge will be to ensure that property models used in adjacent process steps are consistent to accurate models applied for CO_2 transport

Thank you for your attention!

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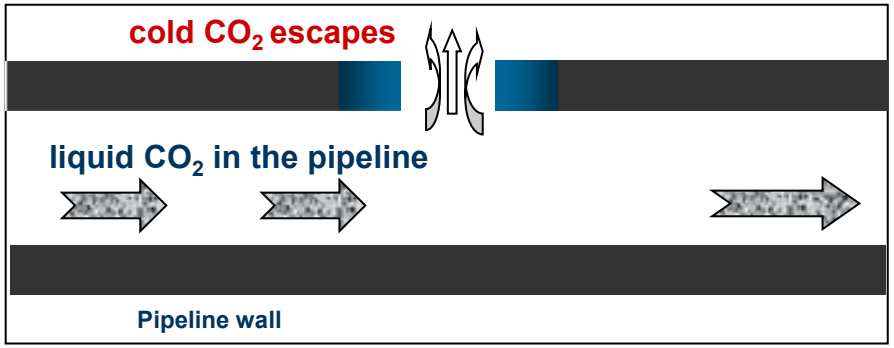
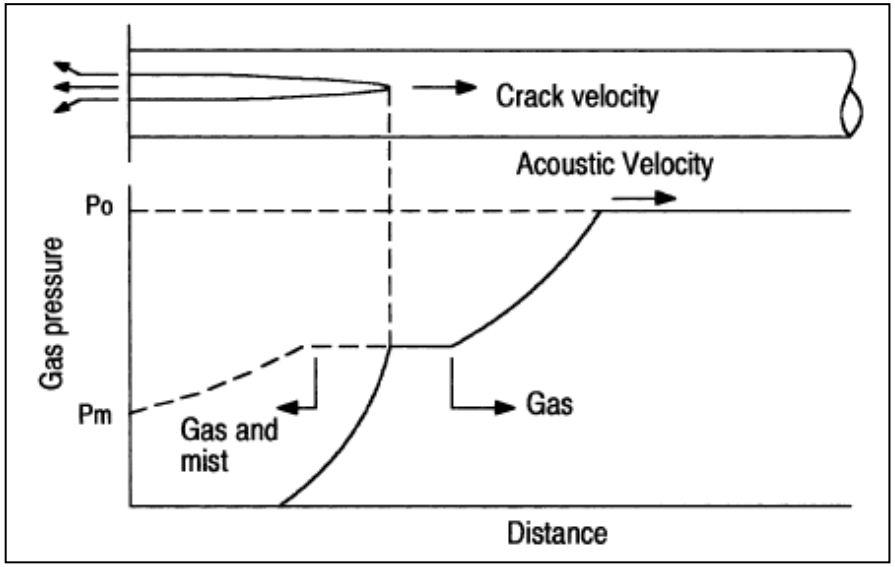
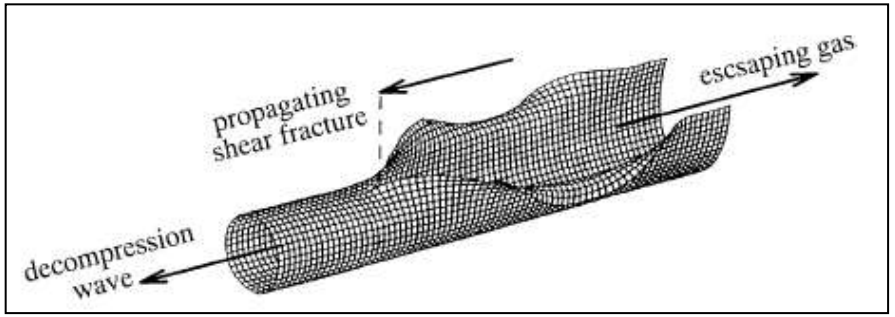
- E.ON for awarding an E.ON Research Award
- E.ON Ruhrgas for the contract "Calculation of Complex Phase Equilibria"
- the federal government of Nordrhein Westfalen in conjunction with EFRE for funding under contract 315-43-02/2-005-WFBO-011Z
- the European Commission for the contract "Seventh Framework Program, Nr. 308809, IMPACTS“
- the DFG for the framework of the collaborative research centre ”Oxyflame“

The „Killer Application“







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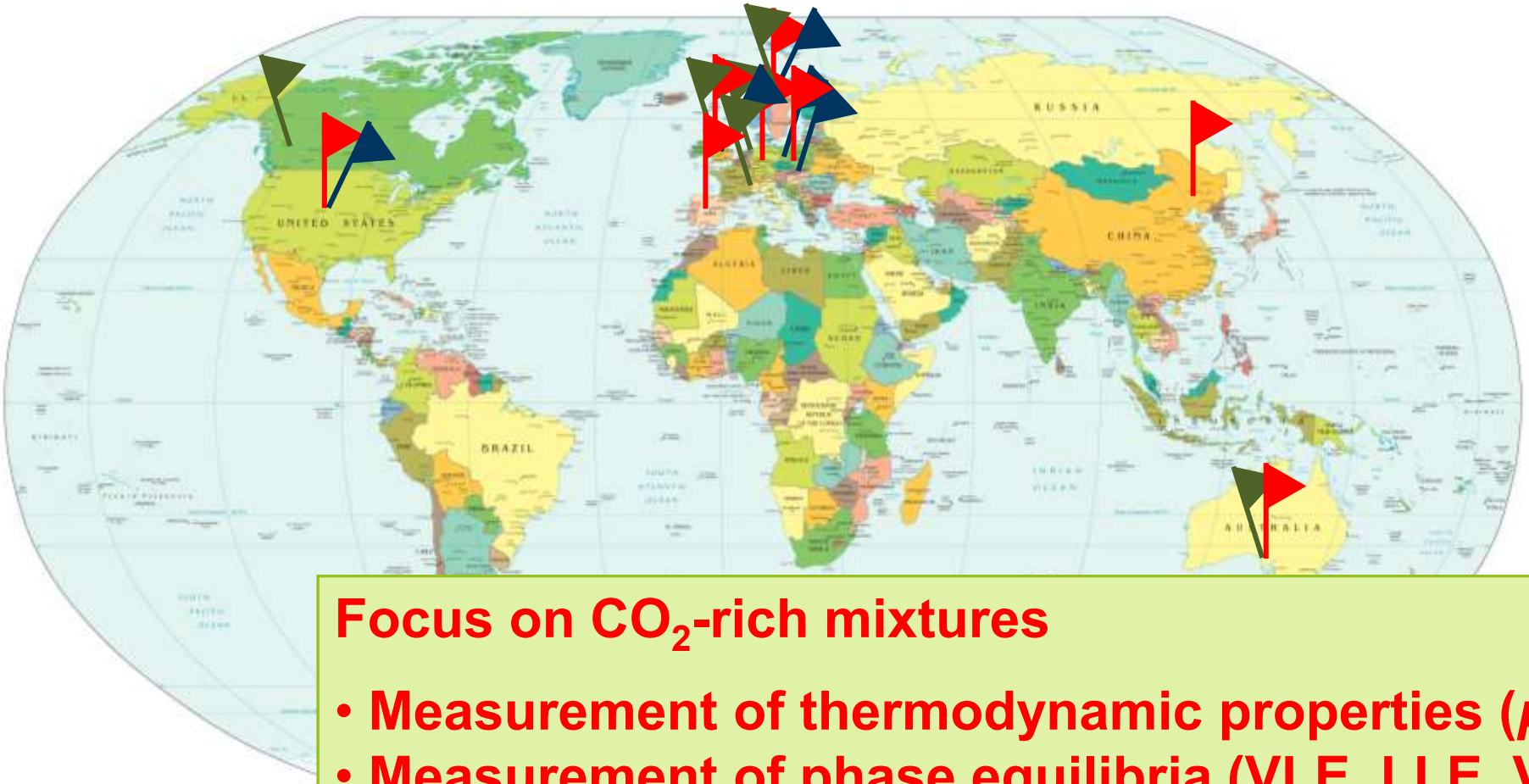
- If a CO_2 pipeline leaks, the mantle cools down drastically, the material becomes brittle
- The crack propagates in both directions
- The pressure loss propagates with about speed of sound
- If the crack propagates faster than speed of sound, small cracks result in a disaster
- ➢ The issue is a **safety issue**, accurate properties required for homogeneous, VLE, VLSE states
- Accurate properties are certainly more important for other applications, but who cares …

International Cooperation



Focus on CO_2-rich mixtures

- **Measurement of thermodynamic properties (*pvT*, *w*)**
- **Measurement of phase equilibria (VLE, LLE, VLSE)**
- **Measurement of transport properties (viscosity)**

- **Accurate property models for CO_2-rich mixtures**
- **Description of phase equilibria including solid phases**
- **Improvement of phase equilibrium algorithms**

- **Test of new property models for various applications**