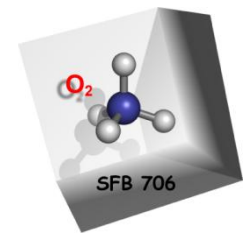




Thermodynamic Properties for the Heterogeneously Catalyzed Selective Oxidation of Cyclohexane in Carbon Dioxide Expanded Media by Experiment and Molecular Simulation

Thorsten Merker¹, Jadran Vrabec², Hans Hasse¹



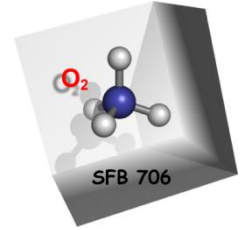
¹Laboratory of Engineering Thermodynamics,
TU Kaiserslautern, Germany

²Thermodynamics and Energy Technology,
University of Paderborn, Germany



Computational
Molecular Engineering

DFG SFB 706: Selective Catalytic Oxidations Using Molecular Oxygen



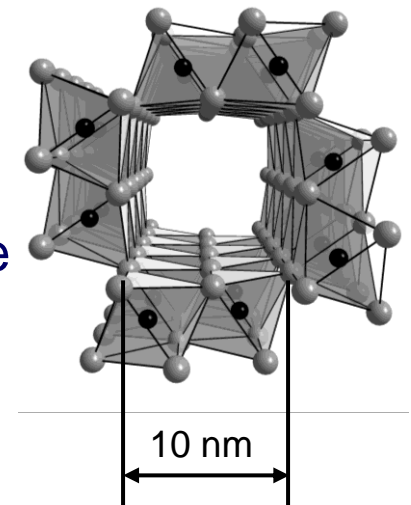
Subproject A2: Novel Octahedral Redox Molecular Sieves for
the Heterogeneously Catalyzed Selective Oxidation of Cyclohexane

Cooperation

- Prof. Gläser, Technical Chemistry, University of Leipzig
- Prof. Schleid, Inorganic Chemistry, University of Stuttgart

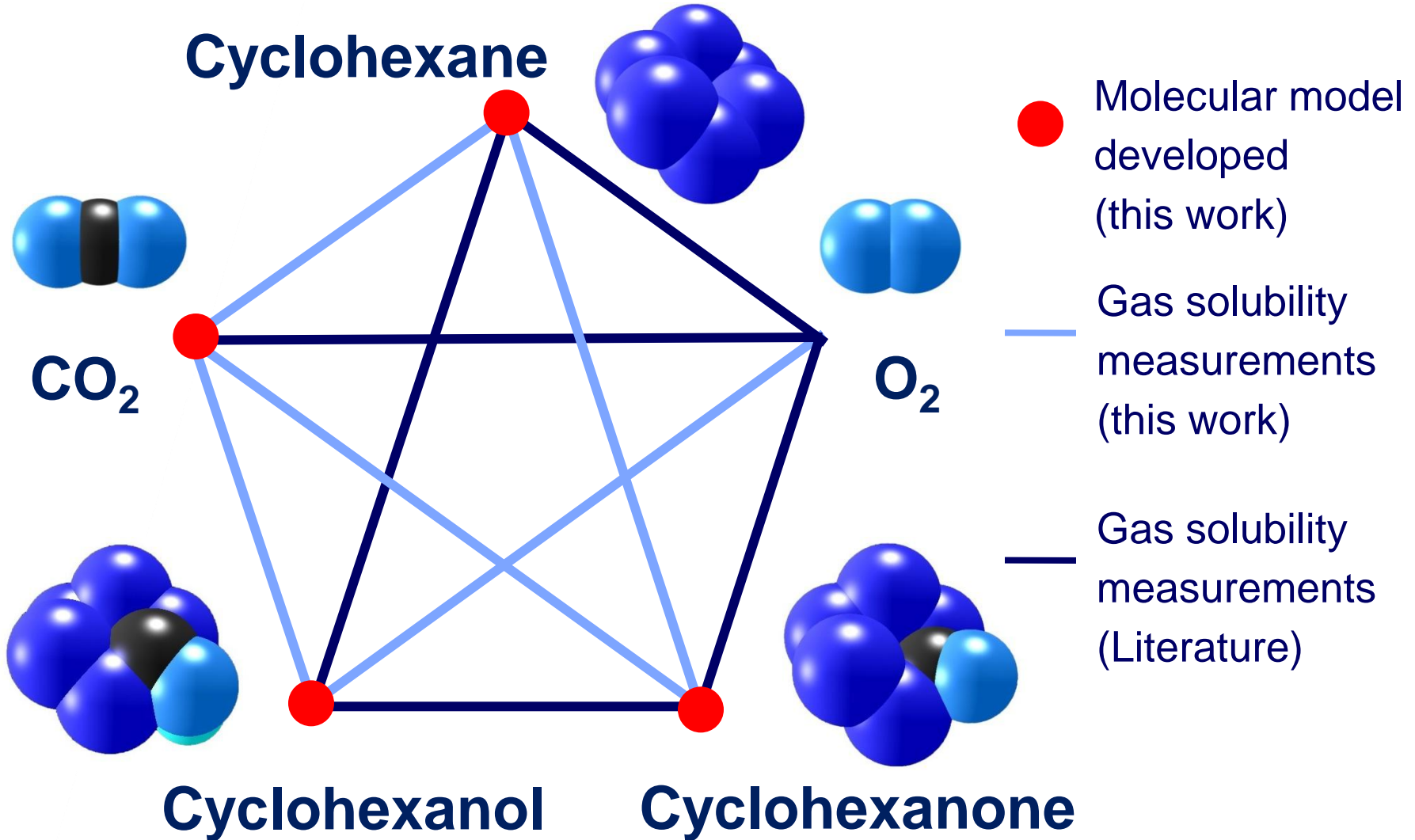
Goal

Experimental investigation and molecular simulation of the
thermodynamic properties of the relevant reaction mixture

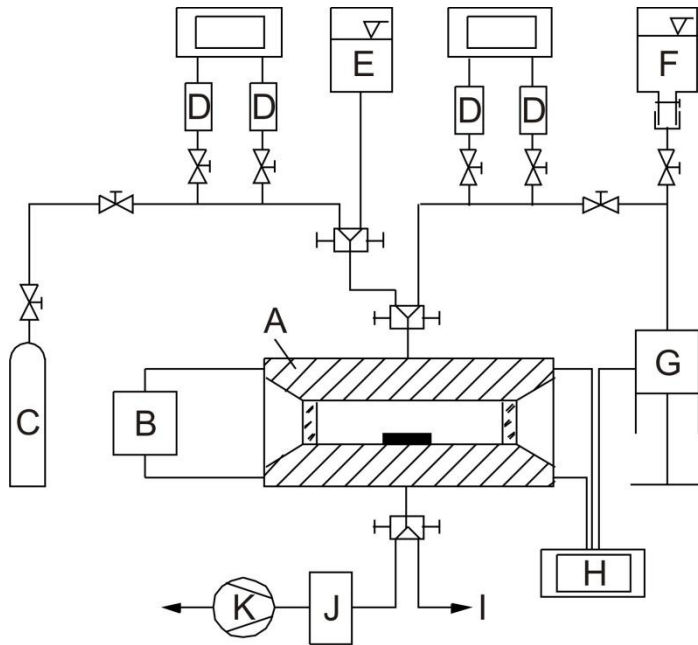


Reacting System

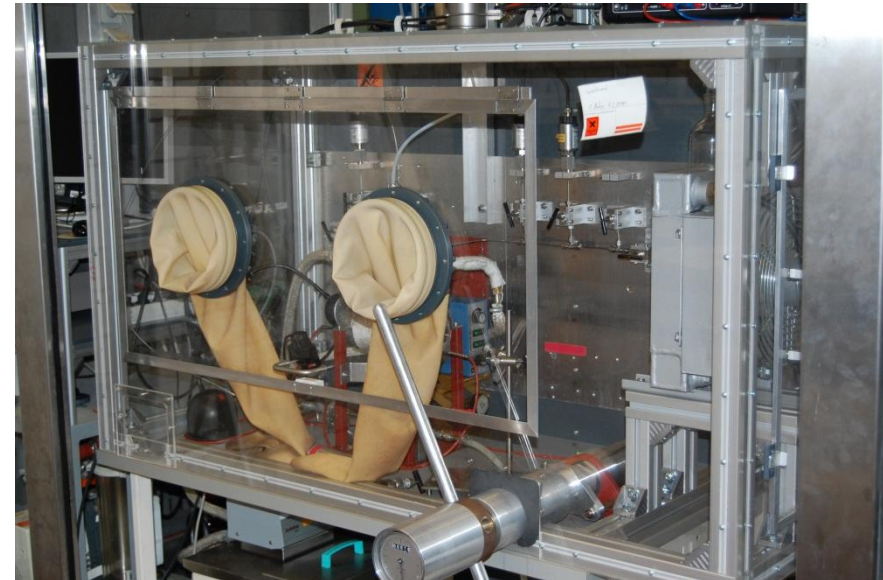
Cyclohexane



Gas Solubility Measurements: Synthetic Method

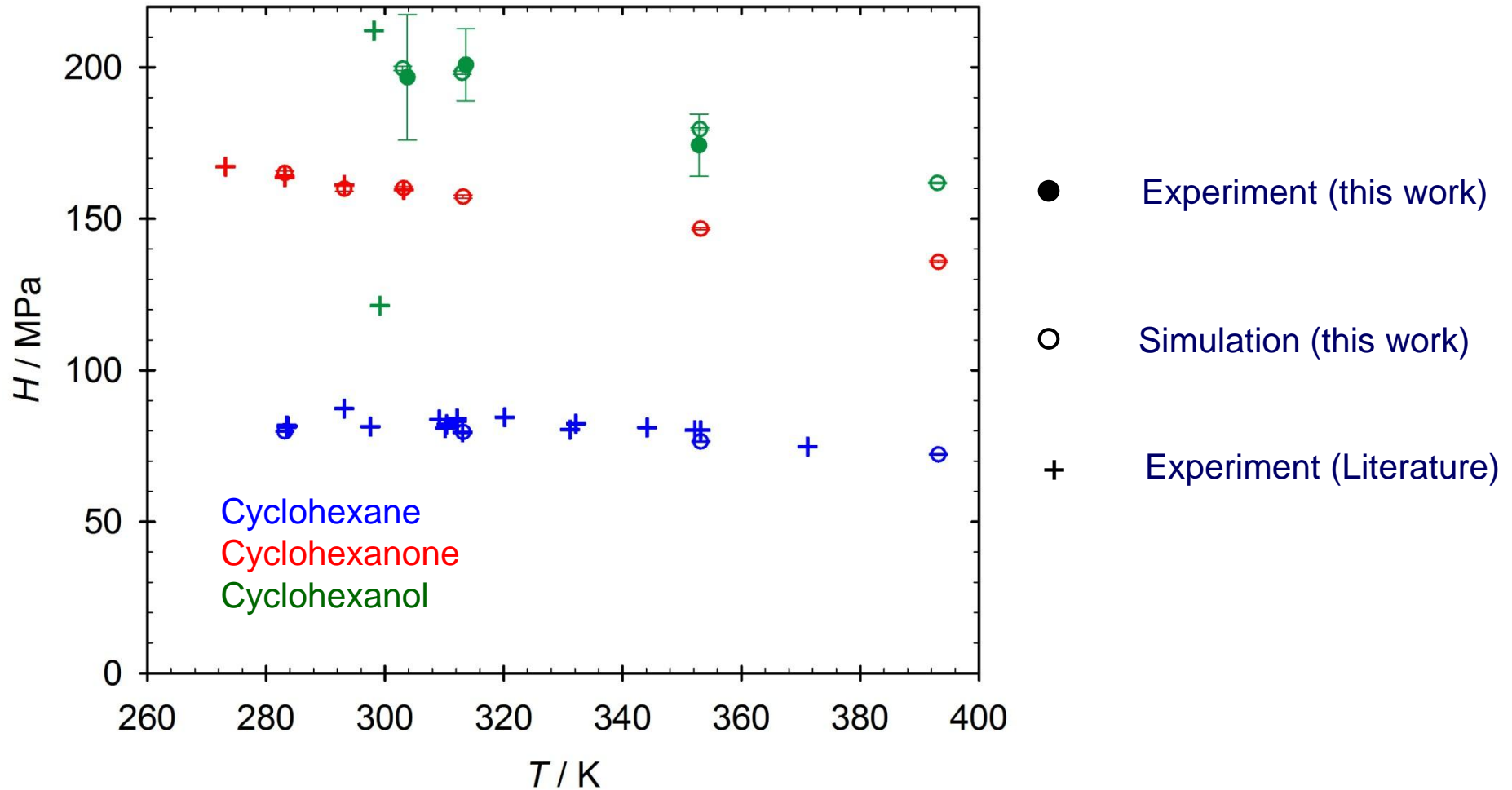


- A: Cylindrical high-pressure equilibrium view cell with two sapphire windows and magnetic stirrer
- B: Thermostat
- C: Container for the gas
- D: Pressure transducers
- E: Tank for rinsing water
- F: Tank for solvent mixture
- G: High-pressure spindle press
- H: AC bridge with three platinum resistance thermometers
- I: Solution outlet
- J: Cooling trap
- K: Vacuum pump



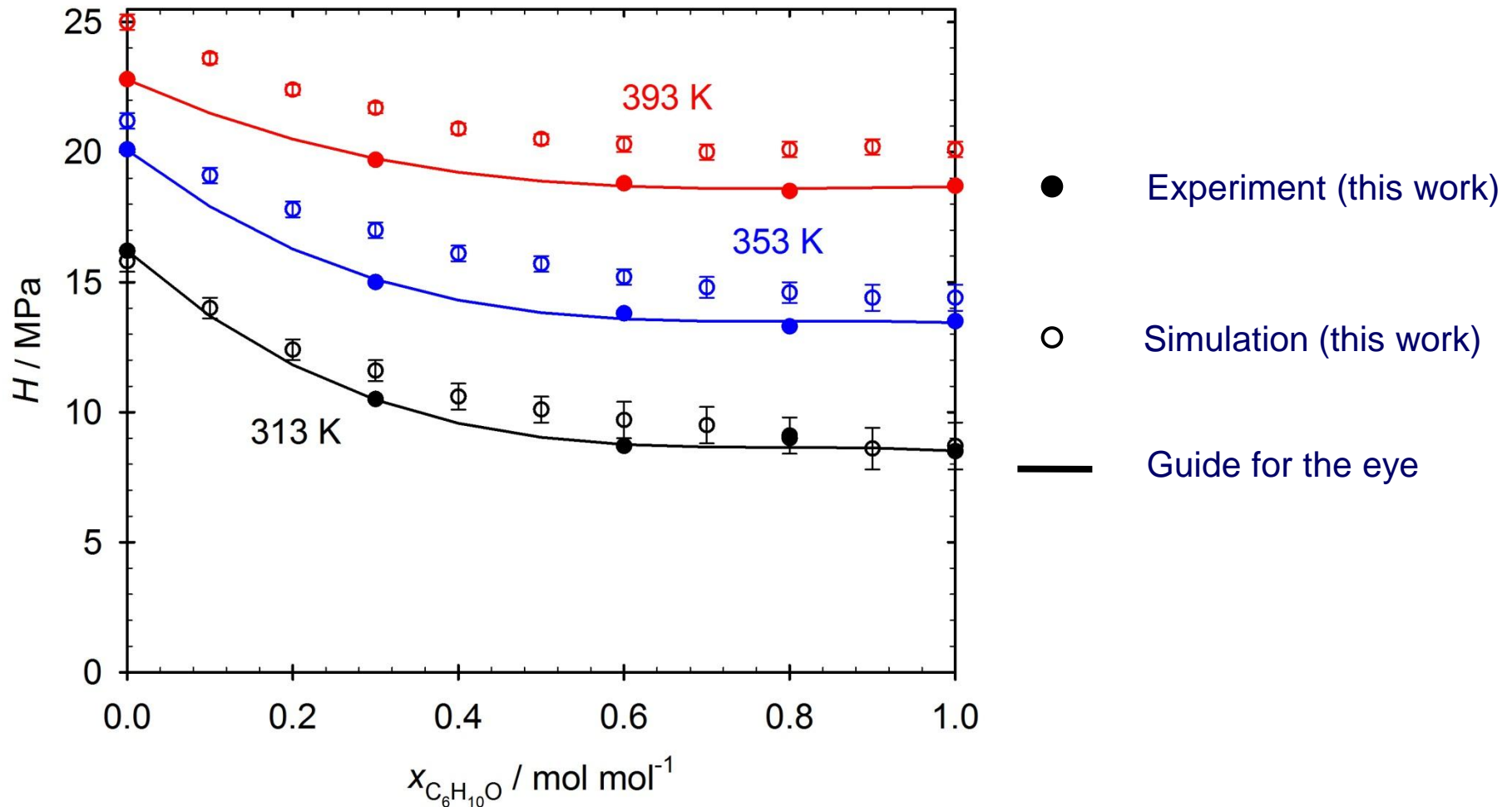
Henry's Law Constant

Oxygen



Henry's Law Constant

Carbon Dioxide in Cyclohexane + Cyclohexanone



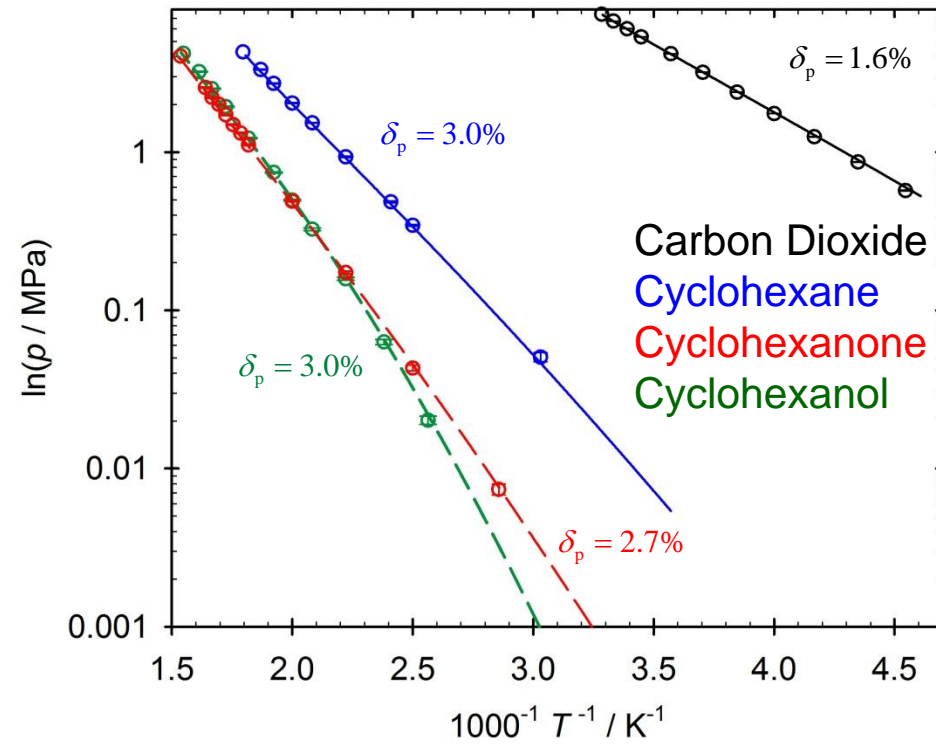
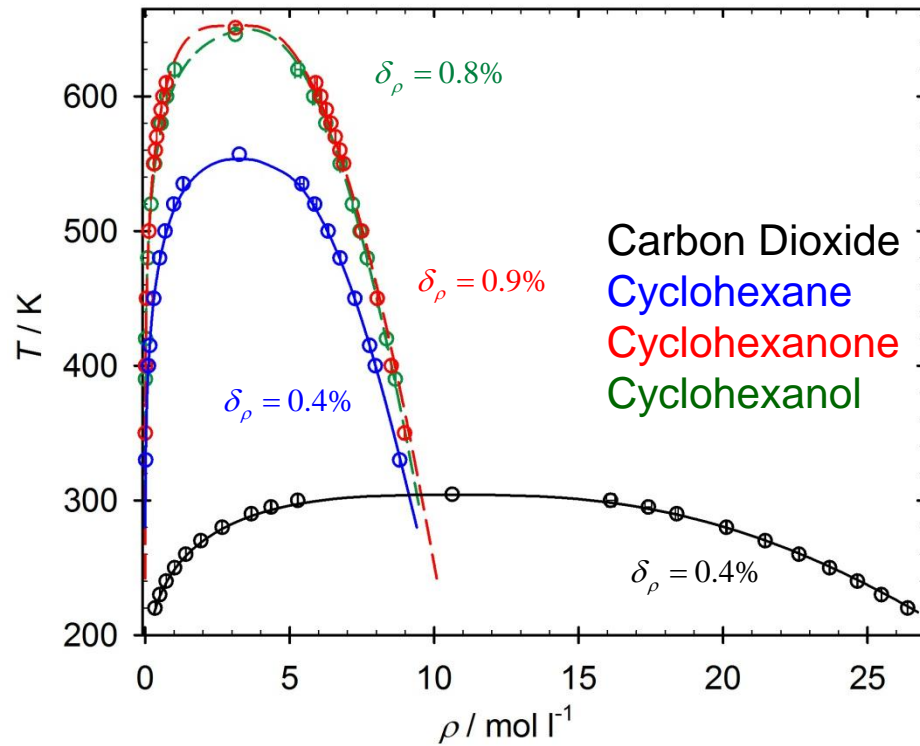


Results

- Simulation in good agreement with experiment for Henry's law constants both for pure solvents and solvent mixtures.

- Henry's law constant of oxygen in cyclohexanol and of carbon dioxide in mixtures of cyclohexane and cyclohexanone is now known.

Molecular Models Developed in This Work



— Equation of State

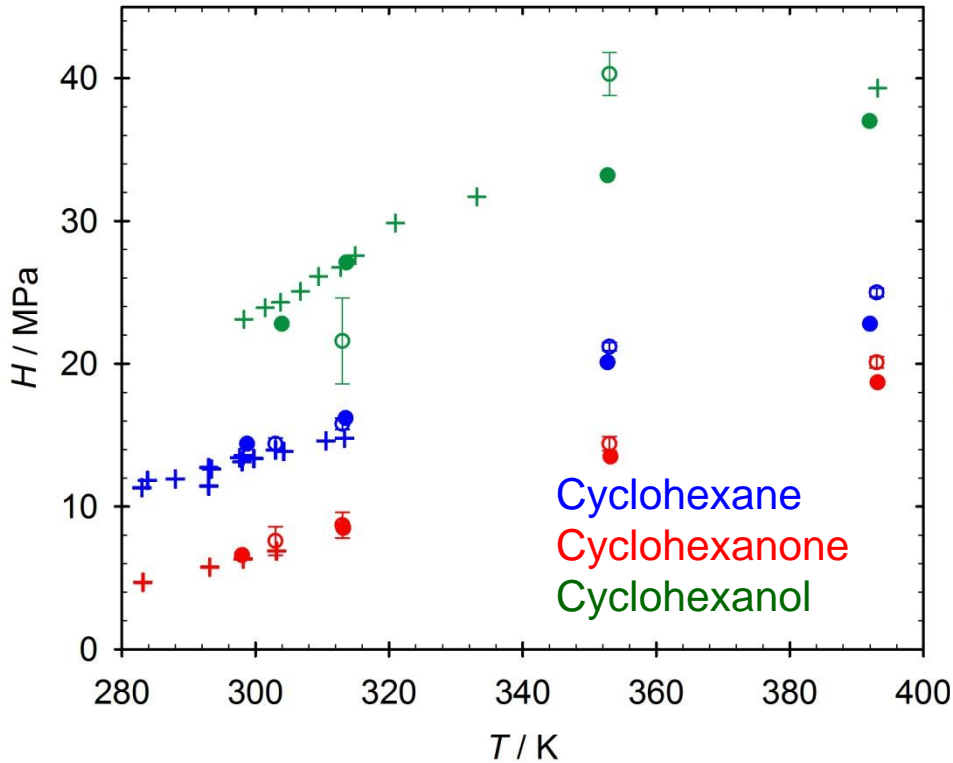
○ Simulation (this work)

- - - DIPPR correlation

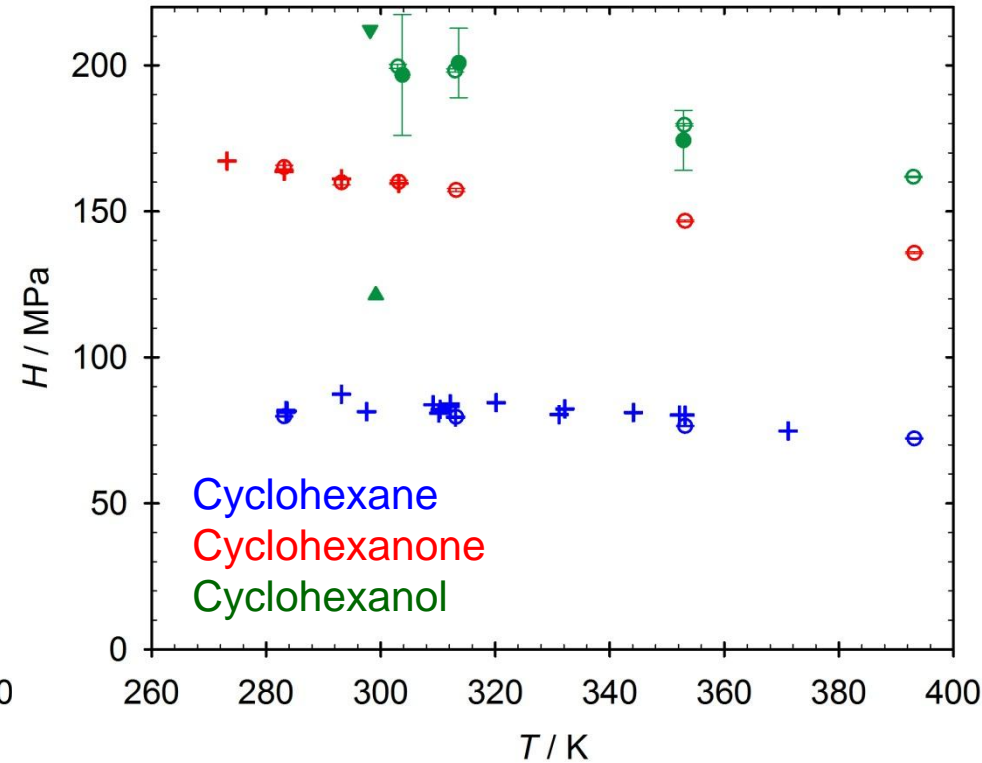


Henry's Law Constant

Carbon Dioxide



Oxygen



● Experiment (this work) ○ Simulation (this work) + Experiment (Literature)

▲ Experiment (Cauquil 1926)

▼ Experiment (Naumenko 1970)