Les propriétés d'équilibre entre phases et masses volumiques

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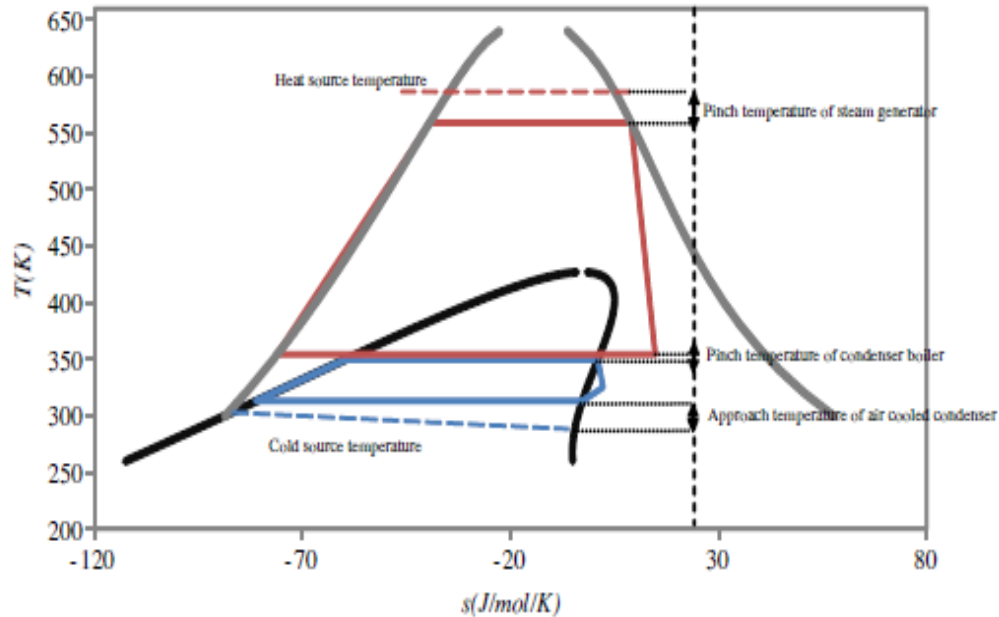
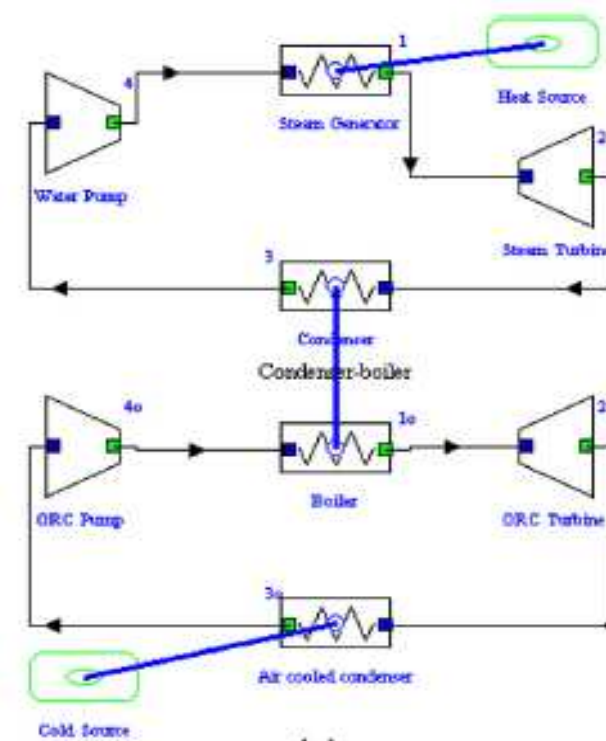Christophe.coquelet@mines-paristech.fr   *Centre of Thermodynamics of Processes*

MOTIVATIONS

○ Example of work done for Edf Chatou (Fluid selection) – Franck David

- The selection of the fluids is mainly based on their energetic performances evaluated on energetic machines.
- The performance (COP) is generally evaluated from a process simulator and confirmed after several tests on existing machines.

TS diagram of two stage ORC

Example of ORC (Bo LIU, 2014)
Simulated using Thermoptim™

MOTIVATIONS

○ Developement of equations of state and phase diagrams understanding
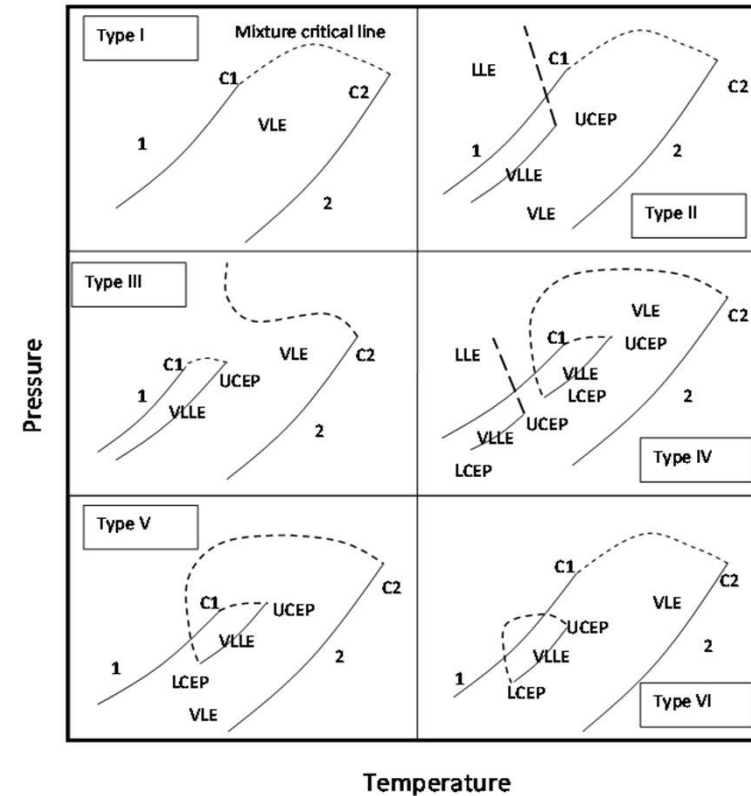
- **Objectives**

- Phase diagrams representation

    Knowledge of phase diagram is essential
    (azeotrope, critical point, relative volatility,
    conditions of apparition of liquid liquid
    equilibrium, solubility in lubricant

- Density predictions

    Estimation of the densities of both vapor and
    liquid phasse with the maximimum of
    accuracy

Scott and van Konynenburg classification.

Properties

○ Phase equilibrium measurements

- What can we measure?
  - Temperature
  - Pressure
  - Composition
  - Volume (variation of volume) or density
  - Speed of sound
  - Flow
  - Luminosity
  - Hardness
  - Etc

- Goal: do not disturb the system during experiments
  - Research on techniques and experimental procedures
  - Size of the equilibrium cell
  - Development of sensors

Experimental Approach

- Selection of the best experimental technique

  – Definition of the objective (number of data, accuracy, number of chemicals, etc..)

  – Knowledge of phase diagram is recommended

  – Prediction using GC EoS or MS are welcome

- Purity of the chemicals

- Required time for the measurements

- Utilization of the data

- Calibration and uncertainties

Calibration

- **Calibration**:

  process of finding a **relationship** between the physical property and the output signal

- Required:

  - New instrument

  - After an insturment has been repaired or modified

  - Before and/or after measurement

  - After an event (shock, sudden shutdown, etc)

- Calibration and errors:

$$process = (measure - standard\ measure) + errors$$

✓ Material
✓ Equipment
✓ Method
✓ Operator
✓ Environment

Two types of uncertainties
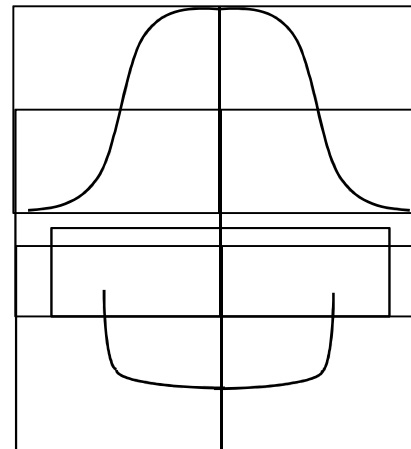
- Uncertainty related to repeatability: type A

    - Ex:

    $$u_{rep}(P) = \sqrt{\frac{1}{N(N-1)} \sum_{k=1}^{N} (P_k - \overline{P})^2}$$
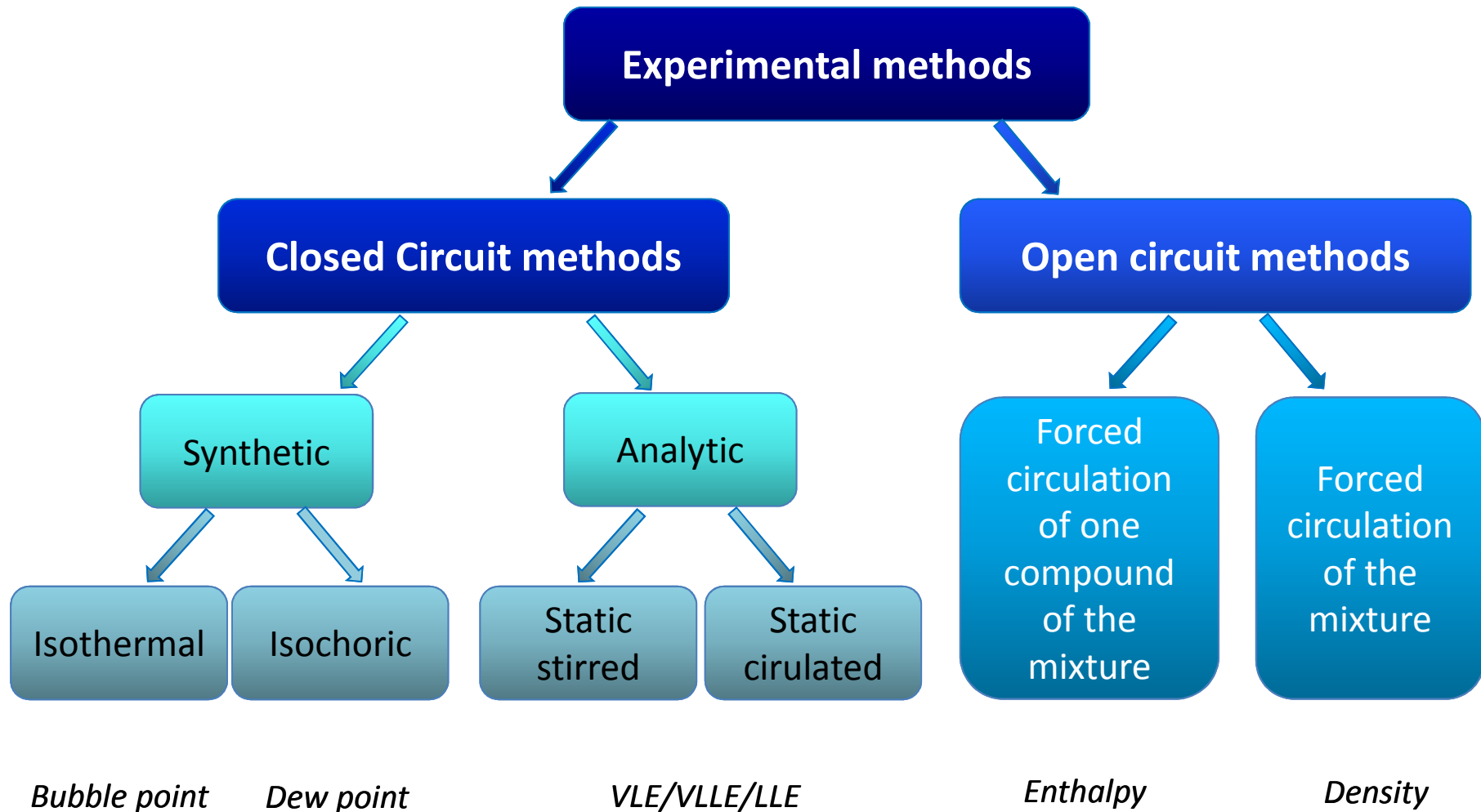
- Standard deviation: type B

    - The uncertainty is supposed to be $\pm a$

    - Different distribution laws:

        - Normal distribution $\quad u_{ref} = \dfrac{a}{2}$

        - Uniform distribution $\quad u_{ref} = \dfrac{a}{\sqrt{3}}$

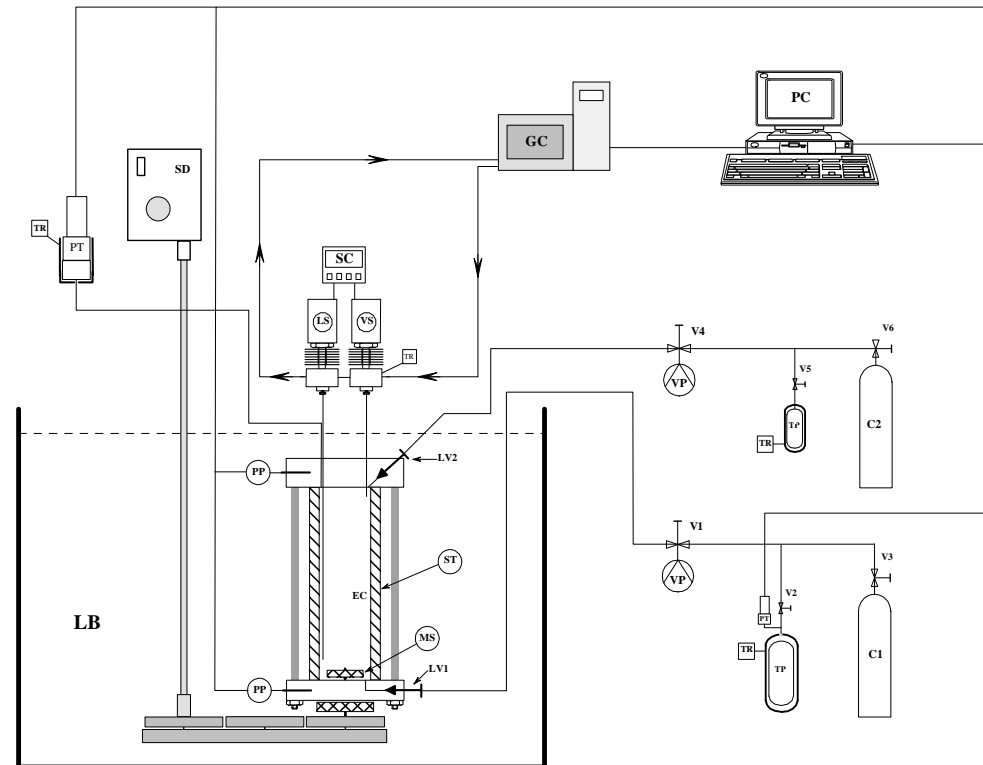   - Arcsine distribution $\quad u_{ref} = \dfrac{a}{\sqrt{2}}$

Experimental Approach

Experimental methods

Closed Circuit methods → Synthetic → Isothermal, Isochoric

Closed Circuit methods → Analytic → Static stirred, Static cirulated

Open circuit methods → Forced circulation of one compound of the mixture, Forced circulation of the mixture

Bubble point   *Dew point*   *VLE/VLLE/LLE*   *Enthalpy*   *Density*

Vapor Liquid Equilibrium Measurement

O Static Analytic method

- Temperature is maintained constant

- Component are added using gas cylinder

- Phase sampling (ROLSI®)

- 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.
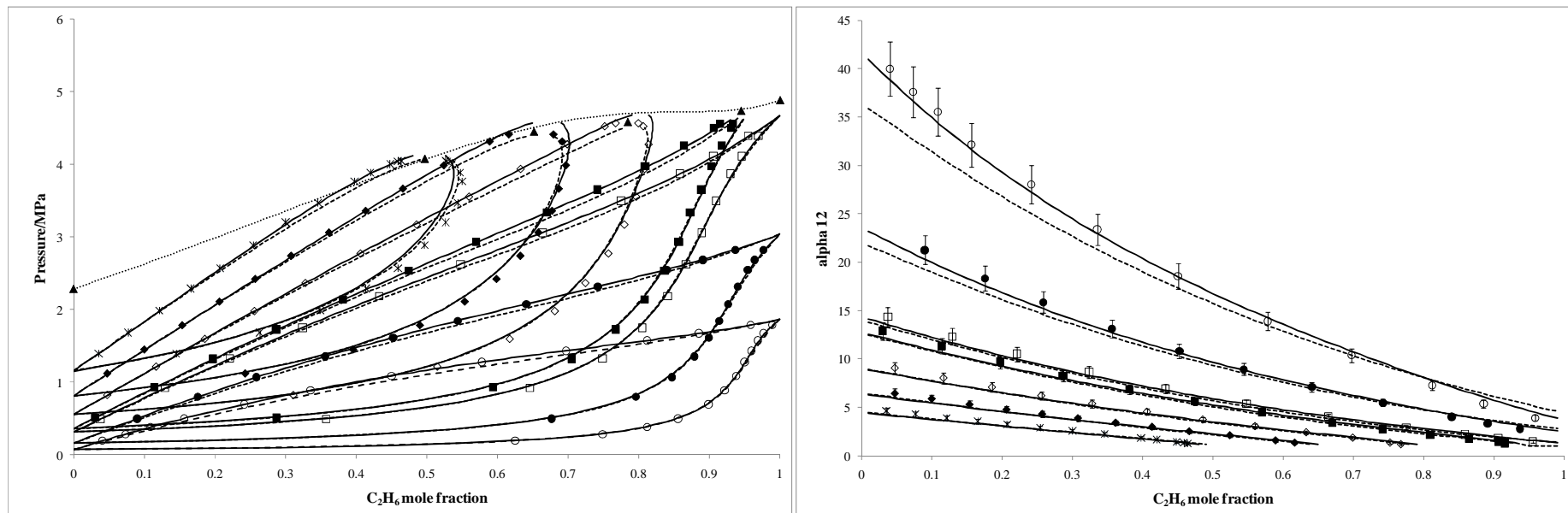
Vapor Liquid Equilibrium Measurement

○ Relative volatility

- Graphic treatment: relative volatility

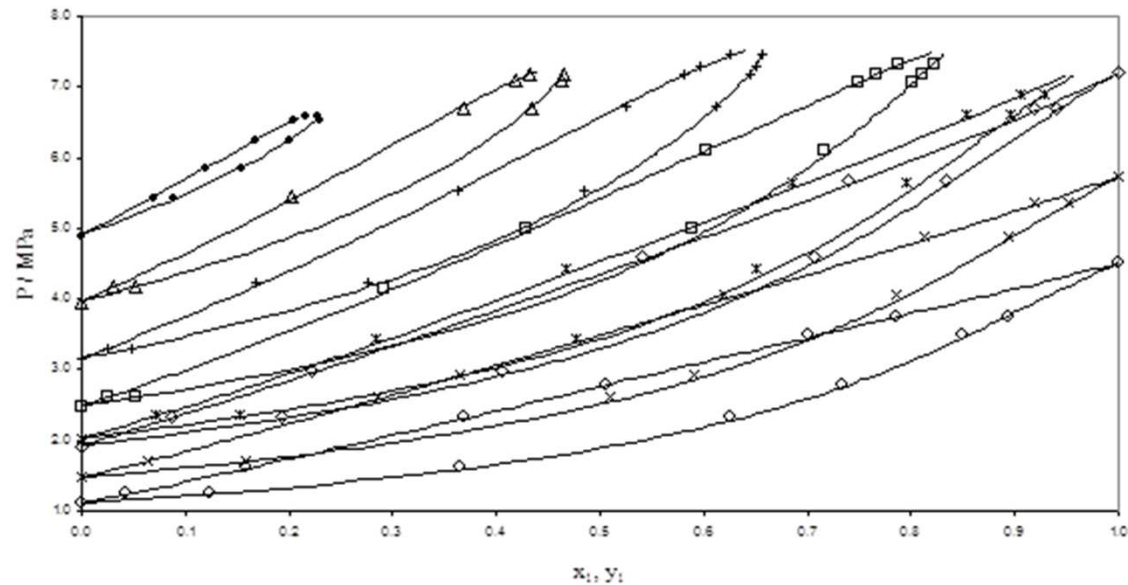$$\alpha_{12} = \frac{y_1}{x_1} \cdot \frac{x_2}{y_2}$$

- Example: Ethane – C4F10

Solid lines: PR
Dashed lines: PSRK

Vapor Liquid Equilibrium Measurement

○ Example of results: CO2 + R32

Pressure as a function of CO2 mole fraction in the CO2 (1) – R32 (2) mixture at different temperatures – VLE Data.
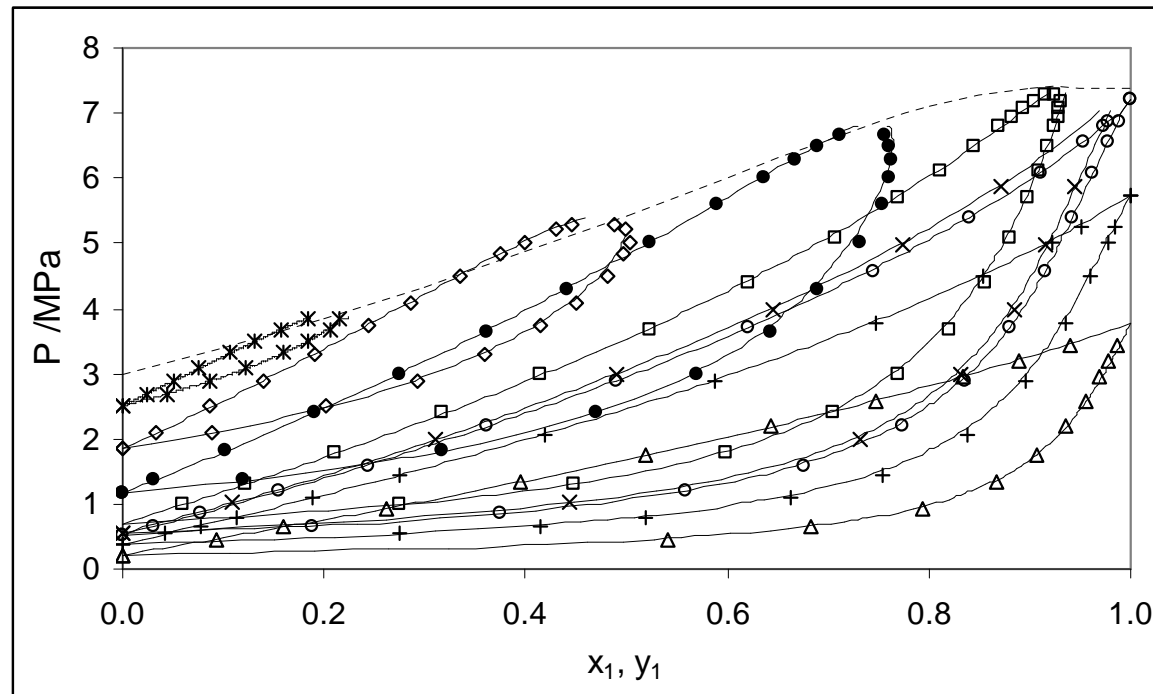o : 283.12 K, □ : 293.11 K, ◊ : 303.13 K, * : 305.15 K, □ : 313.30 K, + : 323.34 K,
Δ : 333.33 K, ● : 343.23 K.
solid lines : calculated with PR EoS, Wong Sandler mixing rules and NRTL activity coefficient model
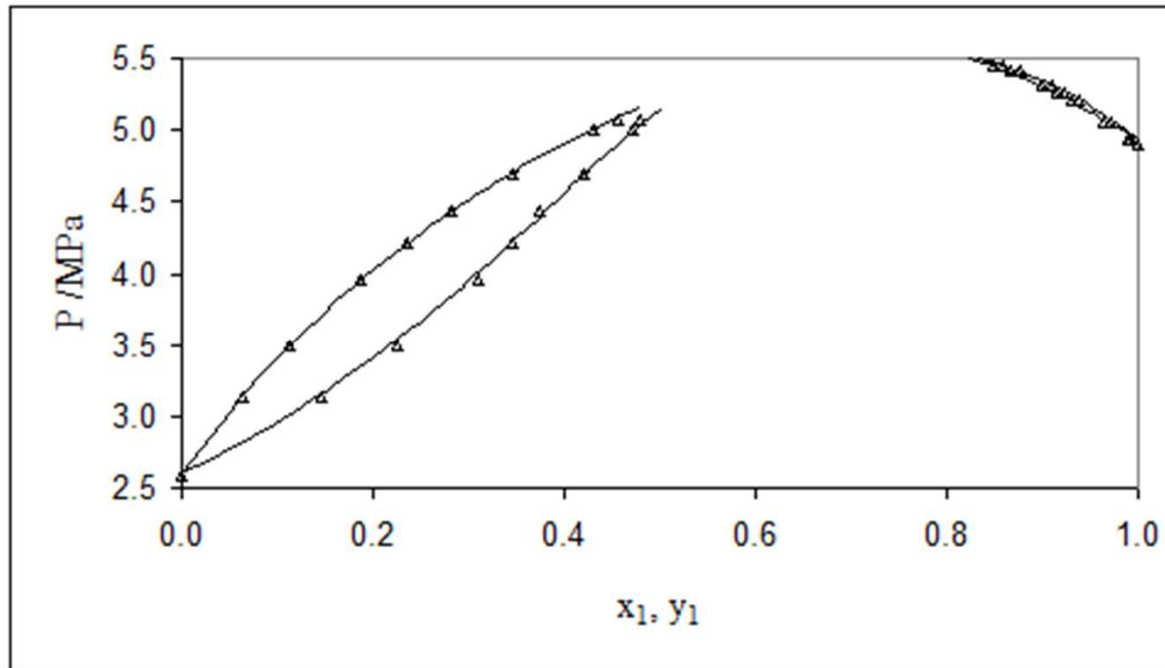
Vapor Liquid Equilibrium Measurement

○ Example of results: CO2 + R227ea

Pressure as a function of CO_2 mole fraction in the CO_2 (1) – R227ea (2) mixture 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. solid lines : calculated with PR EoS, Wong Sandler mixing rules and NRTL activity coefficient model. Dashes line: mixture critical points line.

Vapor Liquid Equilibrium Measurement
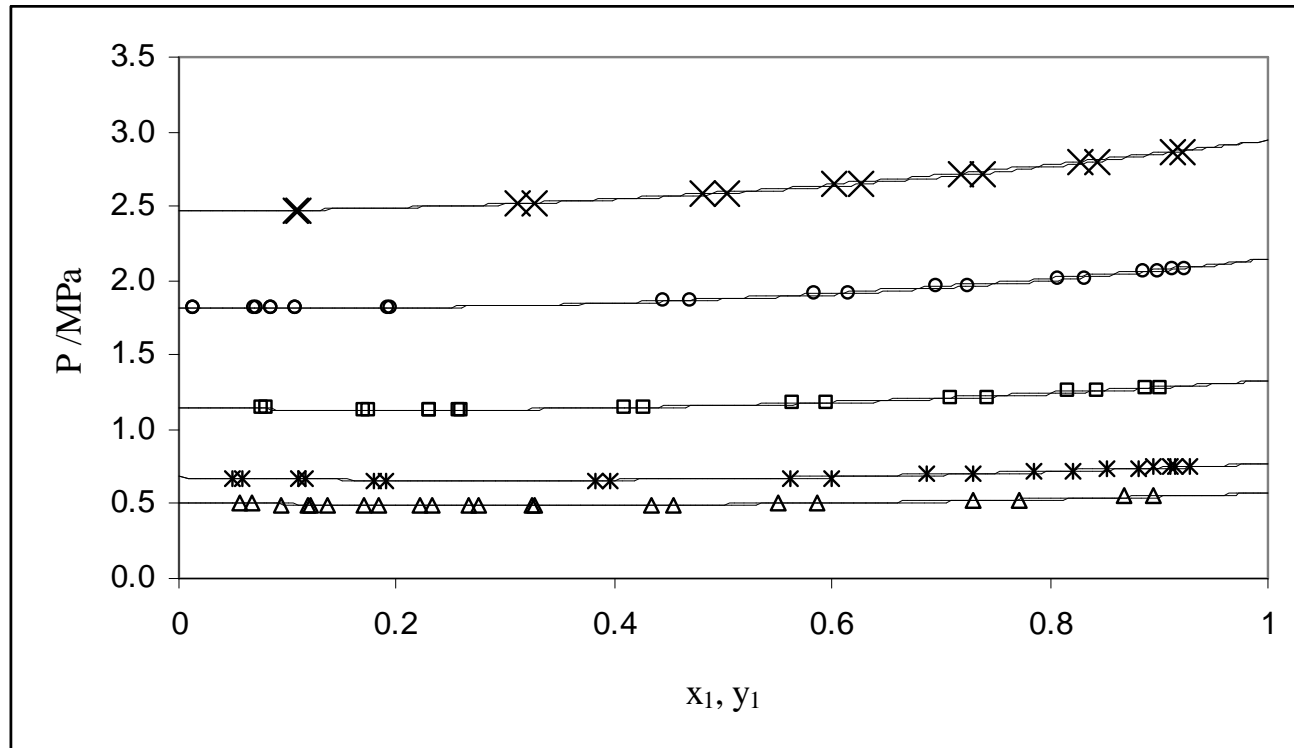
○ Example of results: R32 + propane

Azeotropic behavior

VLE for the R32 (1) + propane (2) system at 343.26 K.
solid lines, calculated with PR EoS and Wong Sandler mixing rules

Vapor Liquid Equilibrium Measurement

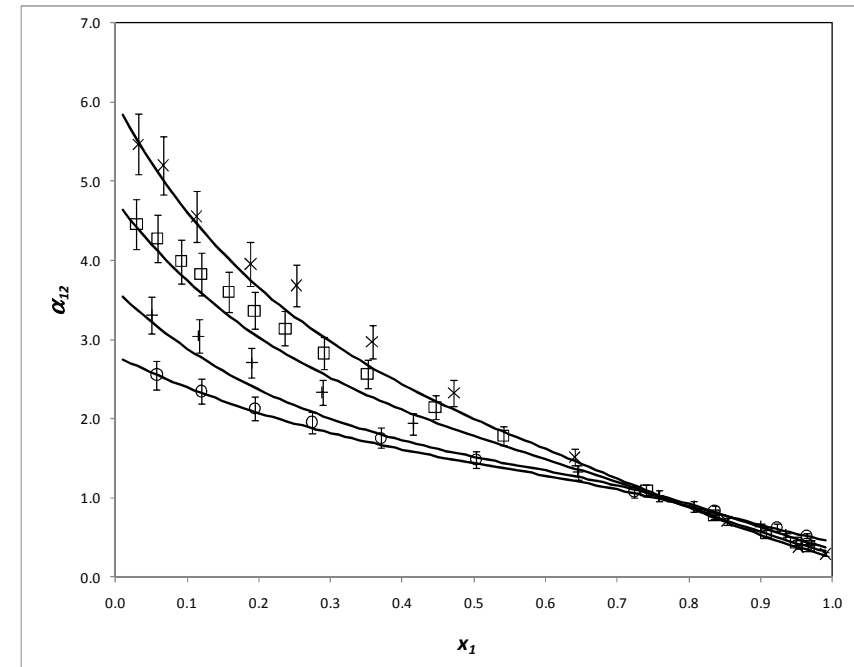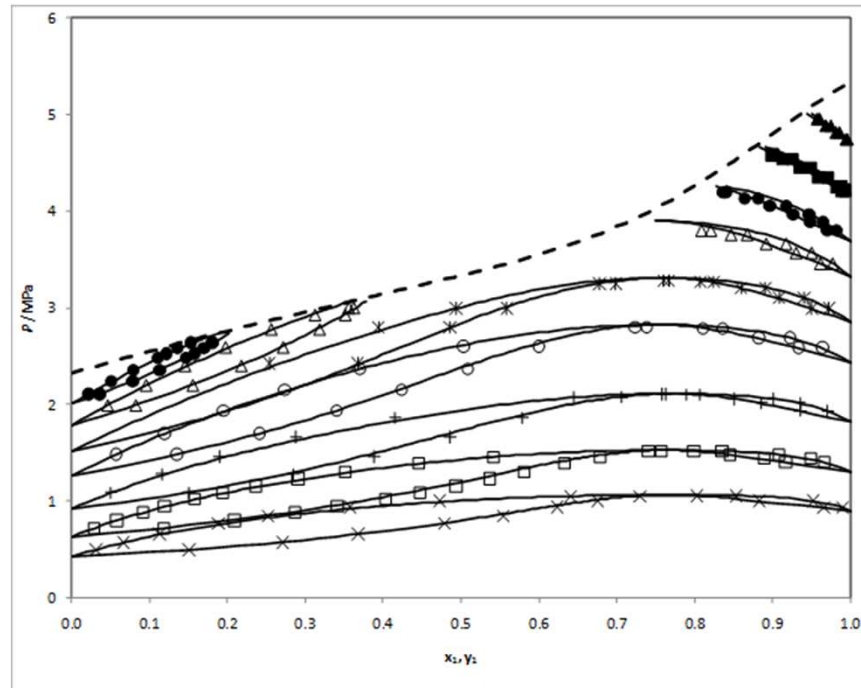○ Example of results: R134a + DME

Azeotropic
behaviour
Min P

Pressure as a function of R134a mole fraction in the R134a (1) + DME (2) mixture at different temperatures. (Δ) 293.18 K, ($*$) 303.17 K, (o) 323.36 K, ($\times$) 343.42 K, ($\square$) 358.15 K. Solid lines: calculated with RK EoS, Huron-Vidal mixing rules and NRTL activity coefficient model.

Vapor Liquid Equilibrium Measurement

○ Example of results: RE170 + DME

Left: Pressure as a function of RE170 mole fraction in the RE170 (1) – R3110 (2) binary mixture at different temperatures. ($\times$)313.28 K, ($\square$) 328.16 K, (+) 343.10 K, (o) 357.12 K, (*) 365.30 K, (Δ) 373.36 K, ($\bullet$) 379.05 K, ($\blacksquare$) 385.84 K and ($\blacktriangle$) 392.83 K. Solid lines: calculated with PR EoS, Wong - Sandler mixing rules and NRTL model. Dashed line: calculated critical point line
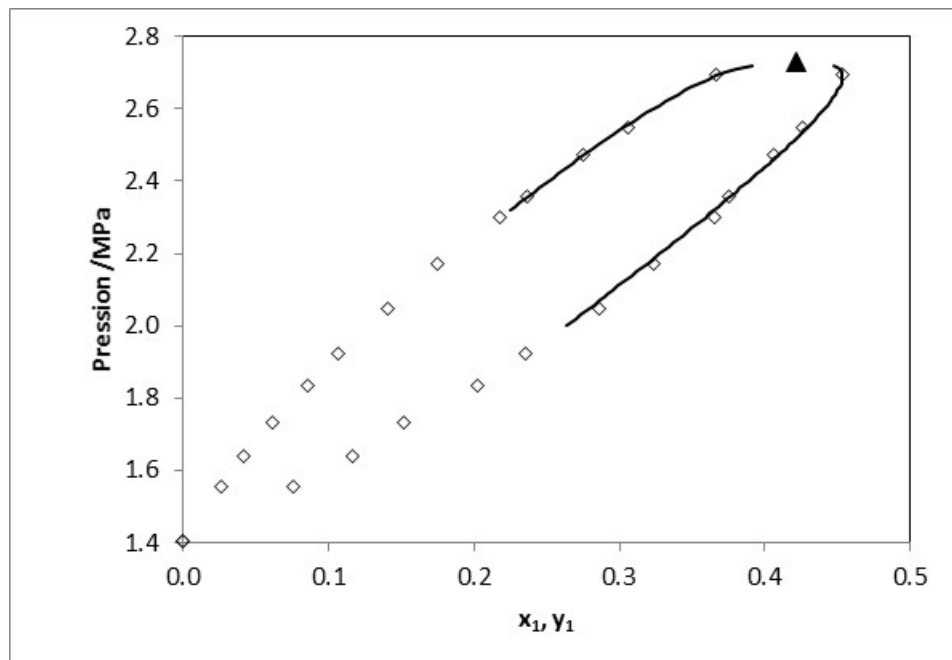
Right: Relative volatility

Data Treatment VLE Mixture

○ Estimation of critical point composition

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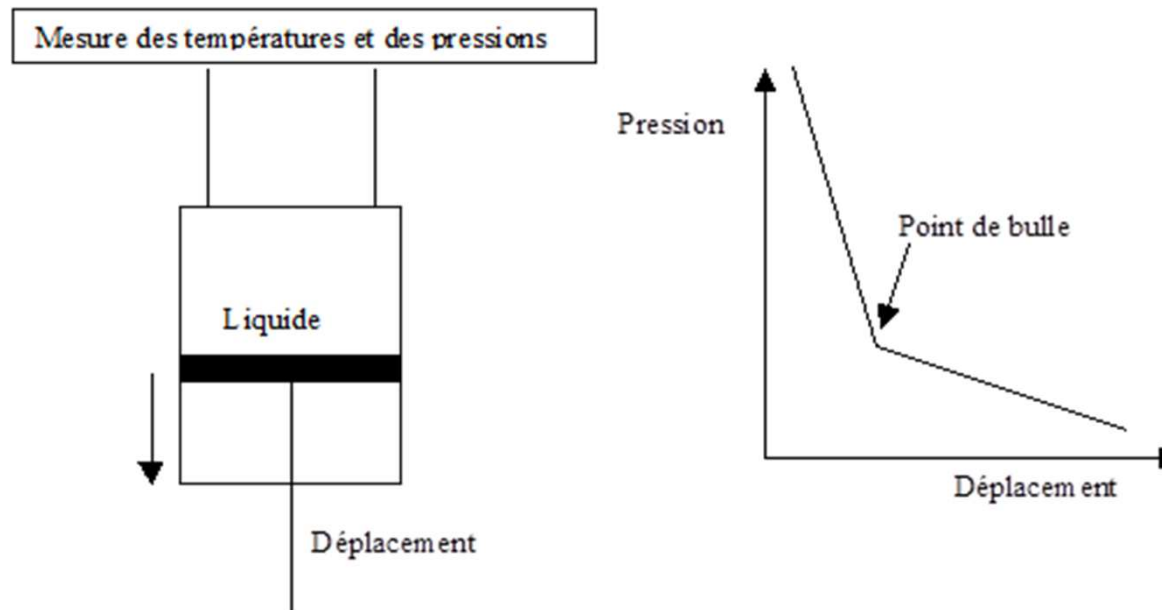$$\frac{1}{2}(y_i - x_i) - x_c = K(P_c - P)$$

H. Madani, A. Valtz, C. Coquelet, Isothermal vapor liquid equilibrium data for the decafluorobutane (R3110) + 1,1,1,3,3-pentafluorobutane (R365mfc) system at temperatures from 333 K to 441K, Fluid Phase equilibria, 2013, 354, 109-113.

VLE of the binary system at 433.65K. (◊) : experimental data , (▲) : mixture critical point
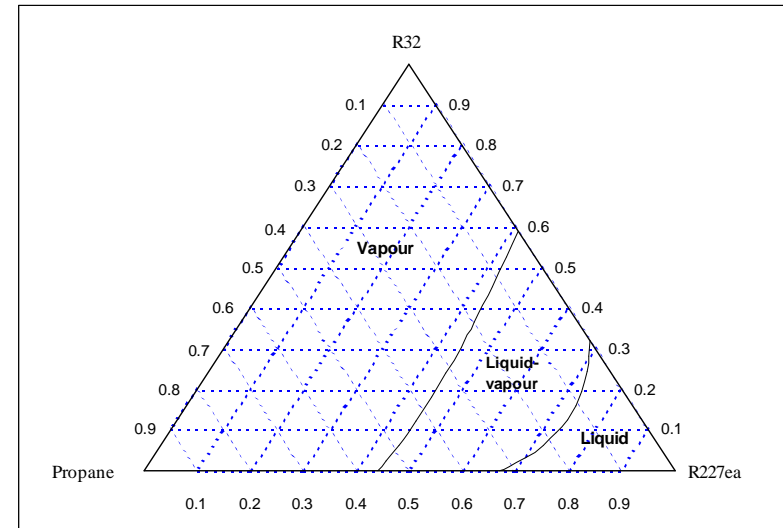
PVT measurement
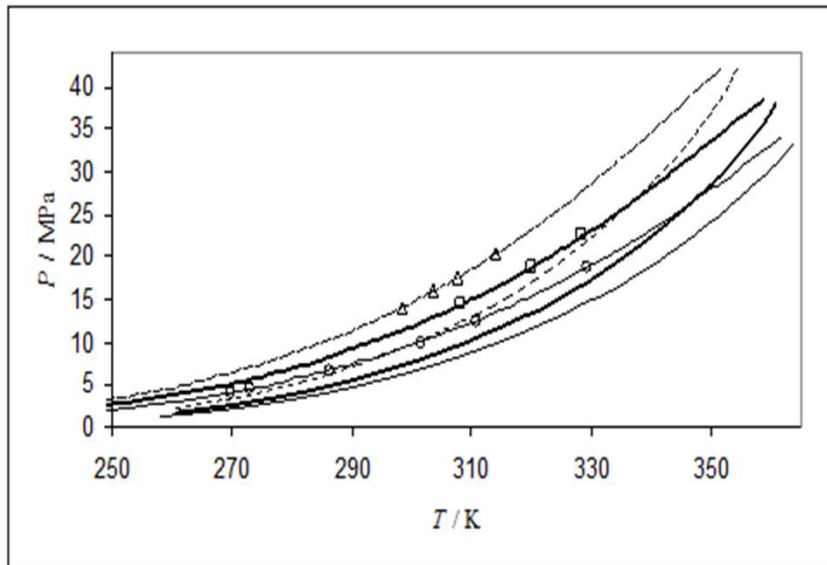
○ Synthetic method

- Determination of bubble pressure
- Variable volume cell
- Possibility to determine density at saturation (after calibration)

PVT Measurements

○ Example of results: R32 + R227ea + propane

Ternary phase diagram: The system R32 (1) + R290 (2) + R227ea (3) at $T = 300$ K and $P = 0.9$ MPa

The system R32 (1) + R290 (2) + R227ea (3). Pressure versus temperature diagram for each composition.
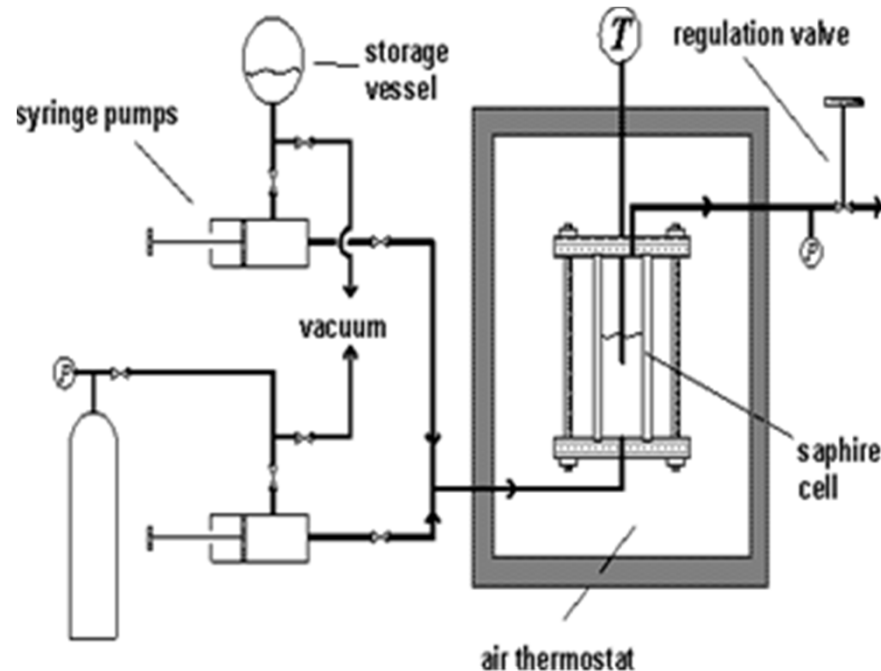
Mixture 1: $x_1 = 0.322$, $x_2 = 0.123$, □: Experimental bubble points, thick line: calculated with RKS EoS and MHV1 mixing rules.

Mixture 2: $x_1 = 0.135$, $x_2 = 0.174$, ○: Experimental bubble points, solid line: calculated with RKS EoS and MHV1 mixing rules.

Mixture 3: $x_1 = 0.493$, $x_2 = 0.127$, Δ: Experimental bubble points, dashed line: calculated with RKS EoS and MHV1 mixing rules.
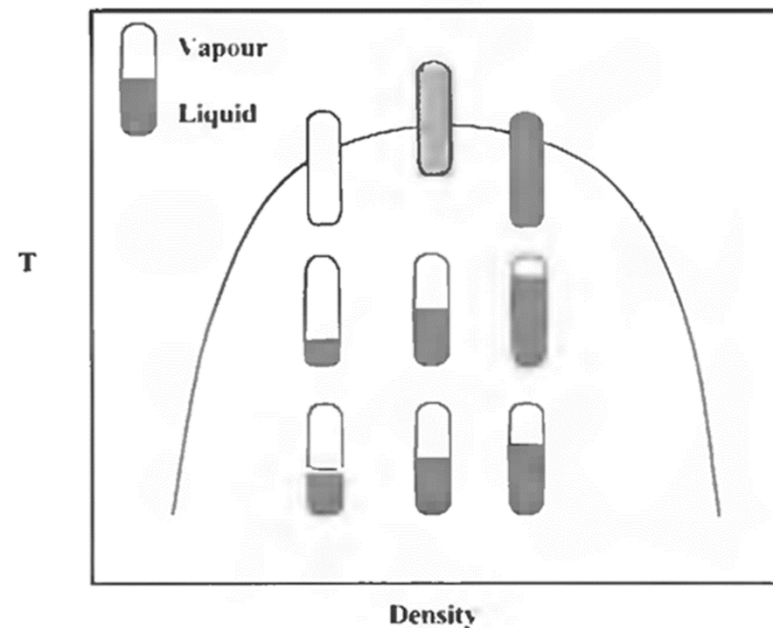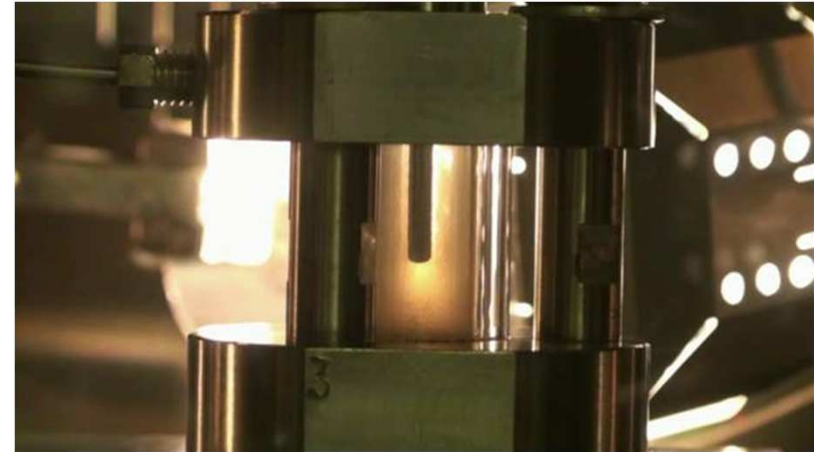
Critical point determination

○ Synthetic method

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.
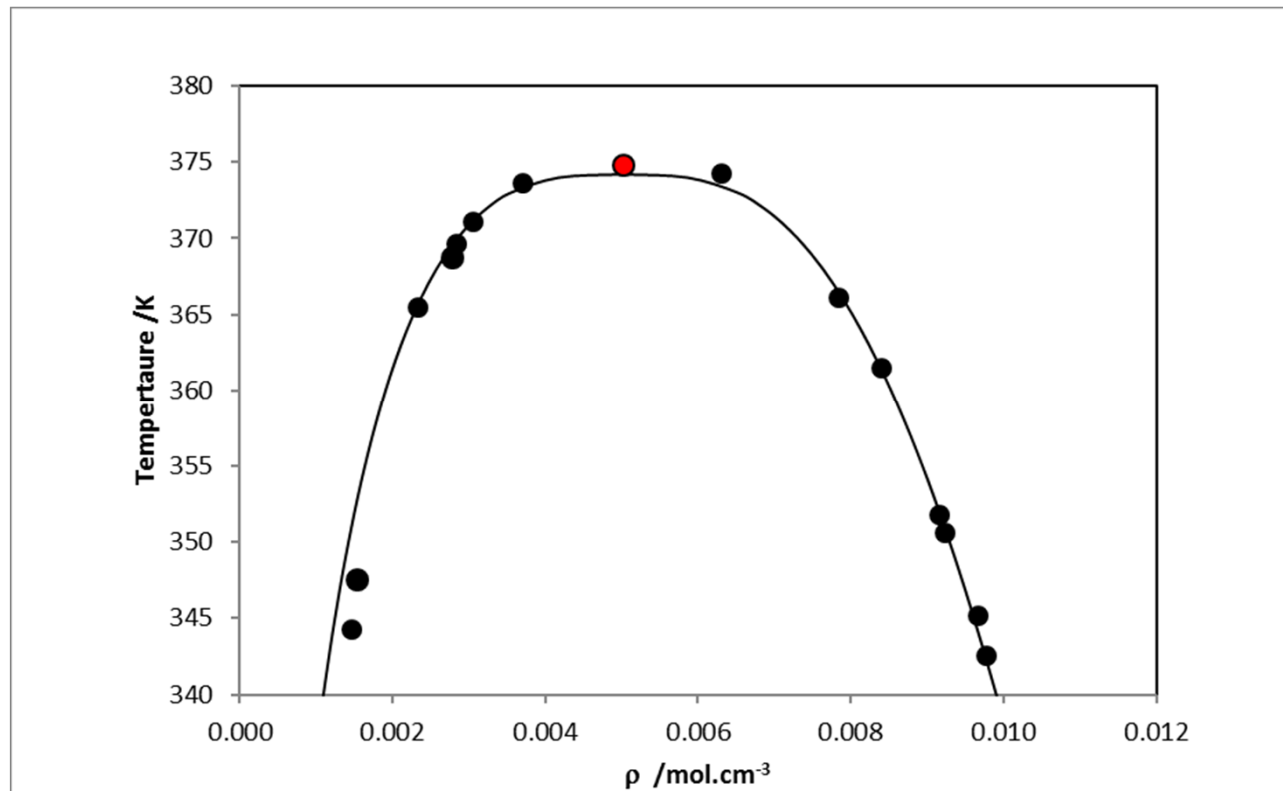
Critical point determination

○ Possibility of density determination around critical point

● 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)
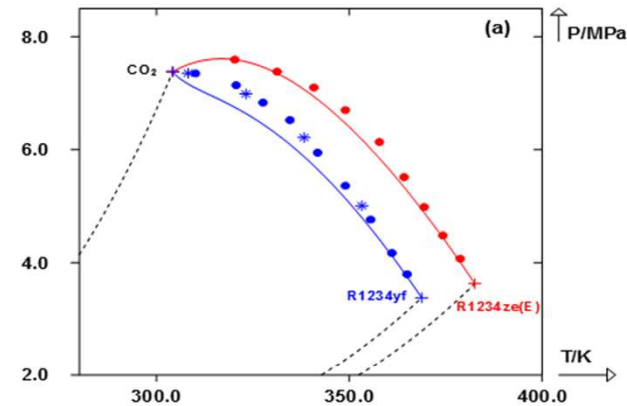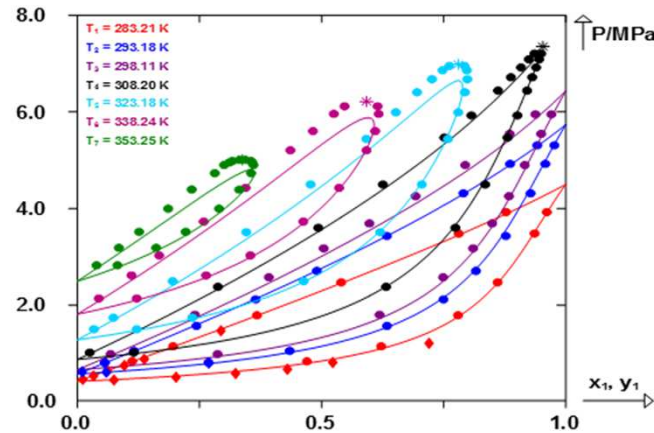
Critical point determination

○ Possibility of density determination around critical point
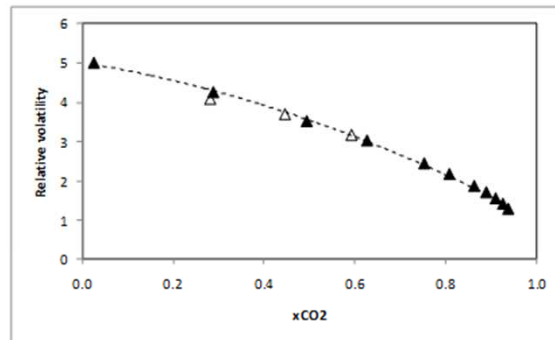
- Exemple: R134a

CO$_2$ + HFO 1234yf

○ Juntaratchat et al. 2014

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) (△) 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
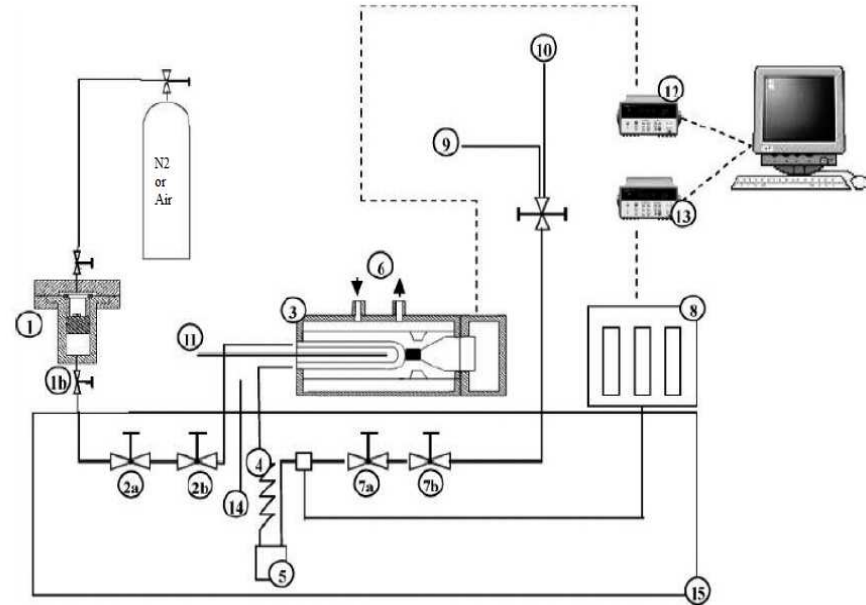
Density Measurements

○ Synthetic method

- **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).
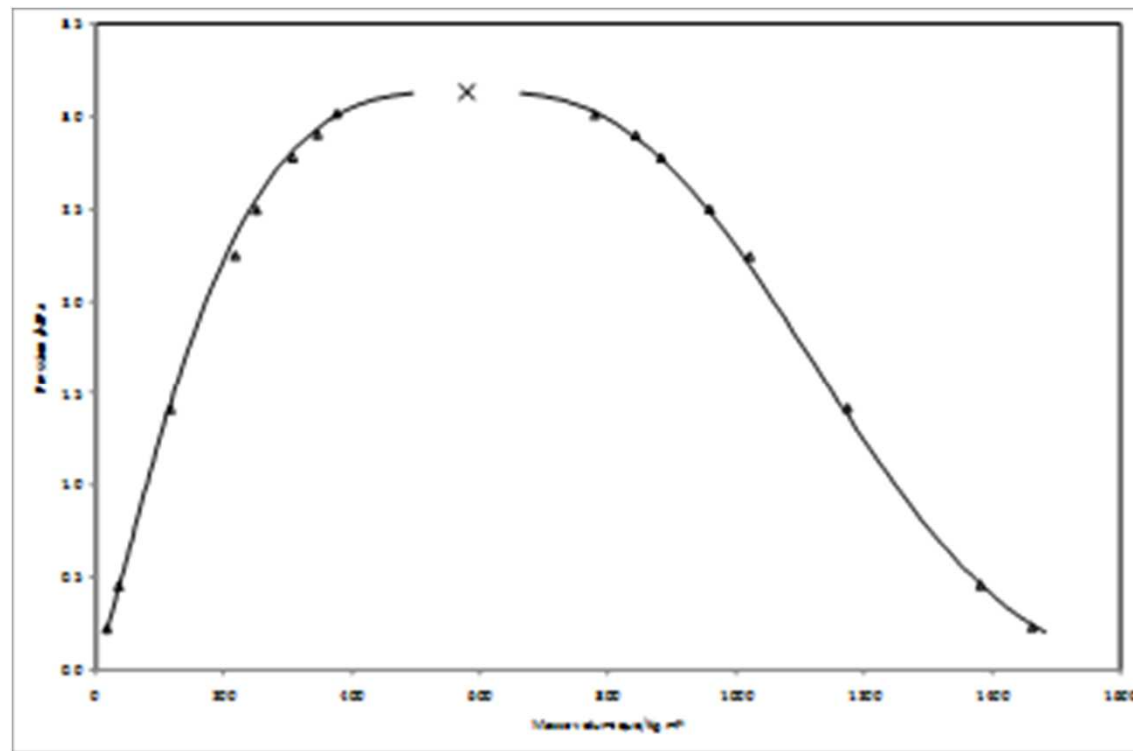
- **Important to control evolution of Z vs pressure**

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

- 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

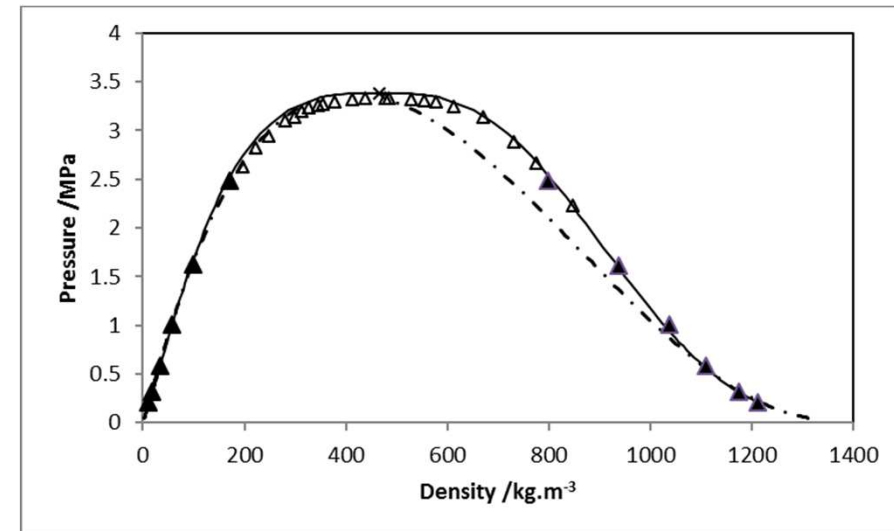$$\rho_g - \rho_l = B(T - T_c)^{\beta}$$

- Combination of these two expressions

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

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

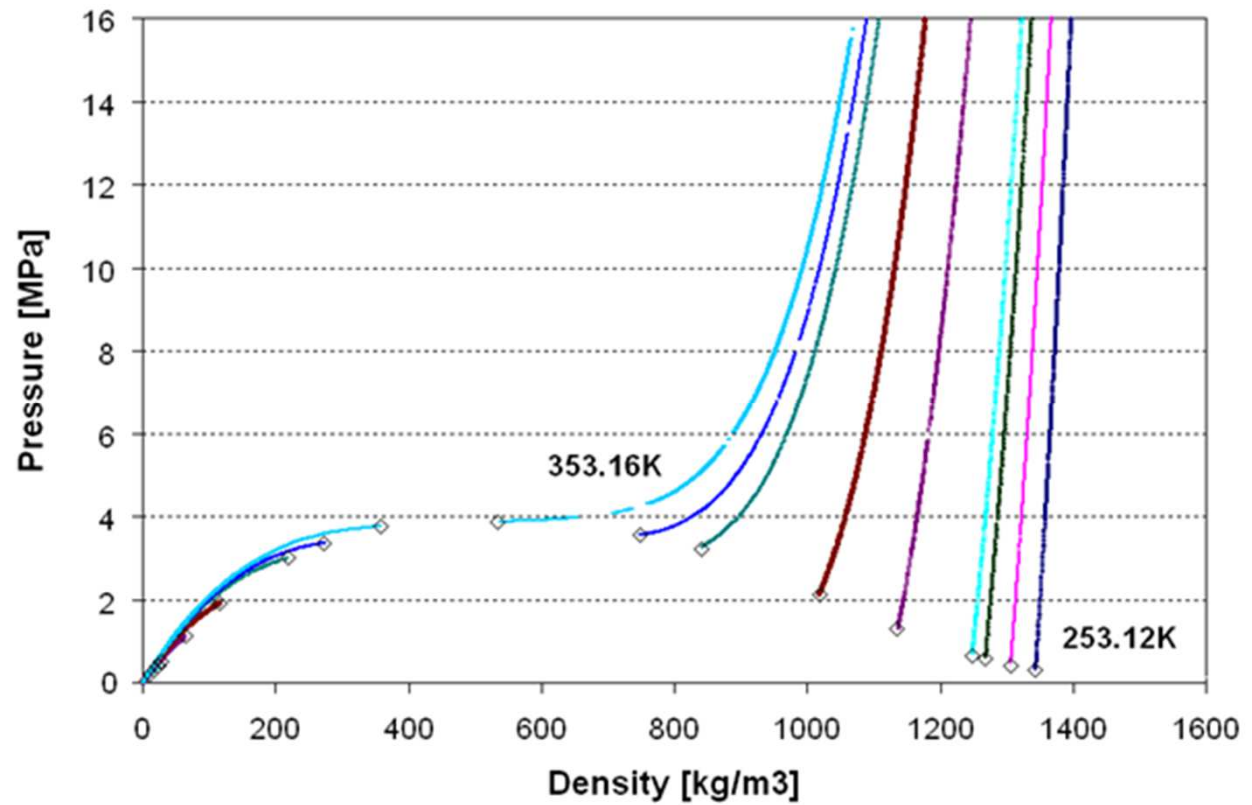- Parameters are fitted considering both vapor and liquid densities at saturation

R1234yf

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

Mixture

- Density measurements

  - FX90 (Atofina)
  - R419a

R125, R134a, RE170 (DME): 77-18-4 in mol%

Conclusion

- Different experimental techniques exist for the measurement of:

  - Vapor Liquid Equilibrium data
    - PTxy
    - PVT
  - Critical point (visual method)
  - Density (vibrating tube or isochoric method)

- Importance of calibration and uncertainties determination

- Data are essential for adjustment of equation of state parameters and fluid selection

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Thank you for your attention

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Example

○ Static analytic method using GC

- Molar fraction

$$u(x_1) = \sqrt{u_{rep}^2(x_1) + \left(\frac{1-x_1}{n_1+n_2}\right)^2 u^2(n_1) + \left(\frac{x_1}{n_1+n_2}\right)^2 u^2(n_2)}$$

idem

Type A

$$u(n_1) = \sqrt{u_{inj}^2(n_1) + u_{corr}^2(n_1) + \left(\frac{\partial n_1}{\partial S_1}\right)^2 u_{rep}^2(S_1)}$$

gas

$$n_1 = a_0 + a_1 S_1 + a_2 S_1^2$$

liquid

$$\overline{S_{1,k}} = \frac{1}{N_k}\sum_{l=1}^{N_k} S_{1,k,l}$$

$$n_1 = \frac{PV_1}{RT}$$

$$n_1 = \rho_1 V_1$$

$$\rho_1 = \frac{A}{B^{\left(1+\left[1-\frac{T}{T_c}\right]^C\right)}}$$

- S of component 1
- N points (k=1...N) are taken for the polynomial correlation

Type B

empirical equation {Component Plus, PROSIM France}

$$u_{rep}(S_1) = \frac{E_{max} S_1}{\sqrt{3}}$$

$$u_{inj}(n_1) = n_1 \sqrt{\frac{u^2(P)}{P^2} + \frac{u^2(T)}{T^2} + \frac{u^2(V_1)}{V_1^2}}$$

$$u_{inj}(n_1) = n_1 \sqrt{\left[\frac{C}{T_c}\left(1-\frac{T}{T_c}\right)^{C-1}\ln B\right]^2 u^2(T) + \frac{u^2(V_1)}{V_1^2}}$$

$$E(S_{1,k,l}) = \frac{\left(S_{1,k,l} - \overline{S_{1,k}}\right)}{\overline{S_{1,k}}}$$

- **Hyp: ±2%**
- •**Type B**