Centre Thermodynamic of Processes

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Generalities

- Joint research group **Mines ParisTech PSL Research university and ARMINES**
- Research and teaching **Department of Energetic and Processes (DEP)**
- Located at Fontainebleau, 60 km in the South of Paris in "Seine et Marne"
- **Staff (around 25 including visitors)**
  - 3 professors
  - 2 researchers
  - 1 research engineer
  - 2 engineers
  - 4 technicians
  - 2 secretaries
  - 5 phD students (on average)
  - 2-3 post-doc (on average)
  - + 4 associate researchers from another institution (university or industry)
- **Budget**
  - Mines ParisTech 50 - 60 k€ (without salaries)
  - Armines 700 k€ (research contracts)

Presentation

- ***From molecular knowledge of fluid to innovative conception of processes***

  - Optimization of existing processes and development of new ones require information concerning molecular behavior

  - Chemical Engineering and Energetic
    - Chemistry (stability, toxicity, chemical reaction, fluid characteristics)
    - Fluid mechanics (transport of the fluid, rheology, etc…)
    - **Thermodynamics (fluid behavior, phase diagram, enthalpy, etc..)**
    - Mass and heat transfers
    - Process control

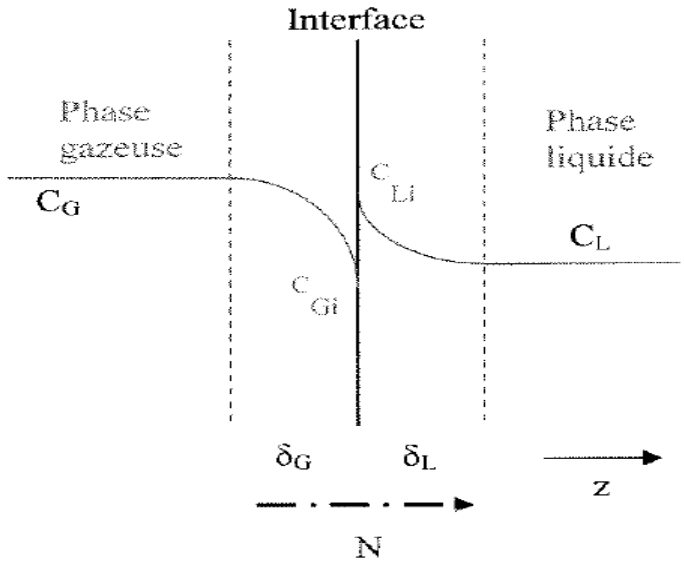
  - Knowledge of phase diagrams and thermophysical properties of fluids are essential for process design and optimization.

Presentation

- Fundamental aspects

- **Mass and heat transfers**
  - Analogy Chilton-Colburn
  - Double layer
  - Non dimensional numbers:

$$\mathrm{Nu} = A + B\,\mathrm{Re}^{a}\,\mathrm{Pr}^{b} \qquad \mathrm{Sh} = A + B\,\mathrm{Re}^{a}\,Sc^{b}$$



- **Phase equilibria, Thermodynamic**
  - Pressure Temperature envelops
  - Bubble point, dew point
  - Enthalpy of mixing, heat of vaporization
  - Densities

Example: Length of a column of absorption

$$Z = HUT.NUT = \frac{G}{K_y A_c a_e} \cdot \int \frac{dy}{(1-y)(y-y^*)}$$

- **Transport properties**
  - *Viscosity, thermal conductivity*
  - *Coefficient of diffusion*

Presentation

Thermophysical properties

- **Thermophysical properties** can be defined as a term '*representing a sort of concept*' of all materials or fluids properties which can affect the **transfer (mass and heat) and storage of heat**

- They are function of the **physical state** and vary with :
  - **physical state variables** (Temperature, Pressure, density, composition)
  - **relevant variables** (dipole moment, acentric factor, etc...)

- Chemical stability is not affected

- **3 categories**

  - **Thermodynamic** defined at *equilibrium state conditions*
  - **Transport** defined at *non equilibrium state conditions* with existing potential gradient like velocity (viscosity), temperature (thermal conductivity) and composition (diffusion coefficient)
  - Other properties such as chemical, optical, electric, magnetic and thermal radiation

Presentation

- Thermodynamic of fluids

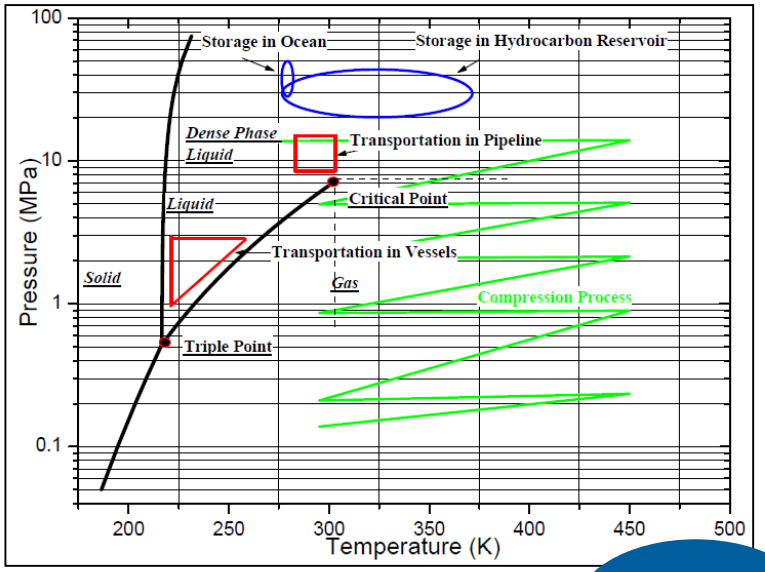
Determination of the phases diagrams and determination of the thermophysical properties of the phases equilibria

Thermophysical properties measurements (VLE, VLLE, gas hydrates, critical points, densities, enthalpies, etc….).

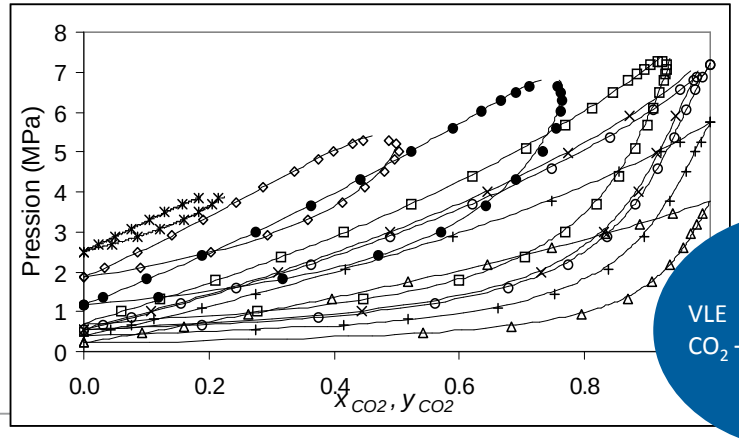
Modeling and data treatment: Development of thermodynamic models.

Conception and realization of experimental set-up .

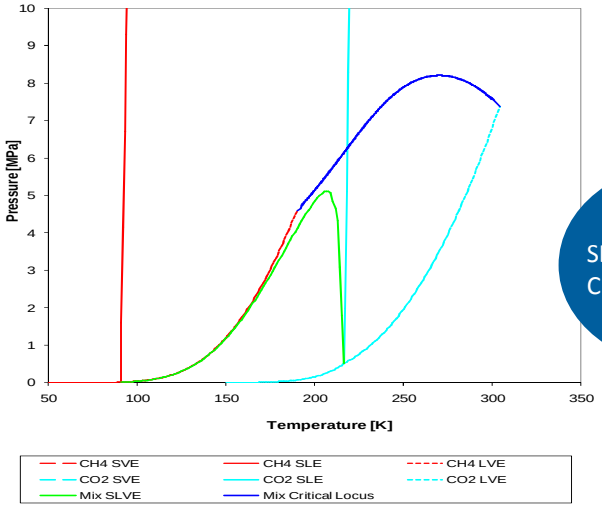
Scientific advice for industrials (process engineer).



CO_2 Transportation



VLE Phase diagram
CO_2 – R227ea

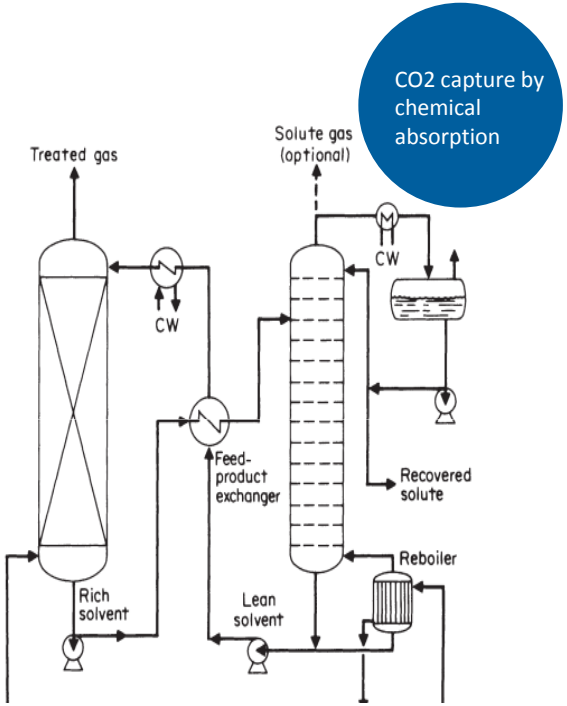


SLV phase diagram
CH4-CO2

Presentation

- ***Three main applications***
  - « Oil and gas engineering », CO_2 Capture Transport and Storage
    - Cryogenics, gas and air separation, natural gas transportation (gas hydrates), water content
  - Fluorinated component: energetic optimization
    - Study of new fluids, optimization of machines
  - Chemistry, Green chemistry
    - Biogas, biorefinery

    (experimental facilities and methodology under development).



Our Tools

- Several home made programs for representation of thermophysical properties
- Molecular simulation
- Apparatus conception platform
  - Equipment design and construction
  - Metrology
- Experimental platform : Thermophysical properties measurement
  - Equipments for phase equilibrium properties measurements
  - Metrology / experimental procedure / calibrations
- Commercial software for thermodynamic calculation and process simulation

Experimental platform:Thermophysical properties measurement

- 5 laboratories:
  - 'High Safety' Laboratory
  - 'Cryogenic' Laboratory
  - 'Gas Hydrates' Laboratory
  - 'Calorimetry ' Laboratory
  - ' Mass transfer and Precipitation ' Laboratory

- 1 workshop

Calvet Calorimeter (C80)

Experimental device using the static-analytic method

Experimental platform:Thermophysical properties measurement

'High Safety' Laboratory

Experimental platform:Thermophysical properties measurement

Apparatus :

- 2 calorimeters (µDSC et C80)
- 2 vibrating tube densimeters LP (+ speed of sound)
- 1 vibrating tube densimeter HP
- 1 viscosimeter (falling ball)

Experimental set-up :

- 1 Static-analytic LP cell : Liquid bath
- 5 Static-analytic HP cells : 1 cryogenic, 1 air oven, 3 liquid bath
- 1 Critical point determination apparatus
- 3 cells « hydrates » (1 with one ROLSI™ sampler)
- 1 dilutor

+ Analytical devices

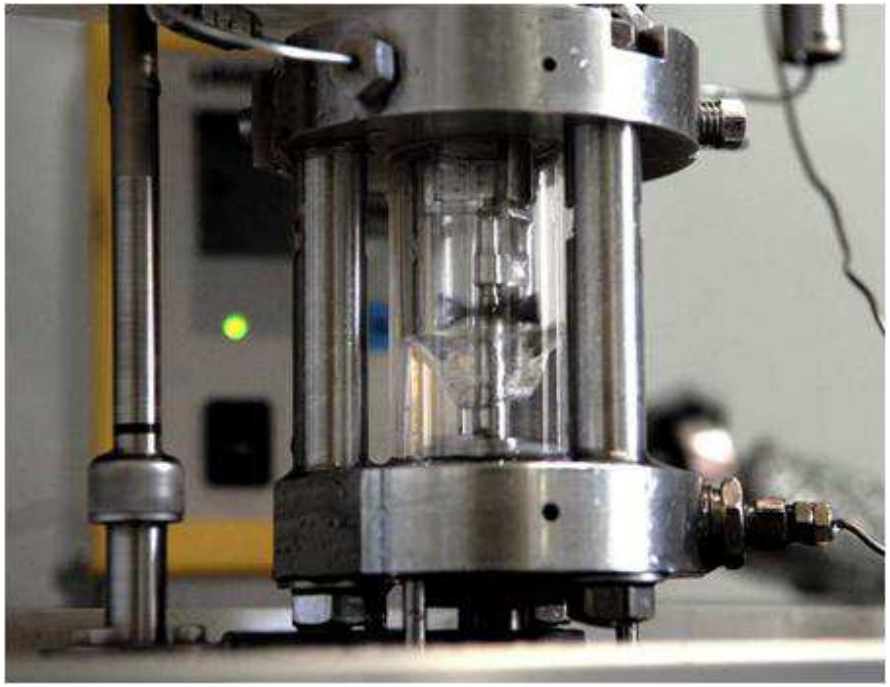
- GC, HPLC, Karl Fisher, Chilled mirror, Refractometer

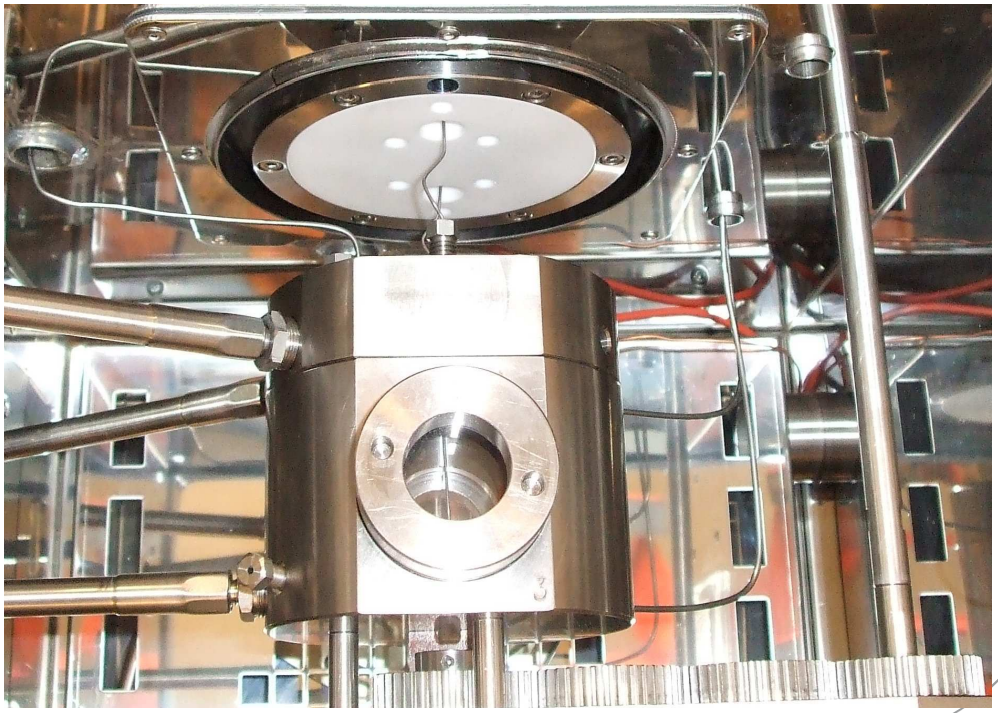
+ Various devices for metrology

- *1 Dead weight balance, and 1 calibration tool for pressure*
- *2 Standard temperature probes for temperature*

Experimental platform:Thermophysical properties measurement

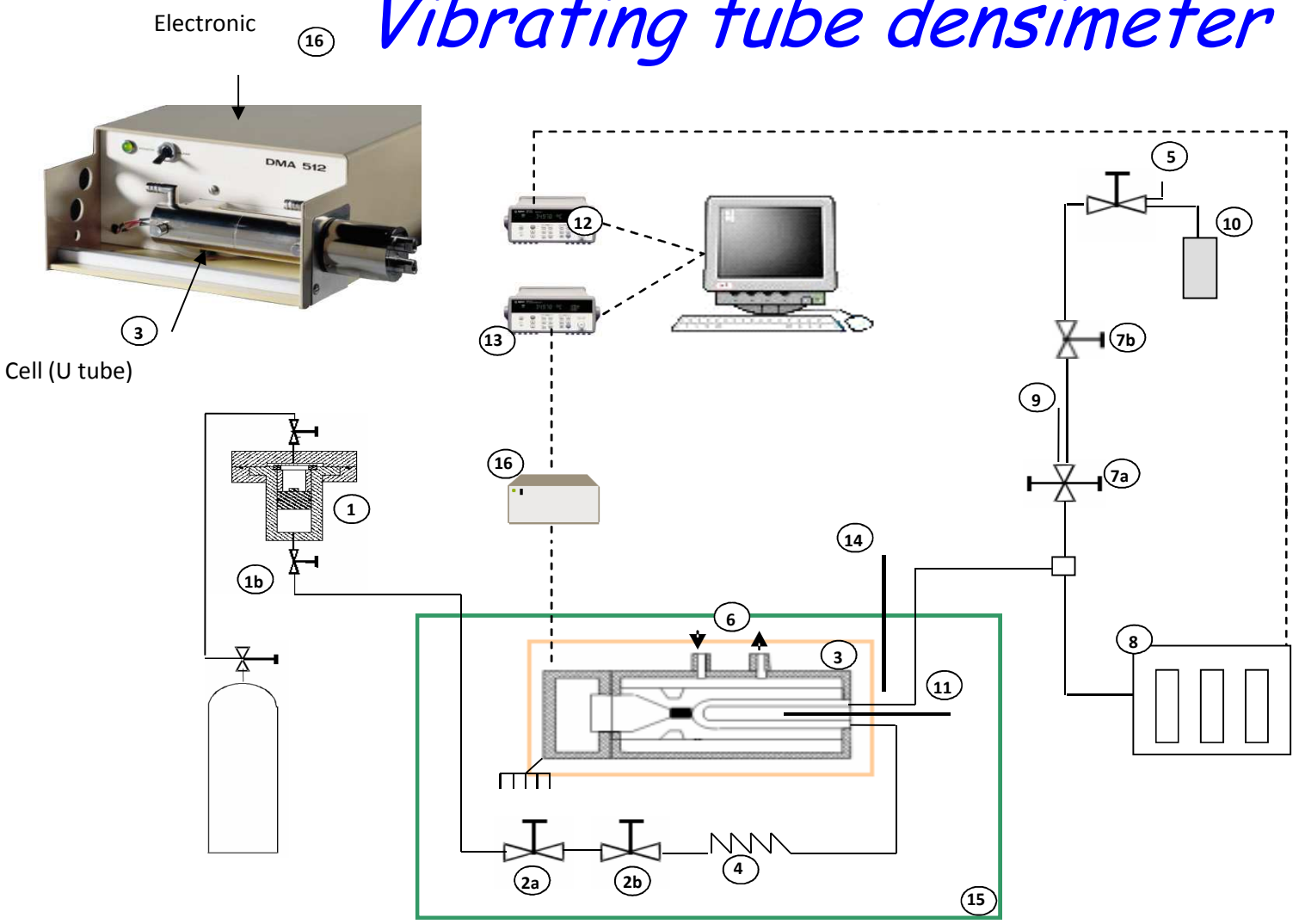
VLE cells





Experimental platform:Thermophysical properties measurement

Vibrating tube densimeter



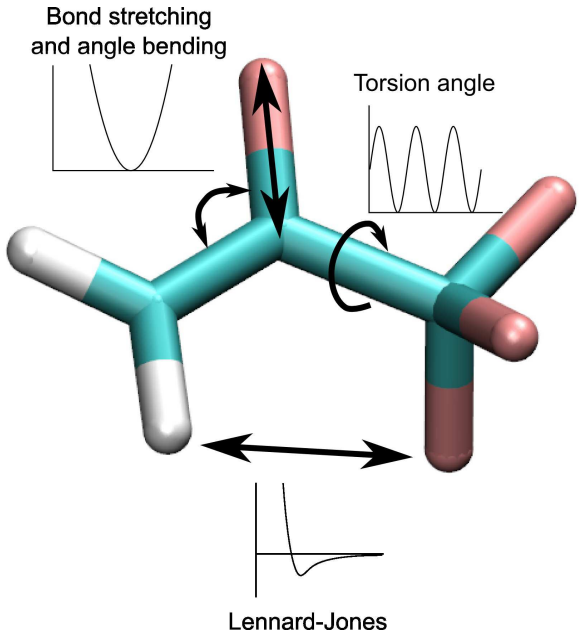
Numerical platform:Thermodynamic properties prediction

- Modeling
  - **Data treatment**
    - Utilisation of conventional tools
    - Examination of derivative properties
    - Determination of other properties considering existing data
  - **Development of equations of state**
    - Critical region calculation -> crossover approach
    - Fluid solid phase diagram prediction -> Yokozeki approach
    - Densities -> cubic EoS approach, SAFT
  - **Projects of software developments**
    - Biogas and natural gas
    - Cleaning of natural gases
    - Refrigerants
  - **Existing home made software**
    - Thermopack
    - thermosoft

Numerical platform: Thermophysical properties prediction

- Molecular simulation

  - **Monte Carlo methods** → Phase equilibrium properties for pure fluids and mixtures (densities, vapor pressures, Pxy diagrams…)
  - **Molecular dynamics methods** → Transport properties (viscosities, thermal conductivities…)
  - Necessity to represent the potentials of interaction between atoms and molecules: several existing force fields (TraPPE, AMBER…)



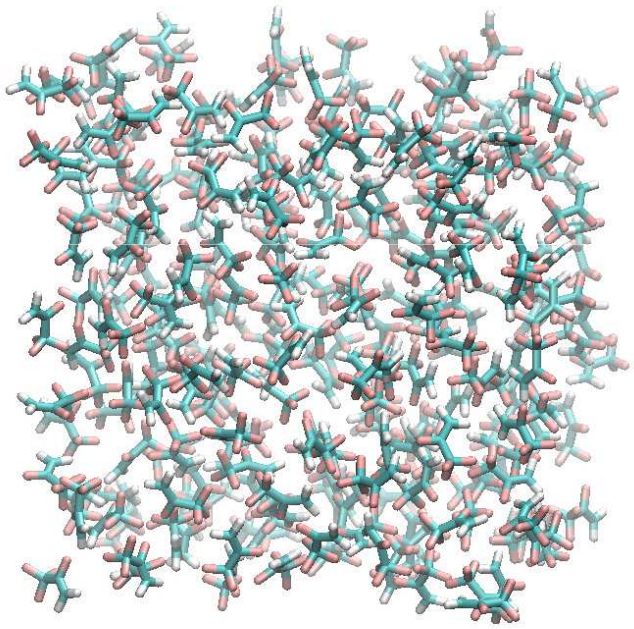
Lennard-Jones type potential of interaction:

$$U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Numerical platform: Thermodynamic properties prediction

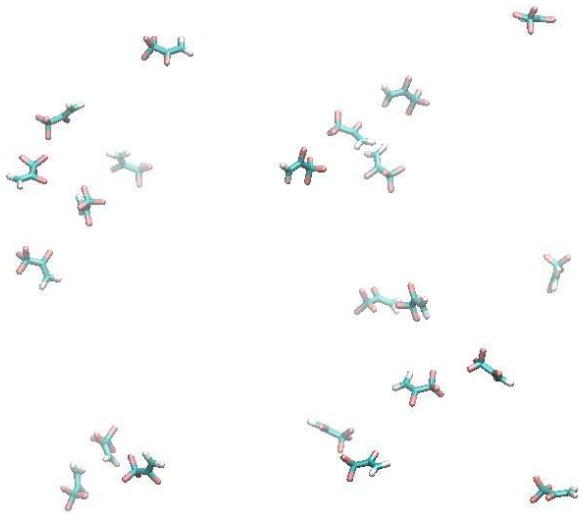
Example of Monte Carlo simulation of HFO-1234yf

Gibbs ensemble (Panagiotopoulos, Mol. Phys. 1987): 2 phases in equilibrium = 2 different boxes



Liquid phase box

Equilibrium



Vapor phase box

Industrial partnership and valorisation of equipments

- **Various research projects** (done and on going) **with industrial partners :**

Air Liquide, EDF, TOTAL, Arkema, Solvay, Petronas, BASF, IFPEN, ENGIE, SHELL, ENITECH, CECA, Saint Gobain

- **Gas Processors Association**

- **Valorisation**: Experimental set-up and ROLSI™

Industrial partnership

Framework contracts

- **Measurements and modeling**
  - PROCESSIUM (Lyon, France)

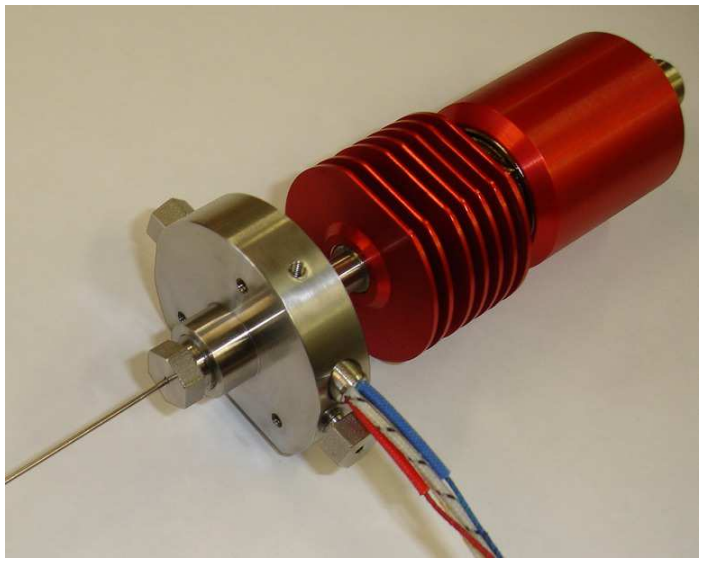
- **Valorization and selling of equipment**
  - TOP INDUSTRIE (Vaux le Pénil, France)

- **Industry**: AIR LIQUIDE

Valorisation: ROLSI™

Licences

- 2 societies
  - EIF
  - Top Industrie



Research Funding

- In 2015

CTP participates in collaboration with other academic groups to several joint projects

- **ANR (Agence Nationale de la Recherche)**
  - SIGARRR (TOTAL)
  - Prediref (ARKEMA)
  - Fluid Story (BRGM)
- **Ademe**
  - Cryocap H2 (Air Liquide)
- **Institut Carnot M.I.N.E.S**
- **Joint industrial project in Collaboration with Heriot Watt University (Scotland)**

Academic network

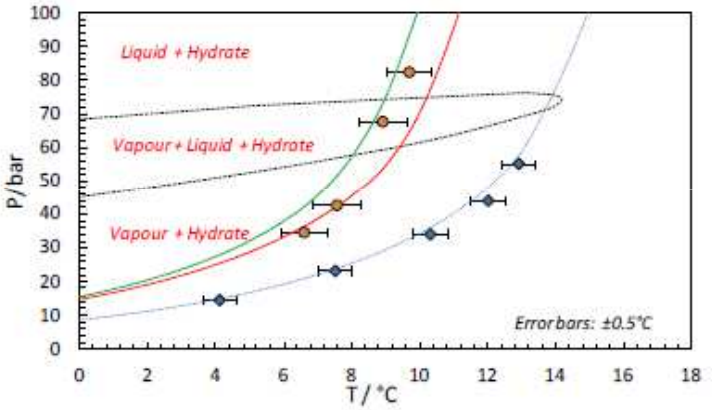
- **Scientific collaborations**
  - *Mines ParisTech - PSL:* CES, Persee, Geosciences, CAS
  - *France:* UCP ENSTA ParisTech, LRGP ENSIC, LSPM Univ. ParisXIII, Rapsodee Mines Albi – Carmaux, SPIN Mines Saint Etienne, TIM Univ. Blaise Pascal
  - *International:* Institute of Petroleum Engineering Univ Heriot Watt, CERE DTU, Politec Milano, TRU Univ Kwazulu Natal
- **Network**
  - SFGP: Thermodynamique des procédés
  - CNRS: GDR Thermodynamique Moléculaire et Procédés
  - CNRS: Technologie des hautes pressions

Example of research collaboration

- **JIP Heriot Watt University**

- **Subject:** Impact of Common Impurities on Carbon Dioxide Capture, Transport and Storage

- **Industrial partners:** CHEVRON, STATOIL, LINDE, PETEX, TOTAL, OMV



- **Joint papers**:

A. Chapoy, C. Coquelet, H. Liu, A. Valtz, B. Tohidi, Vapour-liquid equilibrium data for the hydrogen sulphide (H_2S) + carbon dioxide (CO_2) system at temperatures from 258 to 313 K, Fluid Phase Equilibria, 2013, 356, 223-228

A. Chapoy , M. Nazeria, M. Kapateh, R. Burgass, C. Coquelet, B. Tohidi, Effect of impurities on thermophysical properties and phase behaviour of a CO2-rich system in CCS International Journal of Greenhouse Gas Control, 2013, 19, 92-100.

Example of research collaboration

- Collaboration Mines Paristech (CTP -CES- PERSEE) / EDF

- **Optimisation of ORC (power plant)**
- Screening of fluids
- Implementation of equation of state in home made software Thermoptim™ (Mines ParisTech)
- Utilization for cycle optimization

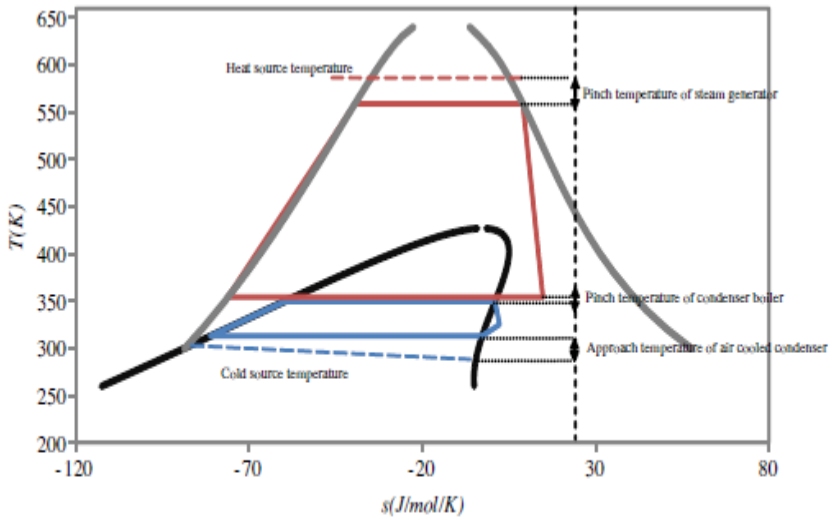


Fig. 2. *T–s* diagram of a two-stage Rankine cycle.

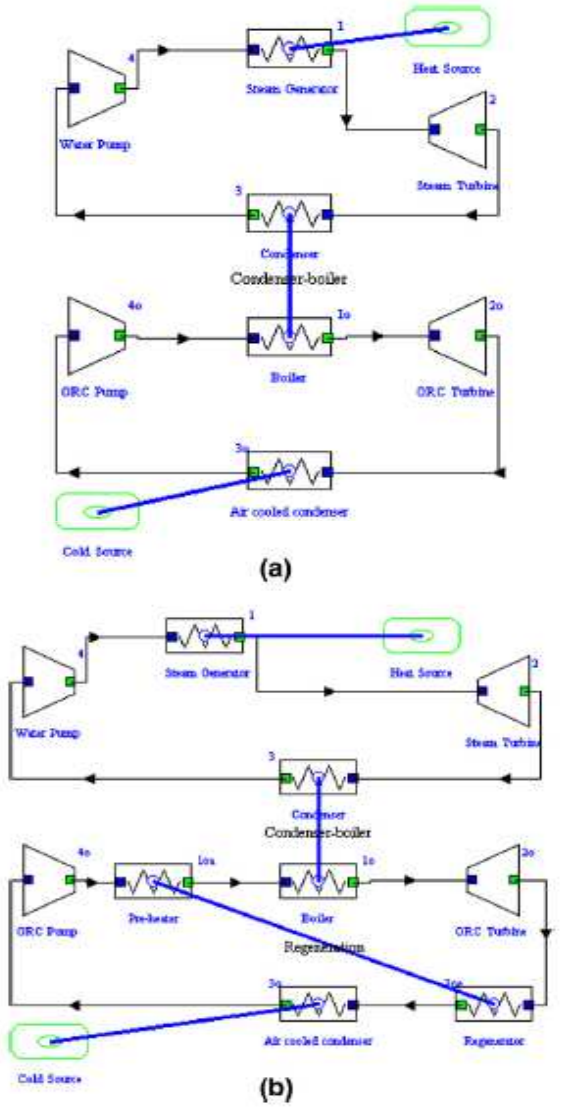
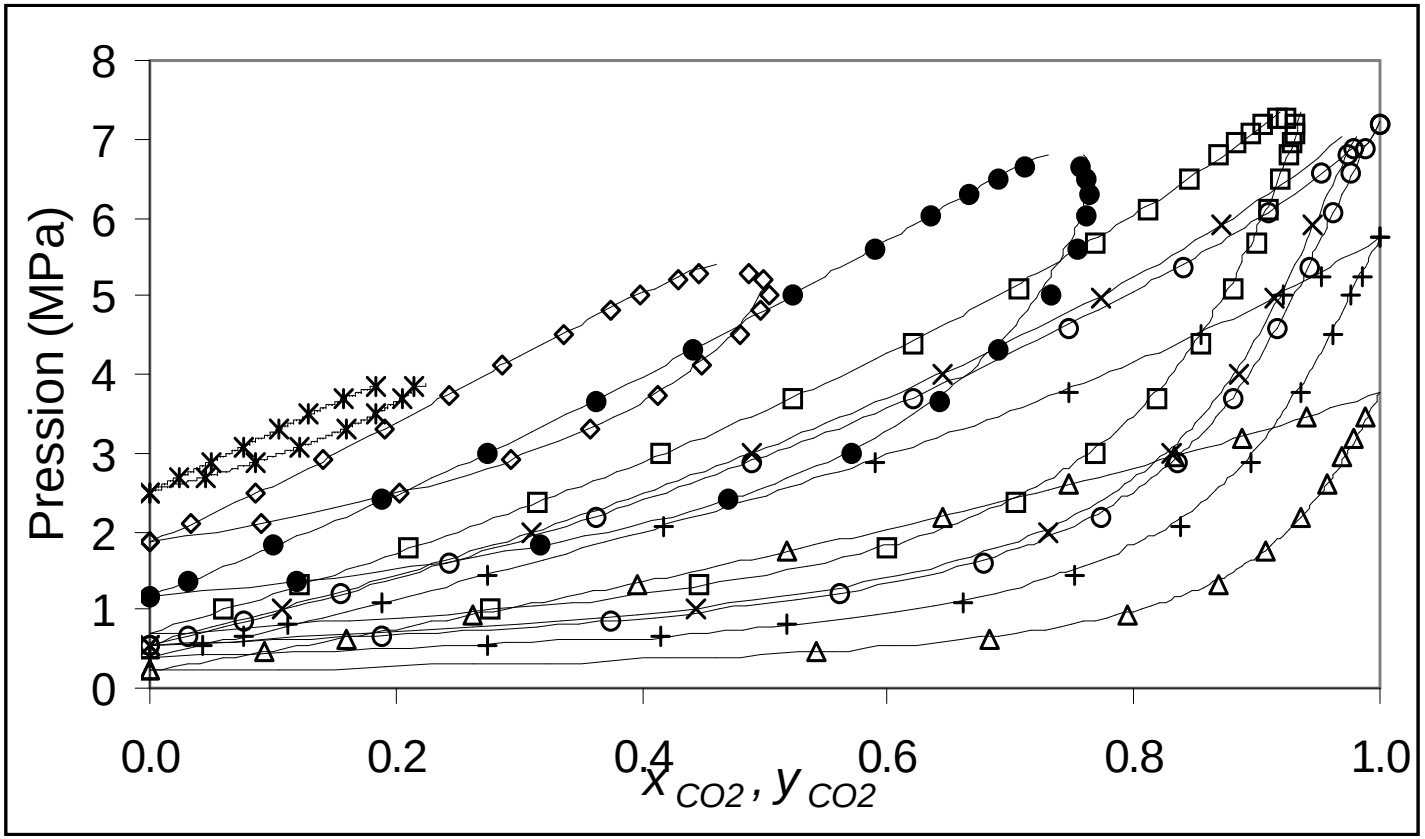


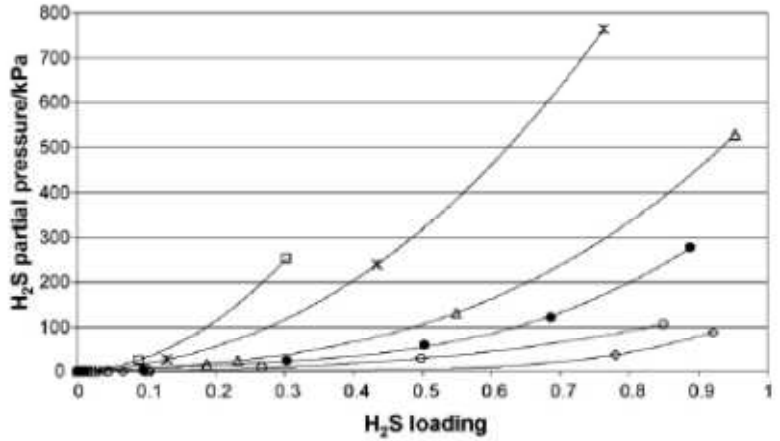
Fig. 1. Structure of two-stage Rankine cycle for electricity production represented in THERMOPTIM™ [27]: (a) basic cycle, and (b) regenerative cycle.

Example of experimental results and modeling

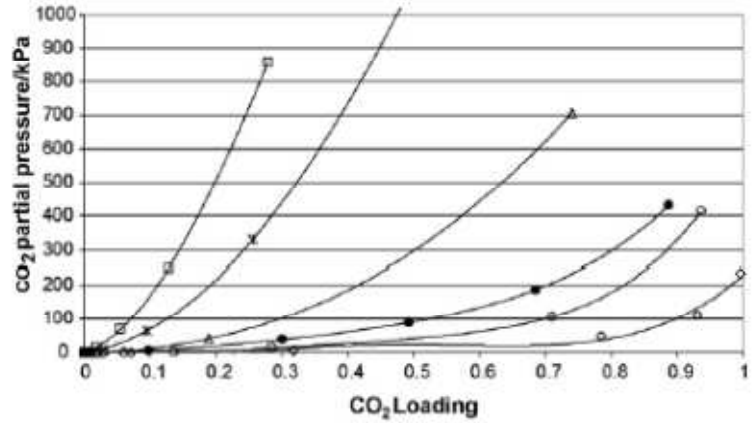
VLE of CO_2 (1) - R227ea (2) at different temperatures : (Δ) 276.01 K, (+) 293.15 K, (o) 303.15 K, (×) 305.15 K, (□) 313.15 K, (●) 333.15 K, (◊) 353.15 K, (*) 367.30K, - : PR EoS



Example of experimental results and modeling



H_2S partial pressure as a function of H_2S loading for $L_{CO_2} = 0$ in 50 wt% MDEA aqueous solution at various temperatures. (◊) $T = 298$ K [5]; (○) $T = 313.15$ K [5]; (●) $T = 323.15$ K (this work); (△) $T = 343.15$ K [5]; (✱) $T = 373.15$ K [5]; (□) $T = 393.15$ K [5]. (—) Tendency curves (regression with third-degree polynomial).



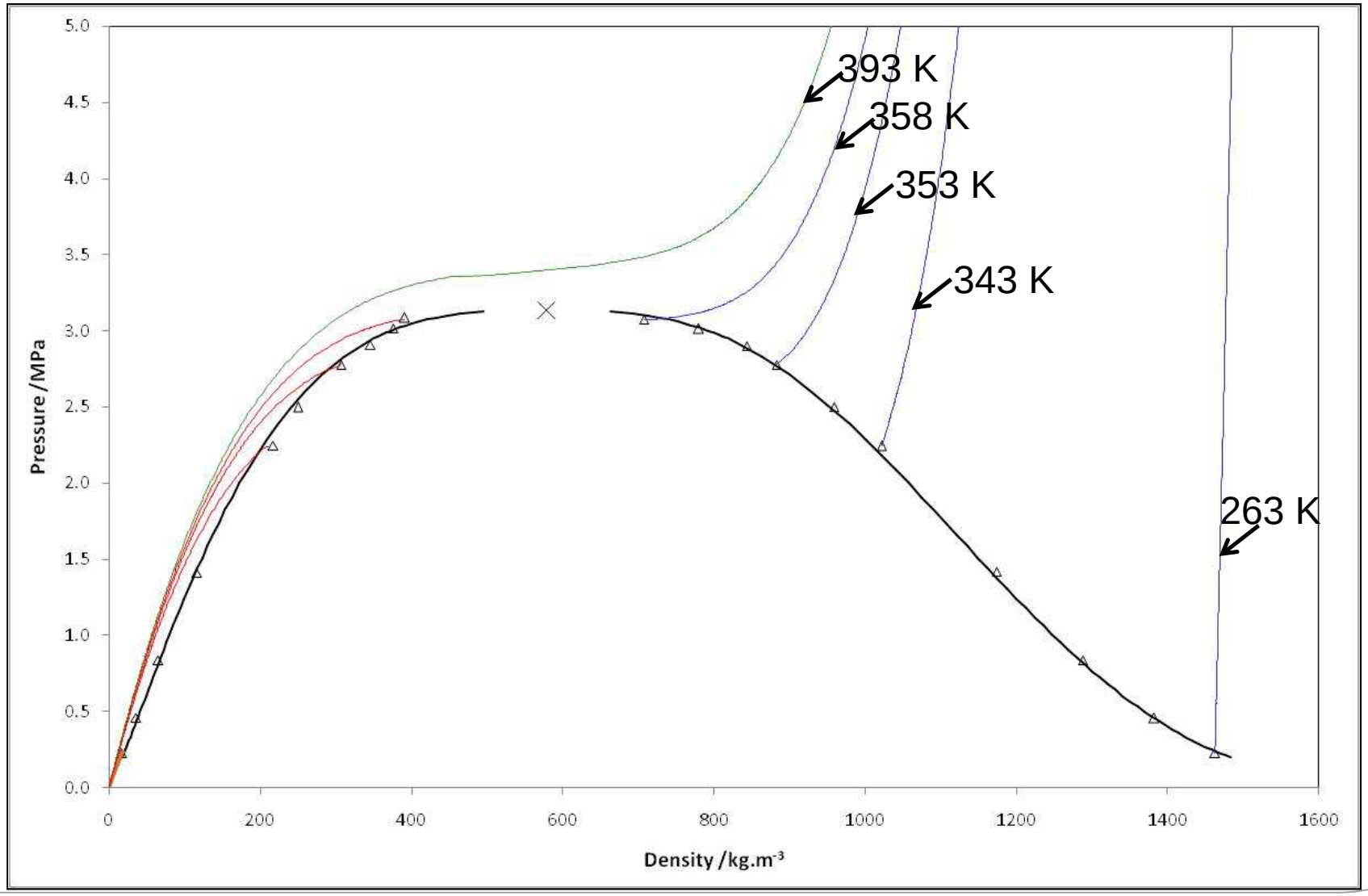
CO_2 partial pressure as a function of CO_2 loading for $L_{H_2S} = 0$ in 50 wt% MDEA aqueous solution at various temperatures. (◊) $T = 298$ K [5]; (○) $T = 313.15$ K [5]; (●) $T = 323.15$ K (this work); (△) $T = 343.15$ K [5]; (✱) $T = 373.15$ K [5]; (□) $T = 393.15$ K [5]. (—) Tendency curves (regression with third-degree polynomial).

Acid gases absorption in amine solutions

CO_2 and H_2S in 50wt % MDEA aqueous solution

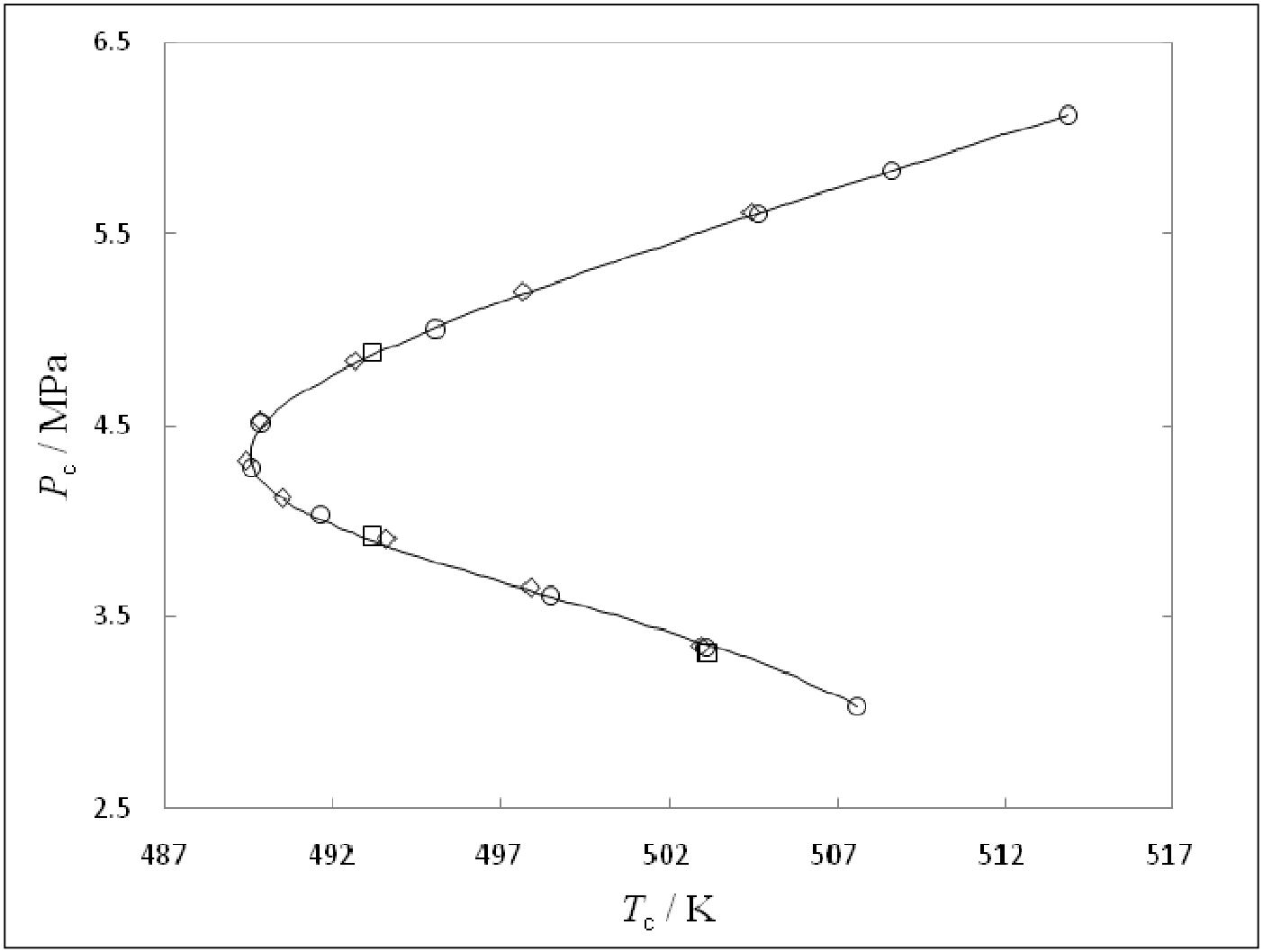
Example of experimental results and modeling

Hexafluoropropylene Pressure-density diagram obtained by using a vibrating tube densimeter



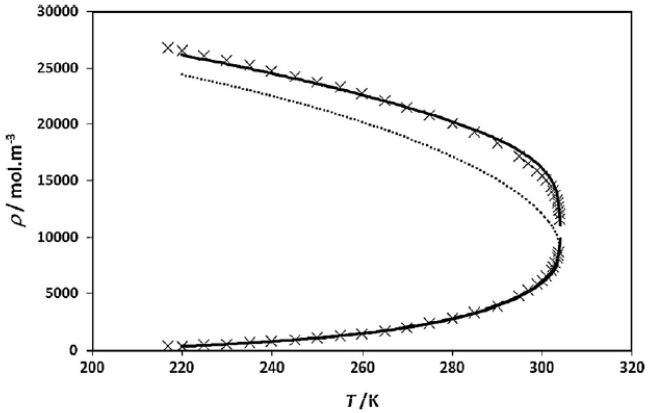
Example of experimental results and modeling

Critical locus of the ethanol + *n*-hexane system. ○: experimental work; ◇,□: literature sources; - : Redlich-Kister correlation

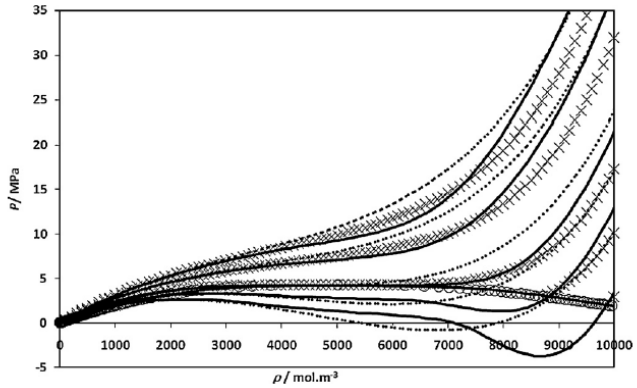


Example of experimental results and modeling

Improvement of EoS to represent thermodynamic properties around critical point

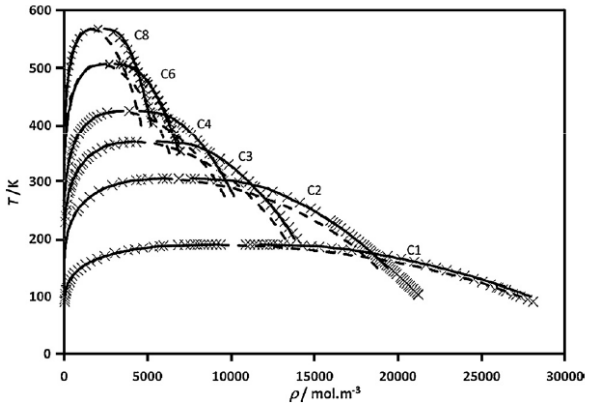


Plot of the coexistence curve of CO2. (-)Crossover RKS (CR-RKS), (---) Classical RKS, (***) experimental data



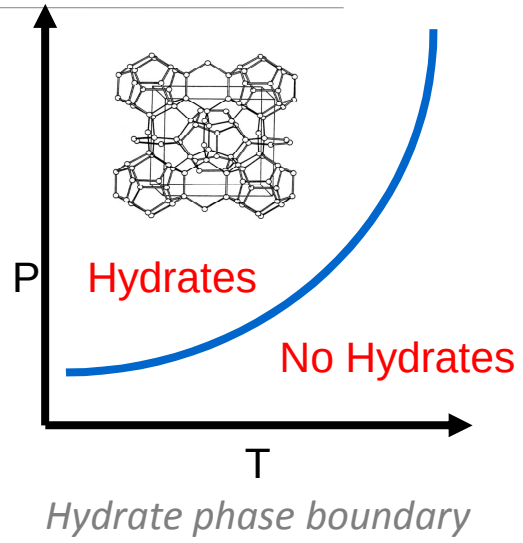
Pressure against density for propane at 330,350,369.89,410 and 440K . (-)Crossover RKS (CR-RKS), (---) Classical RKS, (***) calculated with refprop

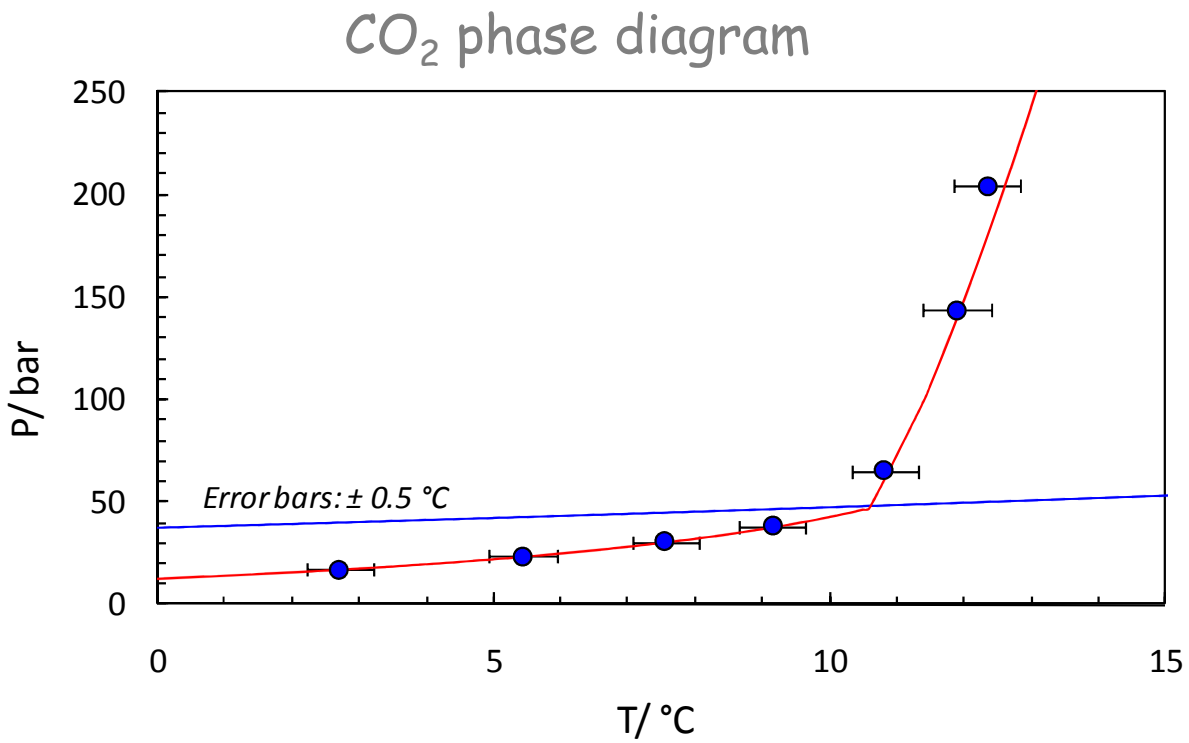
Density fluctuations around critical point



Plot of the coexistence curves for n-alkanes (-)Crossover RKS (CR-RKS), (---) Classical RKS, (***) experimental data

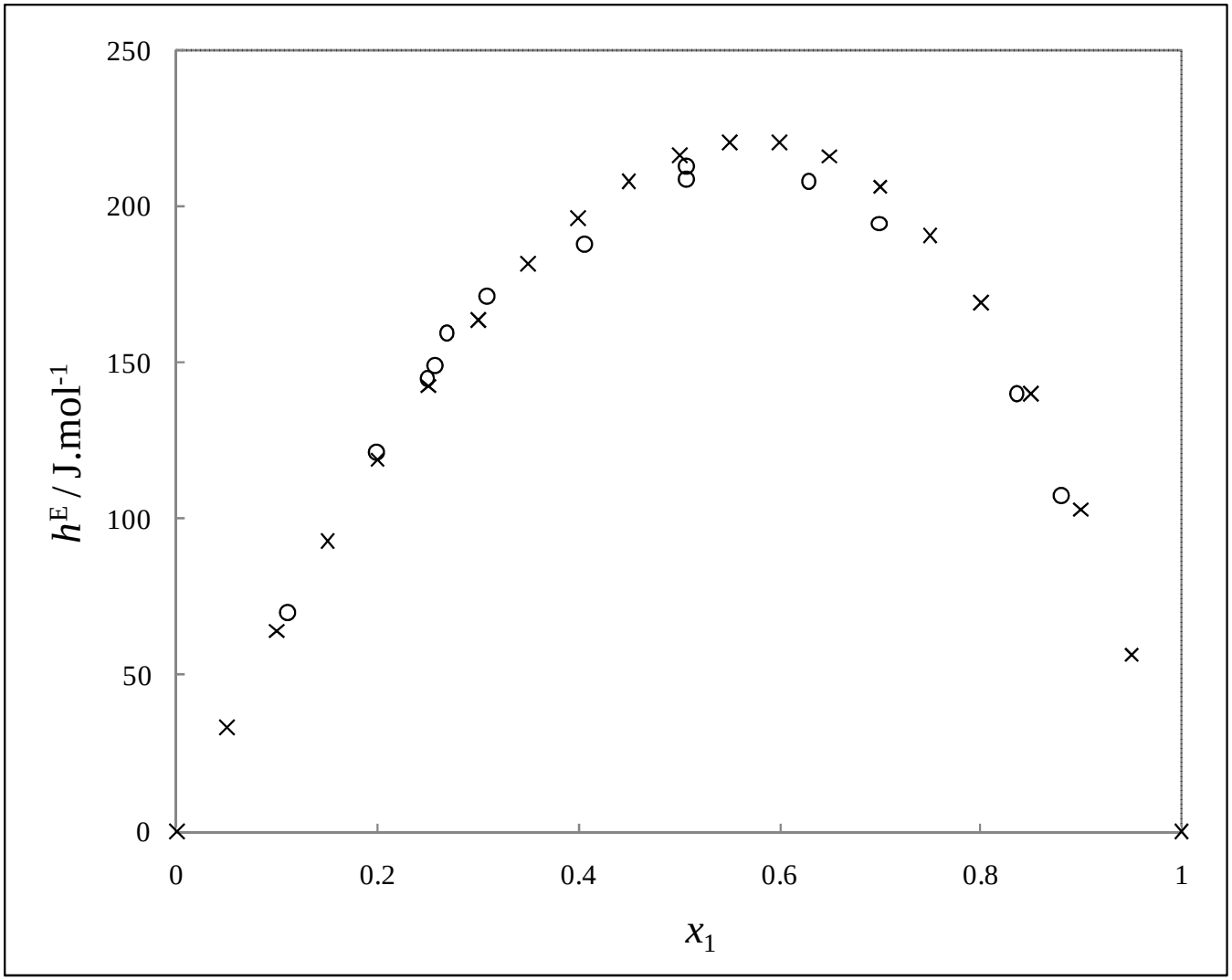
Example of experimental results and modeling





Example of experimental results and modeling

Excess enthalpy of the system cyclohexane (1) + *n*-hexane (2) at 25° C and 1 atm, measured using membrane mixture cell.
○: experimental work, × : literature source.

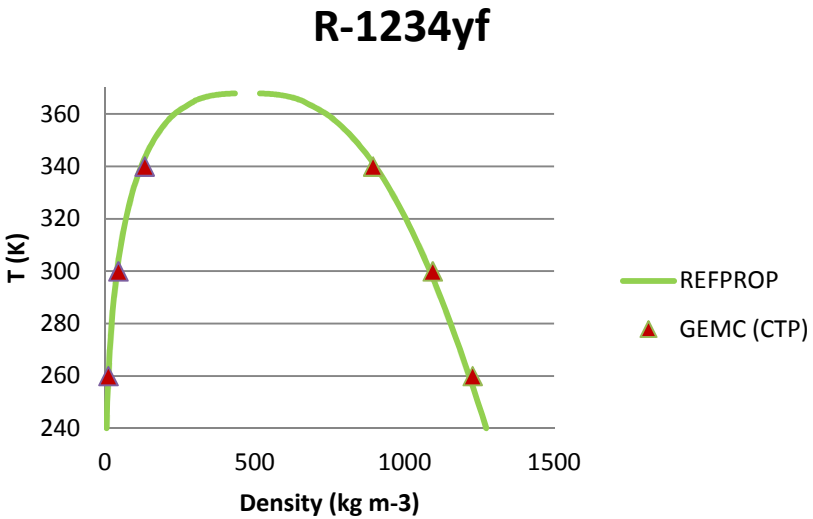


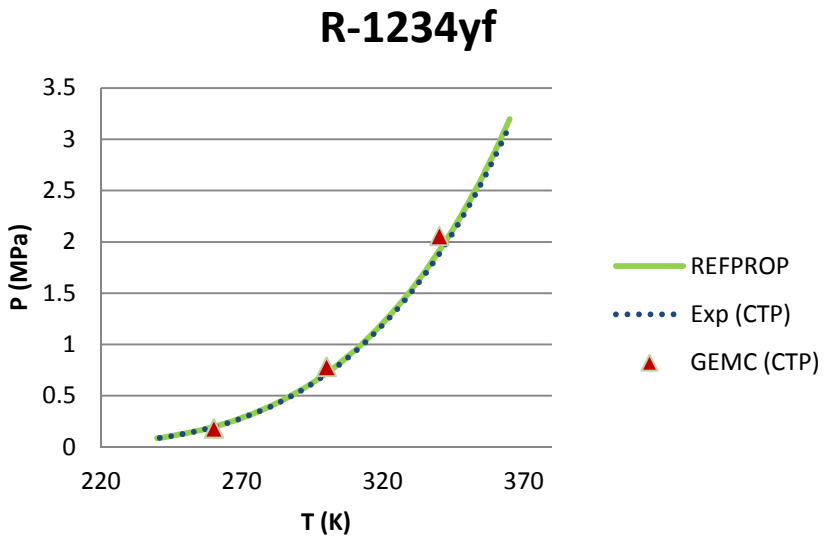
Example of experimental results and modeling

Molecular Simulation

Results concerning HFO-1234yf

- Gibbs ensemble Monte Carlo simulations with Raabe and Maginn force field (JPCB 2010)
- Comparison with REFPROP 9.0 and experimental data (CTP)



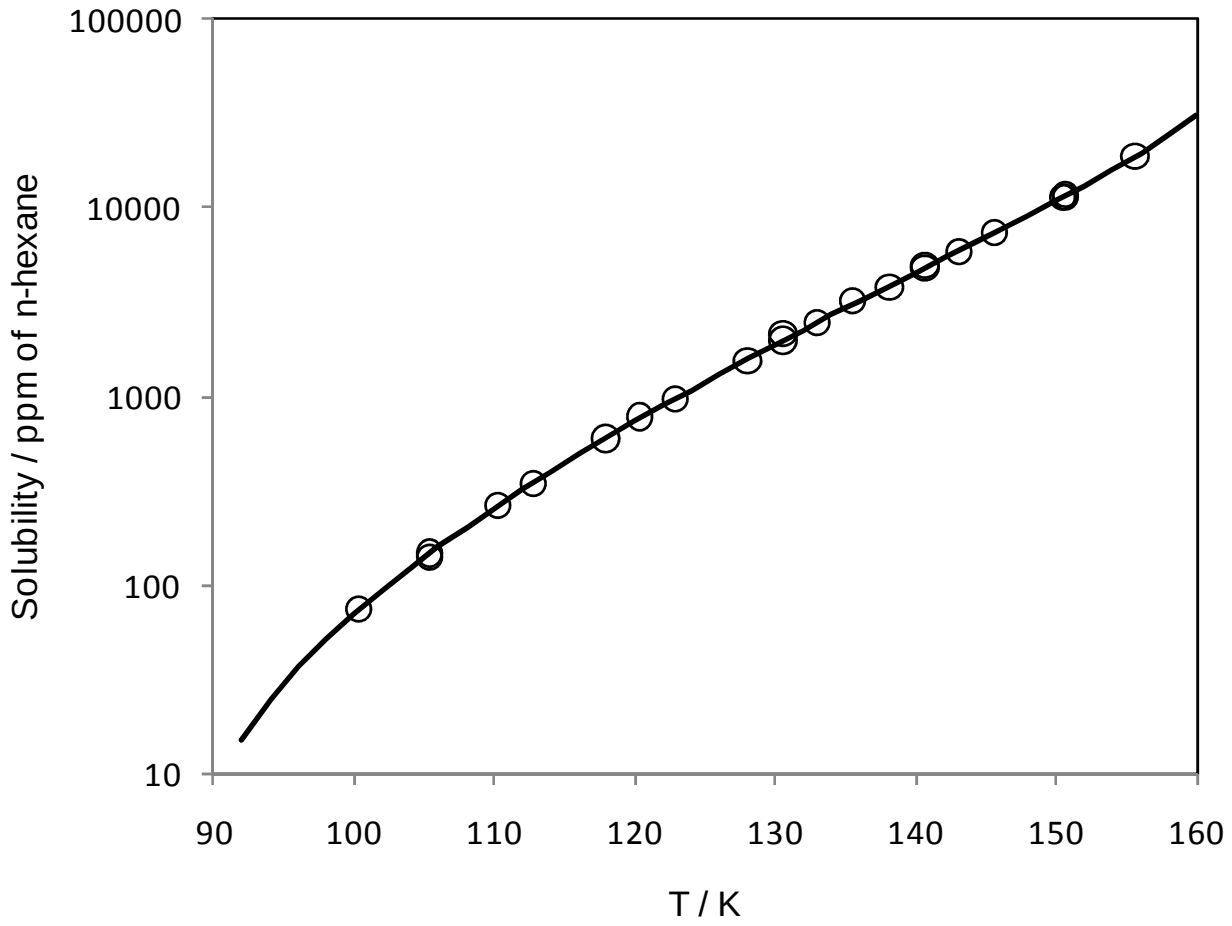


→ Very good agreement between Monte Carlo and other techniques

→ Current extension of this existing force field to other HFO

Example of experimental results and modeling

Solubility of solid n-hexane in liquid methane.
○: experimental results, — : modeling results.



Our Philosophy

"Do the best work in thermodynamics that you possibly can and enjoy it thoroughly. But don´t lose sight of the goal. Thermodynamics comes second. First comes chemical engineering"

J.M. Prausnitz, Fluid Phase Equilibria, 158-160, 110, 1999