Empirical rules of thumb or molecular modelling?

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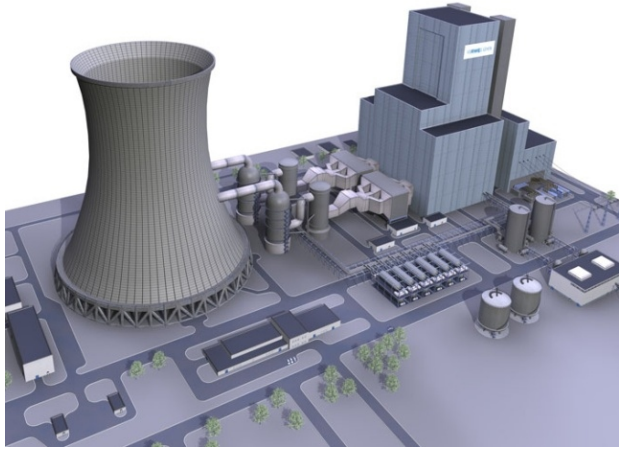
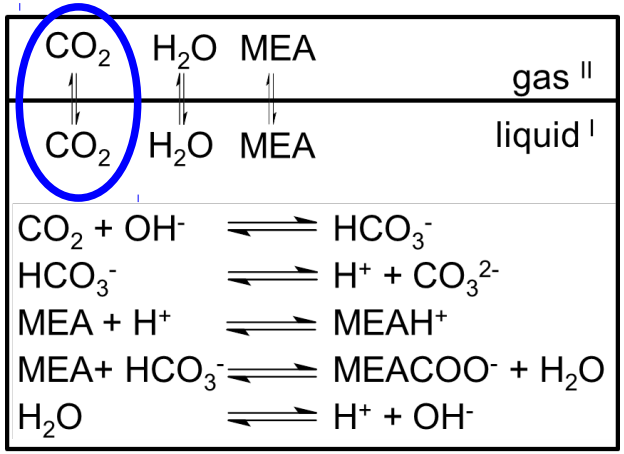
Computational Molecular Engineering

Case study: Analogy between CO_2 and N_2O

Engineering application scenario:

- Gas cleaning by reactive absorption
- Physical gas solubility of CO_2
  - Key property
  - Sometimes impossible to determine





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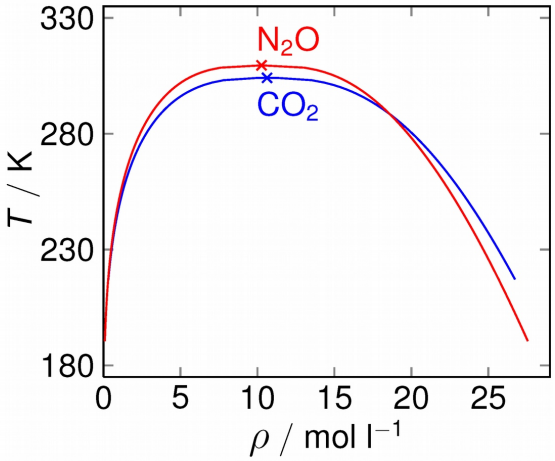
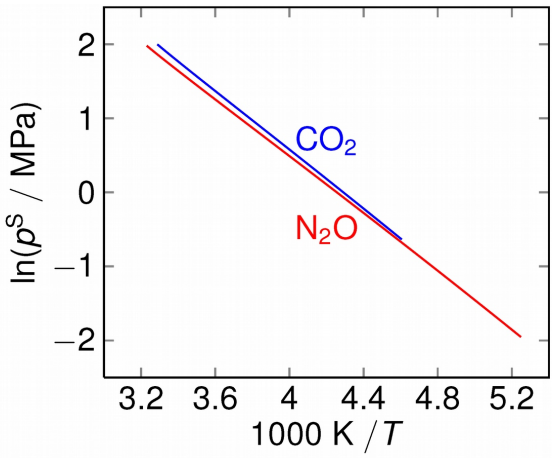
Henry's law: $Py_i\varphi_i = H_i x_i$

Rule of thumb for Henry's law coefficients:

- Analogy with nitrous oxide

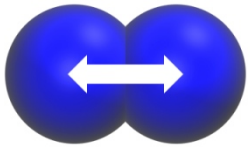
$$R_H = \frac{H_{N_2O,water}}{H_{CO_2,water}} = \frac{H_{N_2O,aqueous\ solution}}{H_{CO_2,aqueous\ solution}} = \text{const.}$$



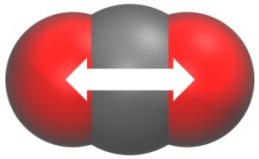


Pure fluid models

Solutes

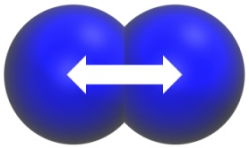


CO_2 (Vrabec *et al.*)

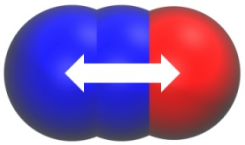


CO_2 (Merker *et al.*)

new molecular models

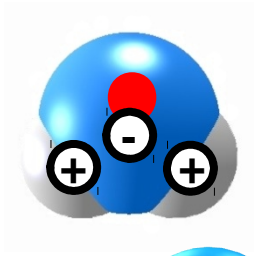


N_2O two-site model

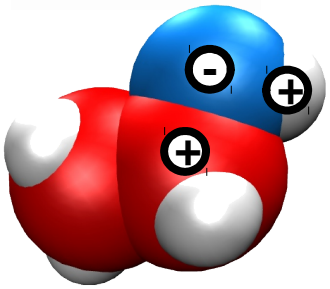


N_2O three-site model

Solvents



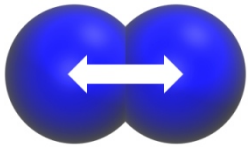
Water (TIP4P/2005)



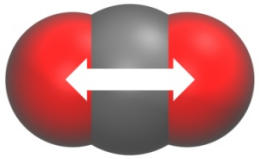
Ethanol (Schnabel *et al.*)

Do mixed solvents containing water and ethanol behave as predicted by the CO_2-N_2O analogy?

New models for nitrous oxide



CO_2 (Vrabec *et al.*)



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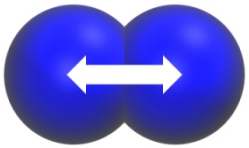
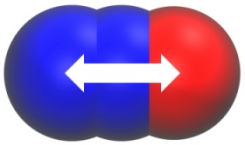
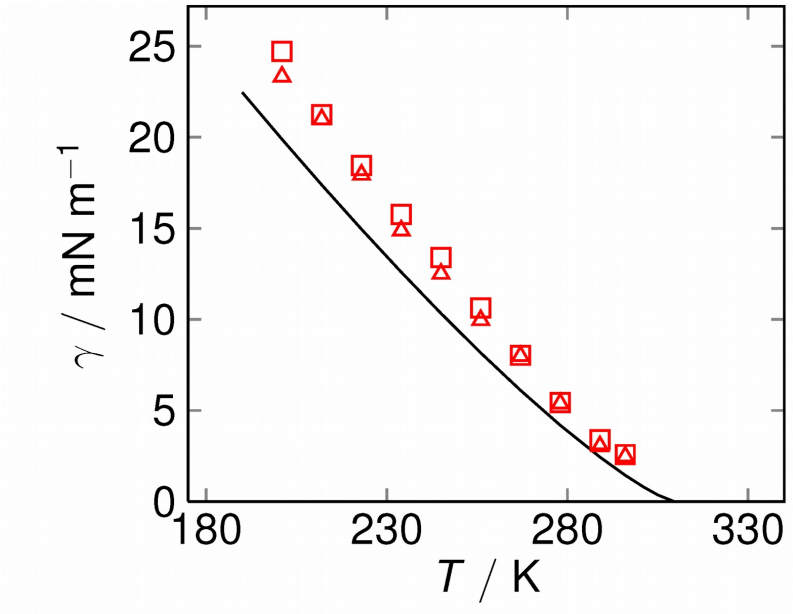


N_2O two-site model



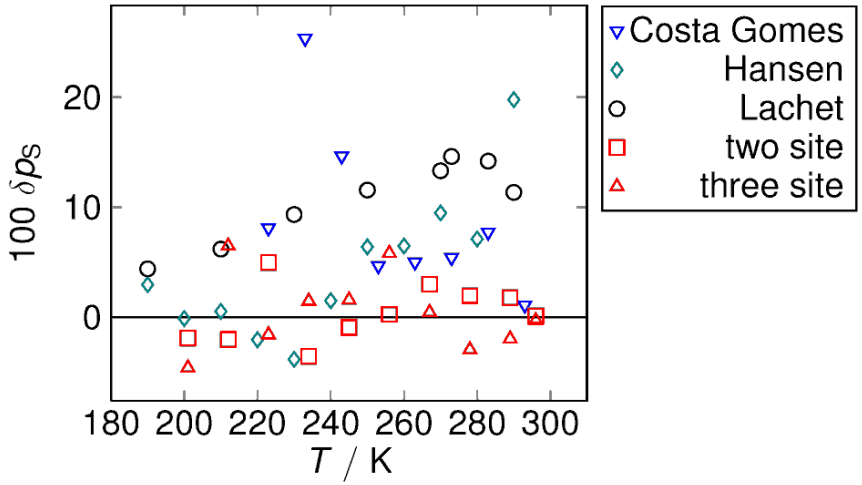
N_2O three-site model

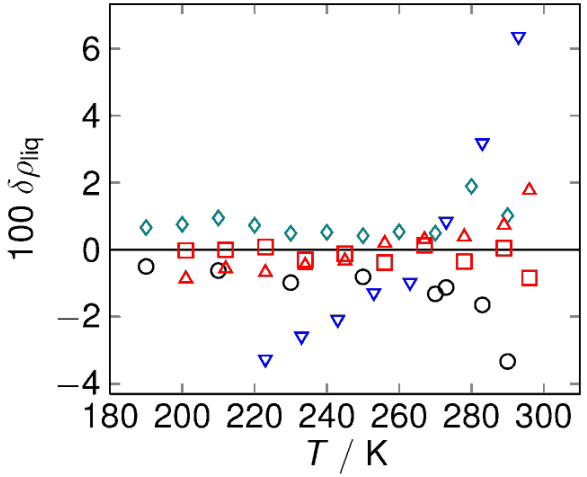
surface tension of N_2O



N_2O two site model, this work
N_2O three site model, this work
— EOS by Lemmon and Span / DIPPR correlation for surface tension

Deviation from Lemmon-Span EOS





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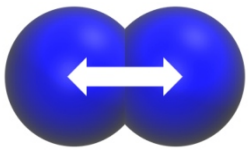

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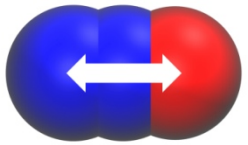

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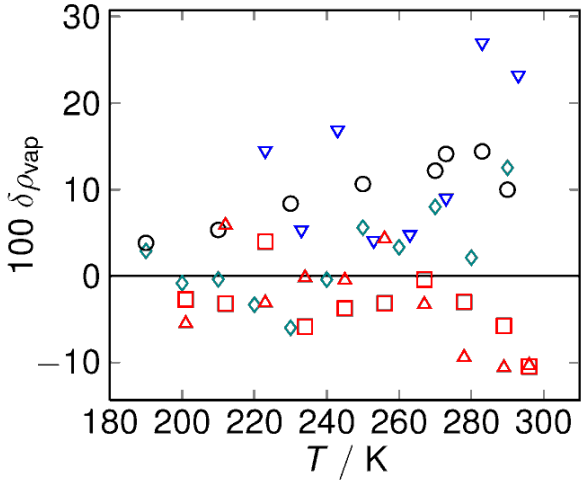
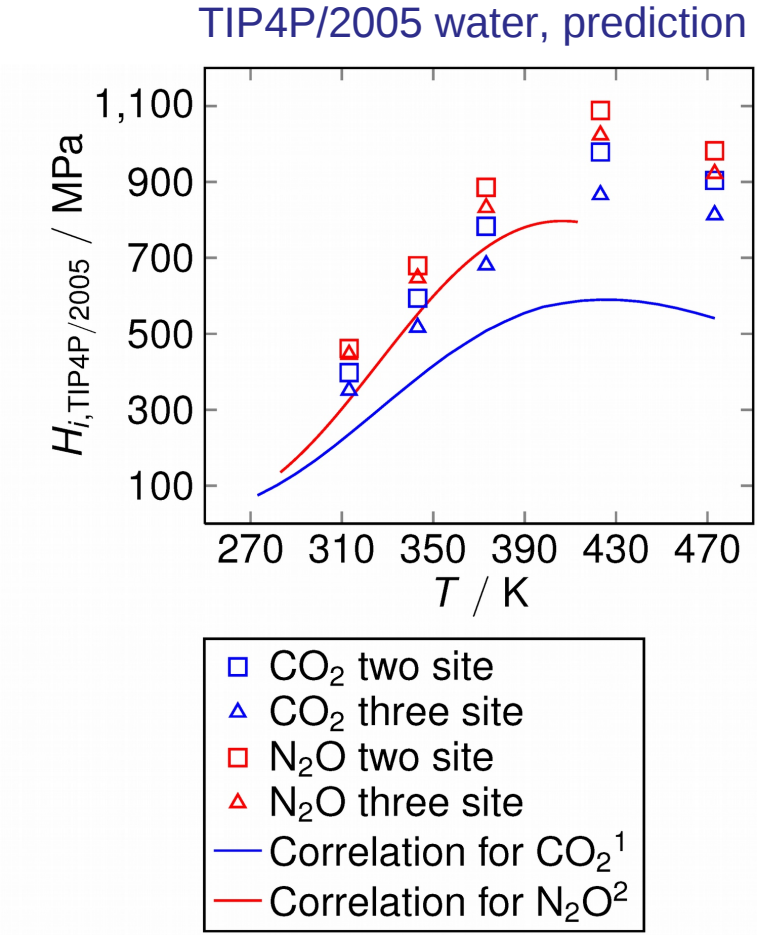


Physical solubility in pure water



- Lorentz-Berthelot combining rule:

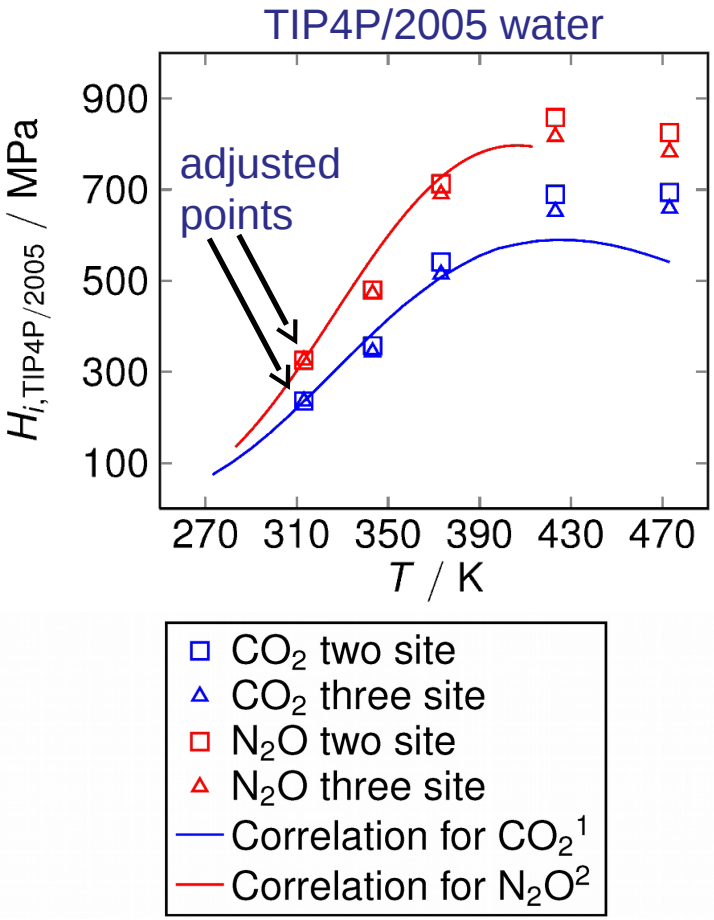
$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$$

- Overestimation of Henry's law constant in all cases
- Adjustment of a binary interaction parameter necessary

1) Rumpf and Maurer, Ber. Bunsenges. Phys Chem. 97 (1993) 85.
2) Penttilä *et al.*, Fluid Phase Equilib. 311 (2011) 59.

Physical solubility in pure water



- Modified Lorentz-Berthelot combining rule:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

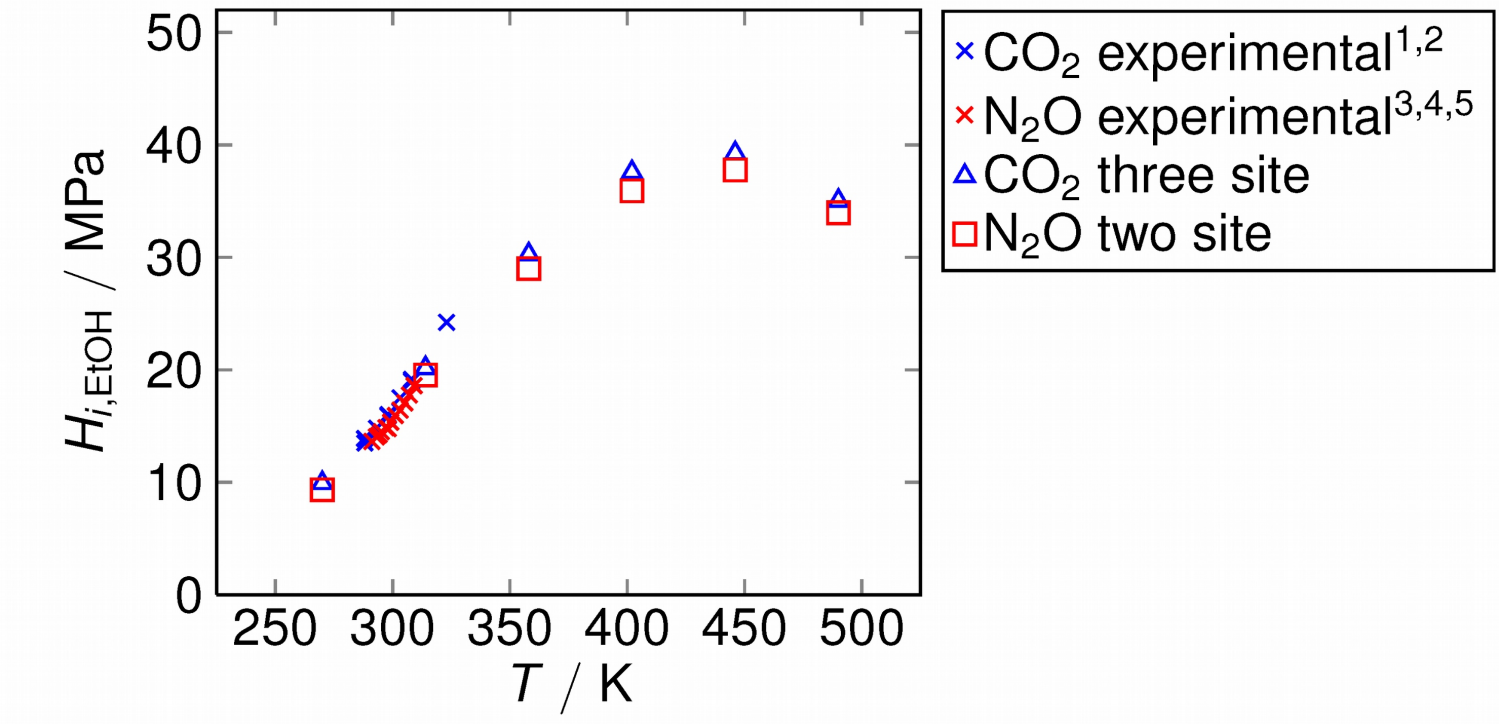
$$\epsilon_{AB} = \xi_{AB} \sqrt{\epsilon_A \epsilon_B}$$

- Temperature dependence is well captured by all models
- Best agreement for two-site model of N_2O and three-site model of CO_2

1) Rumpf and Maurer, Ber. Bunsenges. Phys Chem. 97 (1993) 85.
2) Penttilä *et al.*, Fluid Phase Equilib. 311 (2011) 59.

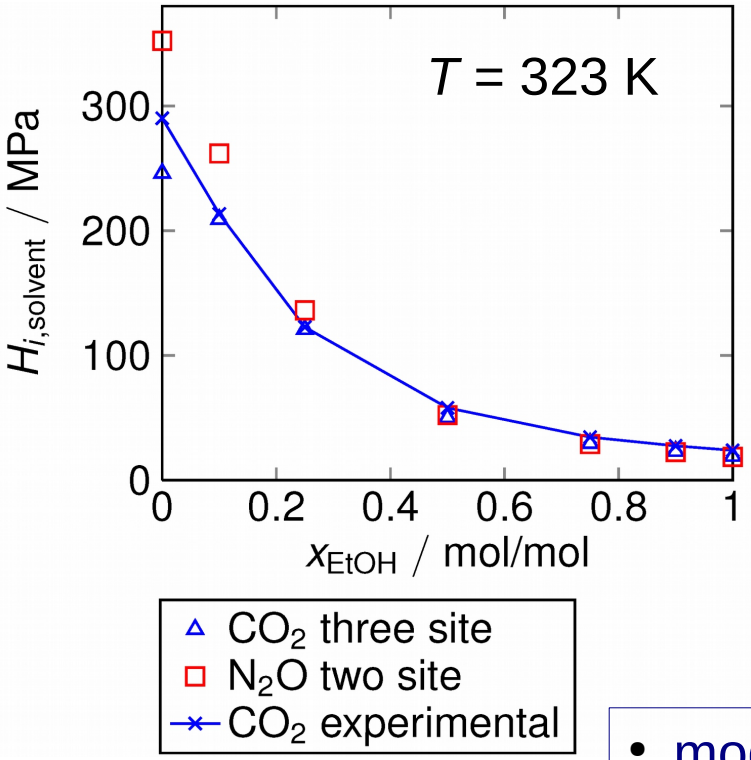
Solubility in pure ethanol

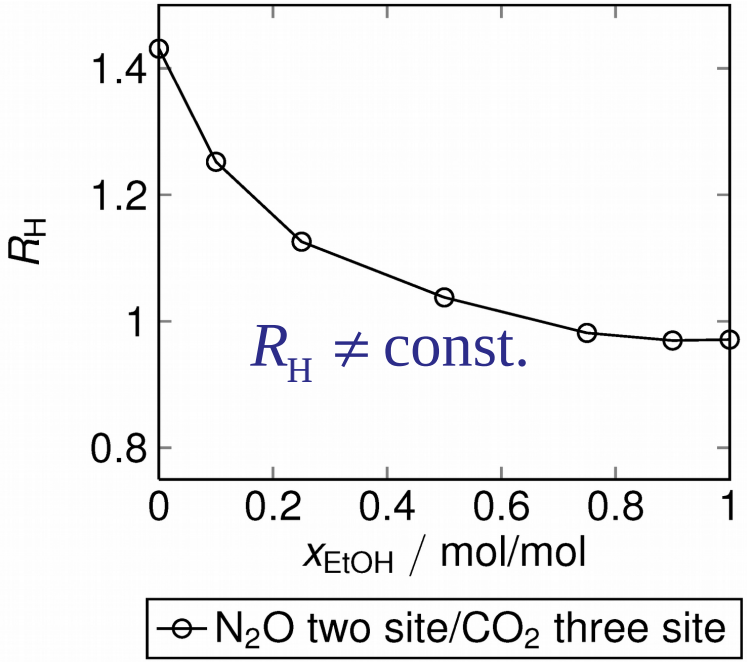
Predictive simulations, i.e. $\xi = 1$ in all cases



1) Postigo and Katz, J. Solution. Chem. 16 (1987) 1015; 2) Dalmolin et al., Fluid Phase Equilib. 245 (2006) 193;
3) Kunerth, Phys. Rev. 19 (1922) 512; 4) Sada et al., Ind. Eng. Chem. Fundam. 14 (1975) 232;
5) Hsu and Campbell, Aerosol Age. 9 (1964) 34.

Mixed solvent: Water + ethanol





- models adjusted to solubility in pure water
- validated for pure EtOH (both), mixture (CO_2)

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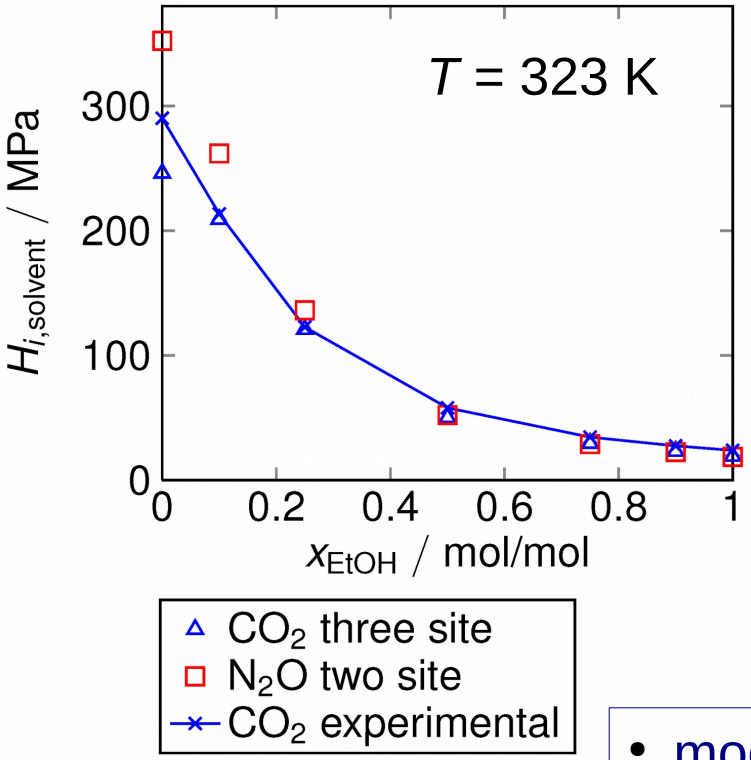

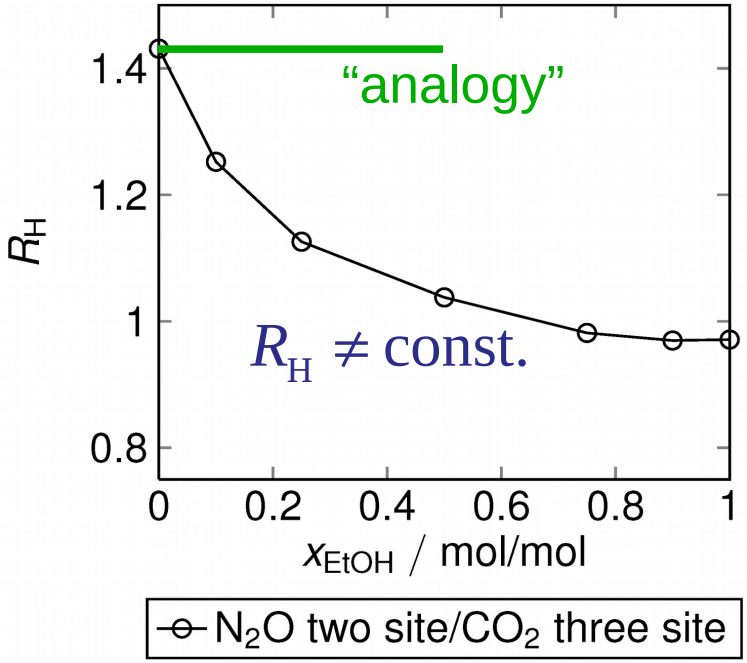

- models adjusted to solubility in pure water
- validated for pure EtOH (both), mixture (CO_2)
- predictive use: breakdown of the "analogy"

Summary

New two-site and three-site (+ quadrupole) models for nitrous oxide

Typical procedure during validation: Select the best model combination

Using validated molecular models, reliable predictions can be obtained

The “analogy” between CO_2 and N_2O breaks down in a simple test case

Outlook

Application to other aqueous mixtures as technically relevant solvents

Crucial: Further development of *ms2idf* (and *ls1idf* for absorption kinetics)