Experimental methods for determining thermodynamic properties near the critical point and data treatment

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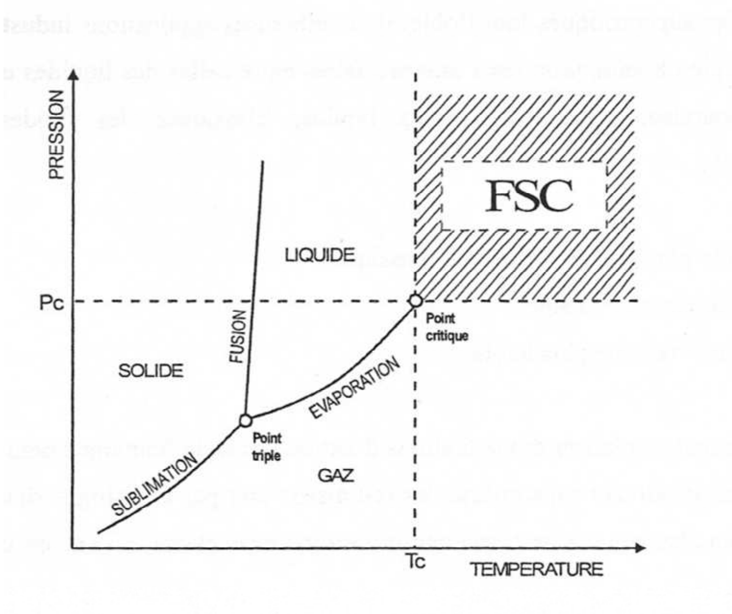
INTRODUCTION

- Supercritical Fluids exhibit very interesting properties.
- Intermediate between a liquid and a gas
- Industrial applications
  - Extraction of chemicals
  - Treatment of heavy hydrocarbons
  - Separation, purification
  - Chemical reactions in supercritical conditions
  - Etc..
- Industries need equations to represent their properties

- Equations require experimental data: phase equilibrium, densities and heat capacities



INTRODUCTION

Phase diagram

- **Objectives of Equation of state**

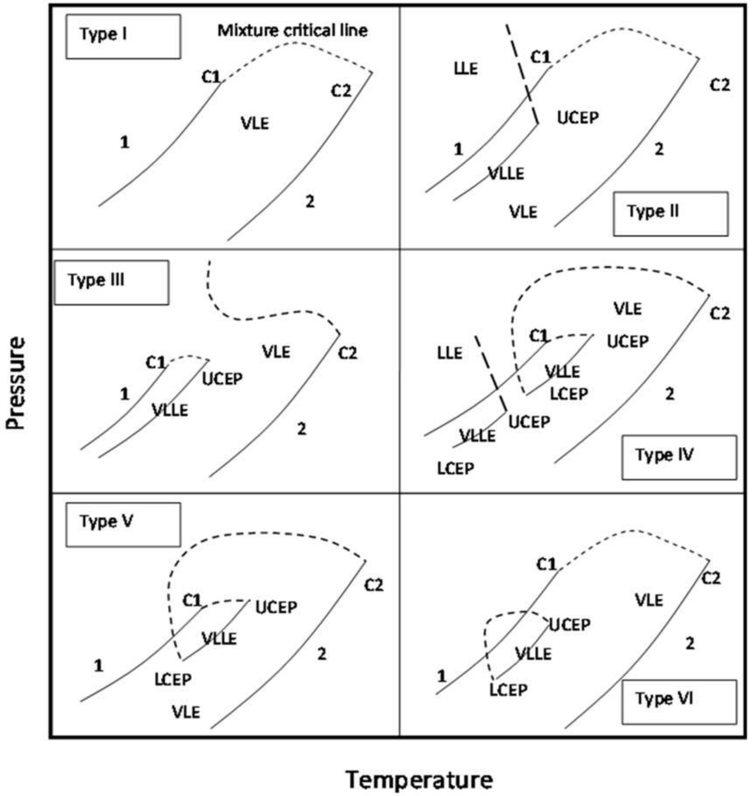
- Phase diagrams representation

  Knowledge of phase diagram is essential (azeotrope, critical point, conditions of apparition of liquid liquid equilibrium

- Density predictions

  Estimation of the densities of both vapor and liquid phases with the maximum of accuracy, estimation of densities in the supercritical phase

- Heat capacities predictions
  - Not discussed here



Scott and van Konynenburg classification.

Thermodynamic properties at the vicinity of the critical point

○ Pure component

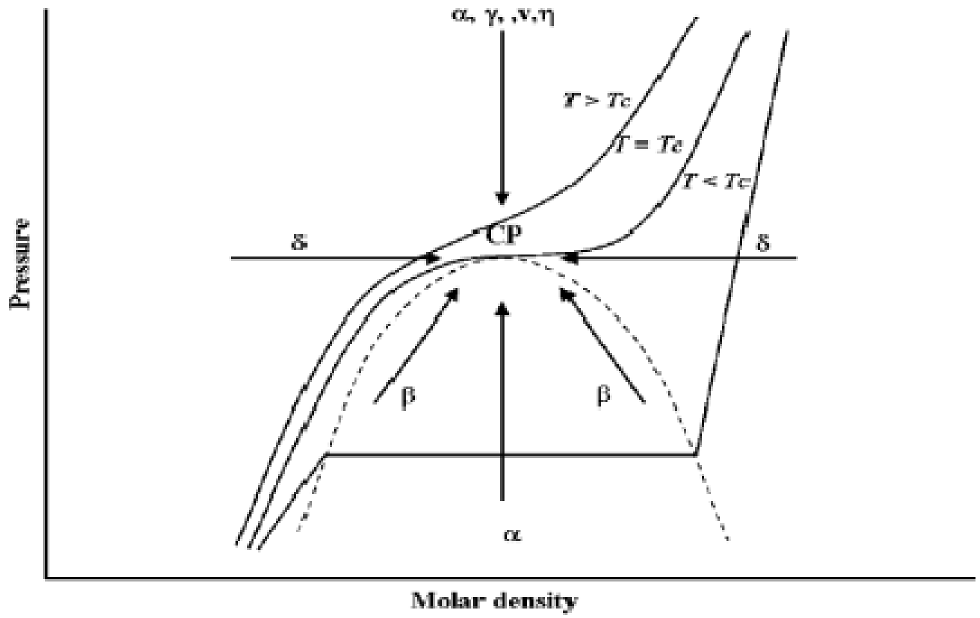
- Assyptotic laws (Scaling law)
- 2nd order phase transition: order parameter (density) (equal to 0, if T>Tc)
- Critical exponents

$\rho_L - \rho_V \propto |T_c - T|^{\beta}$ Coexisting curve

$C_V \propto k_{\alpha 0} + k_{\alpha 1}|\Delta\tau|^{-\alpha}$ Critical isochoric

$\left|\frac{P - P_c}{P_c}\right| \propto \left|\frac{\rho - \rho_c}{\rho_c}\right|^{\delta}$ Critical isotherm

$\chi \propto k_{\gamma 1}|\Delta\tau|^{-\gamma}$ Critical isochoric



Critical exponent	Values
α	0.110
β	0.3255
γ	1.239
δ	4.800

Universal law: $\alpha + 2\beta + \gamma = 2$

Experimental Approach

○ Thermodynamic properties

- **Two main methods:**

  – Open circuit methods

  Circulation of fluid (limiting activity coefficient, critical point, density, etc..

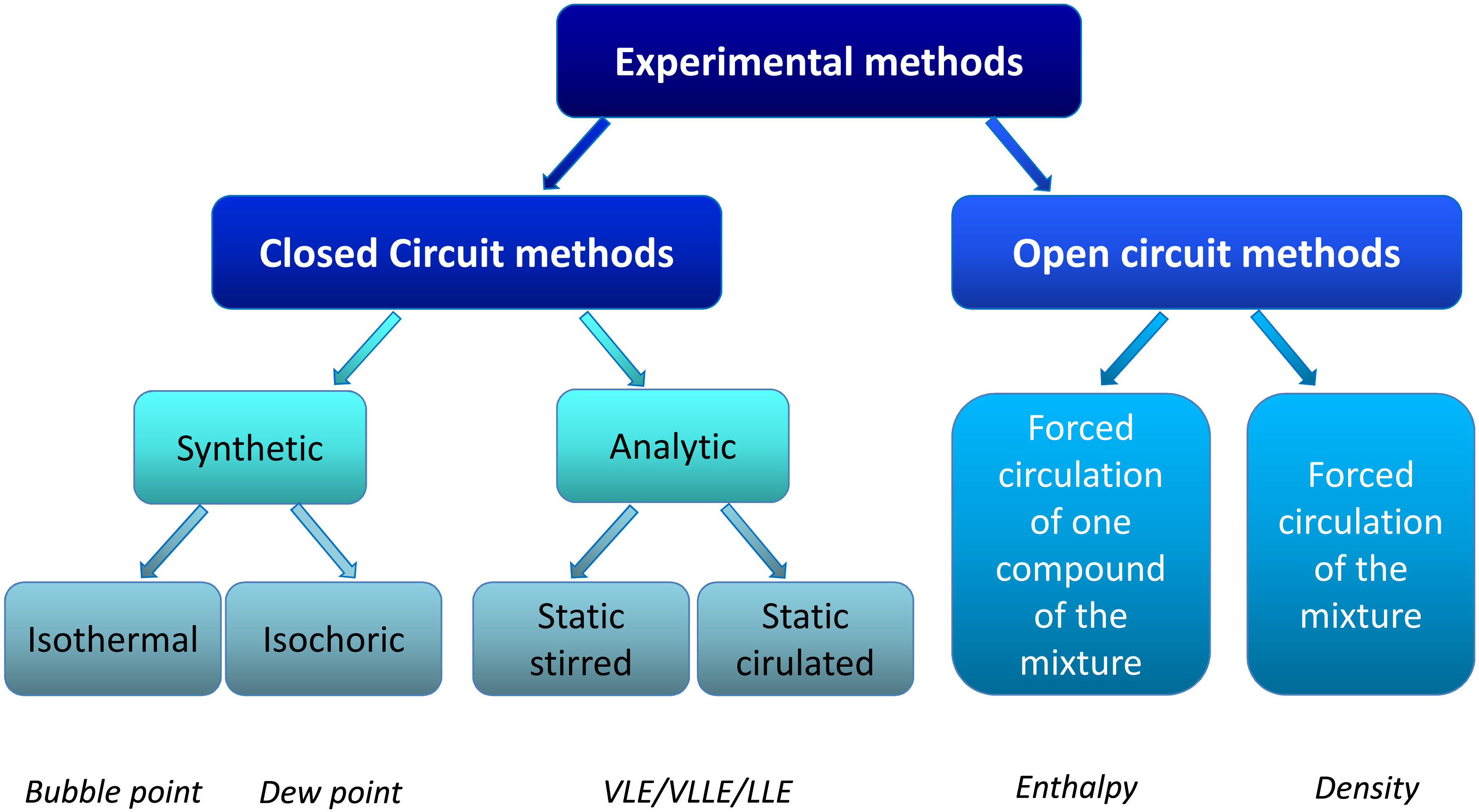
  – Close circuit methods

  Fixed or variable volume

Synthetic and analytic methods

Measurements of T, P, V and compositions for equilibrium properties

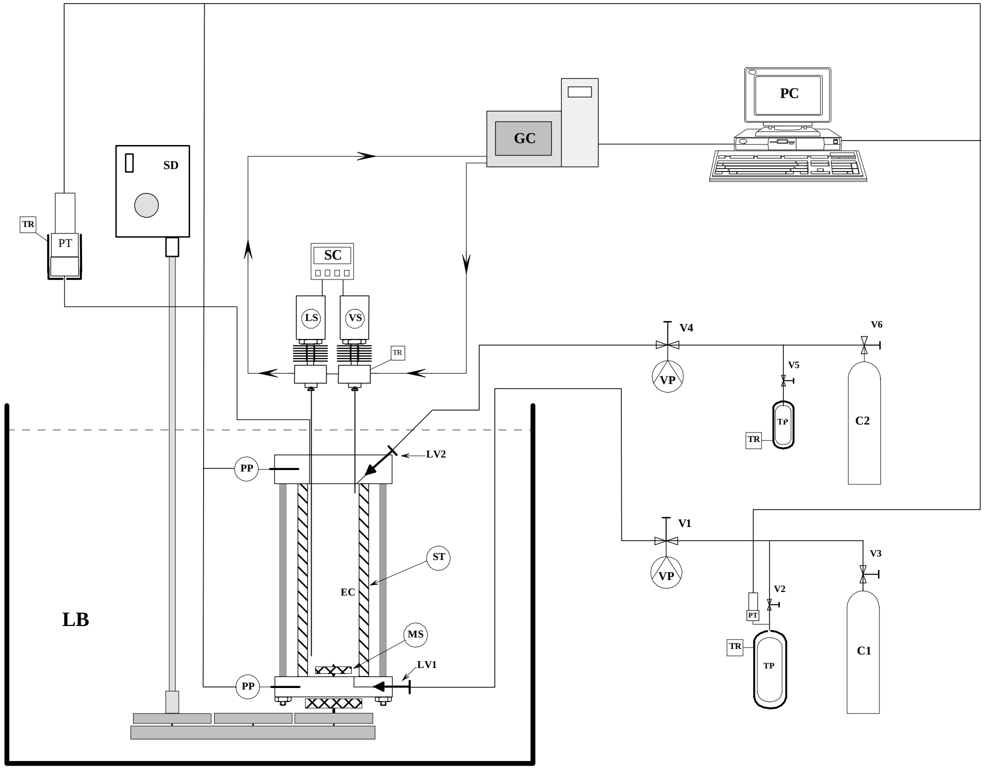
Experimental Approach



Experimental Approach

○ Vapor Liquid Equilibrium measurement

- Static-analytic method
- Temperature is maintained constant
- Component are added using gas cylinder
- Phase sampling (ROLSI(TM))
- Gas Chromatography for the determination of the composition of each phase
- Determination of experimental uncertainty using NIST standard
  – Order of magnitude: u(T)=0.05K, u(p)=0.005 MPa, u(z)=0.005



EC: equilibrium cell; LV: loading valve; PP: platinum resistance thermometer probe; PT: pressure transducer; C1: more volatile compound; C2: less volatile compound; GC: gas chromatograph; LS: liquid sampler; VS: vapor sampler; SC: sample controlling; PC: personal computer; VP: vacuum pump.

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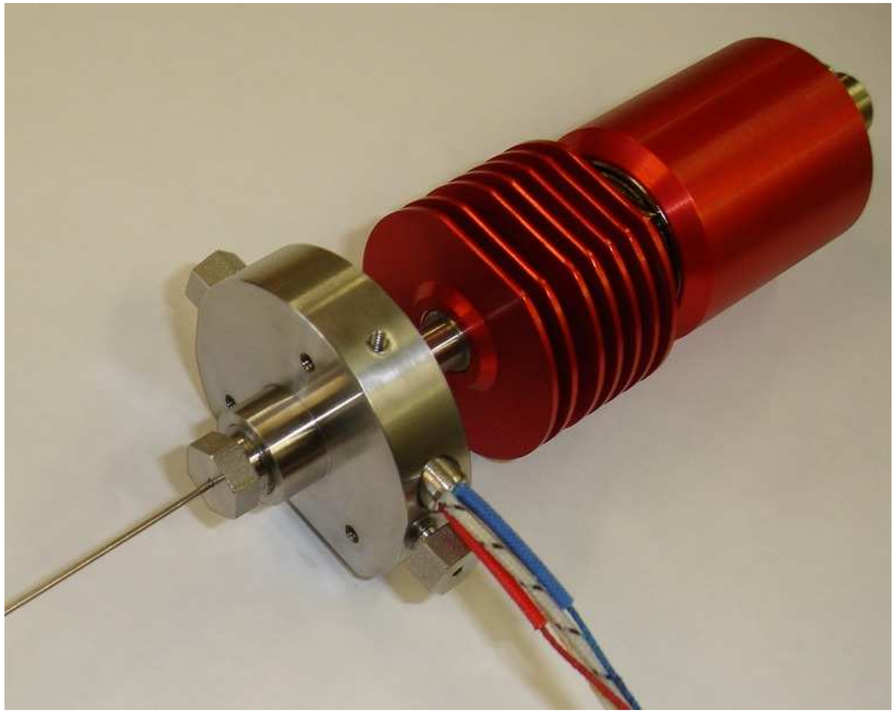

ROLSI™ capillary sampler (Armines's Patent)

Experimental Approach

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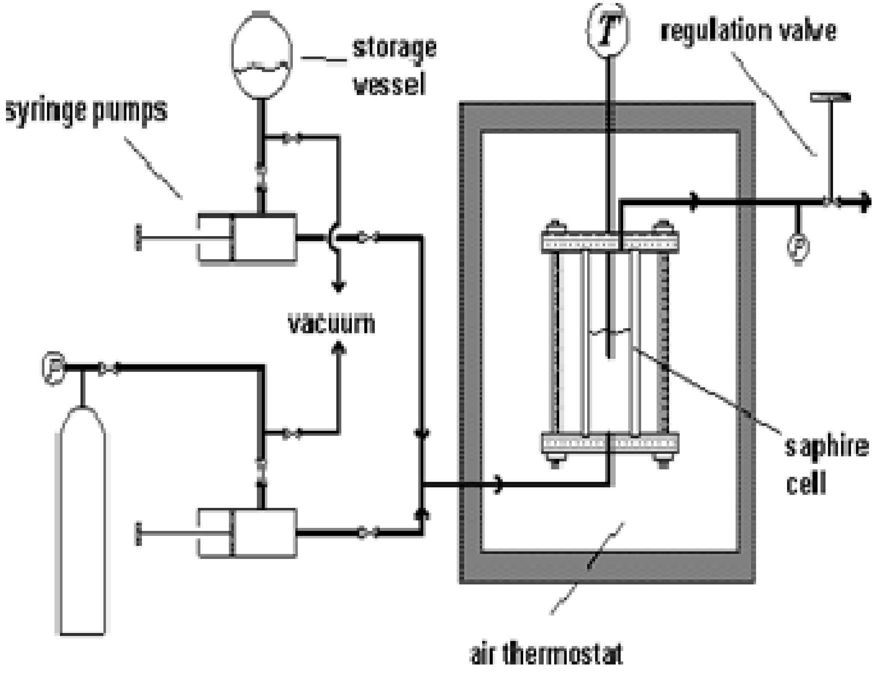
Picture of equilibrium cell

Experimental Approach

- Critical point measurement



Critical points were determined by observing the critical opalescence (dynamic method):

1) A mixture of known overall composition is prepared and sent in the cell

2) The temperature is increased and the flow rate is regulated in order to maintain the meniscus in the middle of the cell

3) At the critical point, the cell becomes orange and the meniscus disappears from the middle of the cell. T_C and P_C are recorded.

Experimental Approach

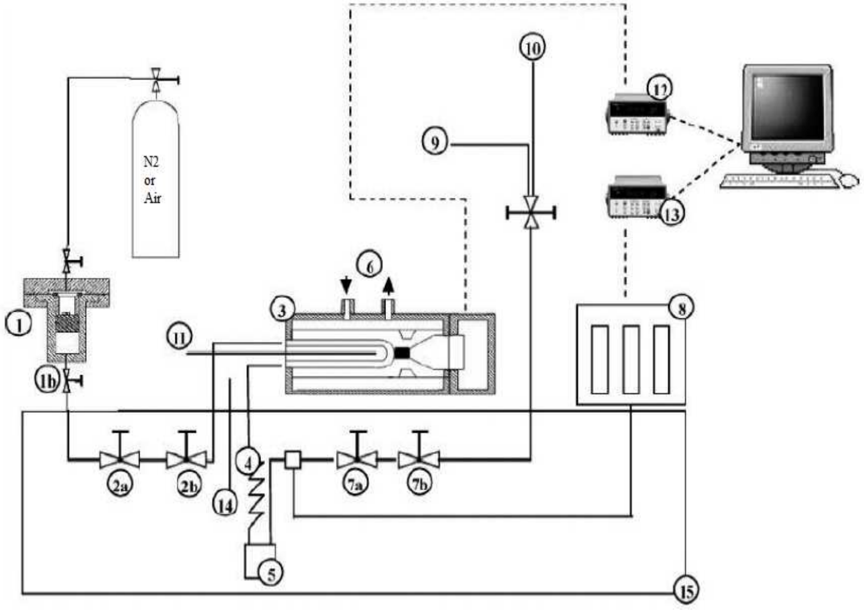
Density measurements

- **Vibrating tube densimeter**

- The measurements are based on the indirect synthetic method. The method is based on the relation between the vibrating period of a dimensional resonator and its vibrating mass.

$$\rho = \left(\frac{M_0}{V_i}\right)\left(\left(\frac{K\tau^2}{K_0\tau_0^2}\right) - 1\right)$$

- The main part of the apparatus is the densimeter cell DMA-512P (Anton Paar KG).

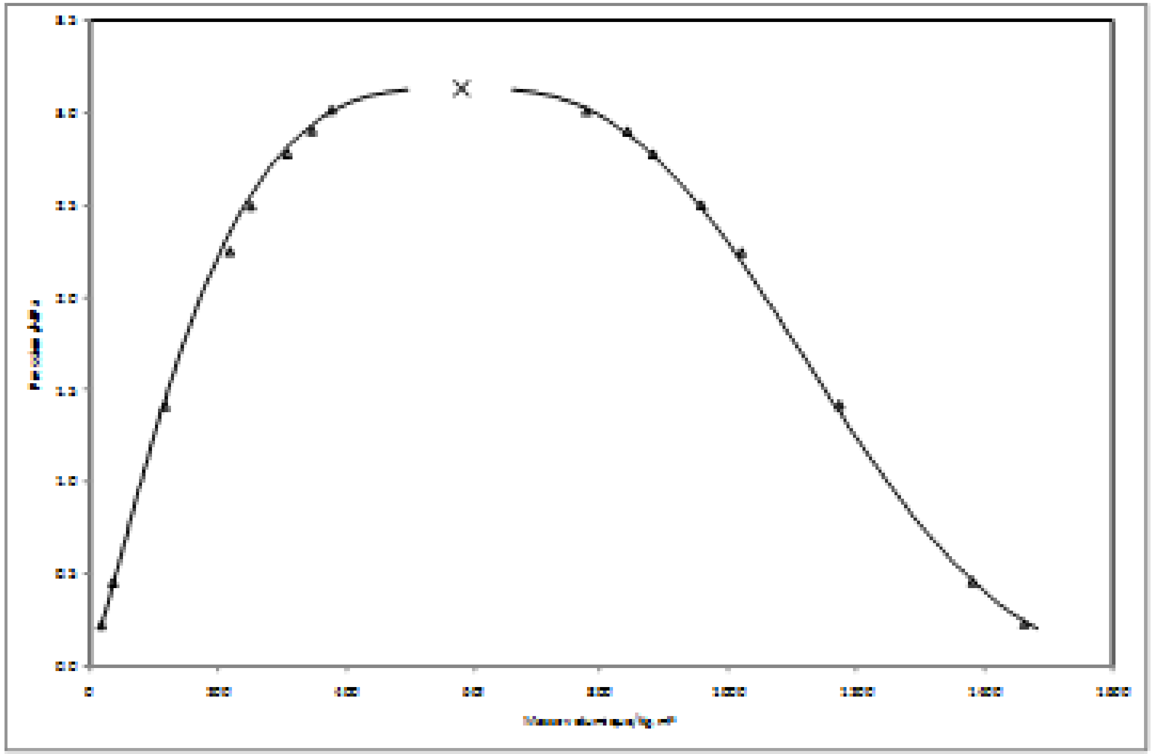


Flow diagram of the vibrating tube densimeter. (1): loading cell; (2a) and (2b): regulating and shut-off valves; (3): DMA-512P densimeter; (4): heat exchanger; (5): bursting disk; (6): inlet of the temperature regulating fluid; (7a) and (7b): regulating and shut-off valves; (8): pressure transducers; (9): vacuum pump; (10): vent; (11): vibrating cell temperature probe; (12): HP 53131A data acquisition unit; (13): HP34970A data acquisition unit; (14): bath temperature probe; (15): principal liquid bath.

Pure component

○ HFO 1216

- Comparison between experimental data (vibrating tube densimeter)
- Estimation of critical properties (Coquelet et al., 2011)



Data treatment

- Rectilinear diameter

$$\frac{\rho_g - \rho_l}{2} - \rho_C = A(T - T_C)$$

- Coexisting curve

$$\rho_g - \rho_l = B(T - T_C)^{\beta}$$

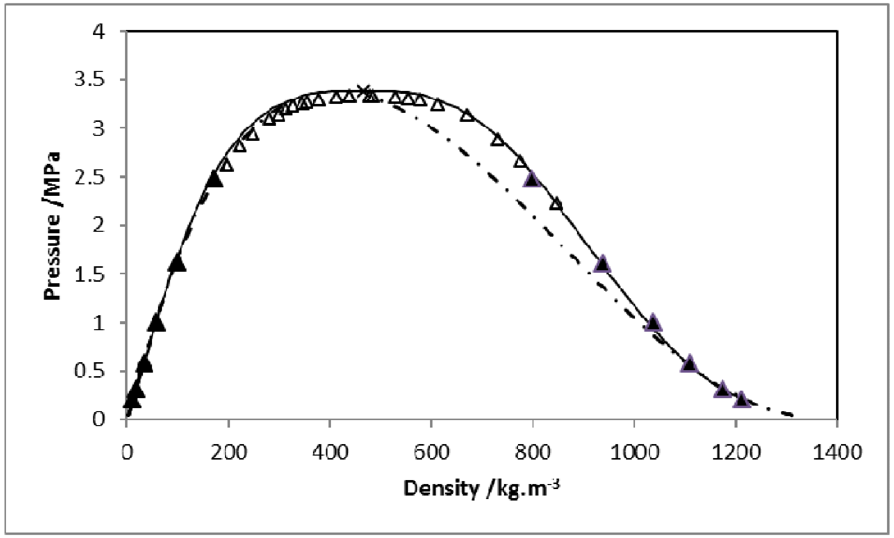
- Combination of these two expressions

$$\rho^L = \frac{1}{2}A(T - T_c)^{\beta} + B(T - T_c) + \rho_c$$

$$\rho^V = -\frac{1}{2}A(T - T_c)^{\beta} + B(T - T_c) + \rho_c$$

- Parameters are fitted considering both vapor and liquid densities at saturation

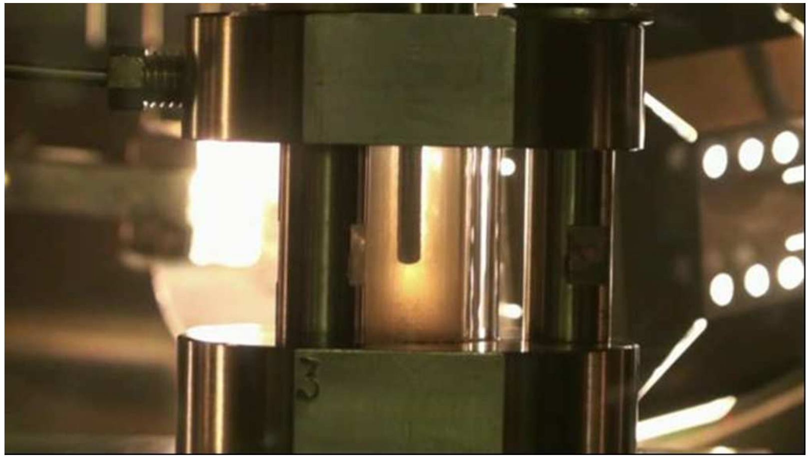
R1234yf

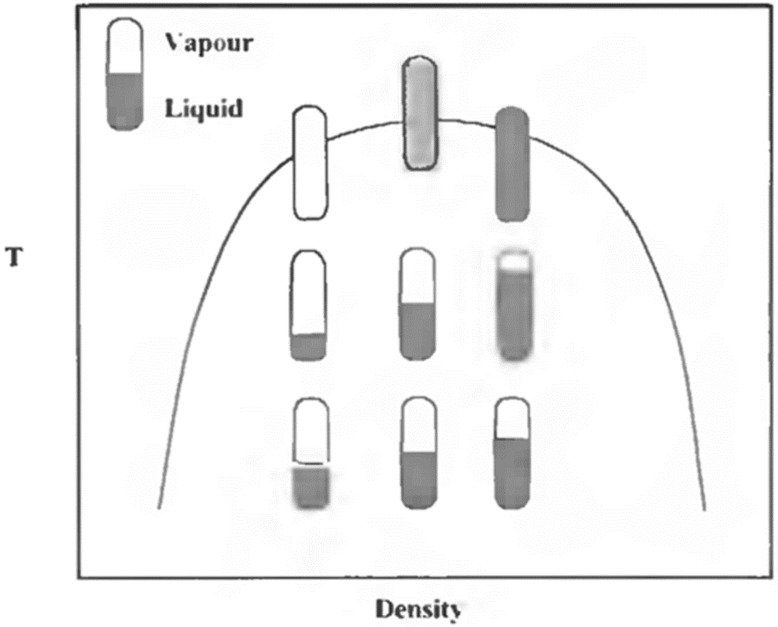


Tanaka et Higashi IJR 33, 2010, 474-479
CTP confidential data

Visual method

- Observation of the vapor liquid interface
- Accurate calibration of the volume of the cell
- Measurement of temperature (for the pressure, we consider the pure component vapor pressure)
- Knowledge of the total mole number using variable volume cell (and density of the fluid the condition of loading)
- Exemple: R134a





Visual method

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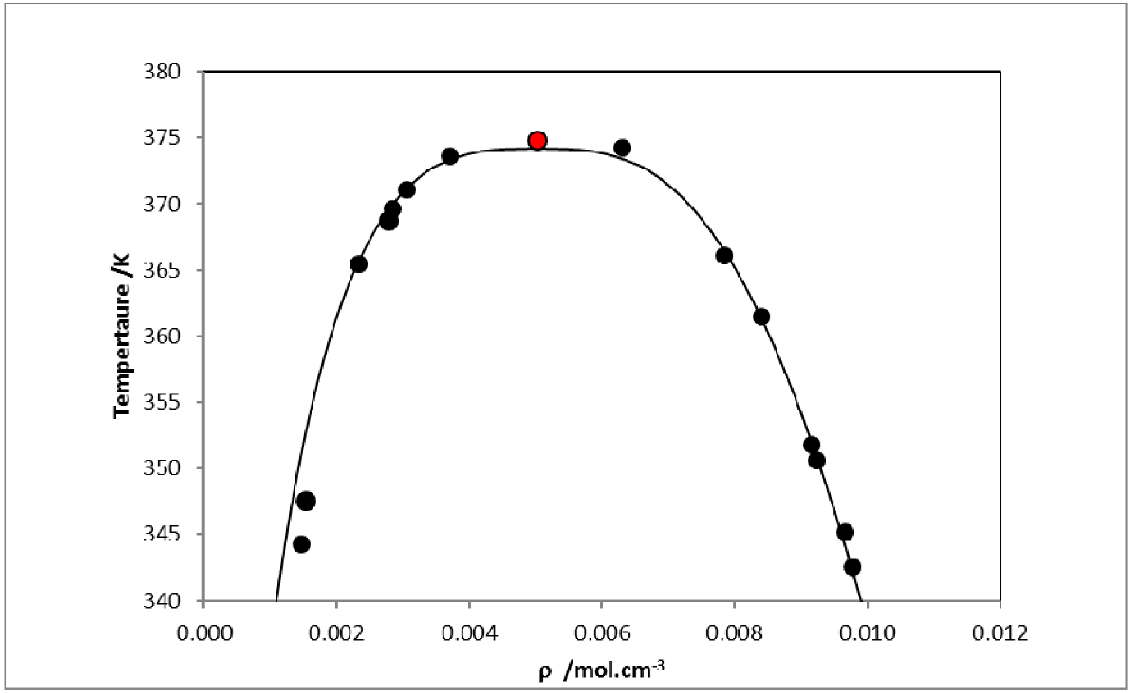
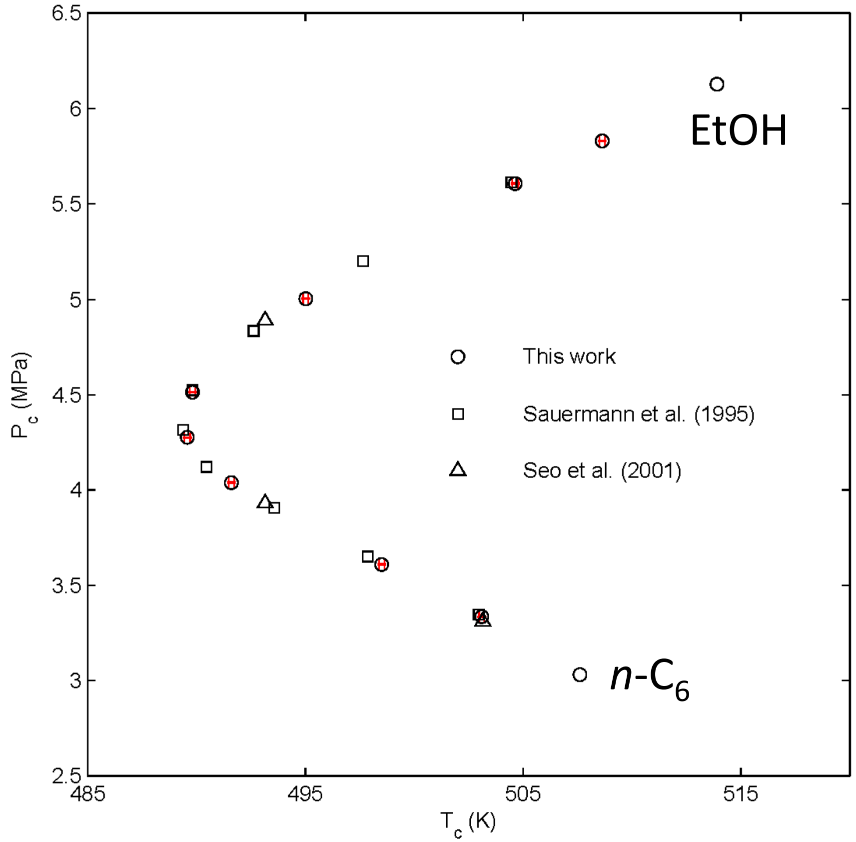
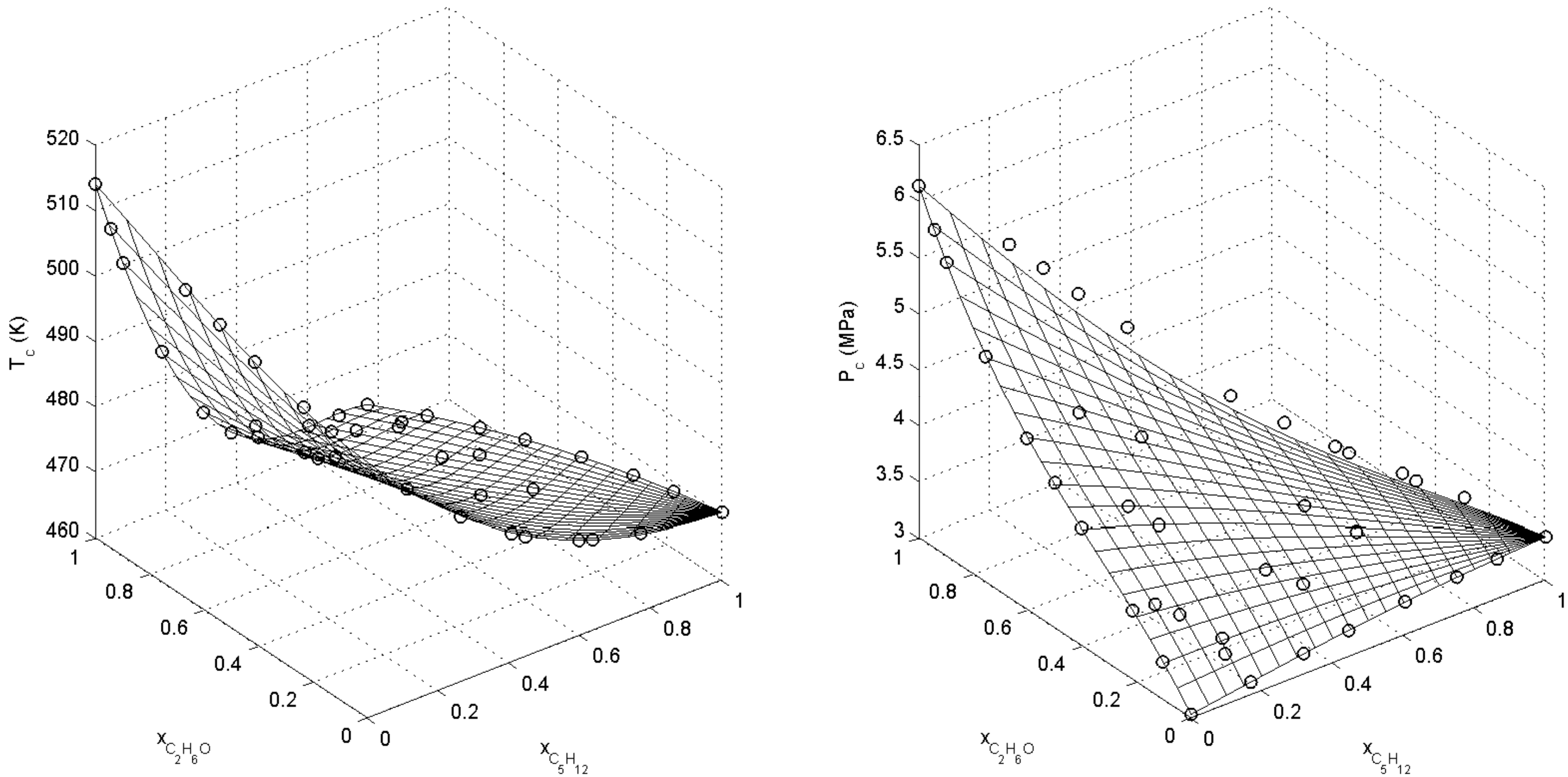


- Redlich Kister type correlation
  - Ethanol + n-hexane binary system: azeotropic behaviour
  - Pentane + ethanol + n-hexane ternary system

Soo et al., 2010



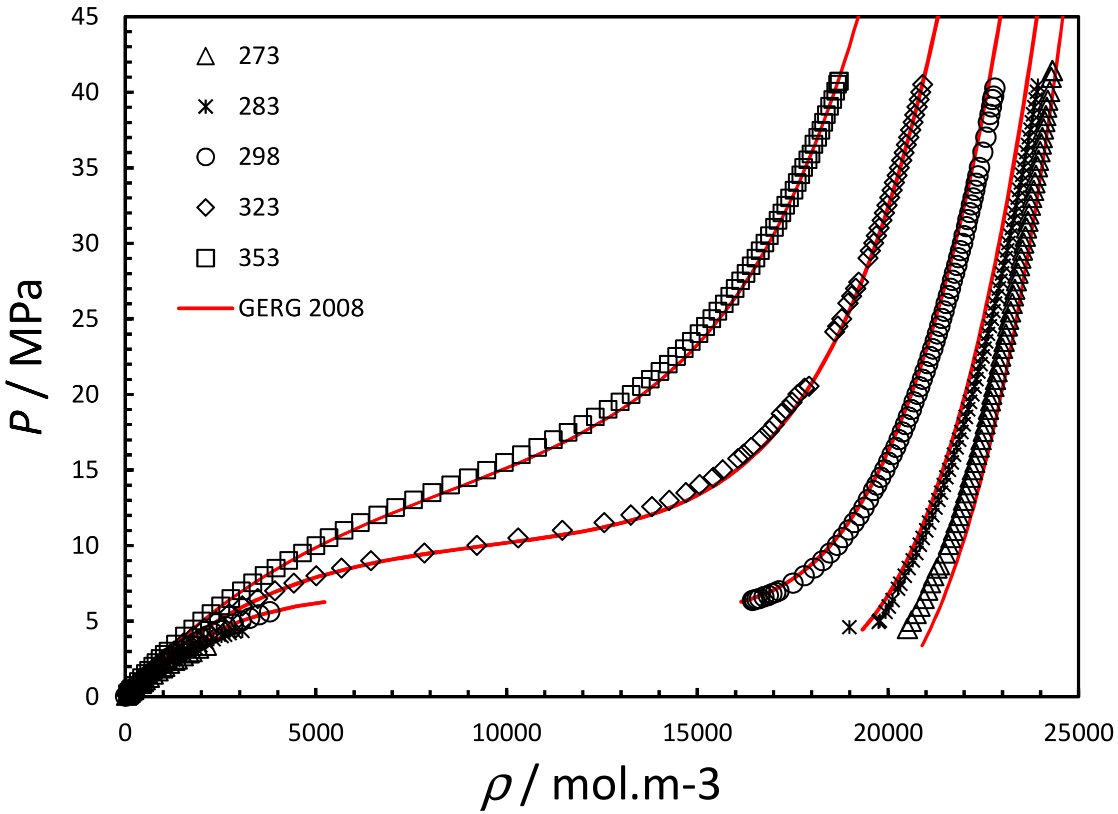
Ethanol + n-Hexane



n-Pentane + Ethanol + *n*-Hexane

Mixture

- Density measurements
  - CO_2 H_2S binary mixture

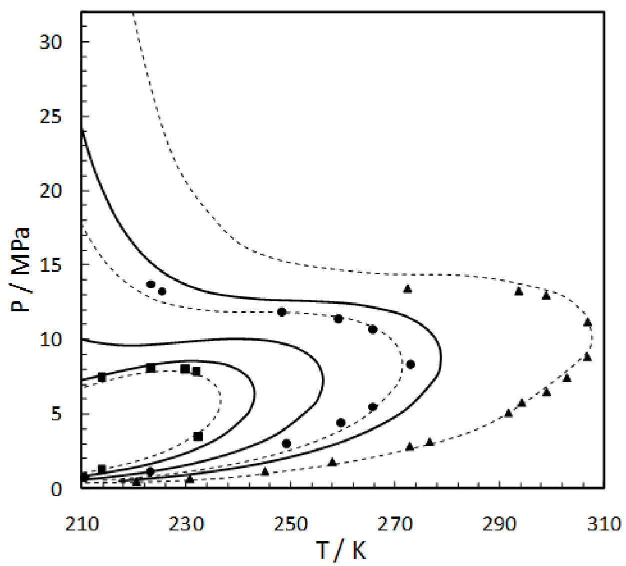


Predicted and experimental densities of the system 0.9505 CO_2 (1) + 0.0495 H_2S (2) system. Red lines: Predictions using the GERG-2008 EoS

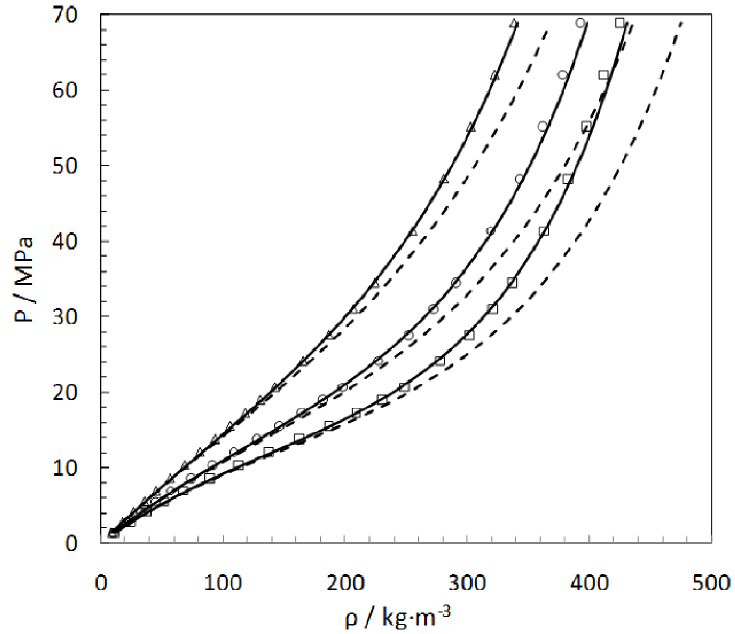
Nazeri et al., 2016

Mixture

- Density measurements
  - CH_4 H_2S binary mixture (**no critical point**)



Predicted phases envelopes with the PR EoS of the methane + hydrogen sulphide system with 0.1101, 0.1315, 0.1803, 0.248, 0.286 and 0.458 mol fractions of H2S.



Experimental and predicted densities of the. Predicted and experimental density of 0.7 mole CH4 + 0.3 mole H2S system. Comparison of PR+Peneloux (continuous curve), PR (dashes) and literature (311 K, 344 K and 411 K)

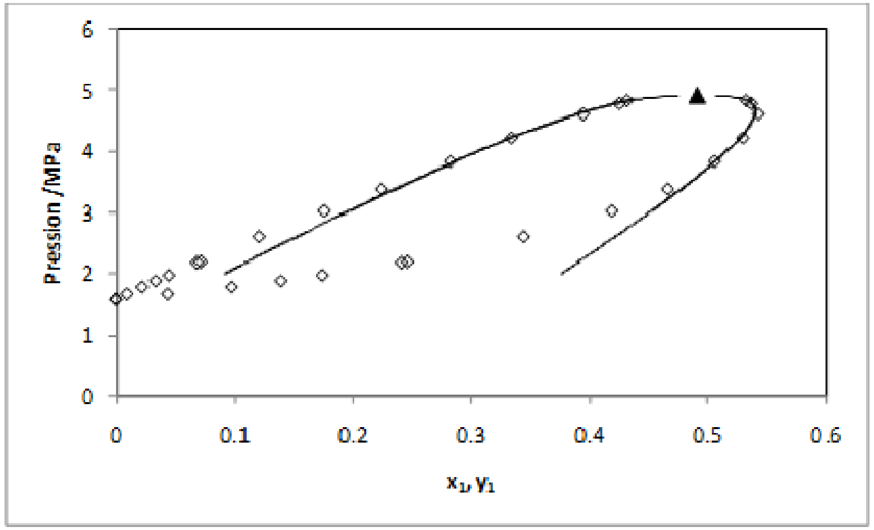
Gonzalez-Perez et al., 2016, submitted

Data Treatment VLE Mixture

- Utilisation of scaling law equations and experimental data to predict correctly the phase diagram close to the mixture critical point

- Equation 1: $$y_i - x_i = C(P_c - P)^{\beta} + D(P_c - P)$$

- Equation 2: $$\frac{1}{2}(y_i - x_i) - x_c = K(P_c - P)$$



VLE of the binary system N_2 (1) – CH_4 (2) at 160K. (◊) : experimental data (Kremer ; 1982), (▲) : mixture critical point

VLE Mixture

- CO + ethylene binary system (El Ahmar et al. 2012)

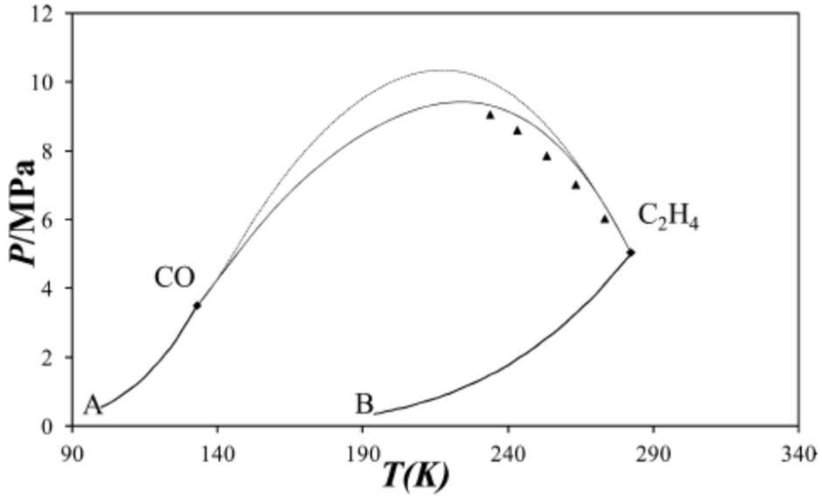


Figure 4. PT diagram for the CO (1) + C_2H_4 (2) system. ♦, critical point value for pure component; ▲, critical point value for the binary system using the scaling laws. Curve ACO (CO pure component vapor pressure) and Curve B–C_2H_4 (C_2H_4 pure component vapor pressure): —, critical loci calculated with the SRK EoS; ···, critical loci calculated with the PR EoS.

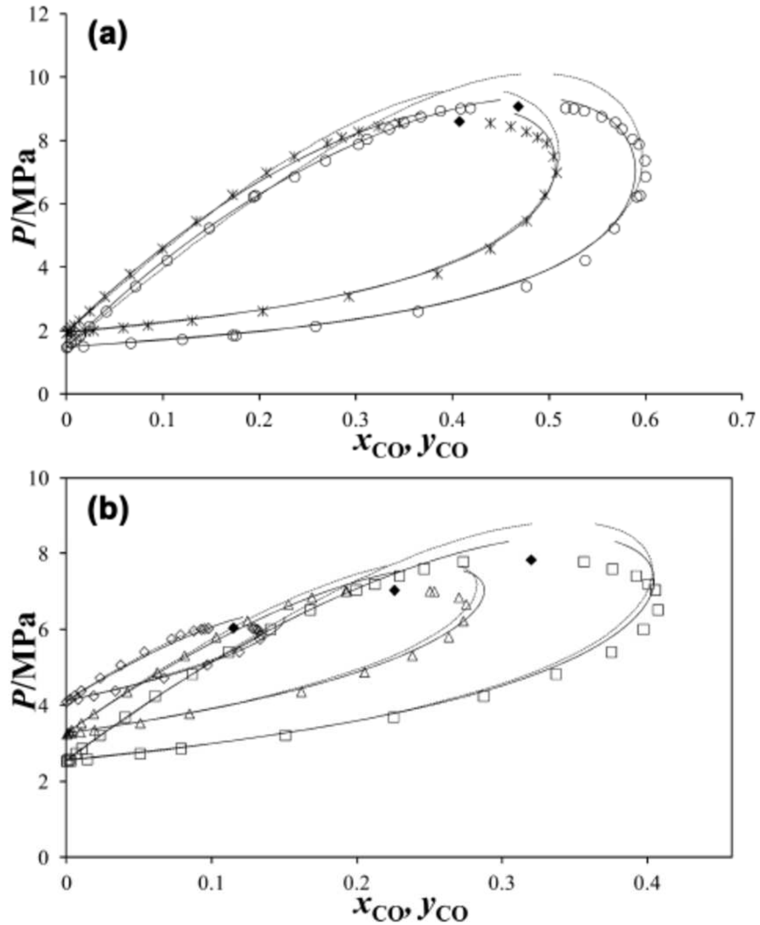


Figure 2. (a) Phase diagrams ($P-x-y$) for the CO (1) + C_2H_4 (2) system at (a) ○, 233.73 K; *, 243.08 K and (b) □, 253.22 K; △, 263.22 K; ◇, 273.18 K. ◆, critical point value; —, SRK EoS; ···, PR EoS.

VLE Mixture

- $CH_4 + C_4F_{10}$
- Estimation of mixture critical point using scaling laws method
- Modeling using PR EOS coupled with WS mixing rule and NRTL activity coefficient equations

Tshibangu et al., 2014

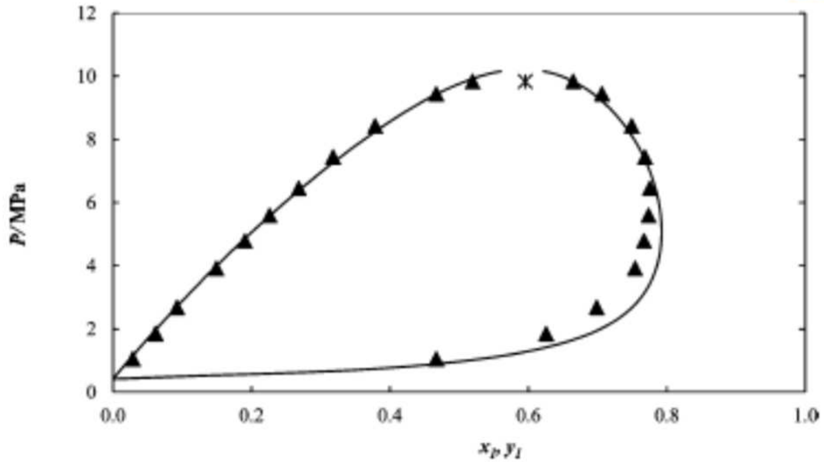


Figure 2. Phase diagram (P–x–y) for the CH_4 (1) + C_4F_{10} (2) system: ▲, 313.09 K —, PR-MC-WS-NRTL model; *, mixture critical point.

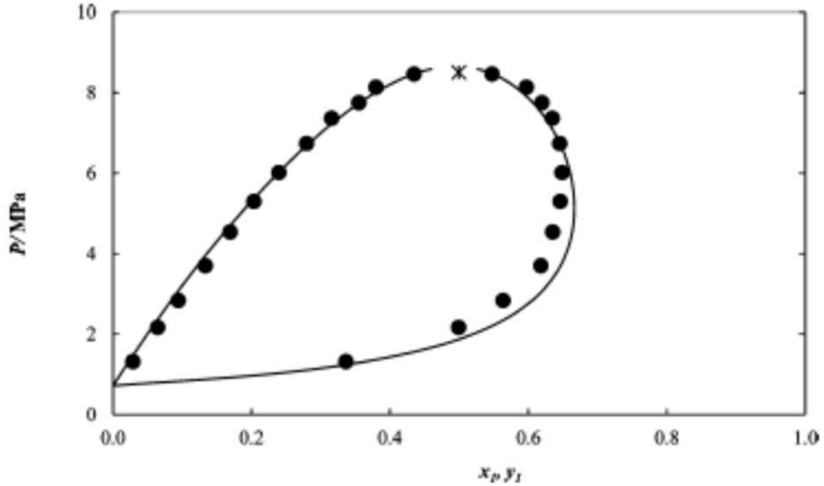
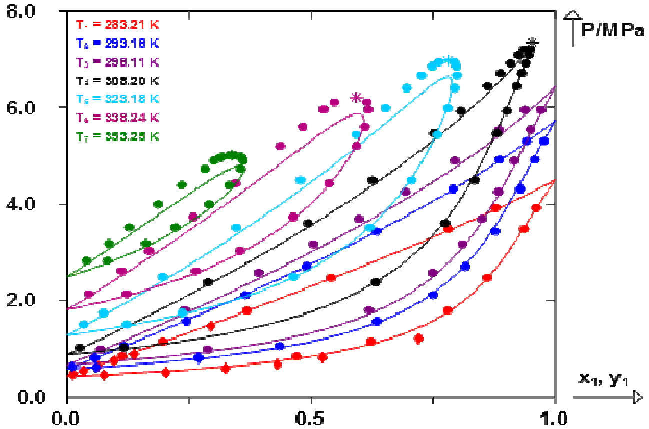
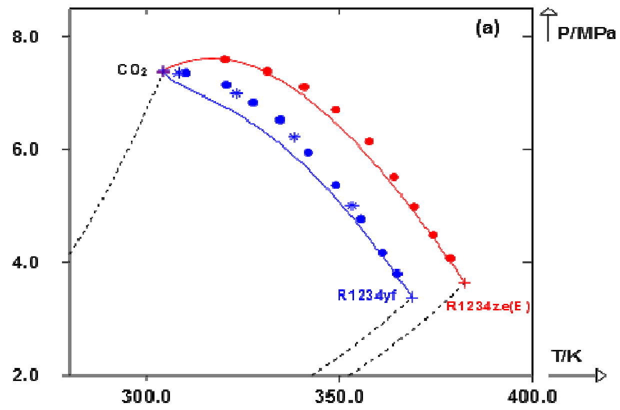


Figure 3. Phase diagram (P–x–y) for the CH_4 (1) + C_4F_{10} (2) system: ●, 332.97 K; —, PR-MC-WS-NRTL model; *, mixture critical point.

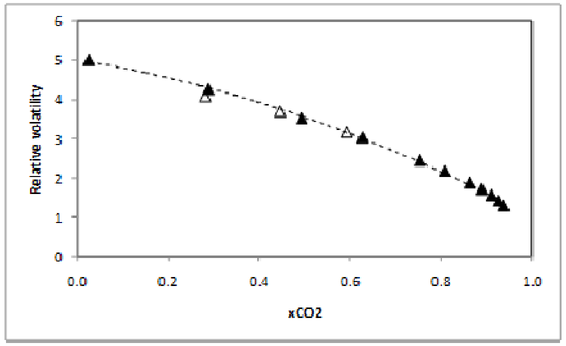
VLE Mixture

- CO_2 + HFO 1234yf





P-T and P-x projections including experimental point and modelling using PPR78



Relative volatility :Juntarachat et al. (2014) (▲) at 308.20 K; Raabe (MS) (2013) (Δ) at 310.92 K.

❖Interest in climatisation and/or refrigeration (low pressure glide)
❖The binary system was investigate using two equipments (critical point and static analytic type)
❖R1234yf is considered as one group
❖Parameters are fitted considering both VLE and critical point experimental data
❖Good agreement is observed with molecular simulation calculation

Conclusion

- Different experimental techniques exist for the measurement of:
  - Vapor Liquid Equilibrium data
  - Critical point (visual method)
  - Density (vibrating tube or isochoric method)

- Data treatment can be done also by using scaling law equations
  - Good test to see the consistency of the data
  - Prediction of some critical properties (T_C, P_C, critical density)

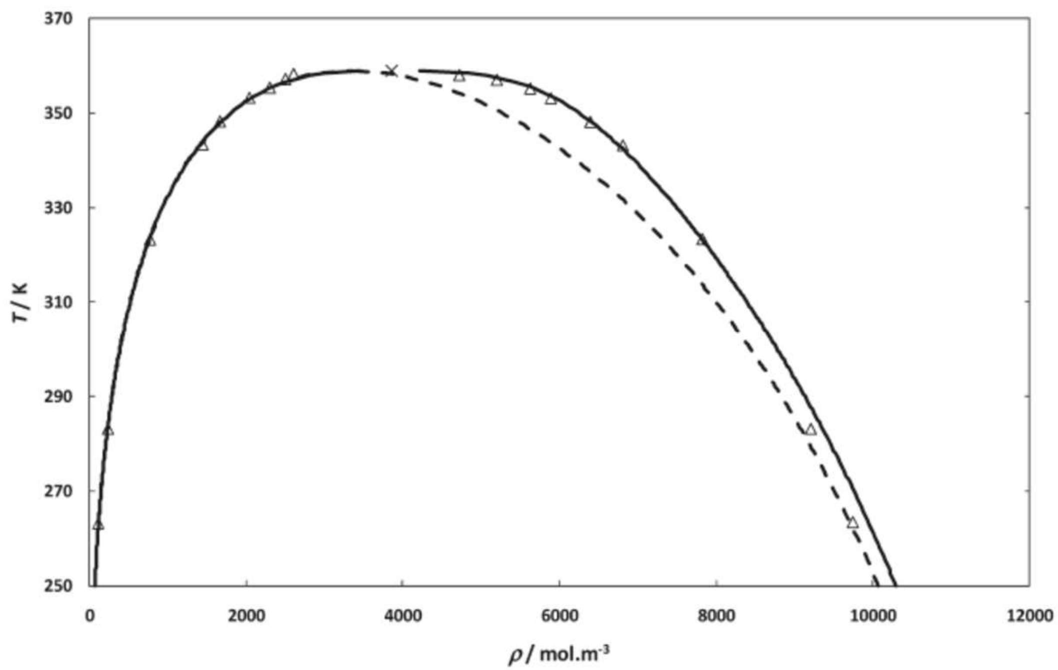
- Data are essential for adjustment of equation of state parameters

Pure component: application of EoS

○ HFO 1216

- Comparison between experimental data (vibrating tube densimeter) and modelling
- Patel Teja EoS is used
- Necessity to apply a correction (Crossover EoS)

Janecek et al., 2015



____: Crossover PT (CR-PT), -------: Classical PT, ×: point critique, (Δ) experimental data Coquelet et al., 2011

Pure component: application of EoS

- HFO 1216

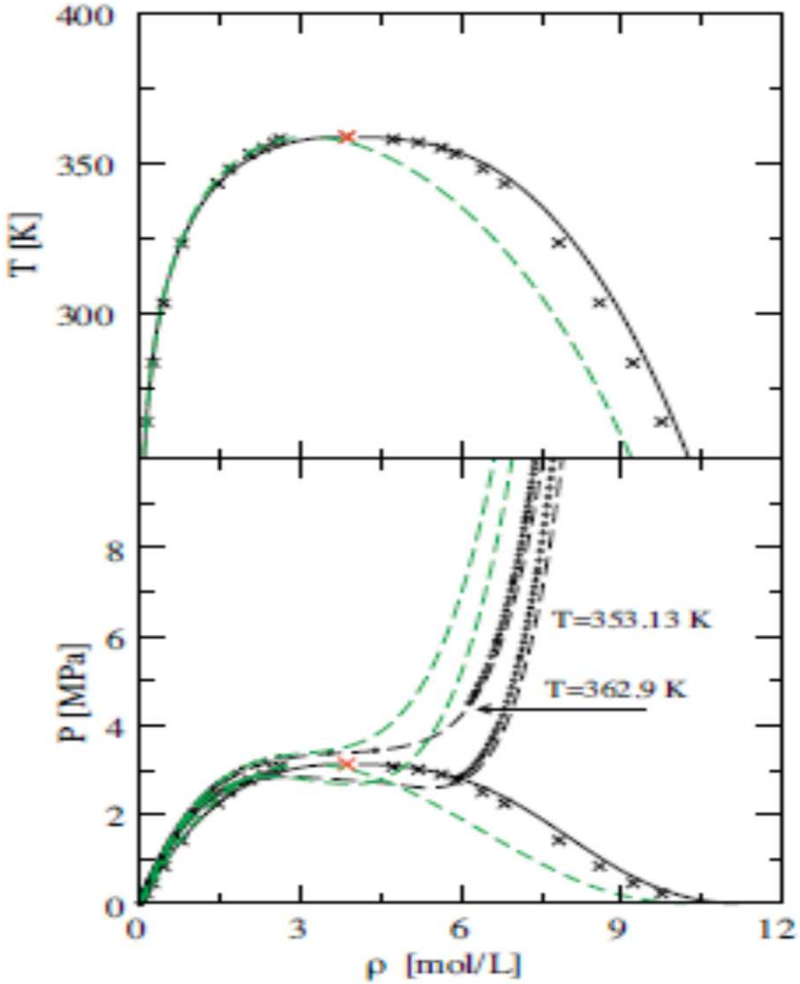


Fig. 10. Phase diagram for hexafluoropropene (R1216). Model C of crossover SRK EoS (solid black lines) is compared with classical SRK EoS with parameters adjusted to reproduce the critical temperature and pressure (green dashed lines). Symbols are the experimental data [43]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)