RUHR-UNIVERSITÄT BOCHUM

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DOCTORAL SCHOOL
CLOSED CARBON CYCLE ECONOMY

New Fundamental Equations of State for an Improved Description of Hydrogen-Rich Mixtures with the Reference Model GERG-2008

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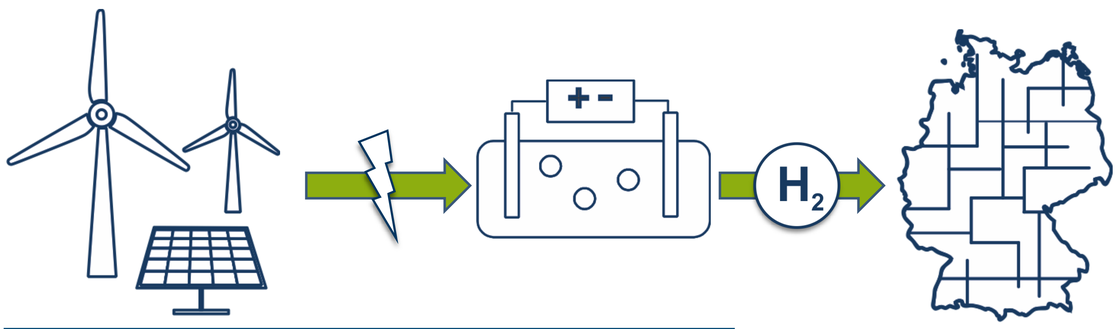
Motivation

- The production of green hydrogen from renewable energies by electrolysis is considered a promising technology for the decarbonization and flexibilization of our energy supply
- The injection of green hydrogen into the natural gas grid allows for a step-by-step substitution of the fossil energy carrier natural gas using the existing infrastructure for distribution and storage of the gas mixture
- The changes in thermodynamic properties resulting from an increased hydrogen injection have to be considered to ensure a safe and efficient operation of the gas grid, gas storage facilities, conversion technologies and a variety of other technical processes

➢ Optimization of the reference model GERG-2008[1] regarding the description of hydrogen-rich natural gas properties in a wide range of temperature, pressure, and composition is required

➢ New equations of state for 20 binary hydrogen mixtures are needed



Fundamental Equations of State for Mixtures

- Equations of state are formulated in terms of the reduced Helmholtz energy α as a function of temperature T, density ρ, and composition $\bar{x}$

$$\alpha(\delta,\tau,\bar{x}) = \frac{a(\rho,T,\bar{x})}{RT} = \alpha^{\mathrm{o}}(\rho,T,\bar{x}) + \alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$$

- The ideal part $\alpha^{\mathrm{o}}(\rho,T,\bar{x})$ describes the mixture behavior of the involved pure components in the reference state of the ideal-gas

$$\alpha^{\mathrm{o}}(\rho,T,\bar{x}) = \sum_{i=1}^{N} x_i[\alpha^{\mathrm{o}}_{\mathrm{o},i}(\delta_{\mathrm{o},i},\tau_{\mathrm{o},i}) + \ln x_i]$$

- The residual part $\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$ considers the molecular interactions of the real fluid

$$\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = \sum_{i=1}^{N} x_i \alpha^{\mathrm{r}}_{\mathrm{o},i}(\delta,\tau) + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha^{\mathrm{r}}_{ij}(\delta,\tau)$$

- The reduced density δ and the reciprocal reduced temperature τ are determined with composition-dependent reducing functions

$$\delta = \frac{\rho}{\rho_{\mathrm{r}}(\bar{x},\rho_{\mathrm{c},i},\beta_{v,ij},\gamma_{v,ij})} \qquad \tau = \frac{T_{\mathrm{r}}(\bar{x},T_{\mathrm{c},i},\beta_{T,ij},\gamma_{T,ij})}{T}$$

- Non-ideal mixture behavior is modelled with a binary-specific departure function

$$\alpha^{\mathrm{r}}_{ij}(\delta,\tau) = \sum_{k=1}^{\mathrm{K_{pol}}} n_k \tau^{t_k} \delta^{d_k} + \sum_{k=\mathrm{K_{pol}}+1}^{\mathrm{K_{pol}}+\mathrm{K_{exp}}} n_k \tau^{t_k} \delta^{d_k} e^{[-\delta^{l_k}]} + \sum_{k=\mathrm{K_{pol}}+\mathrm{K_{exp}}+1}^{\mathrm{K_{pol}}+\mathrm{K_{exp}}+\mathrm{K_{GBS}}} n_k \tau^{t_k} \delta^{d_k} e^{[-\eta_k(\delta-\varepsilon_k)^2-\beta_k(\tau-\gamma_k)^2]}$$

- The adjustable parameters are fitted to experimental data using a non-linear algorithm[2]

Results

Description of the Homogeneous Region

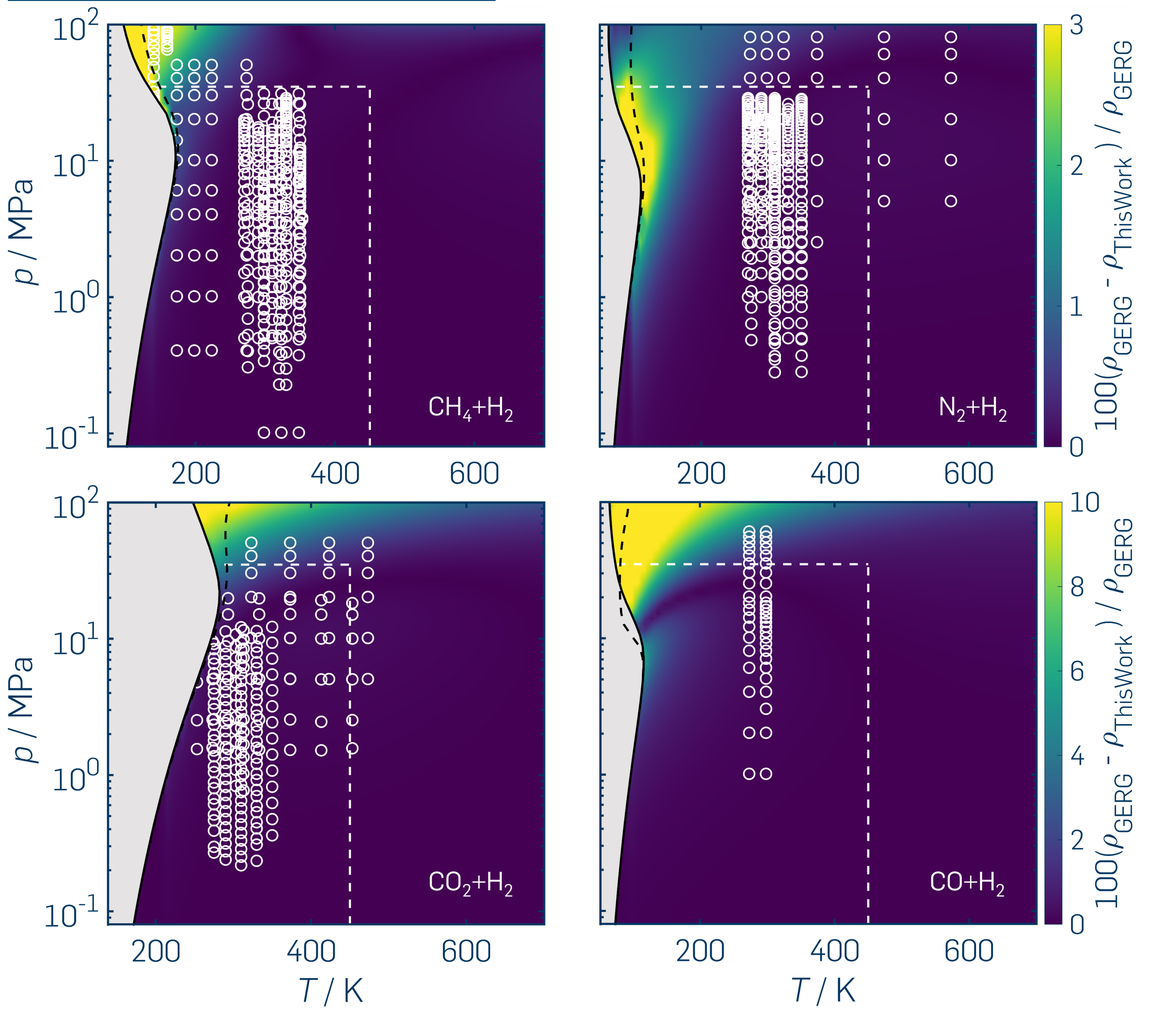


Fig. 1: Percentage deviation in density in the homogeneous region between the new models and GERG-2008[1] at equimolar composition. The white dashed lines represent the normal range of validity of both models and the black dashed lines mark the phase boundary calculated with the GERG-2008.[1] The circles represent the available experimental density data at approximately equimolar compositions.

Description of the Phase Equilibrium

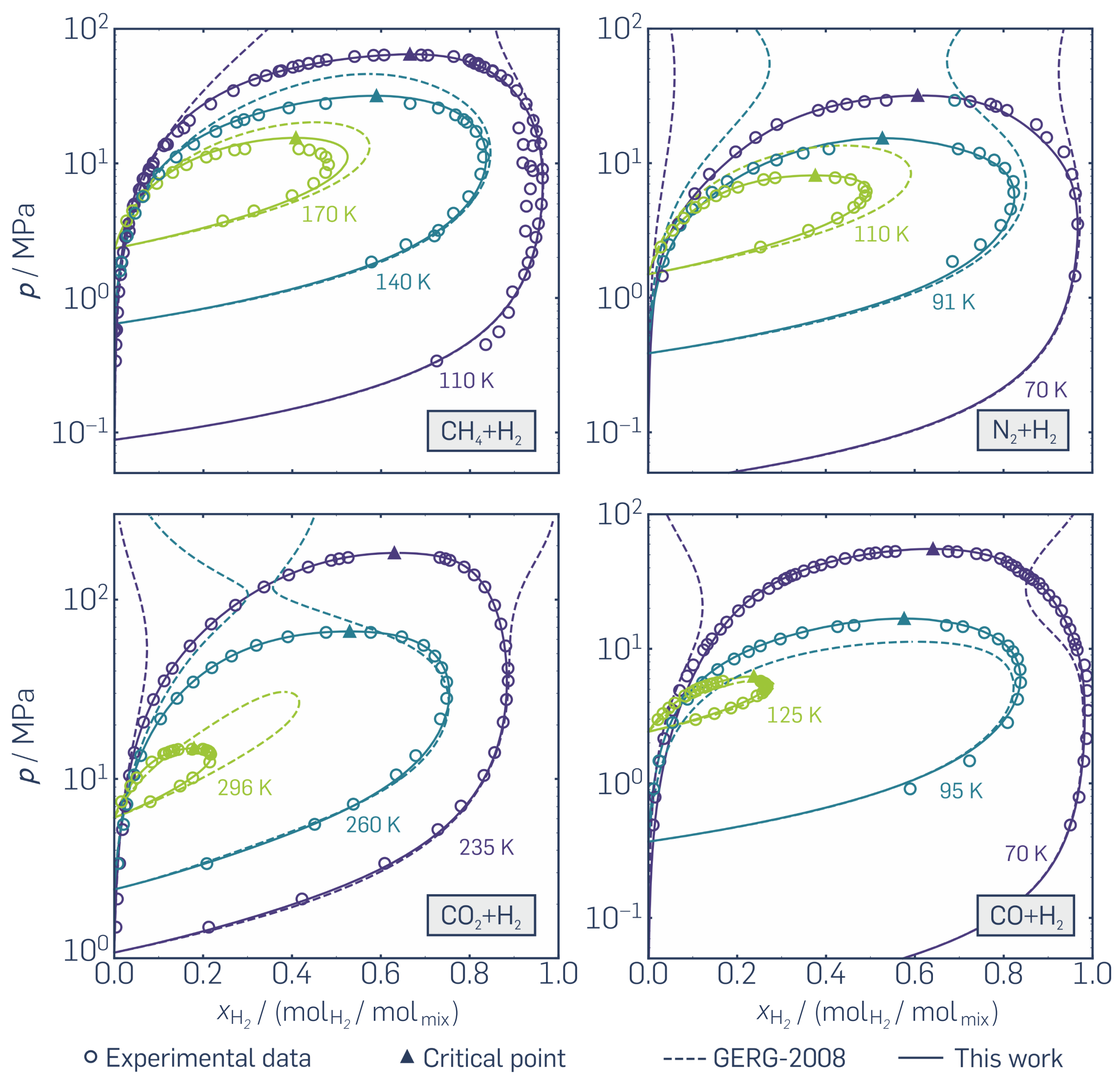


Fig. 2: *p,x*-diagrams of the binary mixtures at selected temperatures calculated with the new models and the GERG-2008[1] compared to experimental phase equilibrium data.

References

[1] Kunz, O., & Wagner, W. , Journal of Chemical & Engineering Data, 57(11), 3032-3091 (2012)

[2] Lemmon, E. W. & Jacobsen, R. T. , Journal of Physical and Chemical Reference Data, 34(1), 69-108 (2005)

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