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
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

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

\[ \rho_c - \rho \propto |T_c - T|^\alpha \] Coexisting curve

\[ C_p \propto k_{\alpha\beta} + k_{\alpha\gamma} \Delta T^{-\alpha} \] Critical isochoric

\[ \left( \frac{P - P_c}{P_c} \right) \propto \left( \frac{\rho - \rho_c}{\rho_c} \right)^\beta \] Critical isotherm

\[ \chi \propto k_{\alpha\delta} \Delta T^{-\delta} \] Critical isochoric

Universal law: \[ \alpha + 2\beta + \gamma = 2 \]

<table>
<thead>
<tr>
<th>Critical exponent</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.110</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.3255</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.239</td>
</tr>
<tr>
<td>$\delta$</td>
<td>4.800</td>
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</tbody>
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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

**Closed Circuit methods**
- Synthetic
  - Isothermal
  - Isochoric
- Analytic
  - Static stirred
  - Static circulated

**Open circuit methods**
- Forced circulation of one compound of the mixture
- Forced circulation of the mixture

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*Bubble point  Dew point  VLE/VLLE/LLE  Enthalpy  Density*
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: \( u(T) = 0.05 \text{K} \), \( u(p) = 0.005 \text{MPa} \), \( u(z) = 0.005 \)

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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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.

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

- 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

\[ \frac{\rho_g - \rho_i}{2} - \rho_c = A(T - T_C) \]

- Coexisting curve

\[ \rho_g - \rho_i = B(T - T_C)^\beta \]

- 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
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

• 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 in the condition of loading)

• Exemple: R134a
• Redlich Kister type correlation
  – Ethanol + n-hexane binary system: azeotropic behaviour
  – Pentane + ethanol + n-hexane ternary system

Soo et al., 2010
n-Pentane + Ethanol + n-Hexane
Mixture

- Density measurements
  - CO$_2$ H$_2$S binary mixture

Predicted and experimental densities of the system 0.9505 CO$_2$ (1) + 0.0495 H$_2$S (2) system. Red lines: Predictions using the GERG-2008 EoS

Nazeri et al., 2016
Mixture

- Density measurements
  - CH$_4$ H$_2$S 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 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:
  \[ y_i \cdot x_i = C \left( \frac{P}{P_c} \right)^\beta \cdot D \left( \frac{P}{P_c} \right) \]

- Equation 2:
  \[ \frac{1}{2} (y_i - x_i) - x_c = K \left( \frac{P_c}{P} - P \right) \]

VLE of the binary system \( \text{N}_2 \) (1) – \( \text{CH}_4 \) (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) + C₂H₄ (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-C₂H₄ (C₂H₄ 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) + C₂H₄ (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$_4$F$_{10}$

- 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
VLE Mixture

- CO₂ + HFO 1234yf

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

- 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

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

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### Graphical Representation

- **Black line**: Crossover PT (CR-PT), **gray dashed line**: Classical PT, **red cross**: point critique, **blue triangle**: experimental data

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**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.)