Thermophysical properties, measurements and uncertainties

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Outline

❑ Introduction

❑ Thermodynamic properties and experimental methods

❑ Transport properties and experimental methods

❑ Uncertainties

❑ Validation of data / Data treatment

    ➢ Pure compounds

    ➢ Mixtures

❑ Conclusion

Importance of thermophysical properties

❑ Availability of accurate thermophysical properties is

important for:

➢ Design and construction of new process plant equipments

➢ Implementation of "more rigorous and sophisticated

   design procedures" in software packages (Raal and
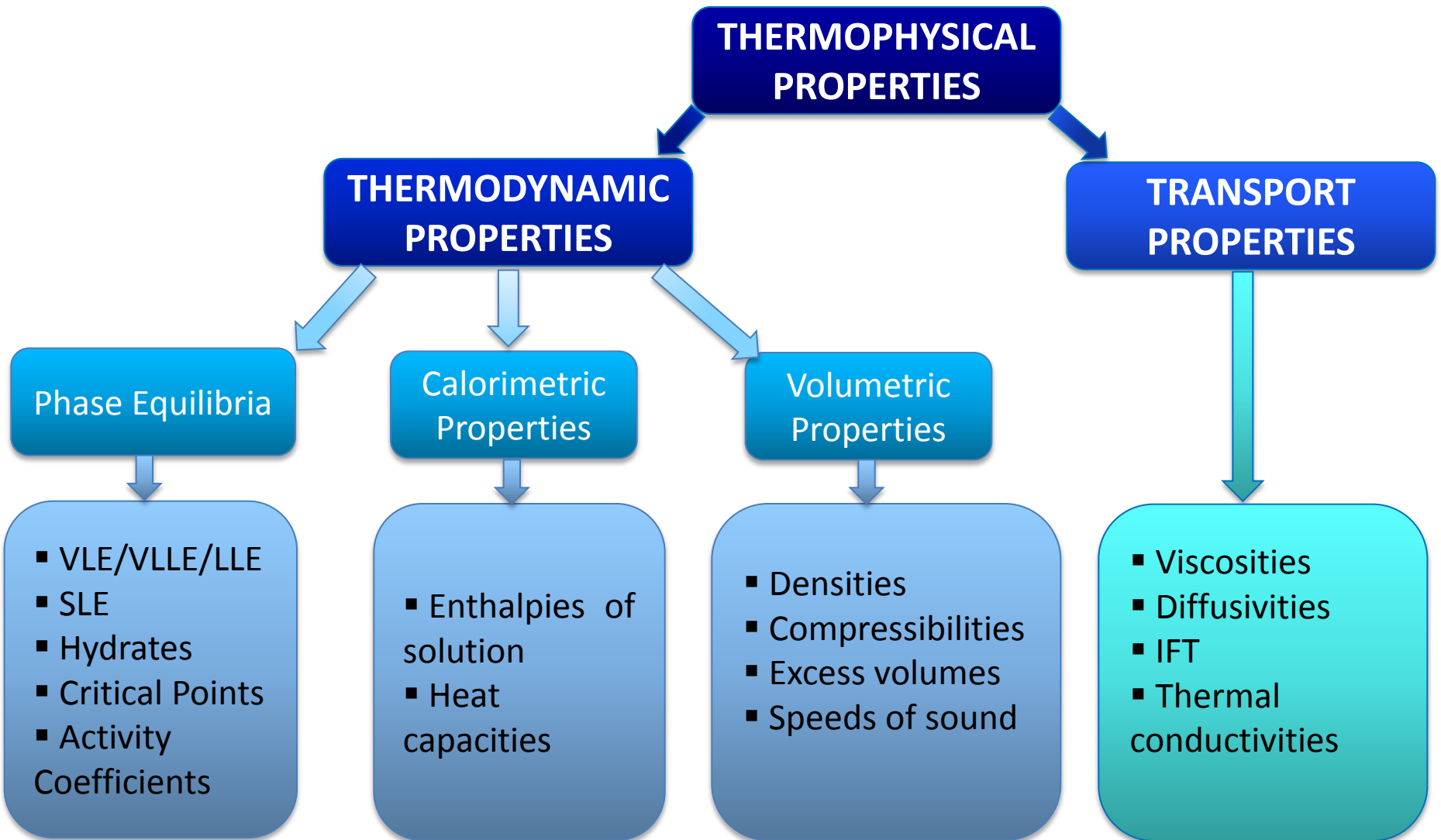
   Mühlbauer, 1984)

Introduction

❑ Thermophysical properties may be divided into two groups:

- ➢ Thermodynamic properties
- ➢ Transport properties

❑ For each experimental measurement, there is:

- ➢ An experimental setup
- ➢ An experimental procedure

❑ For each data measured, we get:

- ➢ A numerical value
- ➢ A unit
- ➢ Its uncertainty

❑ Validation of data and/or data treatment

Properties

❑ What can we measure?

- ➢ Temperature
- ➢ Pressure
- ➢ Composition
- ➢ Volume (variation of volume) or density
- ➢ Speed of sound
- ➢ Flow
- ➢ Luminosity
- ➢ Hardness
- ➢ Etc

❑ Aim: disturb the system as little as possible while being accurate and reliable

- ➢ Research on techniques and experimental procedures
- ➢ Size of the equilibrium cell
- ➢ Development of sensors

Thermophysical properties

THERMOPHYSICAL PROPERTIES

THERMODYNAMIC PROPERTIES

TRANSPORT PROPERTIES

Phase Equilibria

Calorimetric Properties

Volumetric Properties

- VLE/VLLE/LLE
- SLE
- Hydrates
- Critical Points
- Activity Coefficients

- Enthalpies of solution
- Heat capacities

- Densities
- Compressibilities
- Excess volumes
- Speeds of sound

- Viscosities
- Diffusivities
- IFT
- Thermal conductivities

Which experimental method?

❑ The choice of the adequate experimental method

depends on:

➢ The thermophysical property (PTx, density, acivity

coefficient…)

➢ The type of fluid (molar mass, toxicity, stability within

temperature…)

➢ Temperature(s) and pressure(s) of interest

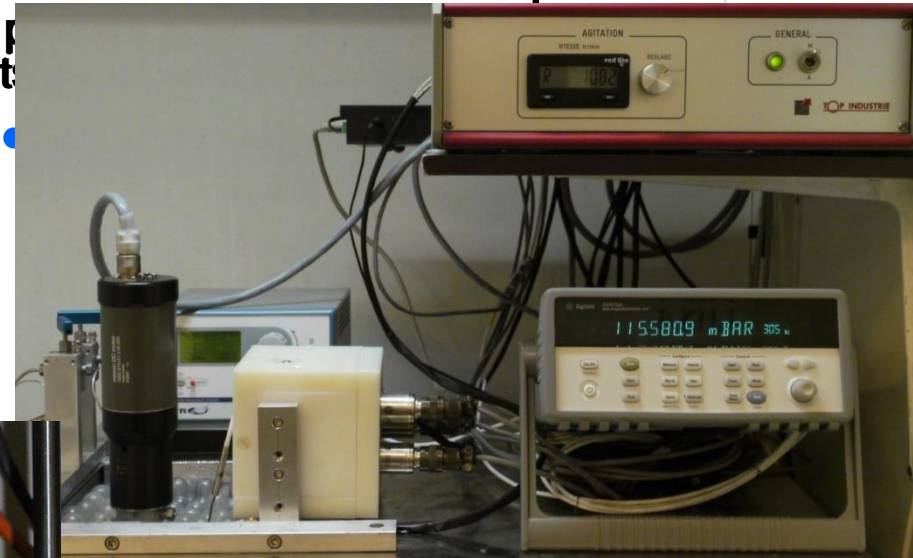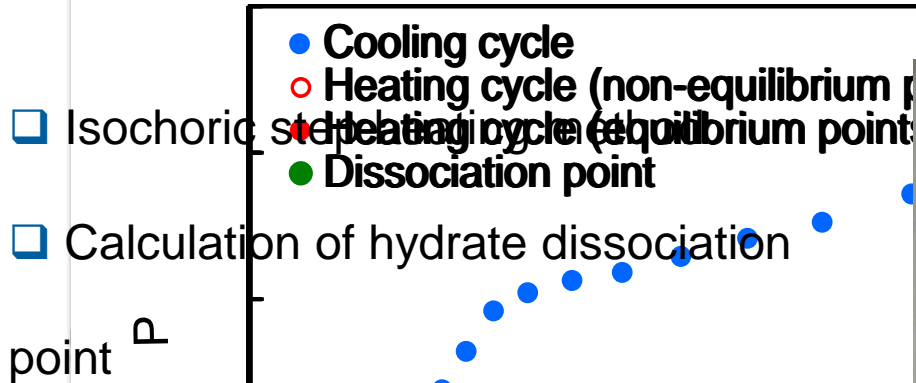# Thermodynamic properties
and
Experimental methods

Experimental methods
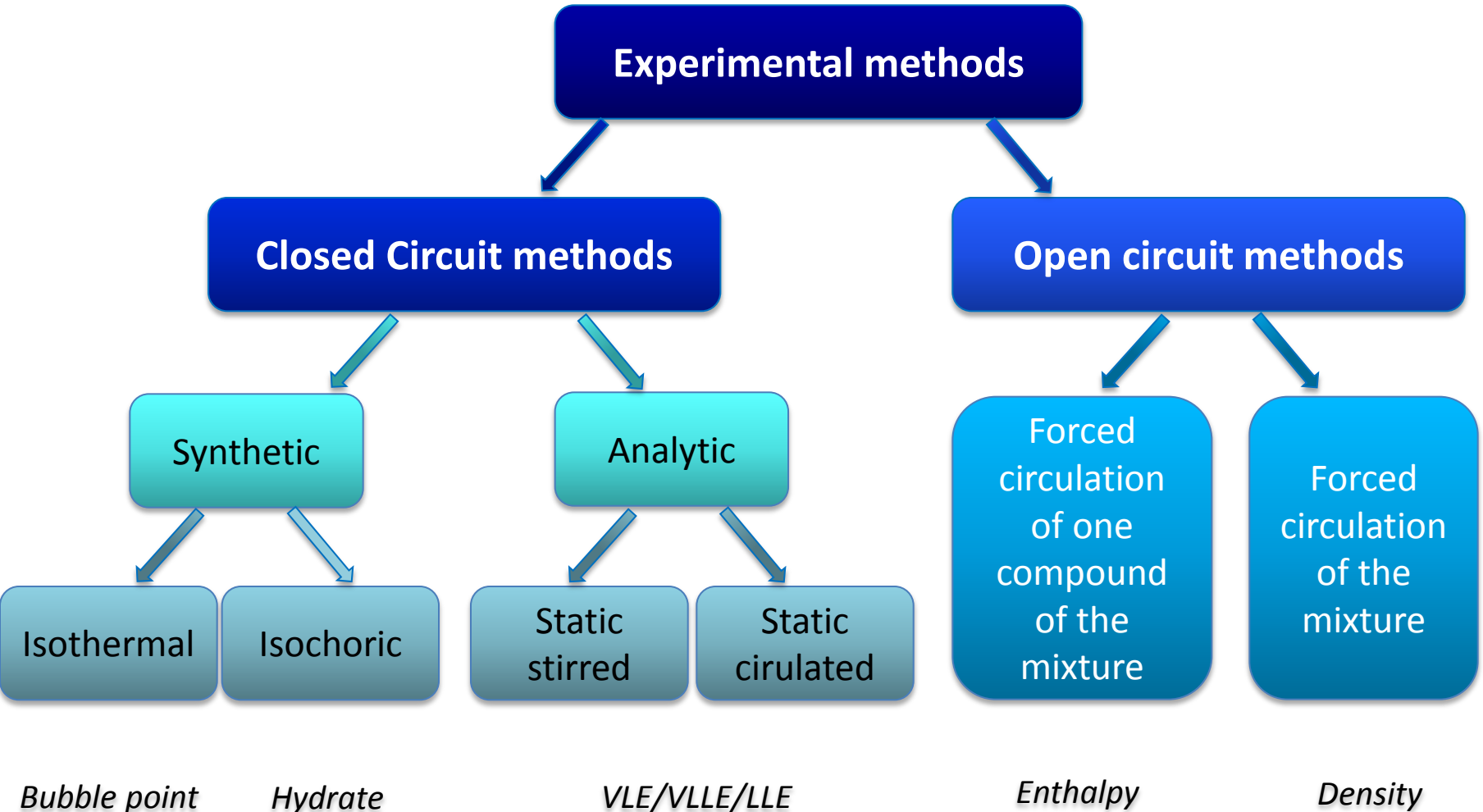
- ❑ Static analytic method

- ❑ Vapour and/or liquid sampling (ROLSI™)

- ❑ Gas chromatography

- ❑ Data obtained: composition of each phase

VLE Equipment

Up to 40 MPa / [300 – 470] K

❑ Isochoric step-heating procedure

❑ Calculation of hydrate dissociation

point

- ● **Cooling cycle**
- ○ **Heating cycle (non-equilibrium point)**
- ● **Heating cycle (equilibrium point)**
- ● **Dissociation point**

P

Equipment for hydrate dissociation points measurements
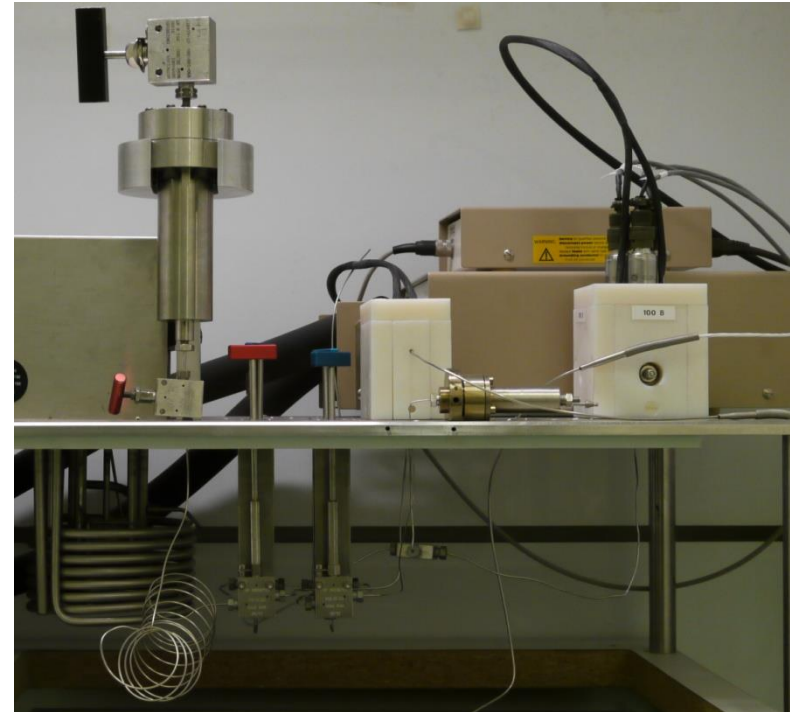
Up to 70 MPa / [200 – 320] K

Densimeter

❑ Indirect synthetic method

❑ Vibrating tube densimeter:

➢ Relation between the vibrating period of a dimensional resonator and its vibrating mass

➢ $$\rho = \frac{m_0}{V_{int}}\left[\left(\frac{K\tau^2}{K_0\tau_0^2}\right) - 1\right]$$

Period of vibration of the tube

Vibrating tube densimeter
Up to 70 MPa / [250 – 390] K

Calorimeter

❑ Open circuit method

❑ T and P are constant

❑ Experimental procedure:

    ➢ T fixed

    ➢ Fluids are loaded into the pumps

    ➢ Fluids are pressurized

   ➢ Circulation at different flow rates ($x_i \in [0 ; 1]$)

Calorimeter

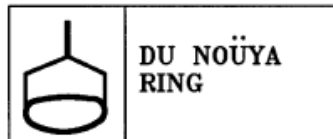Transport properties
and
Experimental methods

Viscosity

- Capillary tube viscosity measurement method

- Consistency of measurements ensured with specific experimental procedure:

  - At each pressure, viscosities determined at different flow rates

  - Laminar flow conditions ensured: check Reynolds number $\mathrm{Re} = \dfrac{\rho VL}{\mu} < 2300$

- Pumping the sample fluid through capillary tube by the piston pump results in dynamic differential pressure (monitored and recorded)

- Poiseuille equation can relate the pressure drop across the capillary tube to the viscosity
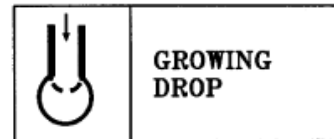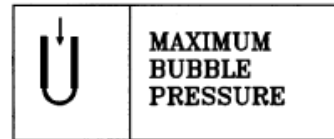
$$\Delta P = \frac{128 L Q \eta}{\pi C D^4}$$

Interfacial tension (IFT)
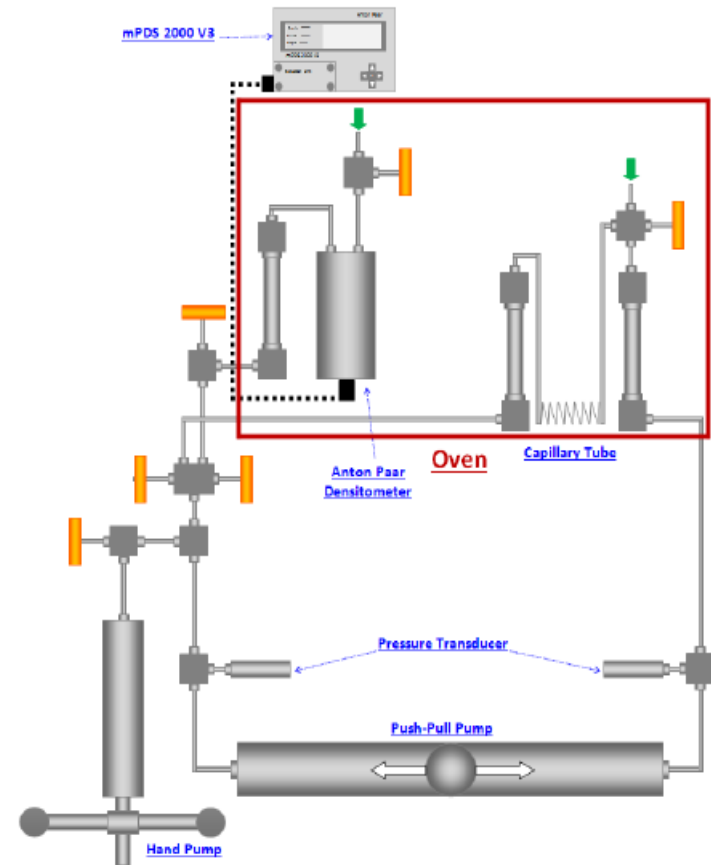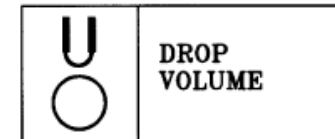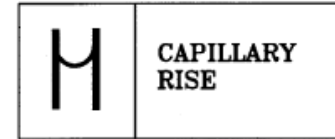
❑ Different methods:

I. Direct Measurement Using a Microbalance
- WILHELMY PLATE
- DU NOÜYA RING

II. Measurement of Capillary Pressure
- MAXIMUM BUBBLE PRESSURE
- GROWING DROP

III. Analysis of Capillary–Gravity Forces
- CAPILLARY RISE
- DROP VOLUME

IV. Gravity–Distorted Drops
- PENDANT DROP
- SESSILE DROP
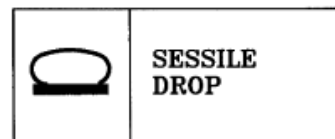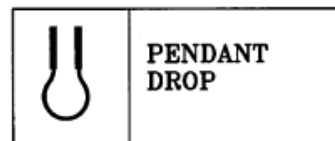
V. Reinforced Distortion of Drop
- SPINNING DROP
- MICROPIPETTE
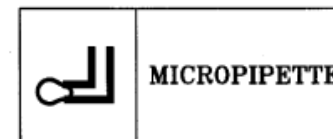
Source: Drelich et al., Encyclopedia of Surface and Colloid Science, 2002

Uncertainties

Definition

❑ Uncertainty:

> ➢ « **Quantitative indication** of the **quality** of a result »

> ➢ « **Doubt** that one has on a result. It corresponds to a **dispersion** that can be reasonably attributed to the **measurement process** »

❑ Estimation:

> ➢ Based on NIST procedure

> ➢ Type A: calculation based on statistical analysis of a set of observations

> ➢ Type B: evaluation by other means:

>> ❖ Ex: distribution law

>> ❖ Calibration

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:
$$u_{rep}(P) = \sqrt{\frac{1}{N(N-1)} \sum_{k=1}^{N} \left(P_k - \overline{P}\right)^2}$$

❑ Type B and distribution laws

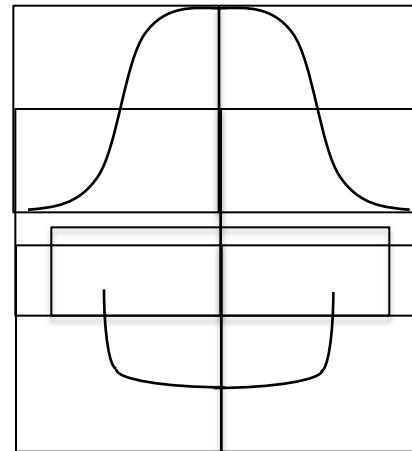➢ The uncertainty is supposed to be $\pm a$

➢ Different distribution laws:

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

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

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

Different sources of uncertainties

○ Exemple: VLE / LLE

	Repeatability	Calibration		
u(P)	$u_{rep}(P)$	$u_{ref}(P)$	$u_{corr}(P)$	**Polynomial correlation to convert the « read » value to the « measured » value**
u(T)	$u_{rep}(T)$	$u_{ref}(T)$	$u_{corr}(T)$	
u(x_i)	$u_{rep}(x_i)$	$u_{inj}(n_j)$	$u_{corr}(n_j)$	$u_{rep}(S_j)$

Standard deviation

Standard deviation

Ca........... of the GC

ume

Polynomial correlation

Repeatability of surfaces at fixed volume

.... several times
- **N volumes are injected lea......g .... surfaces**
- **polynomial correlation between volume and surfaces**
- **polynomial correlation between the number of moles and surfaces**

Example

❑ Molar fraction

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

Type A

idem

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

gas

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

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

liquid

$n_1 = \rho_1 V_1$

Calculation of the covariance matrix

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

Type B

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

❑ Expanded uncertainty:

➢ $$U(P) = \bigcirc{K} \sqrt{u_{rep}^2(P) + u_{ref}^2(P) + u_{corr}^2(P)}$$

Coverage factor

➢ K=2 defines an interval having a level of confidence of ≈ 95%

➢ K=3 defines an interval having a level of confidence of ≈ 99%

Validation of data / Data Treatment

Equations of state

- ❑ Equations of state
  - ➢ Data validation
  - ➢ Pure compounds & mixtures

- ❑ Examples:
  - ➢ Van der Waals type
    - ❖ VPT, SRK, PR

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + ubv + wb^2}$$

  - ❖ Alpha function: Mathias Copeman, Twu et al, etc…

$$a(T) = a_c\,\alpha(T)$$

  - ➢ SAFT type: associating fluids

$$Z = 1 + Z^{seg} + Z^{chain} + Z^{asso}$$

Pure compounds

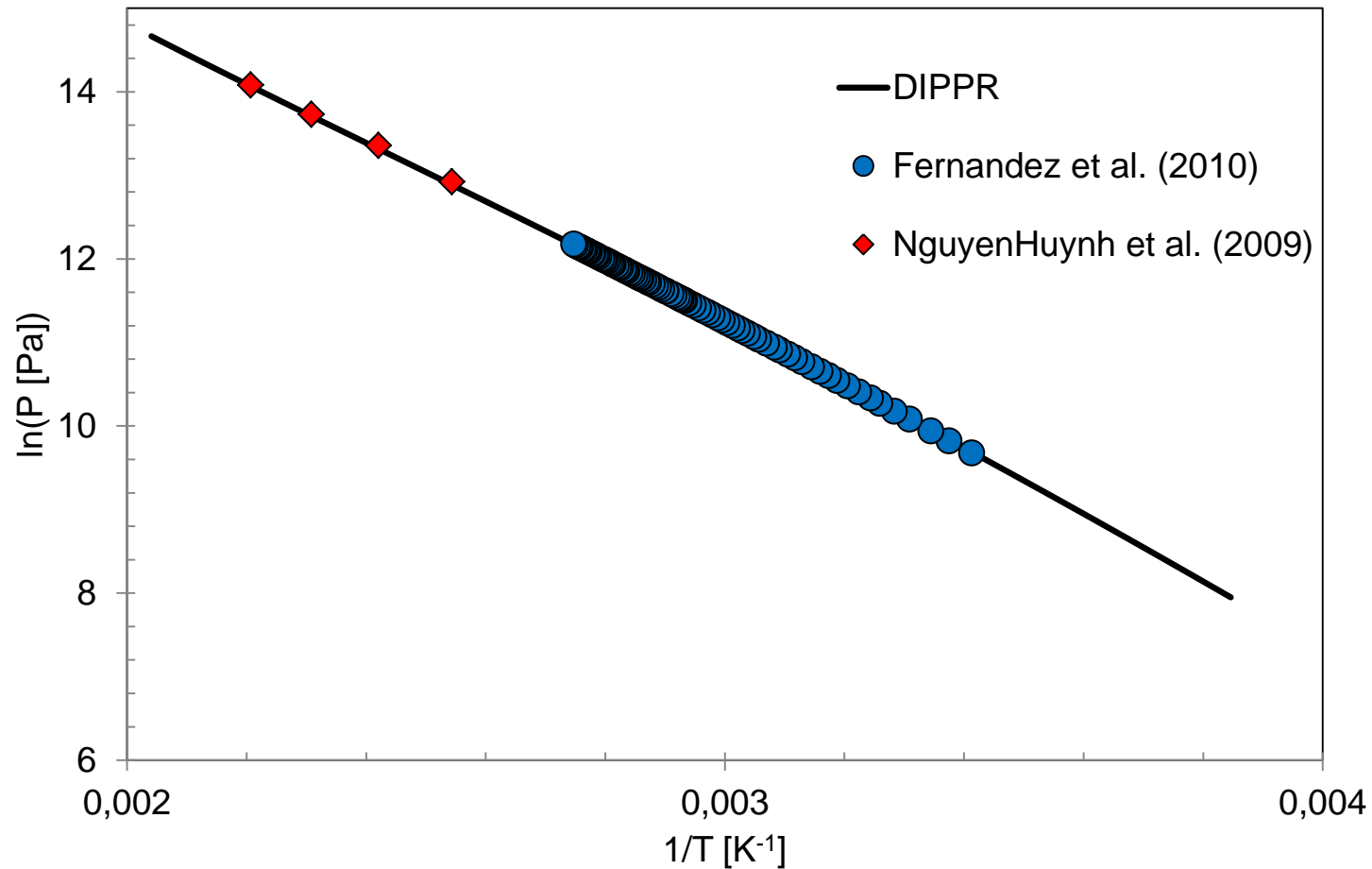○ Data validation: correlations

❑ Antoine equation: $\ln(P^{sat}) = A - \dfrac{B}{C+T}$

❑ Frost Kalkwarf: $\ln(P^{sat}) = A + \dfrac{B}{T} + C\ln(T) + D\dfrac{P^{sat}}{T^2}$

❑ Wagner: $\ln\left(\dfrac{P^{sat}}{P_c}\right) = \dfrac{T_c}{T}\left(A\tau + B\tau^{1.5} + C\tau^2 + D\tau^6\right)$ $\qquad \tau = 1 - \dfrac{T}{T_c}$

❑ Cox: $\ln\left(\dfrac{P^{sat}}{P_0}\right) = \left(1 - \dfrac{T_b}{T}\right)\exp\left(A_0 + A_1 T + A_2 T^2\right)$

❑ DIPPR (Pa): $\ln(P^{sat}) = A + \dfrac{B}{T} + C\ln(T) + DT^E$

O Example: *n*-hexane
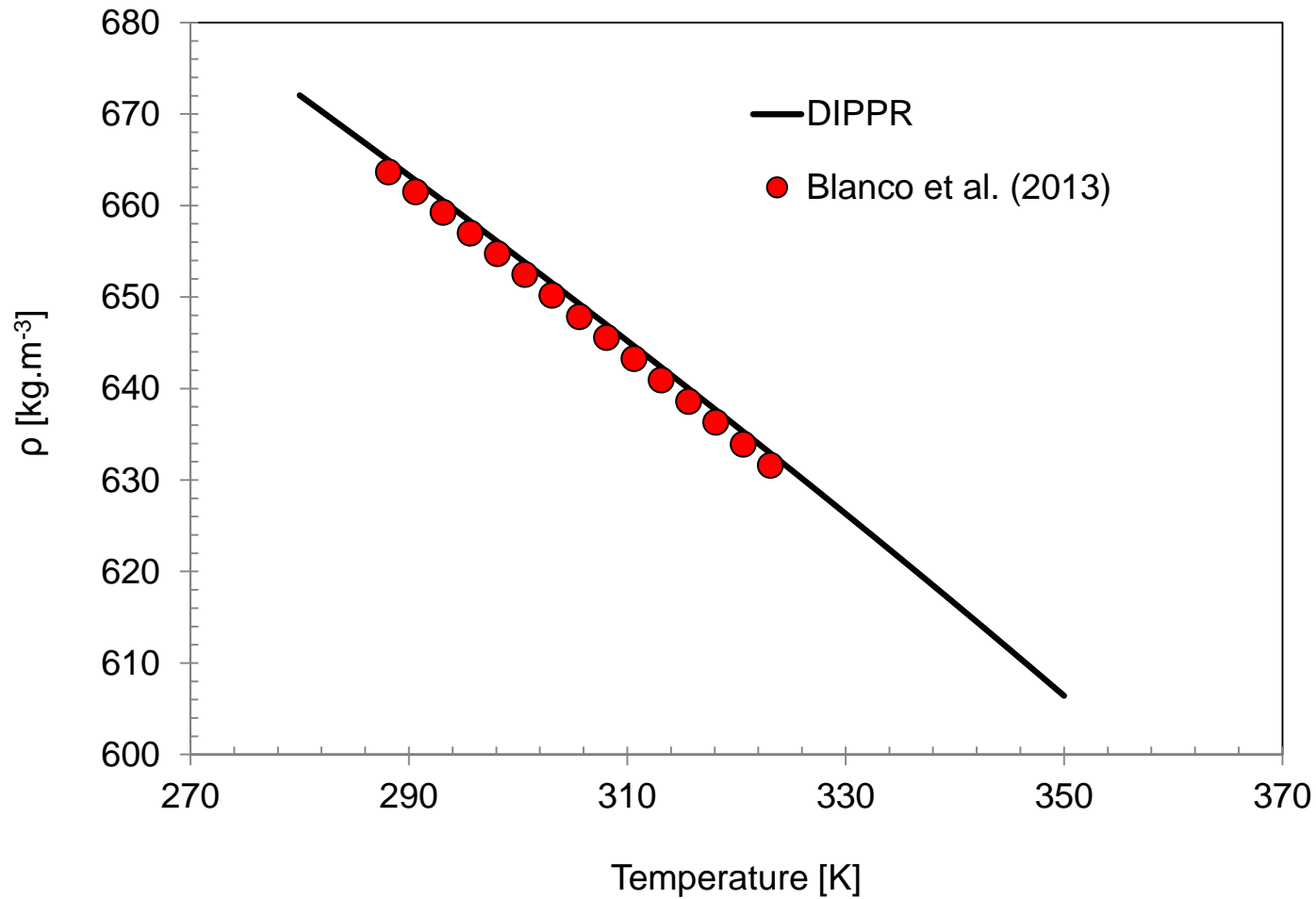
❑ Liquid density

➤ At atm. pressure: DIPPR [kmol.m^{-3}]

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

❑ Isothermal data

➤ Compression factor $Z = \dfrac{Pv}{RT}$

➤ Virial equation (only for vapor phase) $Z = 1 + B(T)\rho$

Density (2/2)
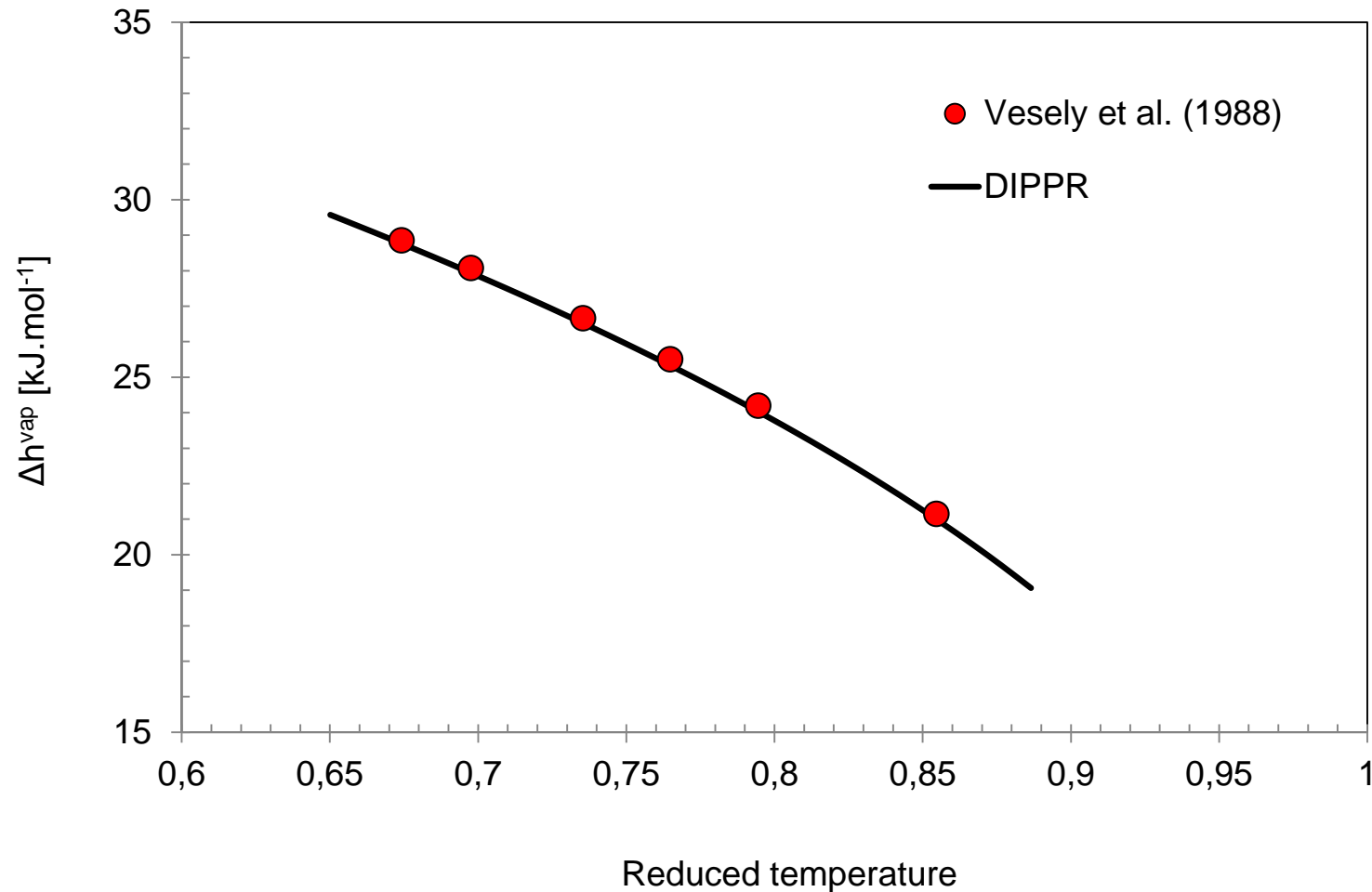
○ Example: *n*-hexane (liquid state)

Enthalpy of vaporization (1/2)

- The Clapeyron equation $\Delta h^{sat} = T\left(v^{V,sat} - v^{L,sat}\right)\dfrac{dP^{sat}}{dT}$

- DIPPR $\Delta h = A\left(1 - T_r\right)^{B + CT_r + DT_r^2 + ET_r^3}$

- Watson (n=0.375) $\dfrac{\Delta h_{T_2}}{\Delta h_{T_1}} = \left(\dfrac{1 - T_{r,2}}{1 - T_{r,1}}\right)^n$

○ Example: *n*-hexane

Mixtures

Vapor – Liquid Equilibria
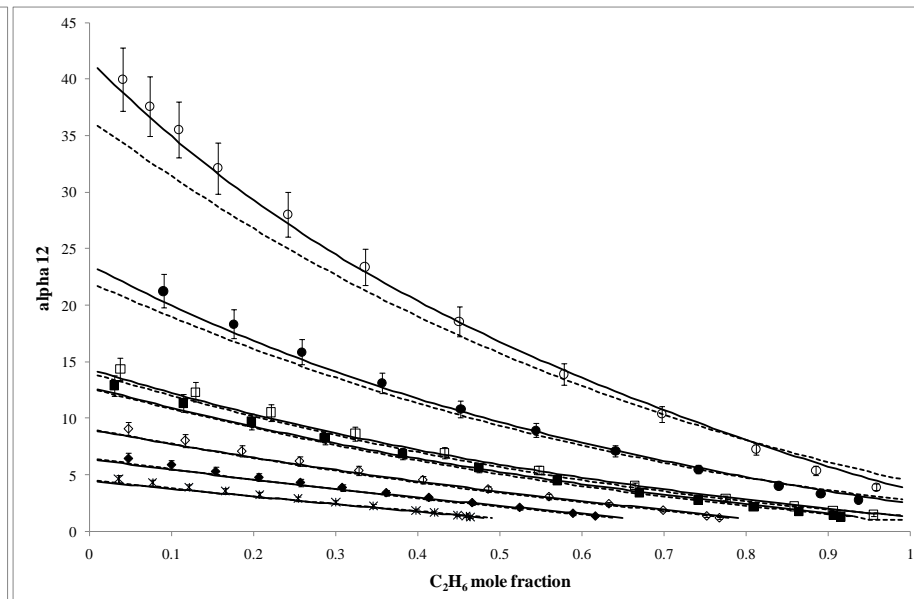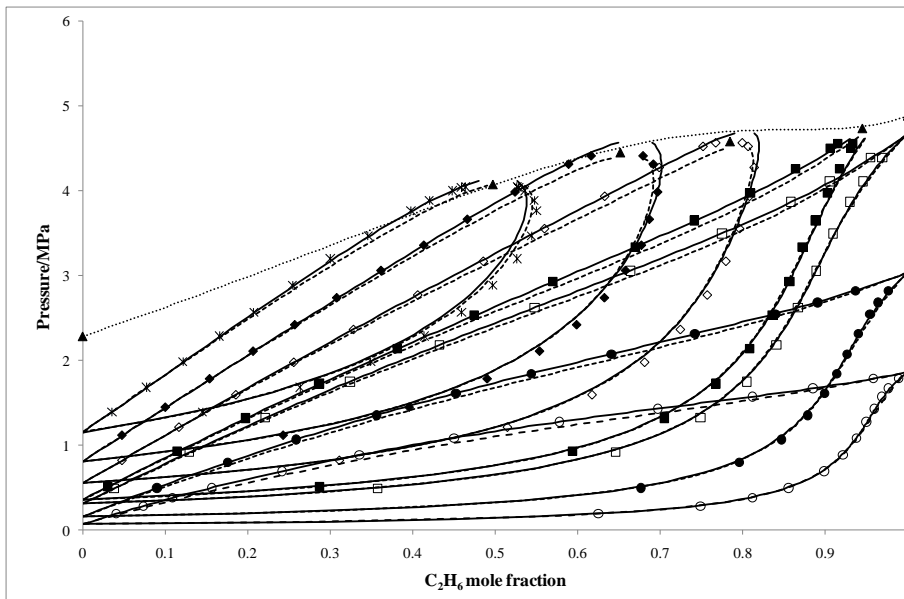
❑ Graphic treatment: relative volatility

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

❑ Example: Ethane – C4F10

Solid lines: PR
Dashed lines: PSRK

❑ Gibbs-Duhem equation

$$\sum_i x_i d\ln\gamma_i = -\frac{H^E dT}{RT^2} + \frac{V^E dP}{RT}$$

Thermodynamic model needed

❑ At equilibrium:

➢ Isothermal – isobaric form

➢ Entire composition range

➢ In low-pressure VLE

$$\int_0^1 \ln\frac{\gamma_1}{\gamma_2} dx_1 = 0$$
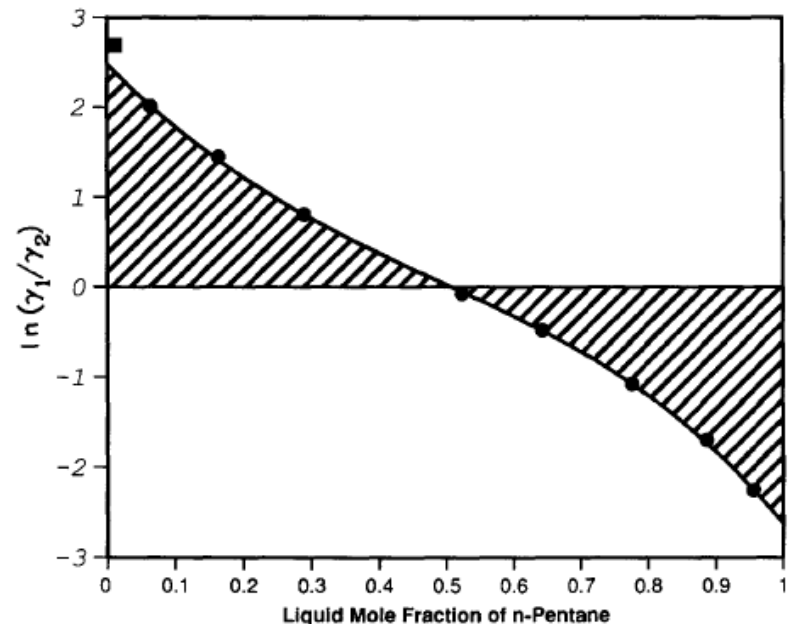
Integral test for the n-pentane/methanol system.
Jackson and Wilsak (1995)

❑ Usually:

Redlich – Kister polynomial correlation

$$Y^E = x_1 x_2 \sum_i A_i \left(x_1 - x_2 \right)^i$$

❑ Problem: number of parameters

❑ Desnoyers and Perron (1997)

$$\frac{Y^E}{x_1 x_2}$$
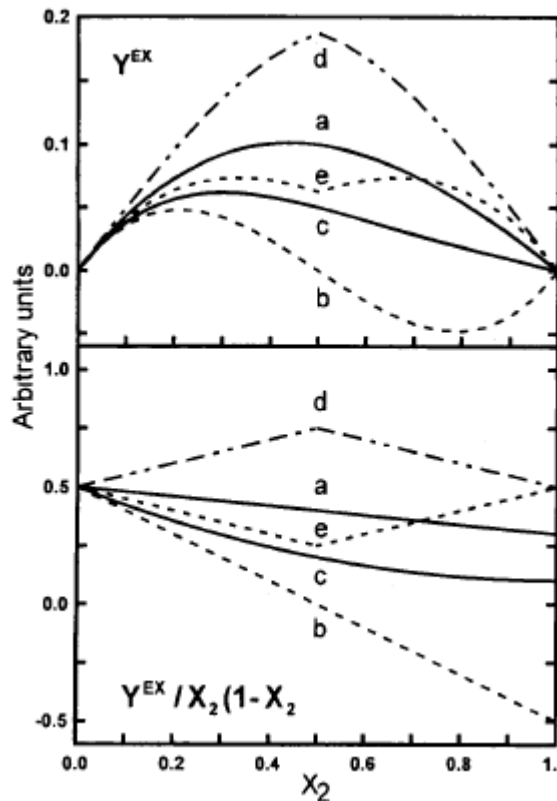
(a): Linear variation. Often mixtures of liquids of similar size and polarity

(b): Linear variation. $Y_2^0 - Y_2^*$ opposite sign $Y_1^0 - Y_1^*$

(c): Mixtures of liquids of different size and polarity

(d): Formation of complex (ex: mixtures of certain alcohols and amines)

(e): Similar to (d)

Example: furan – *n*-hexane

313.15 K – 0.5 MPa
353.15 K – 1 MPa
383.15 K – 1 MPa

Conclusion

Conclusion

Methodes expérimentales
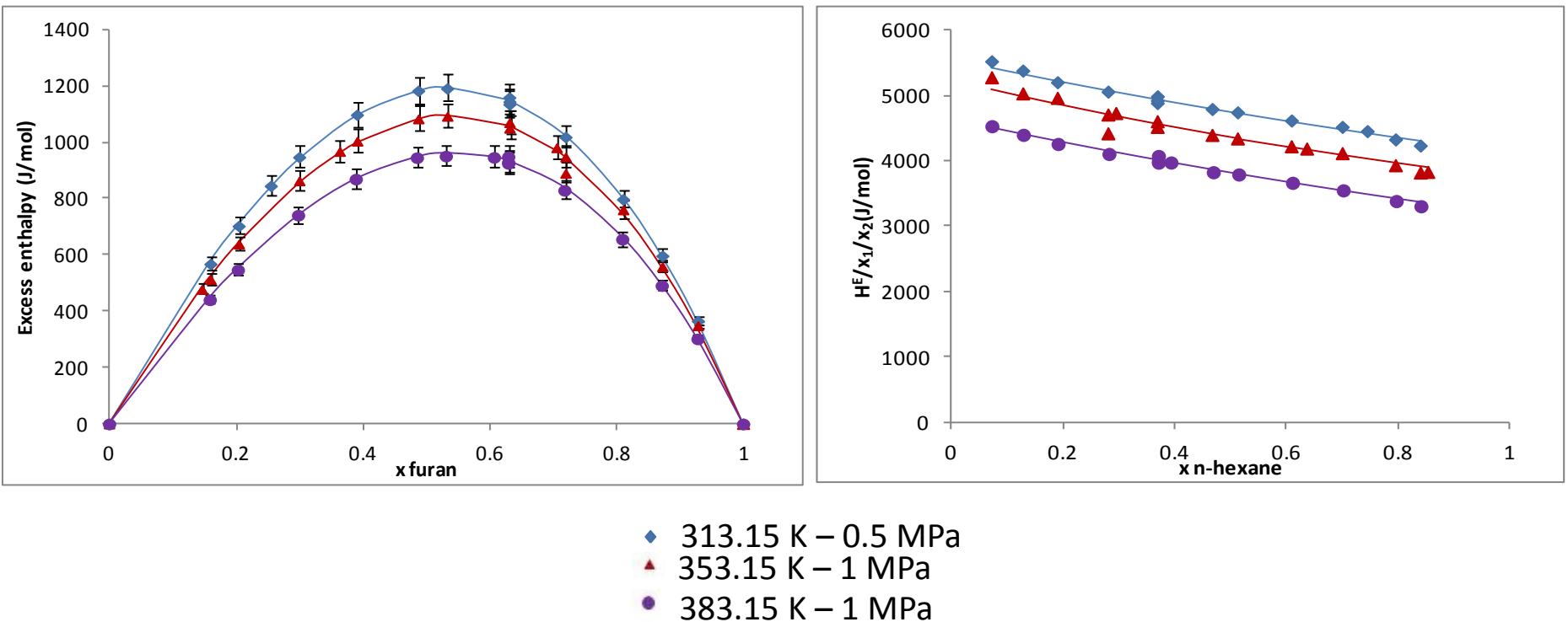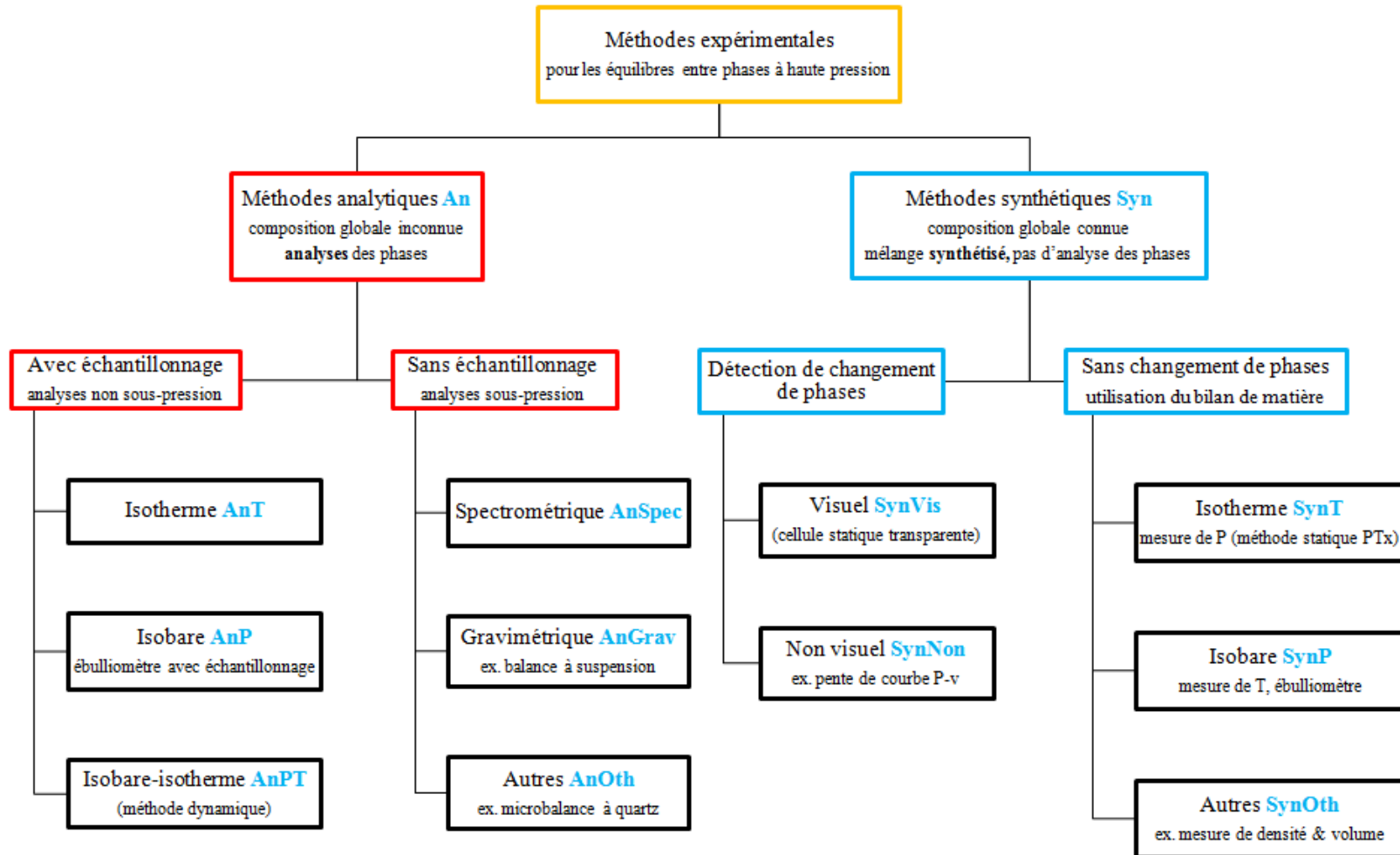pour les équilibres entre phases à haute pression

Méthodes analytiques **An**
composition globale inconnue
analyses des phases

Méthodes synthétiques **Syn**
composition globale connue
mélange **synthétisé**, pas d'analyse des phases

Avec échantillonnage
analyses non sous-pression

Sans échantillonnage
analyses sous-pression

Détection de changement de phases

Sans changement de phases
utilisation du bilan de matière

Isotherme **AnT**

Isobare **AnP**
ébulliomètre avec échantillonnage

Isobare-isotherme **AnPT**
(méthode dynamique)

Spectrométrique **AnSpec**

Gravimétrique **AnGrav**
ex. balance à suspension

Autres **AnOth**
ex. microbalance à quartz

Visuel **SynVis**
(cellule statique transparente)

Non visuel **SynNon**
ex. pente de courbe P-v

Isotherme **SynT**
mesure de P (méthode statique PTx)

Isobare **SynP**
mesure de T, ébulliomètre

Autres **SynOth**
ex. mesure de densité & volume

Experimental techniques for Phase Equilibria measurements at high pressures (Dohrn et al. 2010)

Thank you for your attention

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