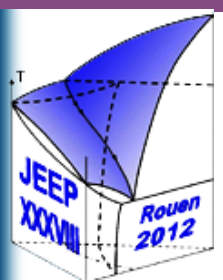
Using Accurate Models for Process Modeling

Journées d'Etude des Equilibres entre Phases

Rouen - 29 et 30 mars 2012



Olivier Baudouin (ProSim)

Stéphane Déchelotte

Alain Vacher

ProSim

Outline

- What are Steady State Process Simulation Software?
- Importance of Thermodynamics inside Simulation Software?
- Approaches used for Fluid Phase Equilibria
  - Homogeneous Approach (Equations of State)
  - Heterogeneous Approach (G^E Models)
  - New Mixing Rules for Equations of State (EOS / G^E)
  - SAFT Equations of State
  - Specific Models
- Description of a Thermophysical Properties Calculation Server

Steady-State Process Simulator

Tools performing rigorous mass and energy balances for all the operating units of a continuous process in steady state operation

- Calculation of **all process streams characteristics** (flowrate, temperature, pressure, composition, physical properties,...)
- Calculation of **performance of equipments**
- Calculation of **all process data required for equipment sizing**
- Calculation of **data required for energetic analysis** of a process (Pinch…)

Typical Process Industries Served

- **Chemical & Petrochemical Processing**
  (ammonia and fertilizer plants, olefins, ethylene crackers, polymers, fine & specialty chemicals, inorganic chemicals, intermediates, solvent recovery,…)
- **Oil & gas production**
  (Offshore platforms, on-shore fields and facilities, LNG plants and terminals, gas dehydration, gas sweetening, NGL plants, gas processing, pipelines,…)
- **Petroleum refining**
  (Crude/vacuum distillation, hydrocracking, FCCU, isomerization, alkylation, hydrotreaters, sulfur recovery, reformers, cokers, lube processing…)
- **Energy**
  (Combined cycle/cogeneration, nuclear, coal processing, gasification combined cycles, water and utilities,…)
- **…and many other fields**
  (Air separation, carbon capture & storage, bio-fuels, pharmaceuticals, pulp & paper, biochemicals, food and food intermediates,…)

⇨ **Operating companies as well as E&C (Engineering & Construction) companies in these fields**

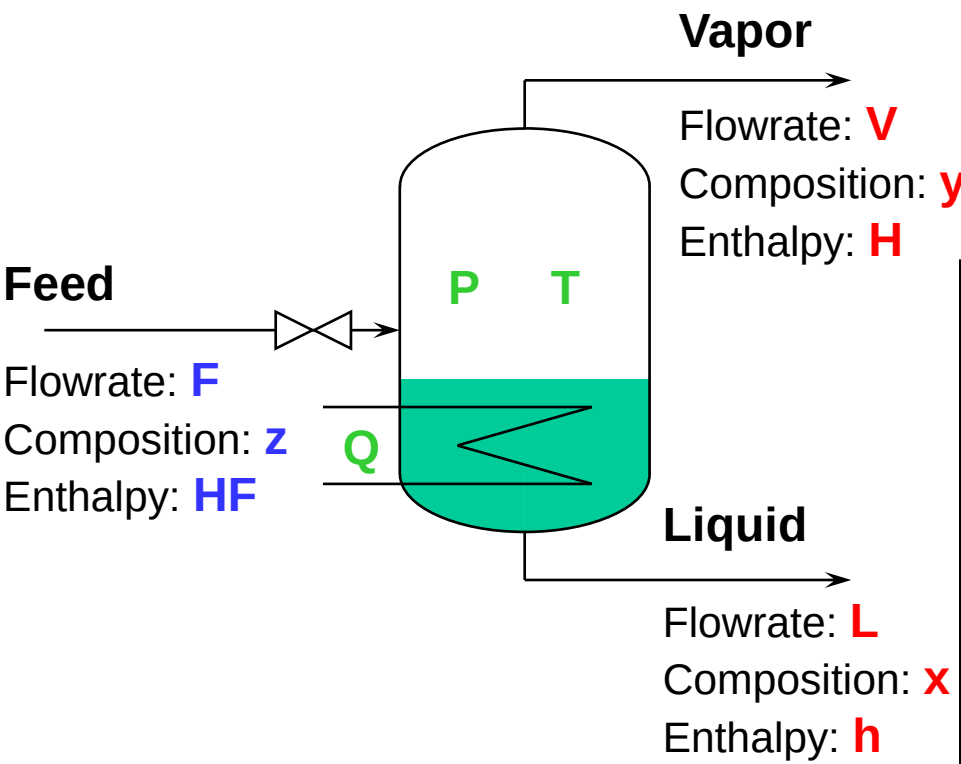
⇨ **For conceptual design, optimization, and performance monitoring**

Useful Throughout the Process Lifecycle

- ⇨*R&D, lab.*
- ⇨*Conceptual development*
- ⇨*Process Engineering*
- ⇨*Detailed Engineering*
- ⇨*Construction & Commissioning*
- ⇨*Operations*

⇨ ***from experimental data regression …***
…to optimization of a complete process unit or plant

Example of a Flash-Unit (without chemical reaction)



Data: F, z, HF
Parameters: P, T, Q
Variables: V, L, y, x, H, h

Equations

Global mass balance: $L + V - F = 0$

Partial mass balances: $L \cdot x_i + V \cdot y_i - F \cdot z_i = 0$

Enthalpy balance:

$$L \cdot h(T,P,x) + V \cdot H(T,P,y) - F \cdot HF(T,P,z) - Q = 0$$

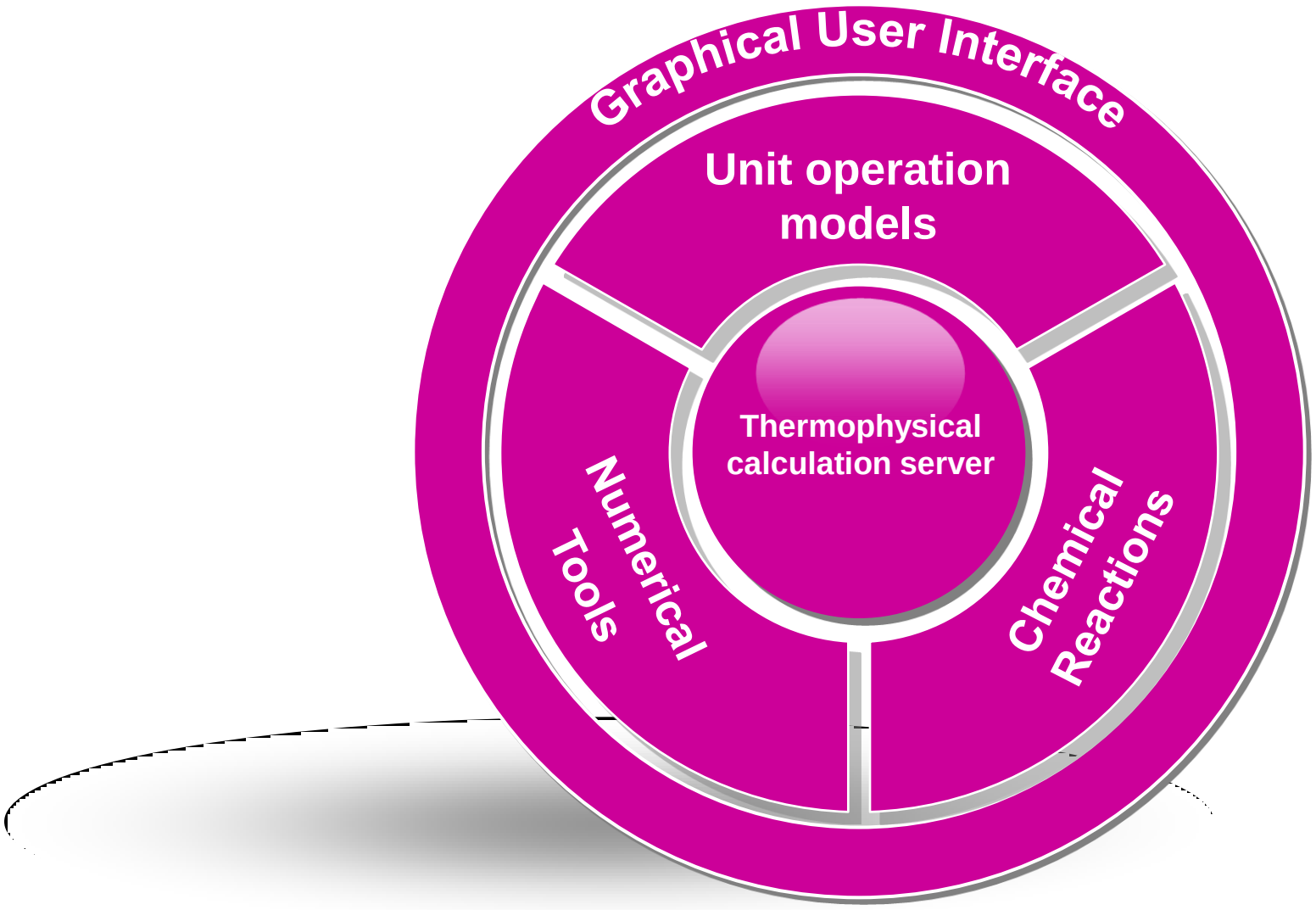
Thermodynamic equilibrium relations:

$$f_i^V(T,P,y) = f_i^L(T,P,x) \quad \text{or} \quad y_i = K_i(T,P,x,y) \cdot x_i$$

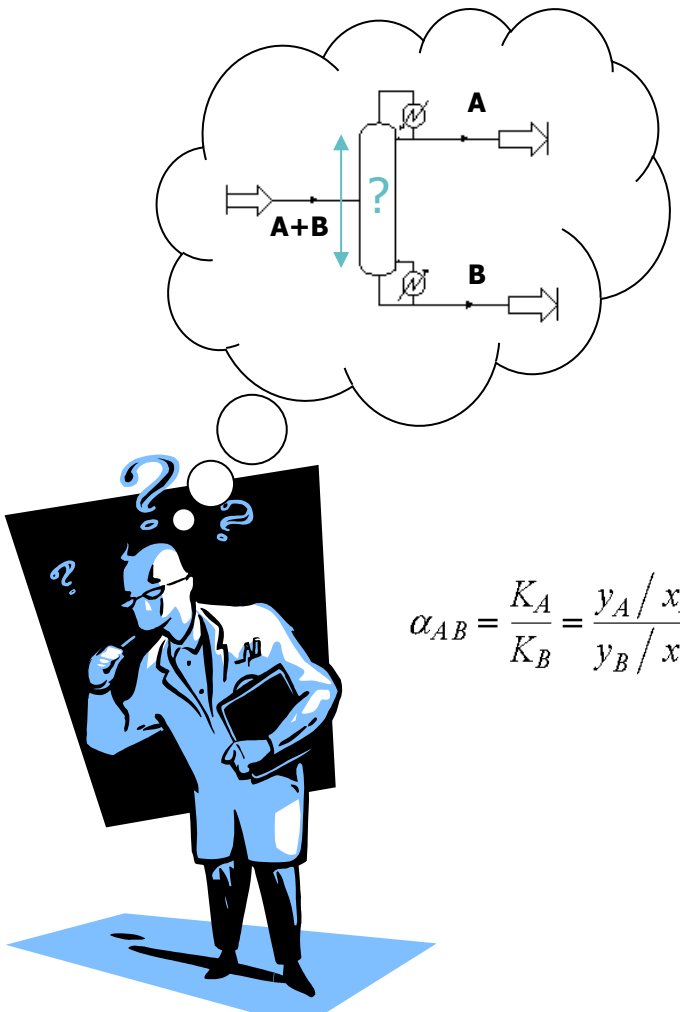
Constraints: $\Sigma x_i = 1$ $\Sigma y_i = 1$ $\Sigma z_i = 1$

⇨ Thermophysical properties
⇨ Numerical algorithms
⇨ Chemical reaction models
⇨ Unit operation models

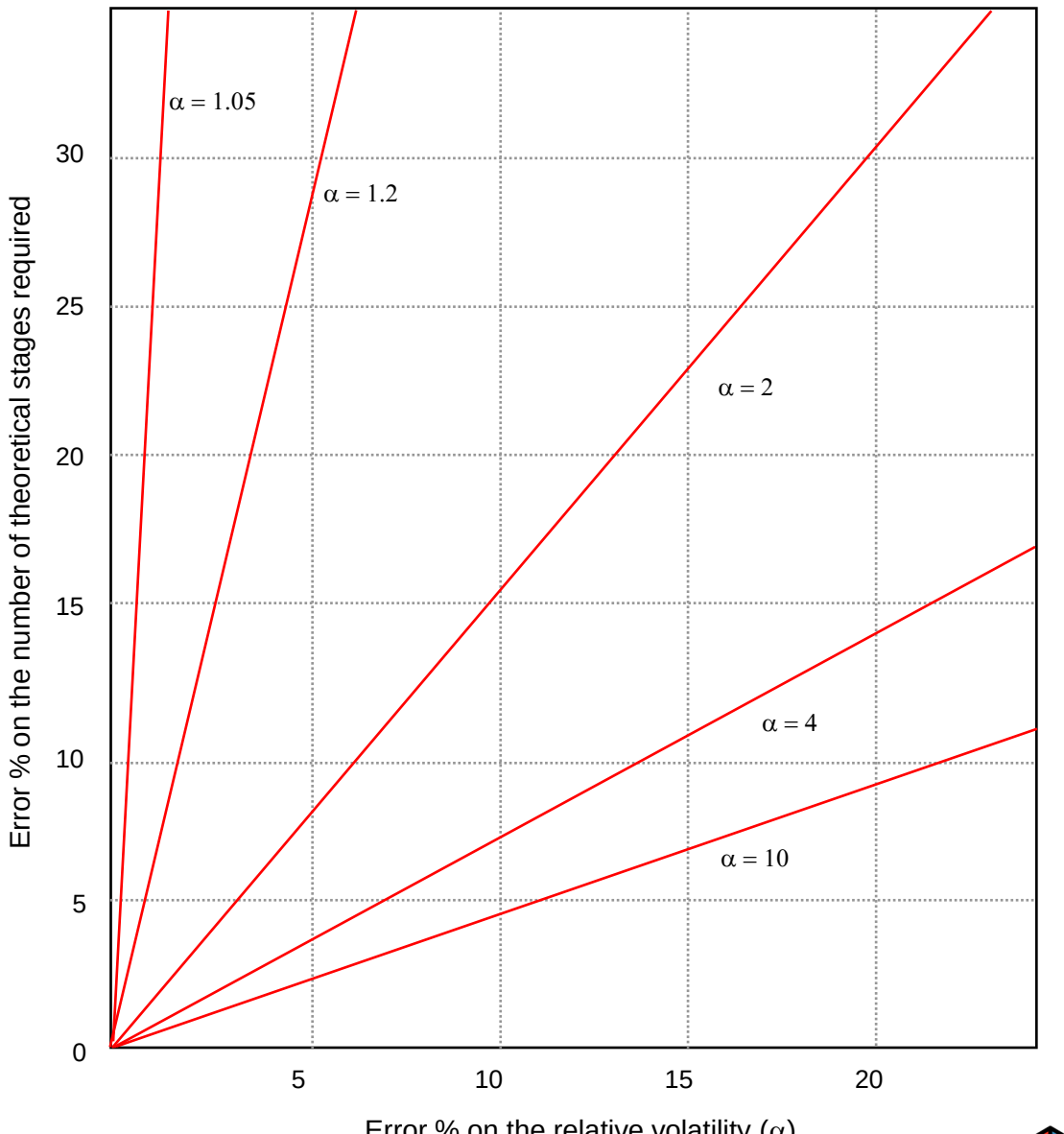
Software Architecture



Conception of a Distillation Column
Influence of Relative Volatility



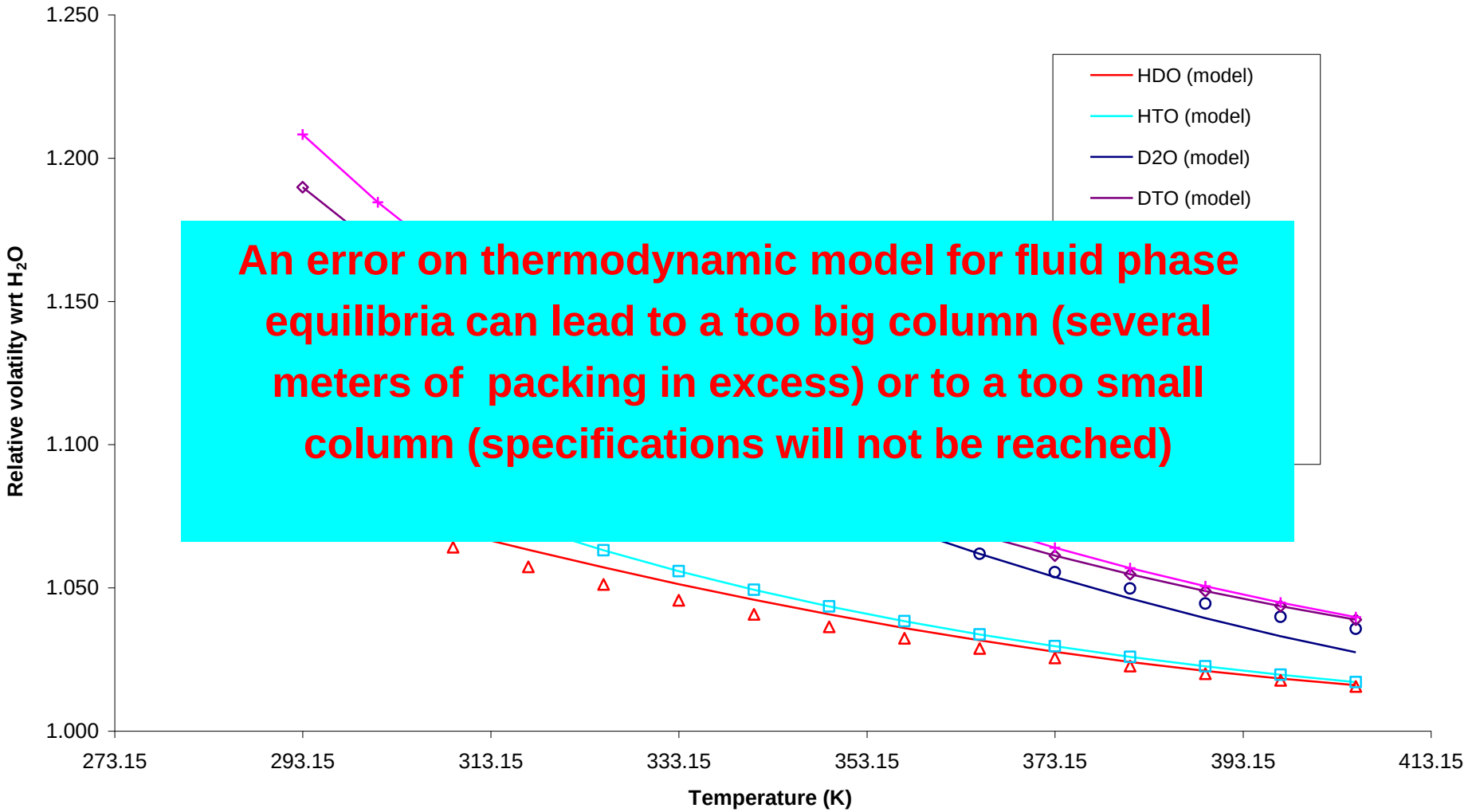
$$\alpha_{AB} = \frac{K_A}{K_B} = \frac{y_A / x_A}{y_B / x_B}$$



Conception of a distillation column
Influence of relative volatility

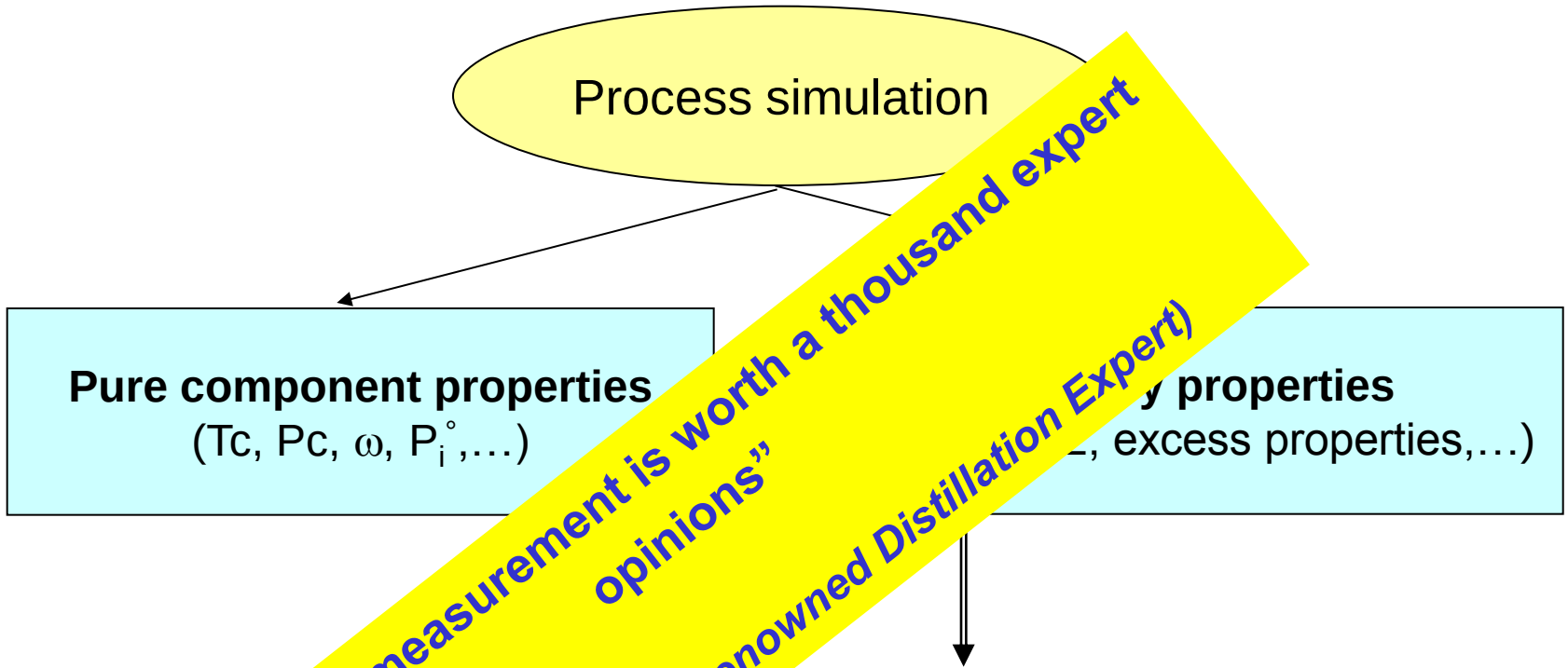
Relative volatility of H_2O/x (x=HDO, HTO, D_2O, DTO, T_2O)

W.A. Van Hook, Vapor Pressures of the Isotopic Waters and Ices, The Journal of Physical Chemistry, 1968, Vol. 72, No 4, p. 1234-1244



An error on thermodynamic model for fluid phase equilibria can lead to a too big column (several meters of packing in excess) or to a too small column (specifications will not be reached)

Data Required For Accurate Results



"One good measurement is worth a thousand expert opinions"

Henry Kister (World-renowned Distillation Expert)

- Basi
  - multi-components system can be deducted from t of the behavior of the pure substances and the bi
  - Only erimental data of pure substances and binary systems are required

Simulis® Thermodynamics

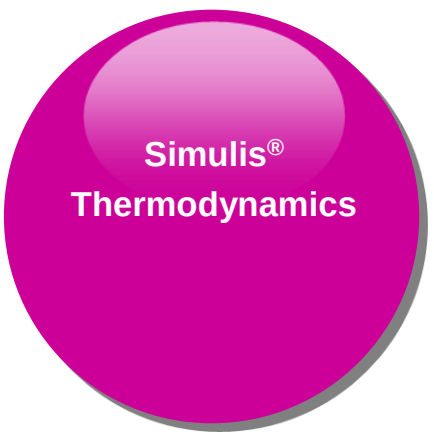
Software component

for computing

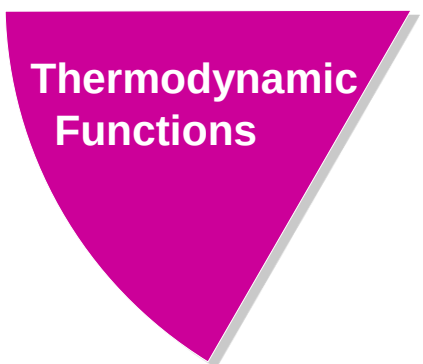
thermophysical properties

and **phase equilibria** on pure substances or **mixtures**

in **MS-Excel®, MATLAB® or other applications**



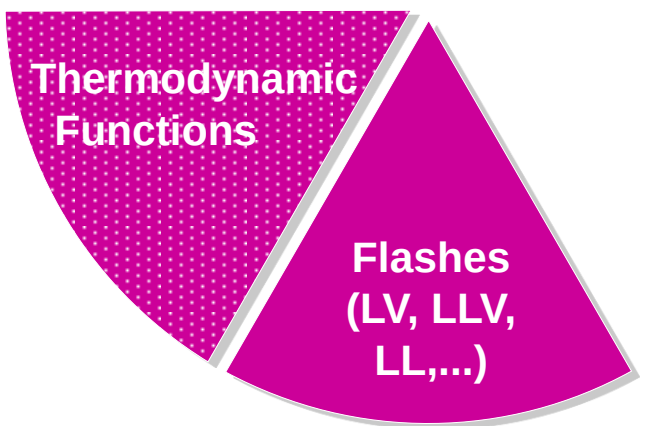
Simulis® Thermodynamics



⇨To compute thermo-physical properties

(Transport, Compressibility, Thermodynamic, Non-ideal and their derivatives)

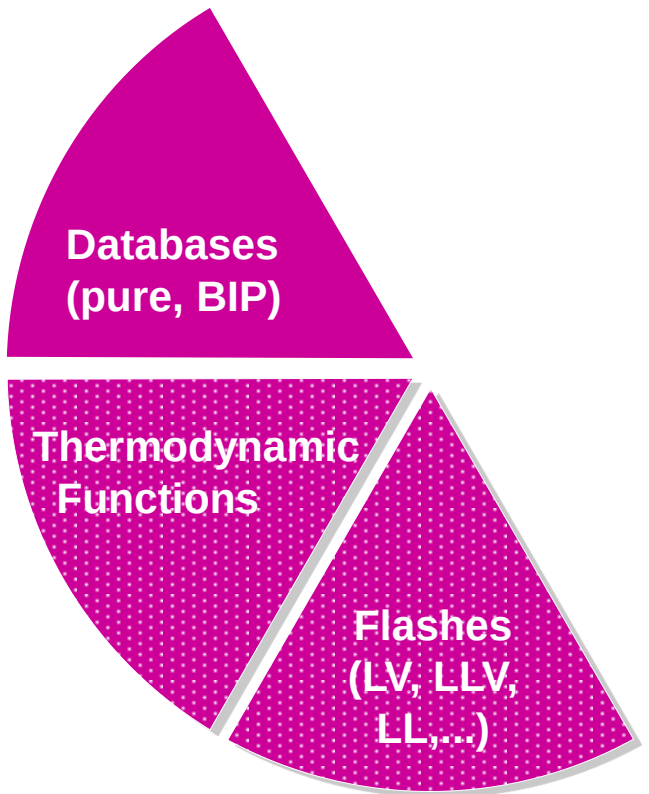
Simulis® Thermodynamics



⇨ **To compute phase equilibria**

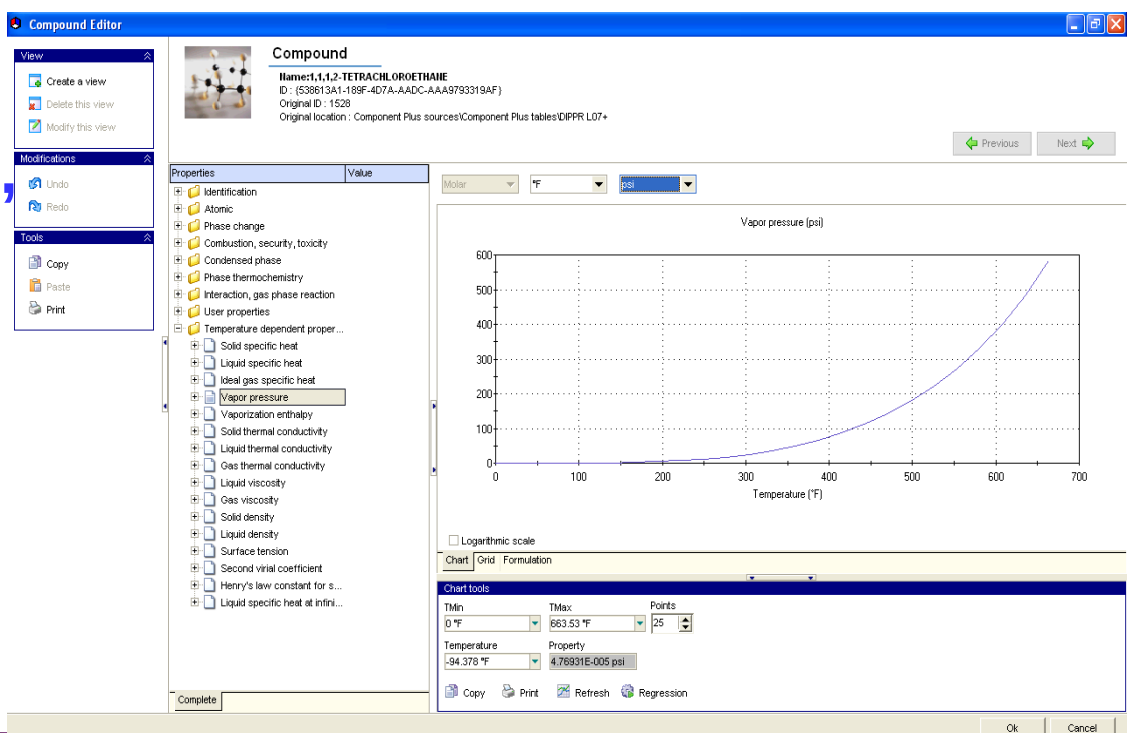
(Vapor-liquid, liquid-liquid, vapor-liquid-liquid flashes)

Simulis® Thermodynamics

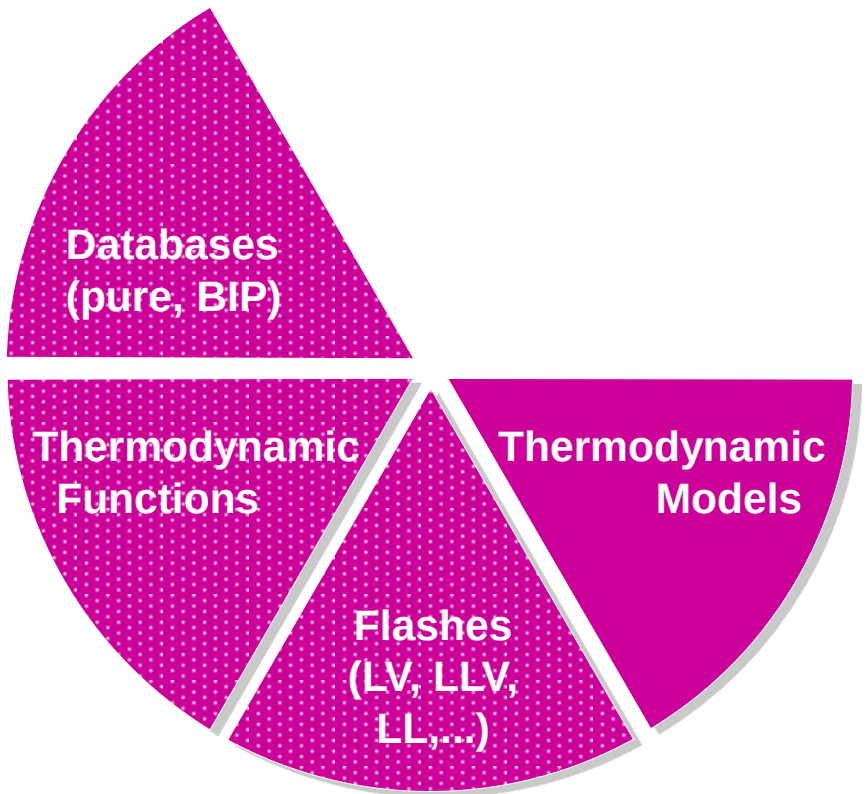


Pure Compound Properties

- **Supplied with a database of over 2 000 compounds based on AIChE's DIPPR® database (public release 2005)**
  - ✓ 125 constant properties (molar weight, critical temperature,…)
  - ✓ 16 temperature dependant properties (Cp, Pi°, λ, ΔHvap …)
- **Optionally the last public version of the DIPPR® database can be supplied**
- **All properties can be edited, modified, plotted,…**
- **Pure compound properties can be estimated**
- **Or regressed from experimental data**



Simulis® Thermodynamics



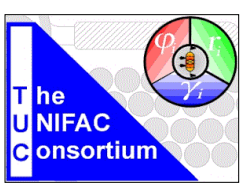
A Range of Thermodynamic Models

Equations of State

- Soave-Redlich-Kwong (SRK)
- Peng-Robinson (PR)
- Predictive Peng-Robinson (PPR78)
- Lee-Kesler-Plöcker (LKP)
- BWRS
- Nakamura
- NRTL-PR
- PPC-SAFT
- etc…

Activity coefficients models

- NRTL
- UNIQUAC
- UNIFACs (Larsen, Dortmund,…)
- Wilson
- etc…



Combined approach models

- MHV2
- MHV1
- PSRK
- etc…

Specific systems

- Pure Water (NBS/NRC steam tables - IAPS,1984)
- Chao-Seader, Grayson-Streed
- Sour-Water
- Carboxylic acids
- Formaldehyde
- etc…

Electrolytes

- Edwards
- UNIQUAC electrolyte
- ULPDHS
- Amines
- etc…

Equation of State Approach

Equations of State derived from van der Waals Theory (1873)

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Repulsive term (volume of molecules, **b**)

Attractive term (internal pressure, **a**)

At critical point ($T=T_c$, $P=P_c$) :

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T = \left(\frac{\partial^2 P}{\partial \upsilon^2}\right)_T = 0$$

$$P_C = \frac{RT_C}{V_C - b} - \frac{a}{V_C^2}$$

$$\left(\frac{\partial P}{\partial \upsilon}\right)_T = -\frac{RT_c}{(\upsilon_c - b)^2} + \frac{2a}{\upsilon_c^3} = 0$$

$$\left(\frac{\partial^2 P}{\partial \upsilon^2}\right)_T = \frac{2RT_c}{(\upsilon_c - b)^3} - \frac{6a}{\upsilon_c^4} = 0$$

$$a = \frac{27}{64}\frac{R^2 T_C^2}{P_C}$$

$$b = \frac{1}{8}\frac{RT_C}{P_C}$$

$$Z_C = \frac{3}{8}$$

Equation of State Approach

Redlich and Kwong (1949) : $P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}$ $\alpha = \frac{1}{\sqrt{T}}$

Soave (1972) : $P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}$

$\alpha = \left[1+m\left(1-T_r^{0.5}\right)\right]^2$

Peng-Robinson (1976) : $P = \frac{RT}{V-b} - \frac{a\alpha}{V^2+2bV-b^2}$

$\alpha = \left[1+\left(0.37464+1.54226\,\omega-0.26992\,\omega^2\right)\left(1-T_r^{0.5}\right)\right]^2$

Improvements: **new alpha functions (Boston-Mathias, Mathias-Coppeman, Twu-Bluck-Cunningham-Coon…), volume translation (Peneloux)**

Equation of State Approach

Some other "Classical" Equations of State:

Benedict-Webb-Rubbin (1940) :

$$P = \rho RT + \left(B_0 RT - \left(A_0 + \psi_A\right) - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0 + \psi_E}{T^4} \right) \rho^2 + \left(bRT - a - \frac{d}{T} - \frac{e}{T^4} - \frac{f}{T^{23}} \right) \rho^3$$
$$+ \alpha \left(a + \frac{d}{T} + \frac{e}{T^4} + \frac{f}{T^{23}} \right) \rho^6 + \left(\frac{c}{T^2} + \frac{g}{T^8} + \frac{h}{T^{17}} + T\psi_S \right) \rho^3 \left(1 + \gamma\rho^2\right) e^{-\gamma\rho^2}$$

Lee-Kesler (1975) :

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}} \left(Z^{(r)} - Z^{(0)} \right)$$

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp\left(- \frac{\gamma}{V_r^2} \right)$$

Equation of State Approach

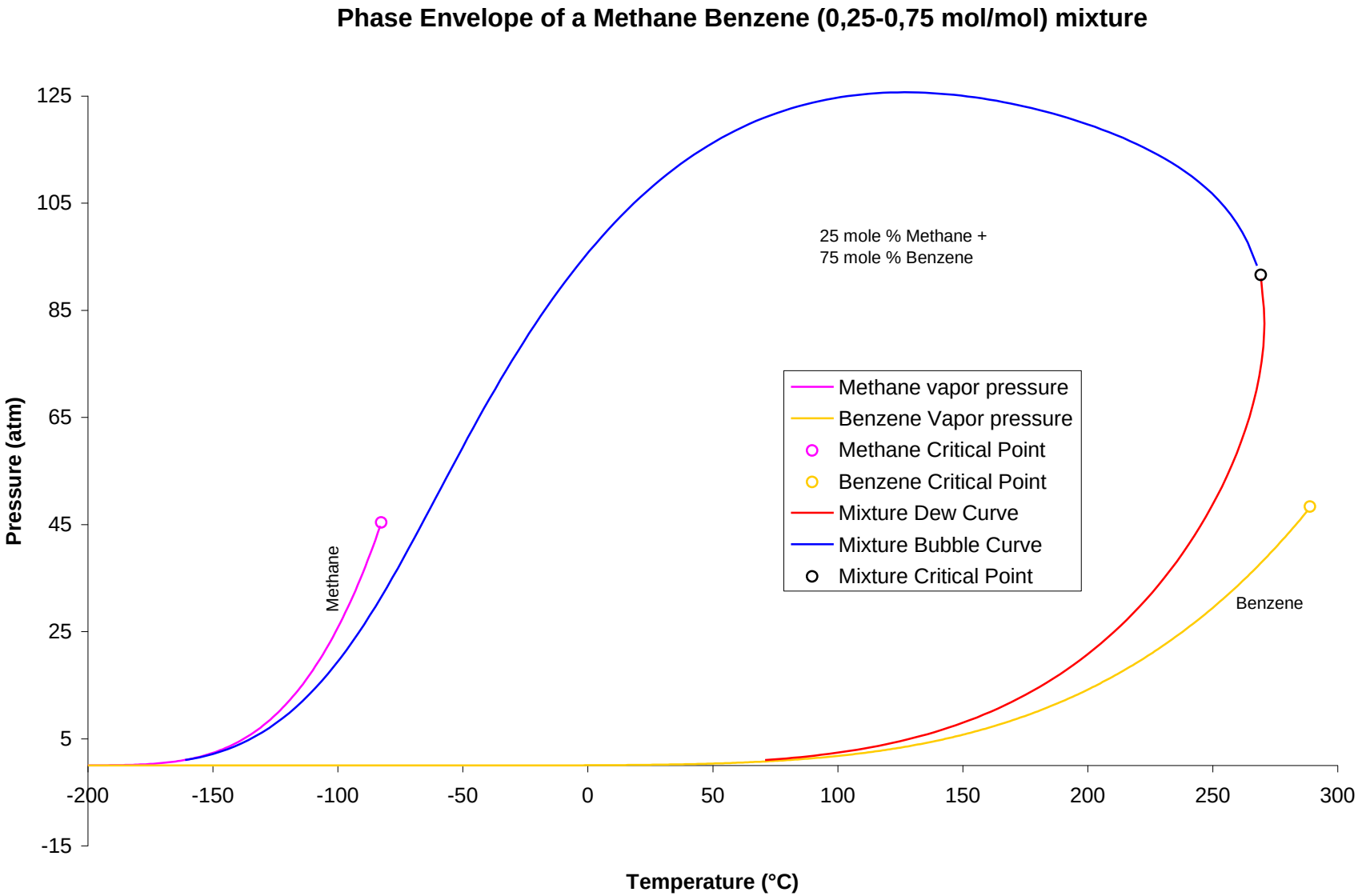
Equilibrium constant (vapor-liquid):

$$K_i(T, P, x, y) = \frac{\Phi_i^L(T, P, x)}{\Phi_i^V(T, P, y)}$$

<u>Application range</u>: «*Systems composed of normal gases, rare gases, nitrogen, oxygen, carbon monoxide, hydrocarbons and some hydrocarbons derivatives. Carbon dioxide, hydrogen sulfide, hydrogen and with some limits, some light polar substances can be included*».

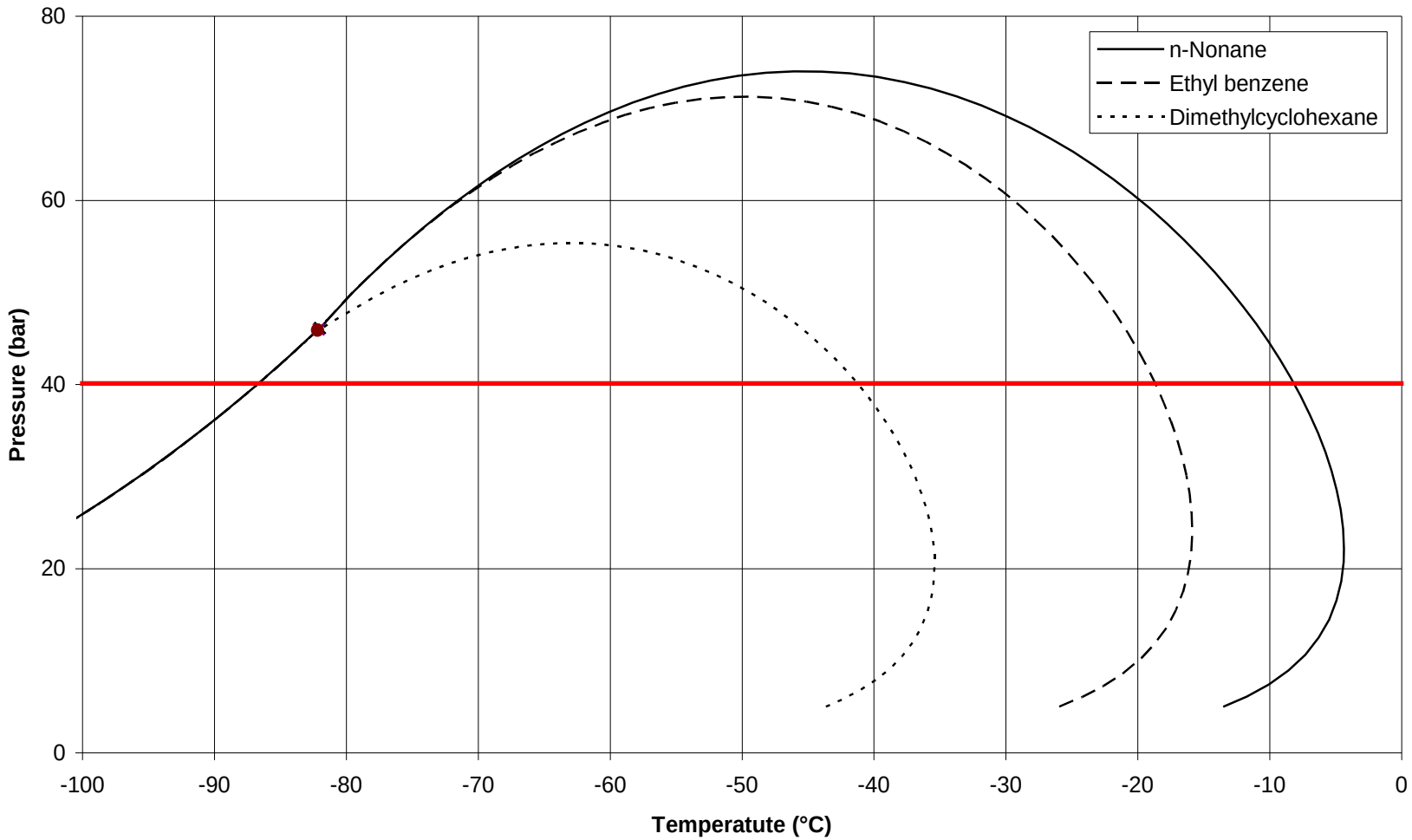
L. Oellrich, U. Plöcker, J.M. Prausnitz and H. Knapp, «Equation of State Methods for Computing Phase Equilibria and Enthalpies, Int. Chem. Eng., 21, 1, pp 1-16 (1981)

Equation of State Approach



Equation of State Approach

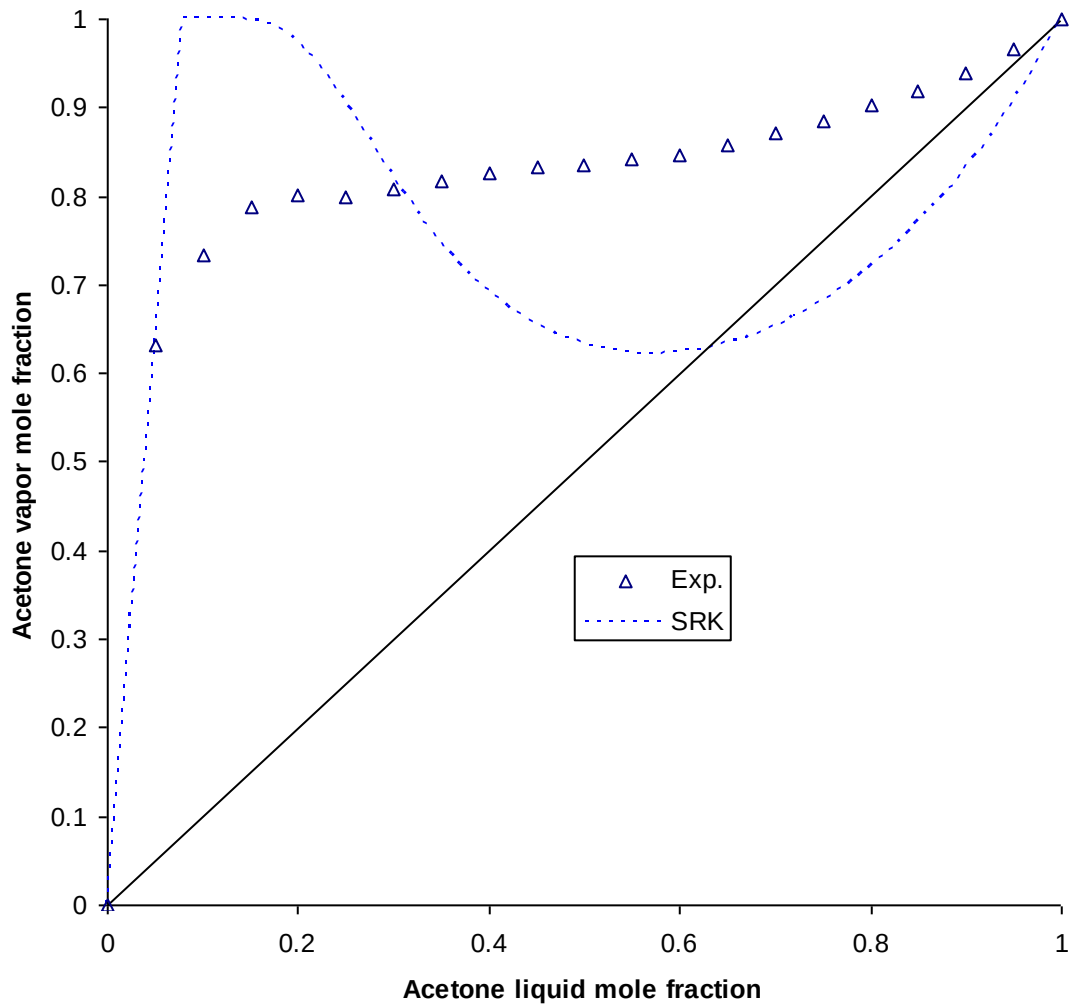
Phase envelopes for mixtures of 99.99 mole % C1 and 0,01 mole % of nC9, dimethylcyclohexane and ethylbenzene with NRTL-PR EoS



Equation of State Approach

Vapor - Liquid equilibrium curve of Acetone - Water mixture @ 760 mmHg

Othmer, D.F., M. M. Chidgar, Sh. L. Levy, Ind. Eng. Chem., 44, 1872 (1952)



Heterogeneous Approach (γ-Φ)

Based on an activity coefficients model in order to take care about the non ideality of the liquid phase:

- Margules
- Scatchard – Hildebrand (Regular solutions)
- Wilson
- NRTL
- Uniquac
- UNIFAC Models
- …

And based on a equation of state usable for vapor phase:

- Ideal gas
- Soave – Redlich – Kwong
- Peng – Robinson
- Lee – Kessler – Plöcker
- …

Heterogeneous Approach (γ-Φ)

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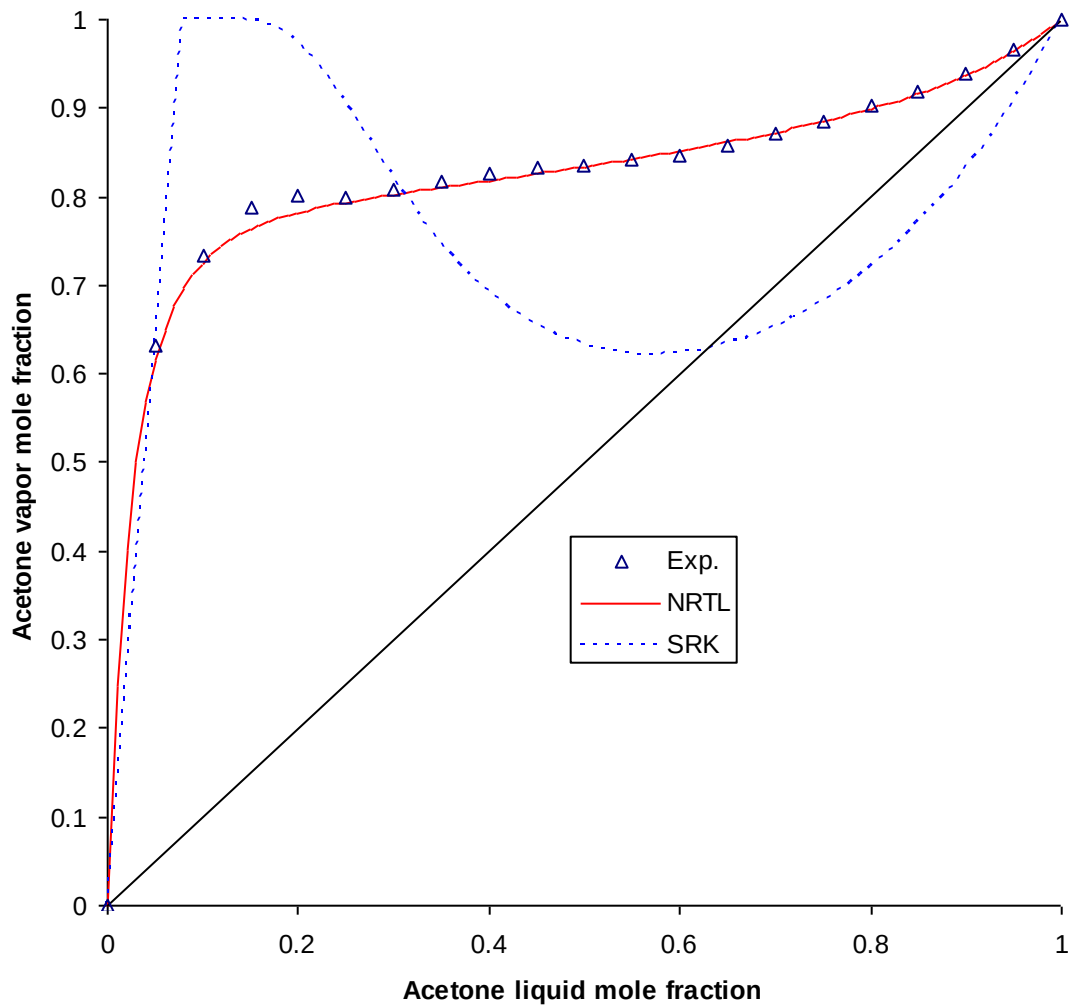

Heterogeneous Approach (γ-Φ)

- **Vapor Phase:** $f_i^V(T,P,y) = \Phi_i^V(T,P,y).y_i.P$

- **Liquid phase:** $f_i^L(T,P,x) = \gamma_i(T,x).x_i.f_i^{0L}(T,P)$

$$f_i^{0L}(T,P) = \phi_i^{0V}\left(T, P_i^0(T)\right) \times P_i^0(T)\, exp\left\{\frac{v_i^{0L}}{RT}\left(P - P_i^0 T\right)\right\}$$

- **Equilibrium constant:**

$$K_i(T,P,x,y) = \frac{\gamma_i(T,X) f_i^{0L}(T,P)}{\phi_i^V(T,P,y)P}$$

Application domain: **Chemical systems where complex chemical or polar interactions take place; low pressure and temperature (far above the critical point)**

Equation of State Approach with Complex Mixing Rules (EoS/G^E)

Use of a unique equation of state for the whole fluid zone including sophisticated mixing rules based on activity coefficient models:

- **Equations of state (cubic)**
  - Soave – Redlich – Kwong
  - Peng – Robinson
  - …
- **Activity coefficients models**
  - Wilson
  - NRTL
  - UNIQUAC
  - UNIFACs
  - …
- **Mixing rules**
  - MHV1
  - MHV2
  - PSRK
  - …

$$f_i(T,P,z) = \varnothing_i(T,P,z)\, z_i P$$

$$H(T,P,z) = \sum_i z_i H_i^*(T,P=0) + \left(H - H^*\right)_{T,P}$$

Equation of State Approach with Complex Mixing Rules (EoS/G^E)

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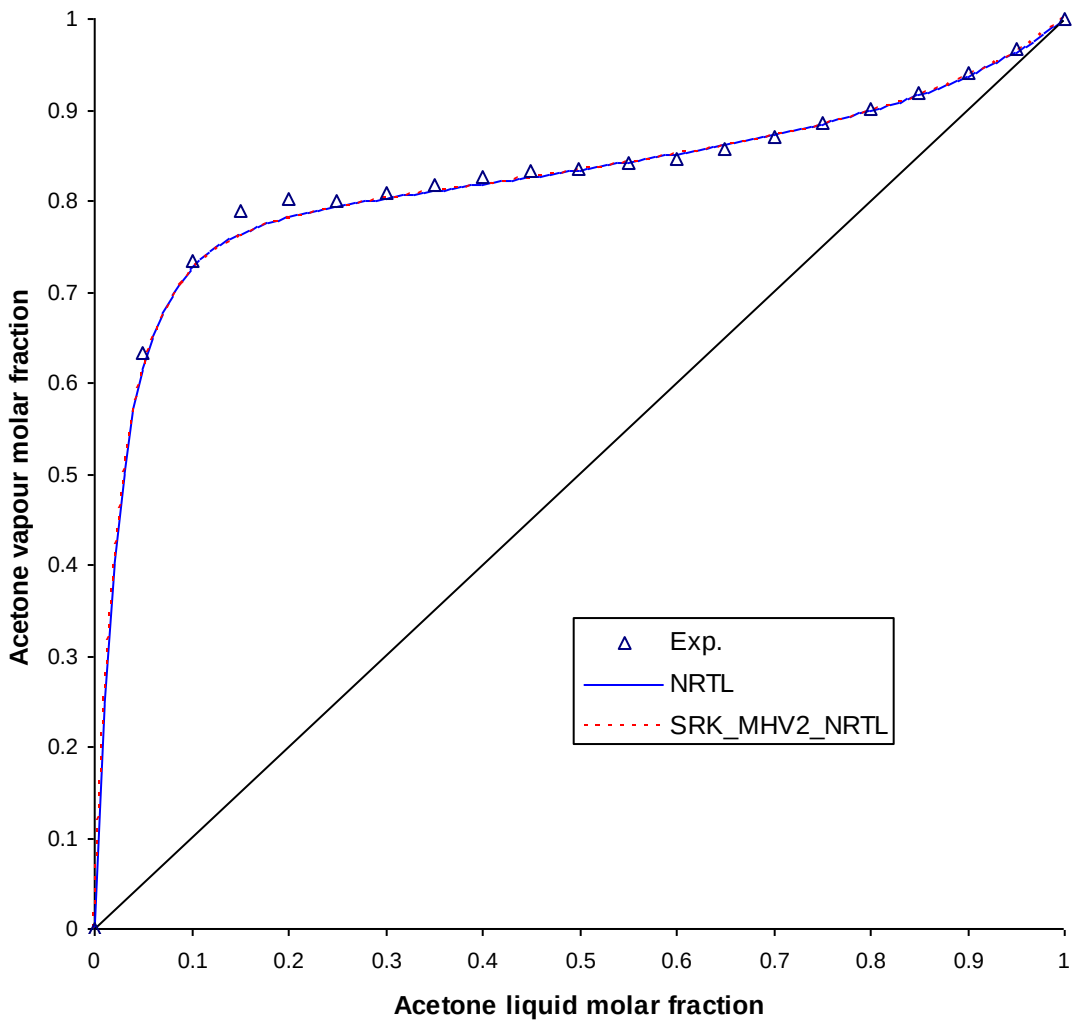
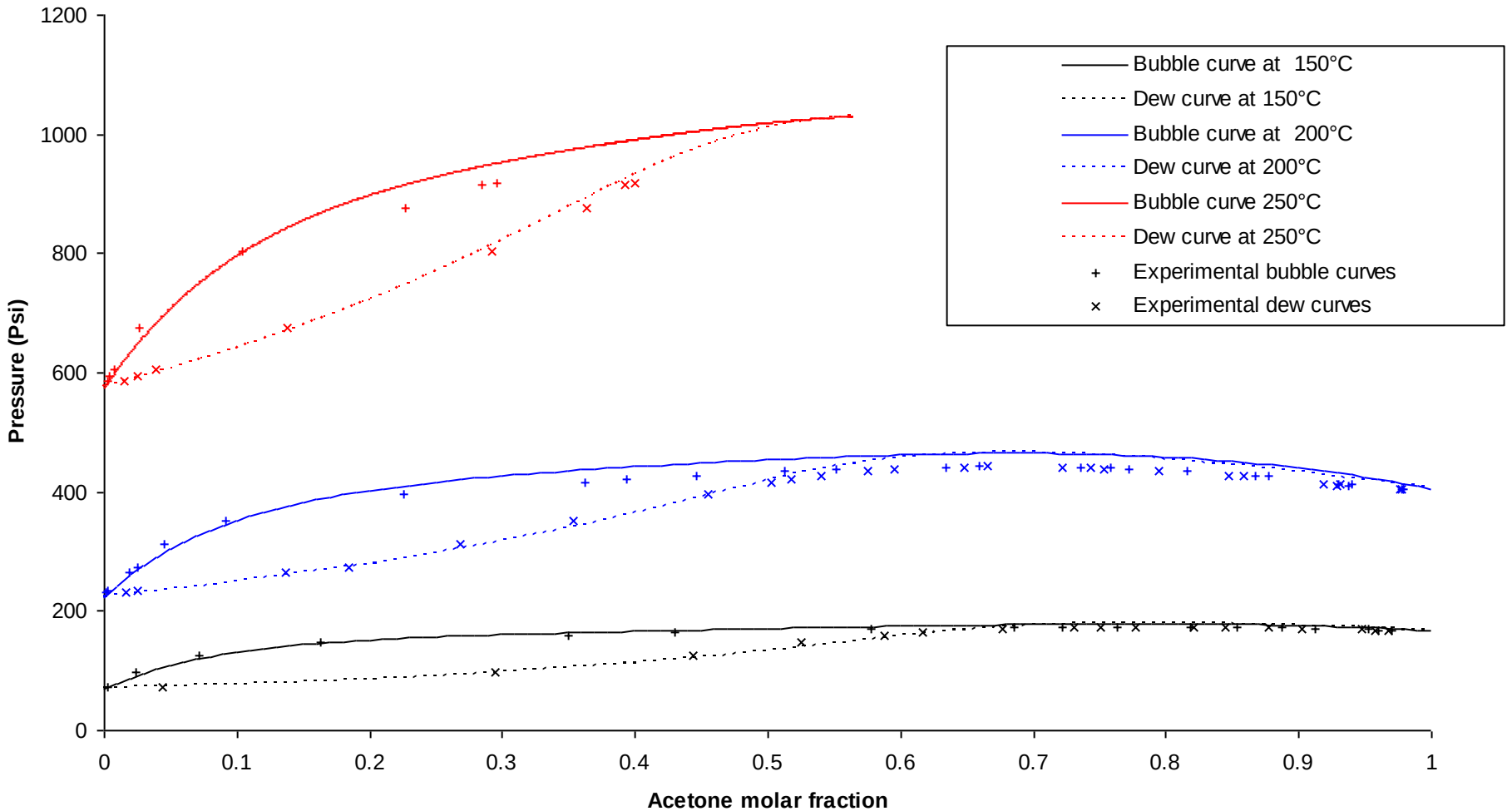


Equation of State Approach with Complex Mixing Rules (EoS/G^E)

Acetone - Water

SRK - MHV2 MR - NRTL

Griswold, J. Wong, S.Y, Chem. Eng. Prog. Symp. Series, 48, N°3 (1952)

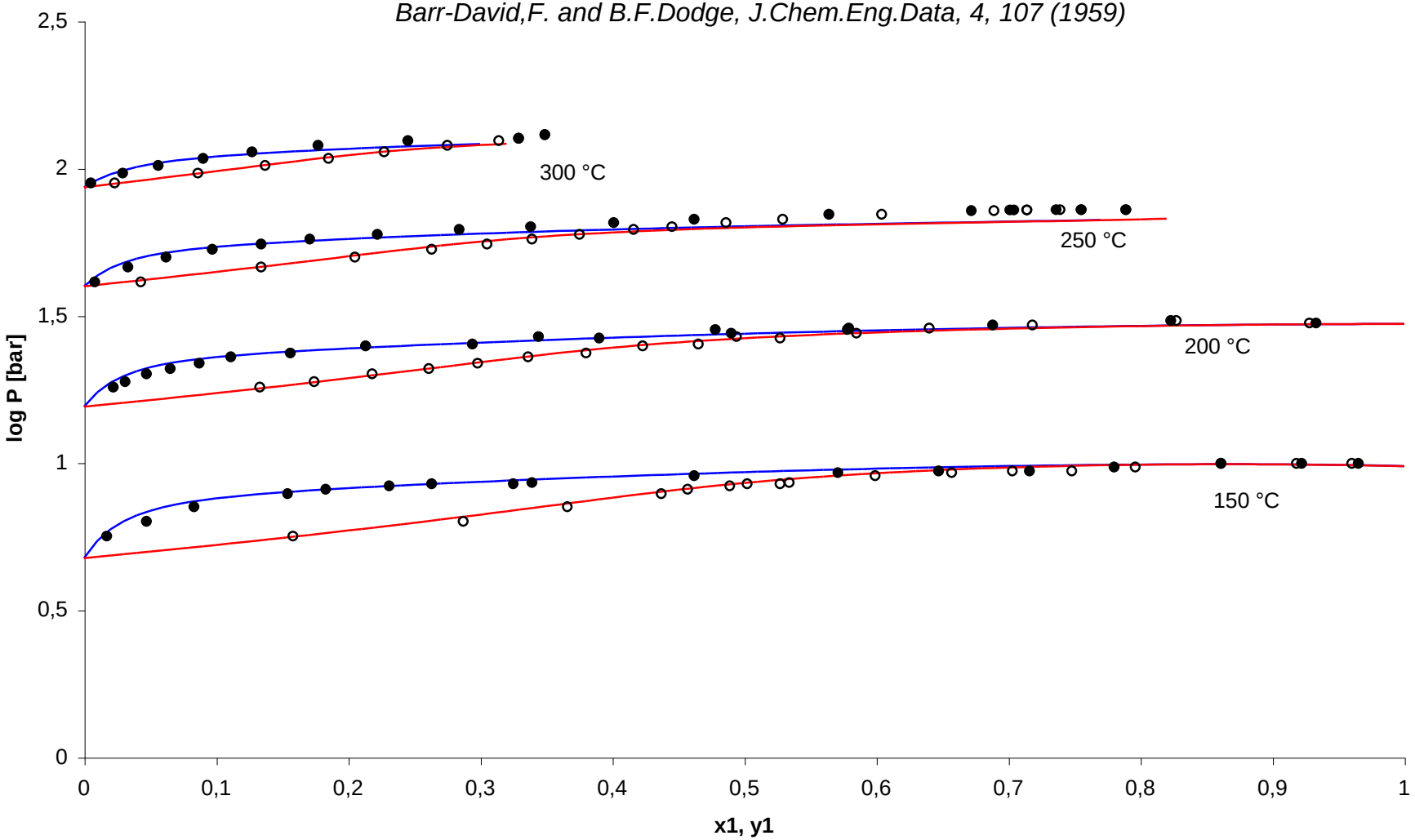


Equation of State Approach with Complex Mixing Rules (EoS/G^E)

Ethanol (1) / water(2)

Comparison of MHV2 in SimulisThermodynamics™ with experimental results

Barr-David,F. and B.F.Dodge, J.Chem.Eng.Data, 4, 107 (1959)



PPC-SAFT

- **Statistical Associating Fluid Theory (Chapman et al. 1990)**

$Z^{residual} = Z^{SAFT} - 1 =$ $m\,(Z^{rep} + Z^{disp}) + Z^{chain} + Z^{assoc}$ + Polar extension (Z^{pol}) μ or Q

☞ $Z^{rep} = Z^{référence\ HS} = f(\sigma, \varepsilon)$

☞ Dispersive-attractive $f(\sigma, \varepsilon)$

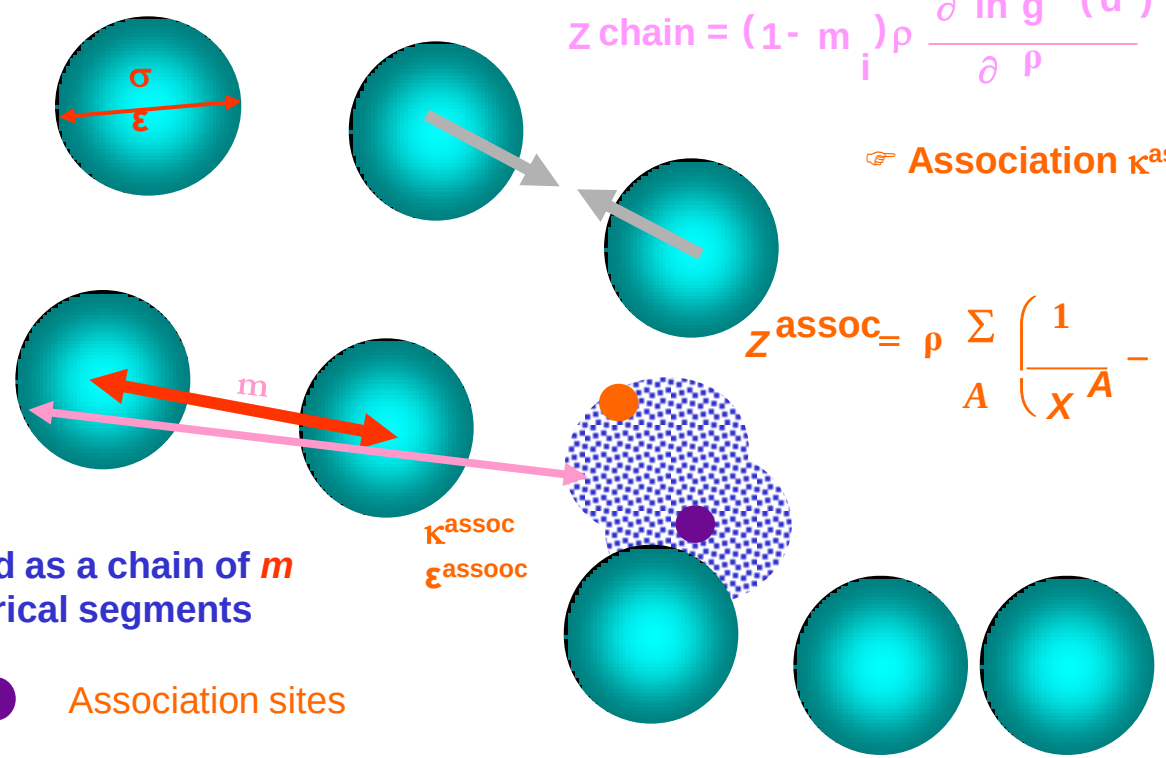
Gubbins et Twu 1978

☞ Chain $f(m,\sigma)$

$$Z^{chain} = (1 - m_i)\rho \frac{\partial \ln g^{HS}(d)}{\partial \rho}$$

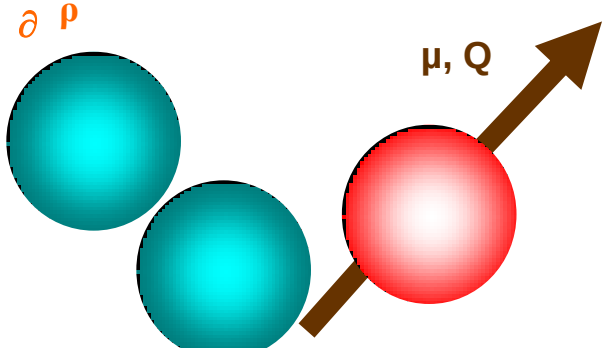
☞ Association κ^{assoc}, ε^{assooc}

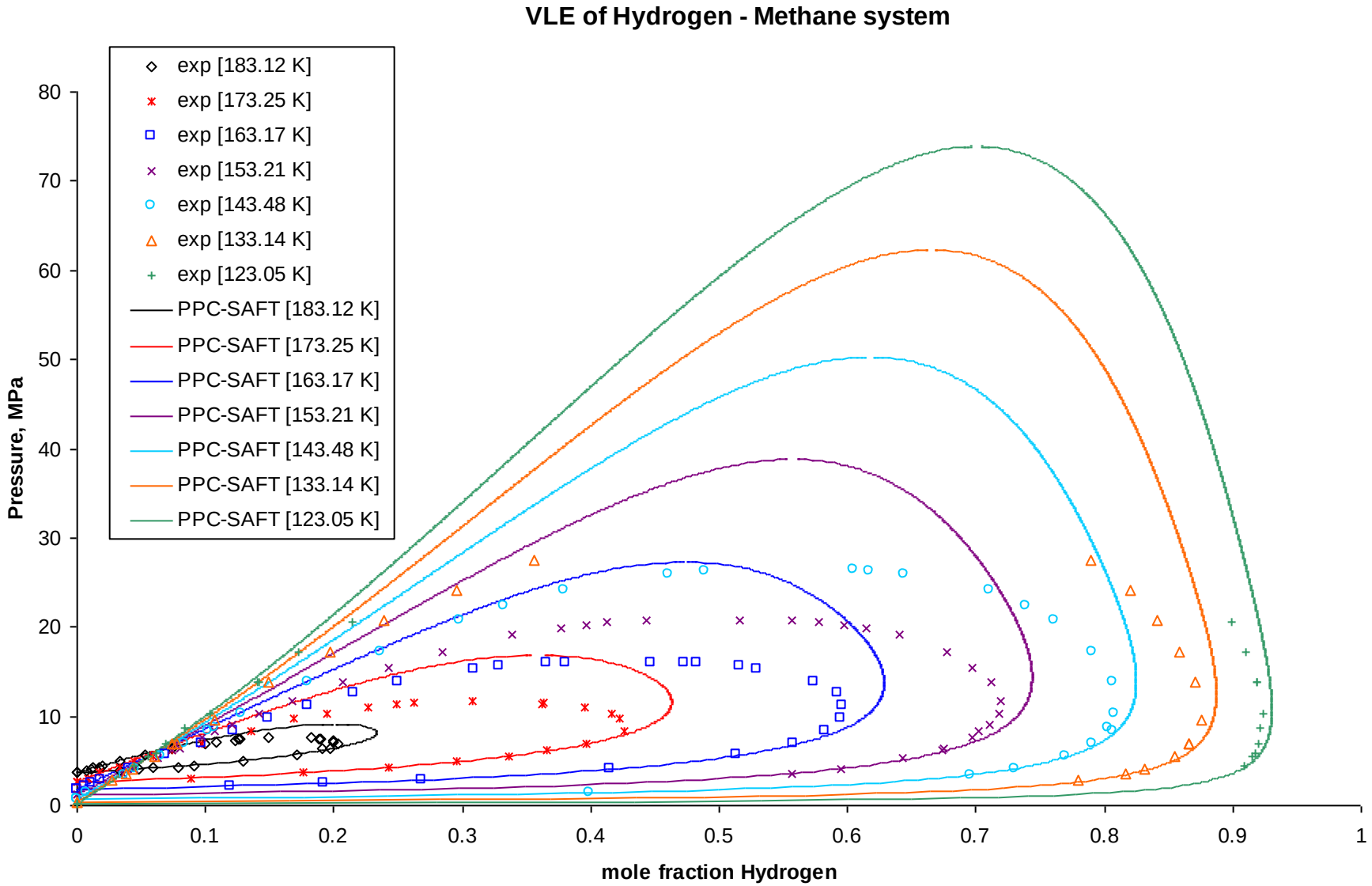
$$Z^{assoc} = \rho \sum_A \left(\frac{1}{X^A} - \frac{1}{2} \right) \frac{\partial X^A}{\partial \rho}, \quad X^A = f(\kappa^{assoc}\ \varepsilon^{assooc})$$

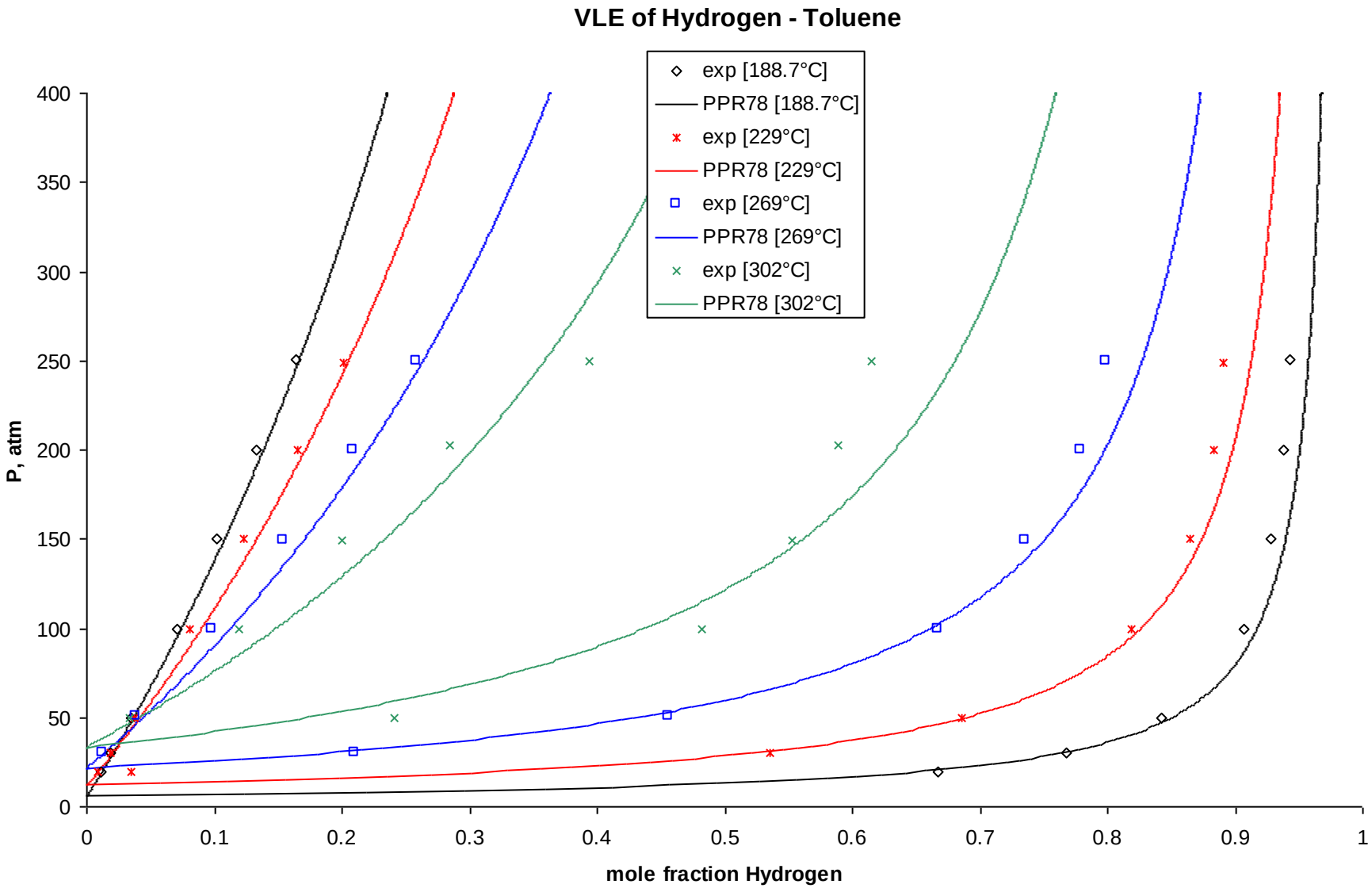


Modeled as a chain of *m* spherical segments

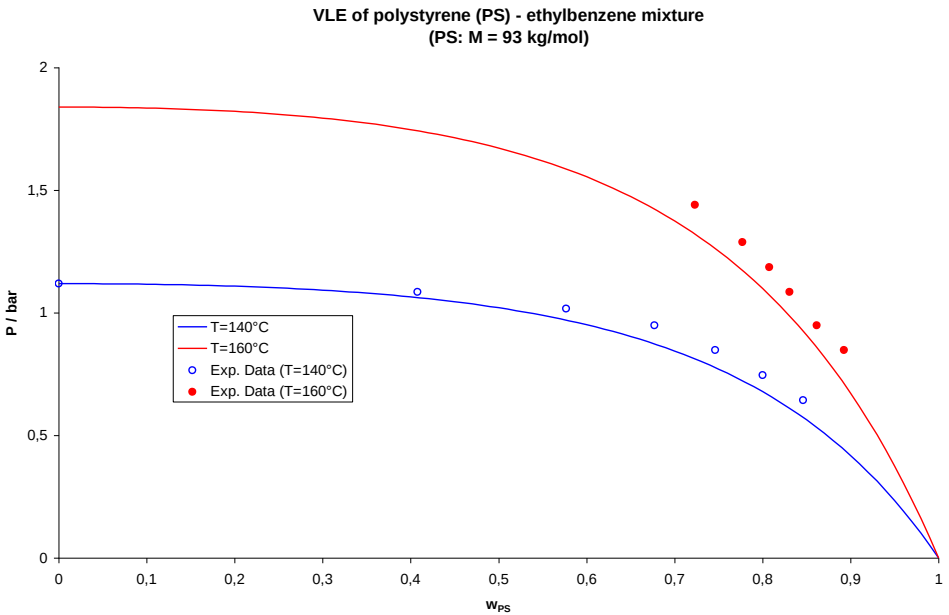
Association sites

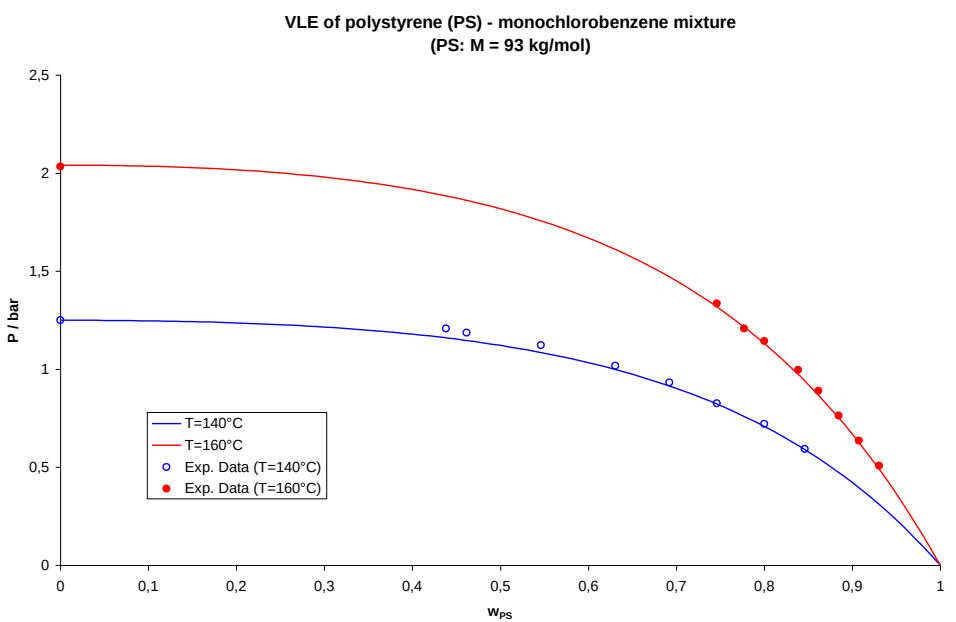



VLE of Hydrogen - Methane system
exp [183.12 K]
exp [173.25 K]
exp [163.17 K]
exp [153.21 K]
exp [143.48 K]
exp [133.14 K]
exp [123.05 K]
PPC-SAFT [183.12 K]
PPC-SAFT [173.25 K]
PPC-SAFT [163.17 K]
PPC-SAFT [153.21 K]
PPC-SAFT [143.48 K]
PPC-SAFT [133.14 K]
PPC-SAFT [123.05 K]
Pressure, MPa
0
10
20
30
40
50
60
70
80
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
mole fraction Hydrogen


VLE of Hydrogen - Toluene
exp [188.7°C]
PPR78 [188.7°C]
exp [229°C]
PPR78 [229°C]
exp [269°C]
PPR78 [269°C]
exp [302°C]
PPR78 [302°C]
P, atm
0
50
100
150
200
250
300
350
400
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
mole fraction Hydrogen

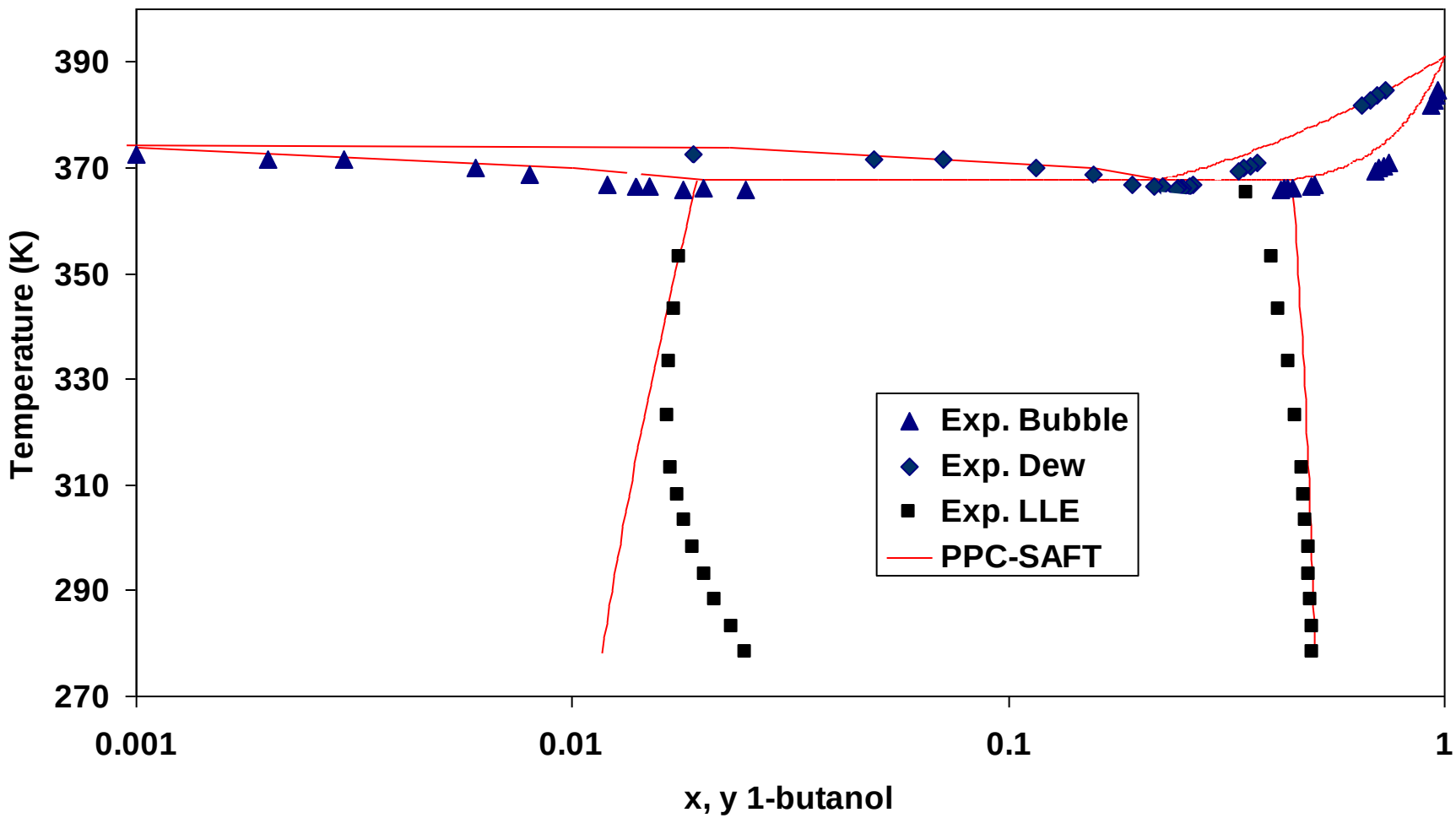
PPC-SAFT



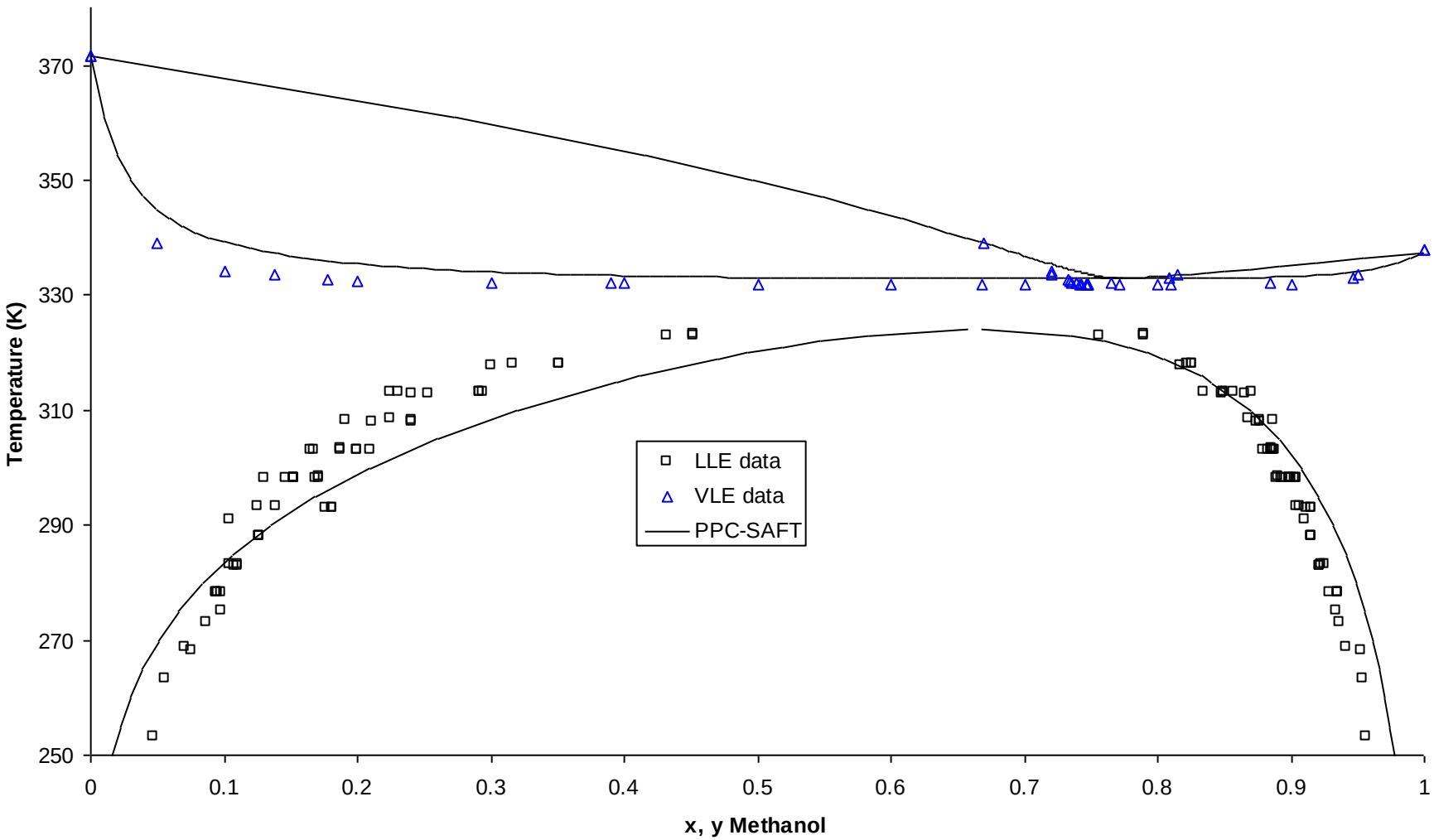


GROSS J., SADOWSKI G., “Modeling Polymer Systems Using the Perturbed-Chain Statistical Associating Fluid Theory Equation of State”, Ind. Eng. Chem. Res., 41, 1084-1093 (2002)

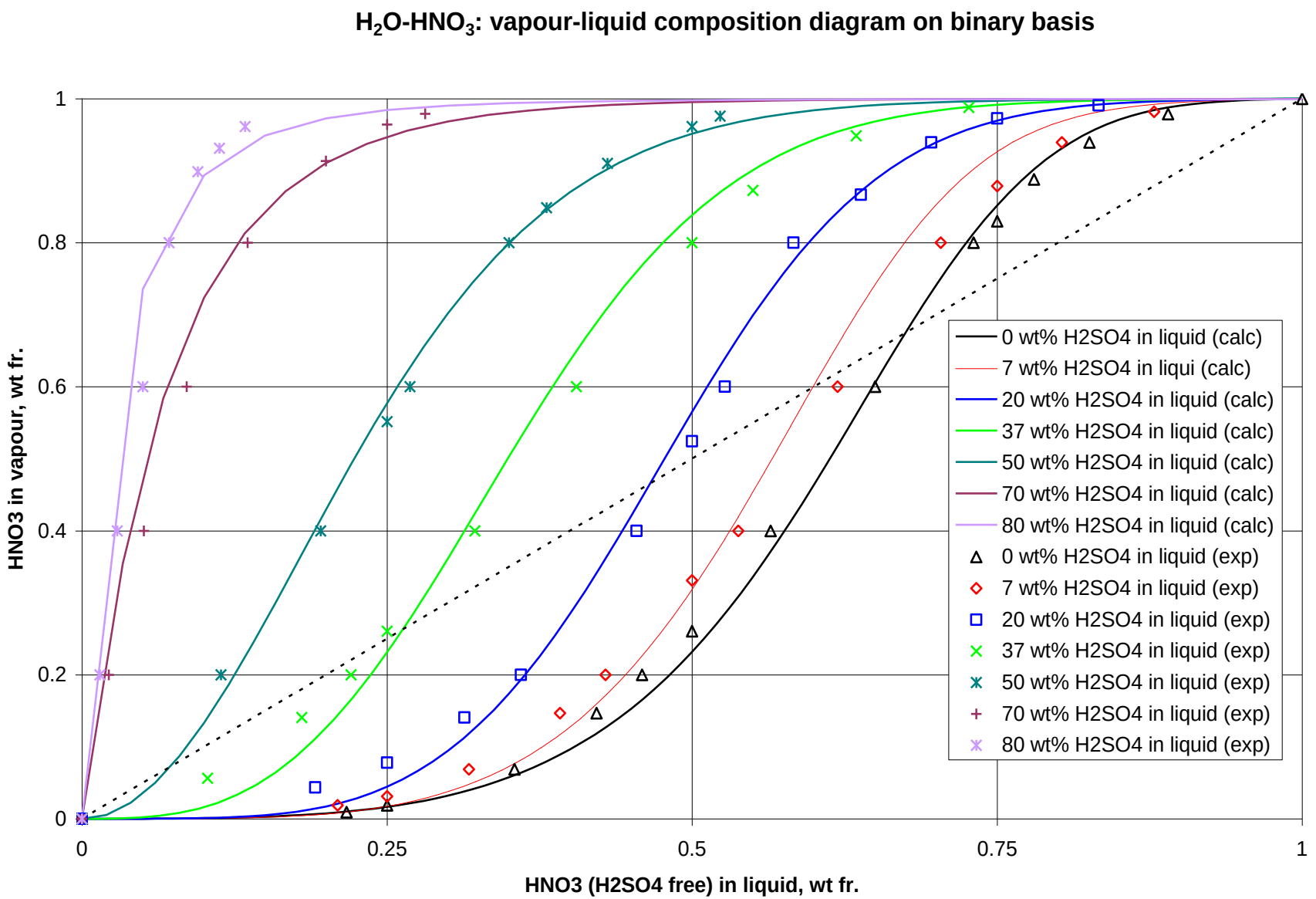
VLLE of Water - 1-Butanol mixture at atmospheric pressure



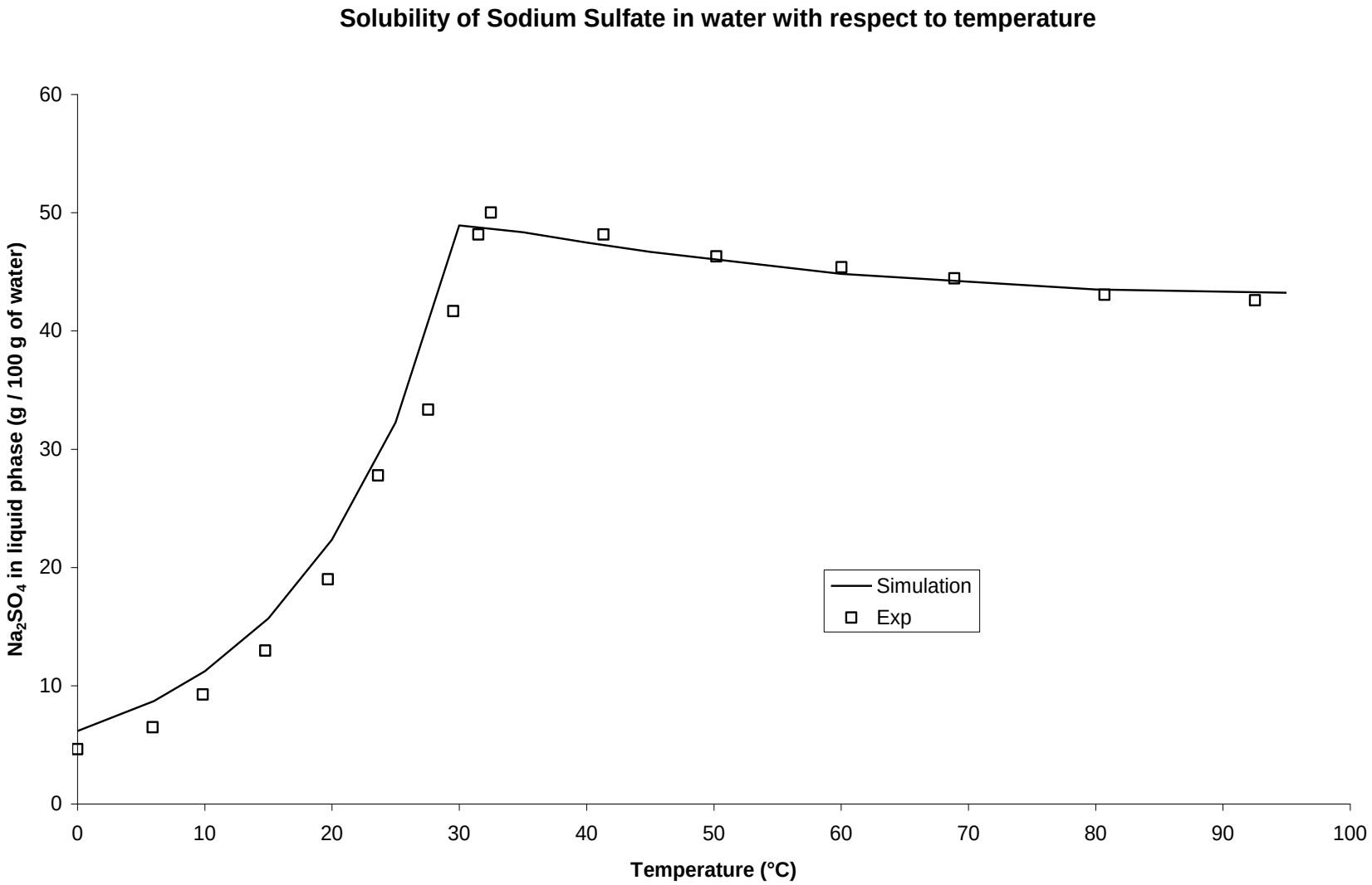
VLLE of Methanol - n-Heptane mixture at atmospheric pressure



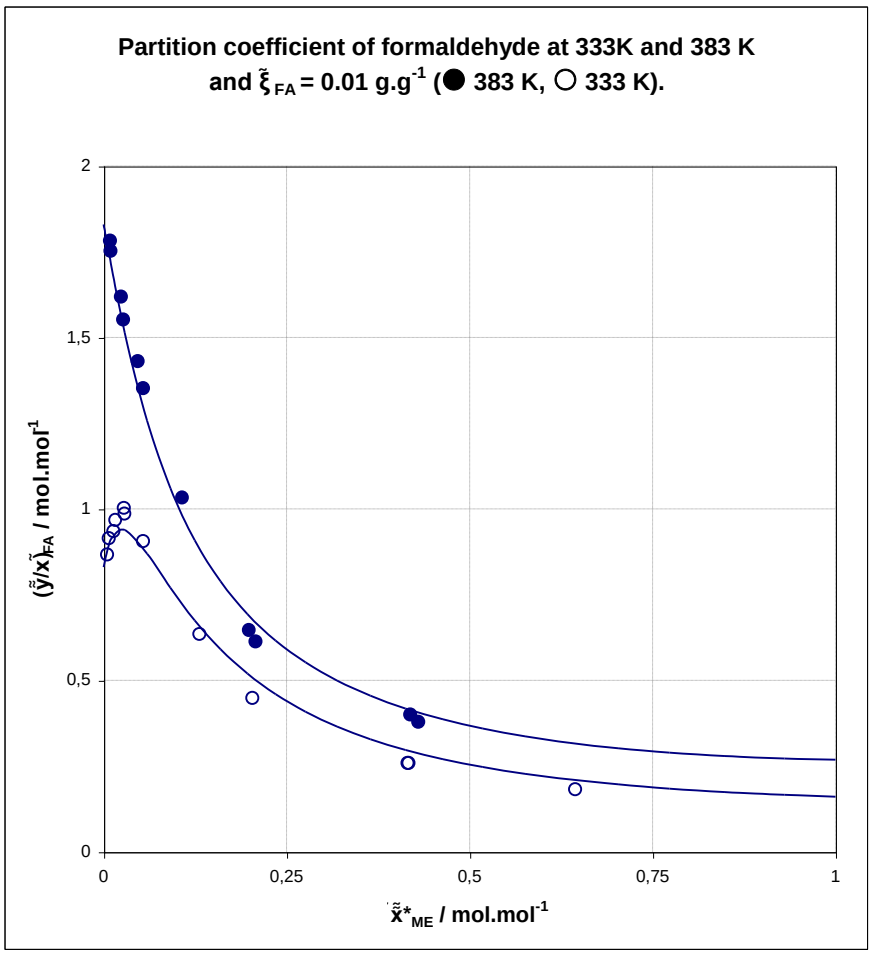
Specific models: Electrolytes



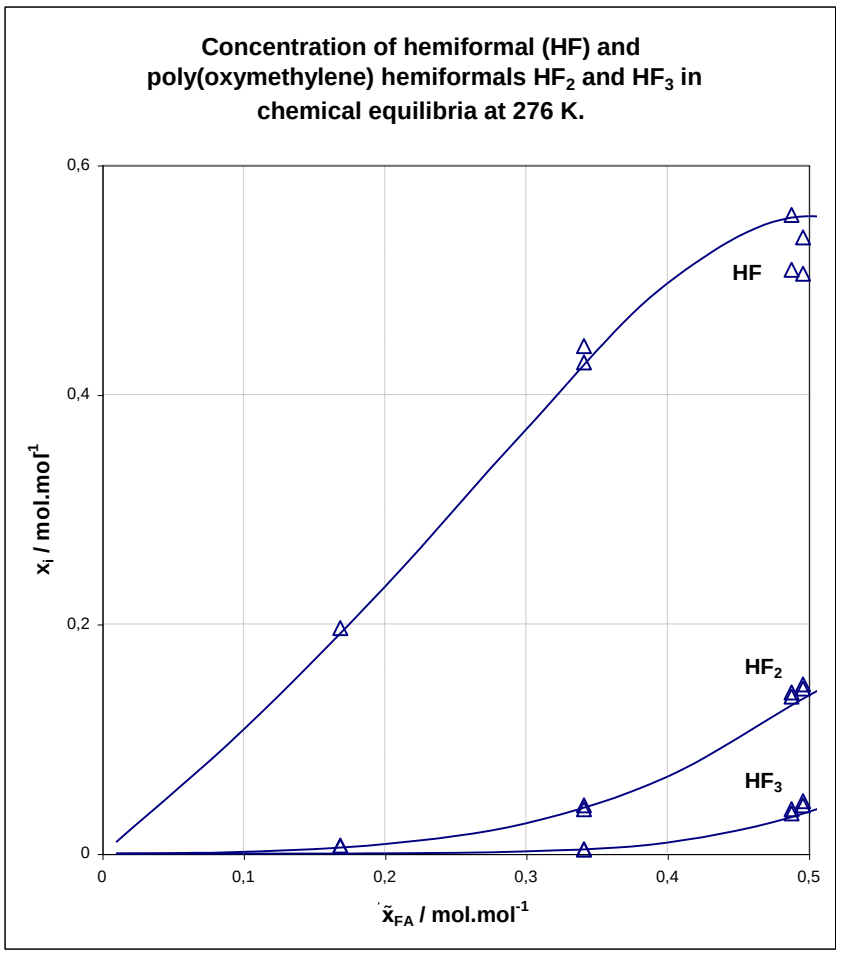
Specific models: Electrolytes



Specific Models: Reactive Systems

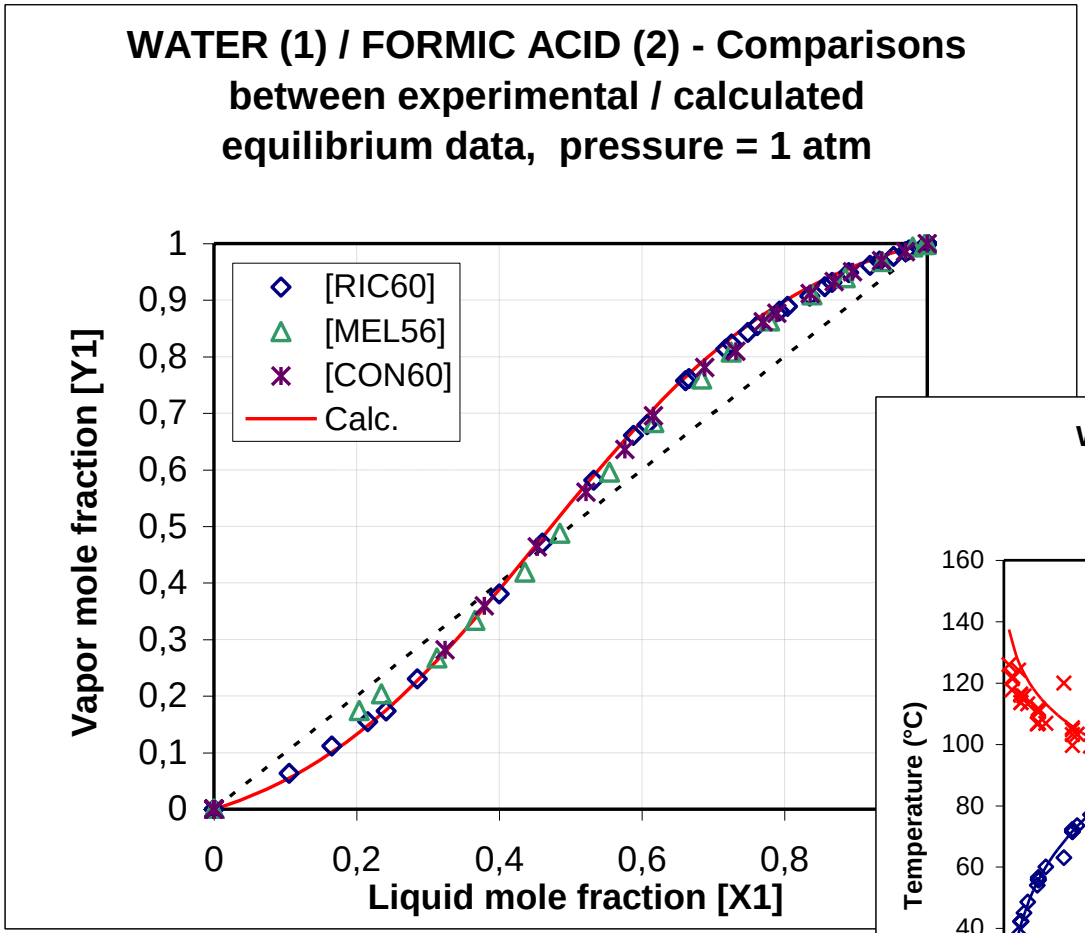


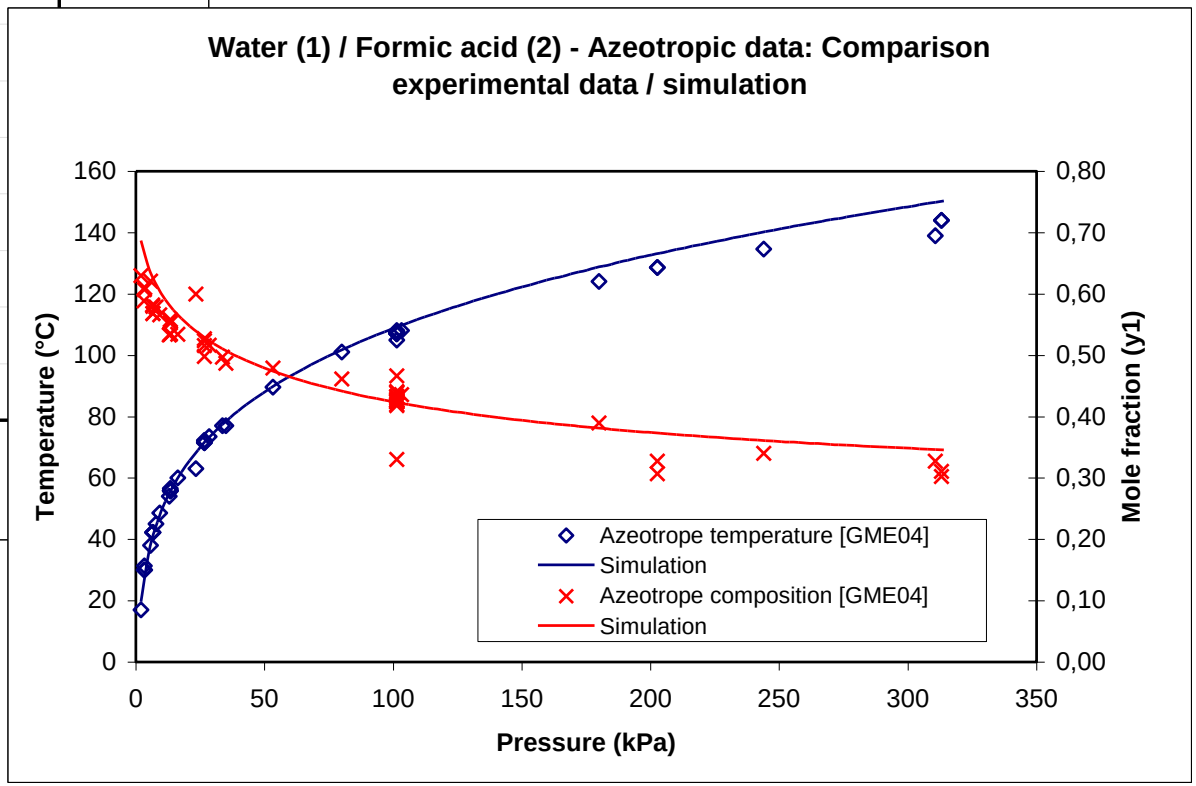
Partition coefficient of FA in the FA-water-methanol system



Concentration of HF, HF2 and HF3 in chemical equilibria at 276 K

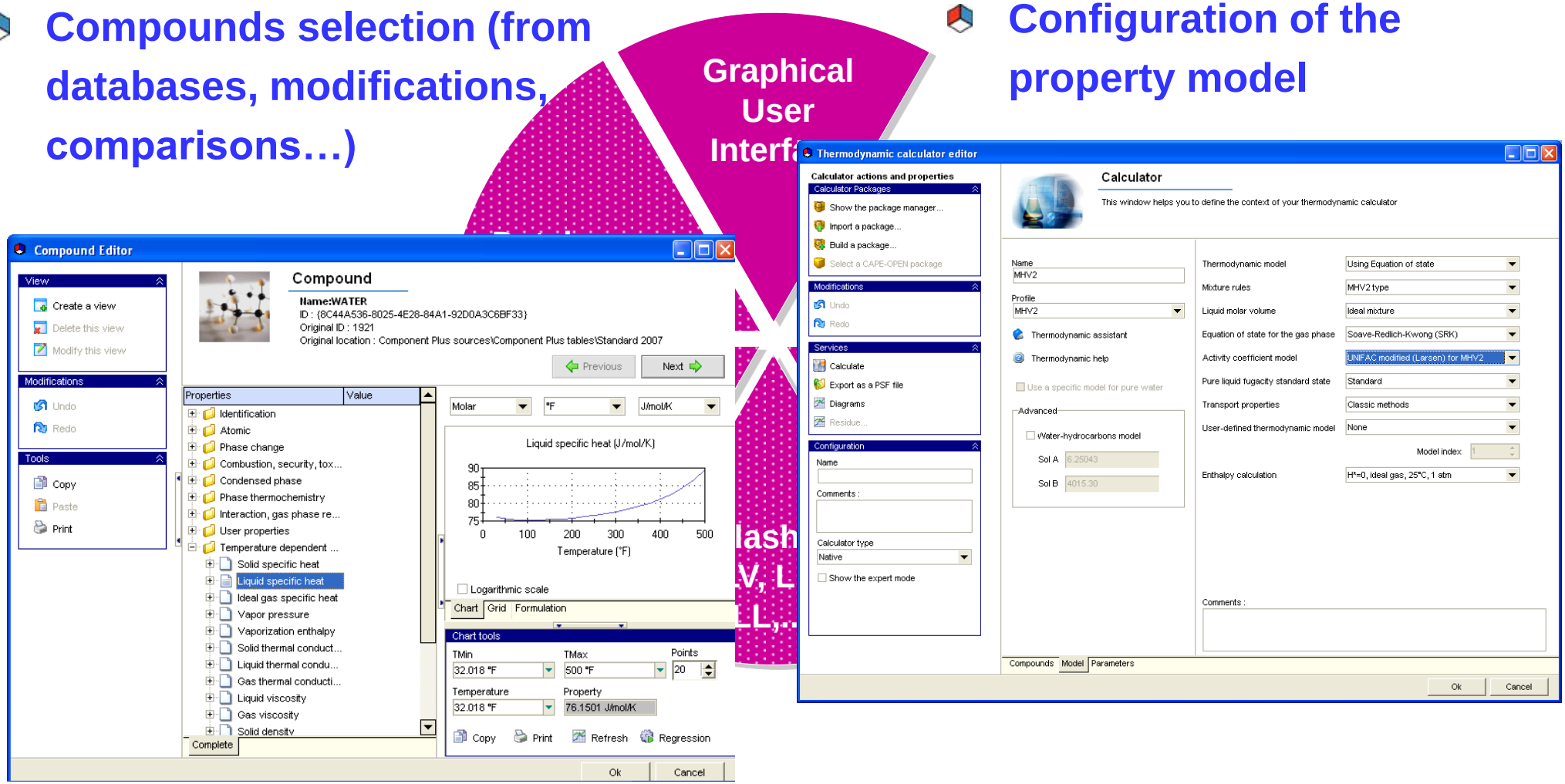
Specific Models: Reactive Systems



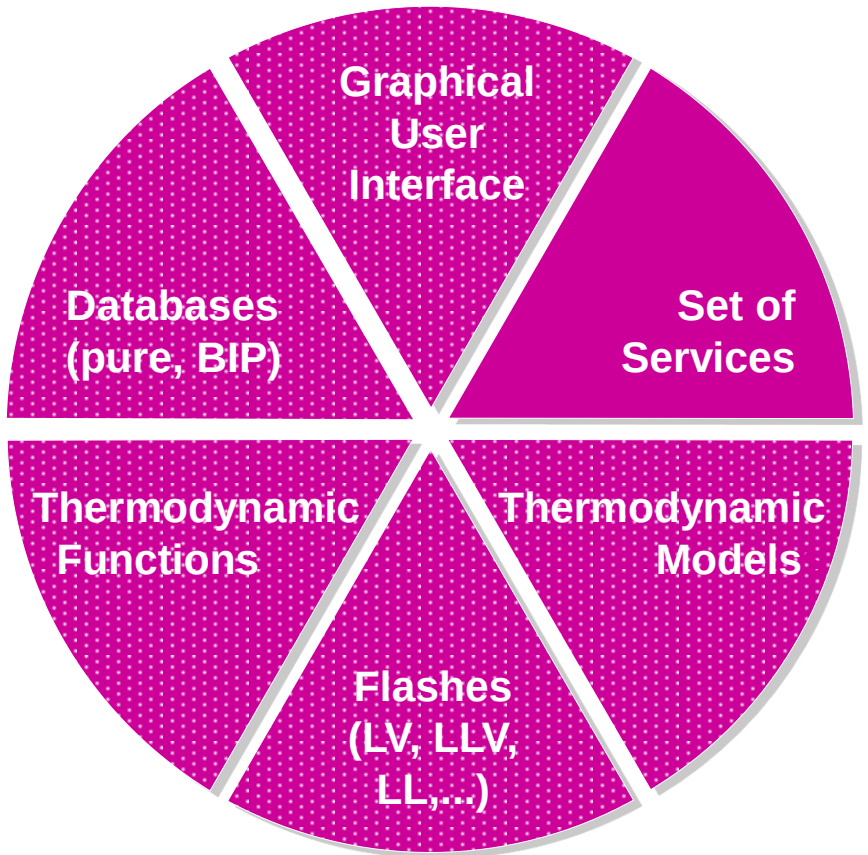


Simulis® Thermodynamics

- **Compounds selection (from databases, modifications, comparisons…)**
- **Configuration of the property model**



Simulis® Thermodynamics

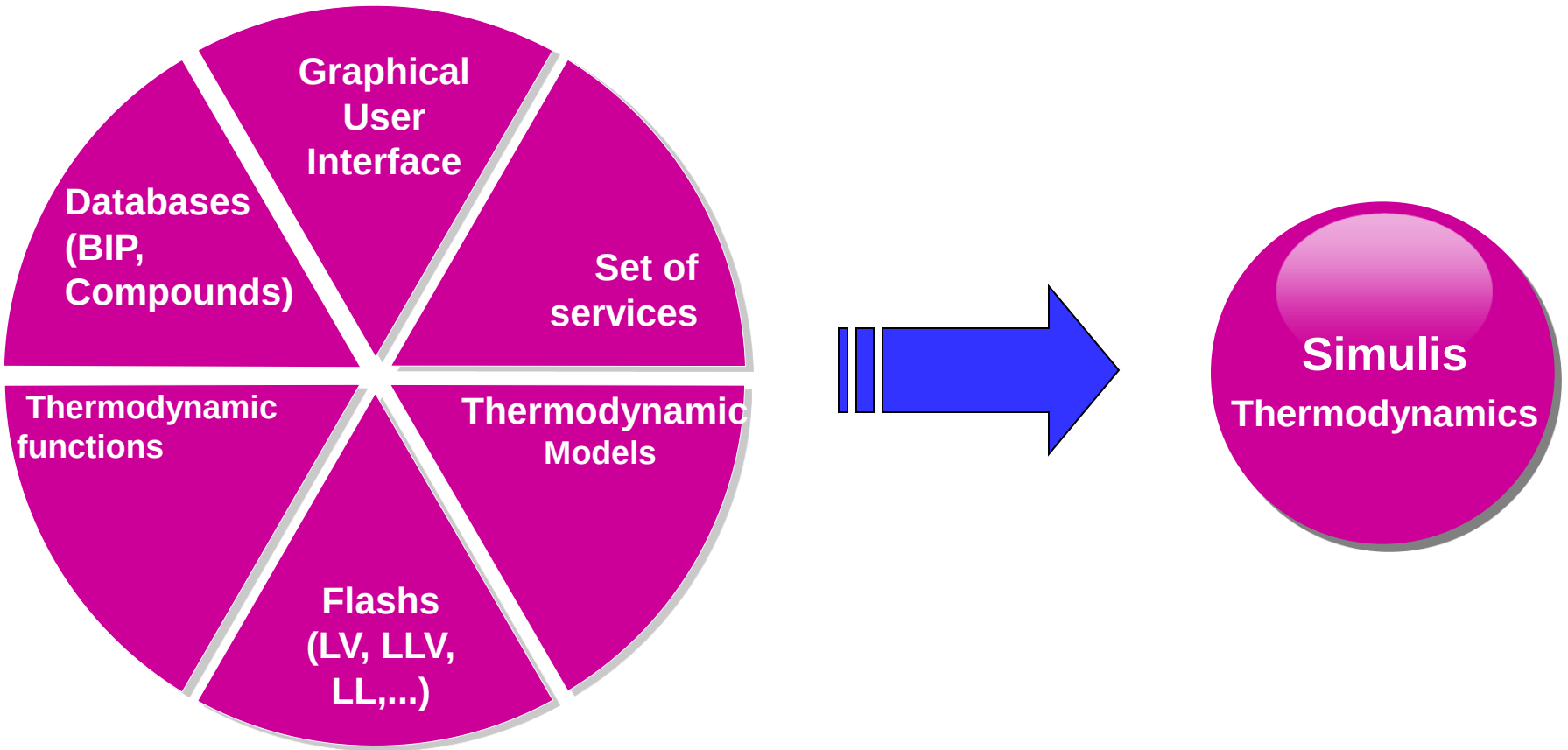


A Range of Services Available

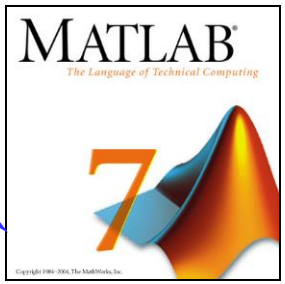
- An interactive calculation service
- Graphical display of properties on temperature, pressure or composition ranges
- Calculation of petroleum fractions properties
- Management of group contribution predictive models
- Estimation of pure component properties
- Data regression of pure components experimental properties
- Unit conversions management tool
- etc…

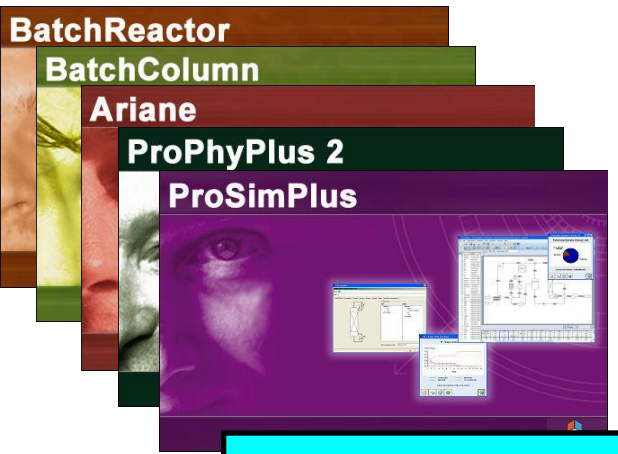
⇨**Provide user with quite all tools required for thermodynamics analysis**

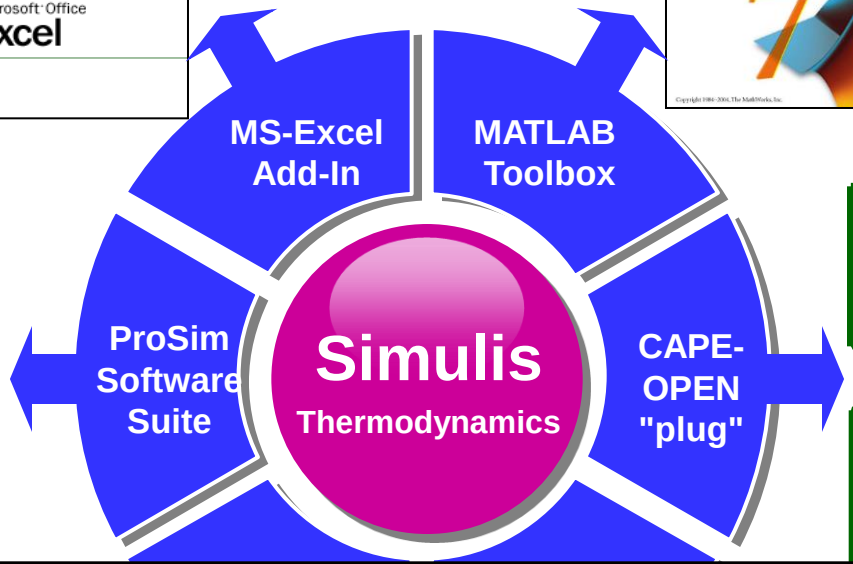
Simulis® Thermodynamics



Simulis® Thermodynamics Can Be Used in a Number of Ways





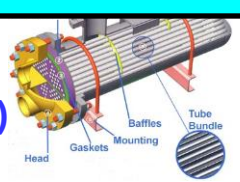


Modeling tool implementing CO Thermo Socket
Aspen Plus, ProII, Aspen HYSYS, HTRI, gPROMS …

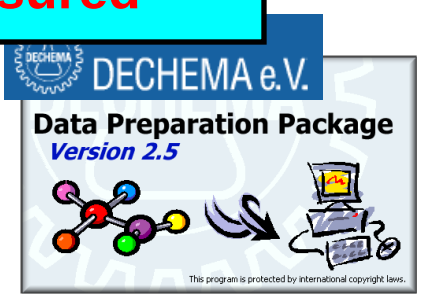
Using Simulis® Thermodynamics, thermodynamic calculation consistency between software is automatically ensured

Tabulate

- **MS-E**
- **Aspen TASC** (PSF file)
- **OLGA** (PVT file) SPT GROUP



Your software
(C++, VB, FORTRAN,…)

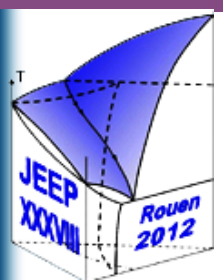


Thank you for your attention!

Using Accurate Models for Process Modelling

Journées d'Etude des Equilibres entre Phases

Rouen - 29 et 30 mars 2012



Olivier Baudouin (ProSim)

Stéphane Déchelotte

Alain Vacher

ProSim

Equation of State Approach with Complex Mixing Rules (EoS/G^E)

$$G^{ex} = RT\left(\ln\Phi - \sum x_i \ln\Phi_i\right)$$

- **Huron – Vidal (Reference state: infinite pressure)**

$$P \to \infty \qquad V \to b \qquad G^{ex} \to \text{mod}\, G^e_\gamma$$

$$\Rightarrow \quad a = b\left[\sum x_i \frac{a_i}{b_i} + \frac{G^e_\gamma\left(T, x_i\right)}{C^*}\right] \qquad b = \sum_i x_i b_i$$

- **Huron – Vidal Modified by Michelsen (Reference state: null pressure)**

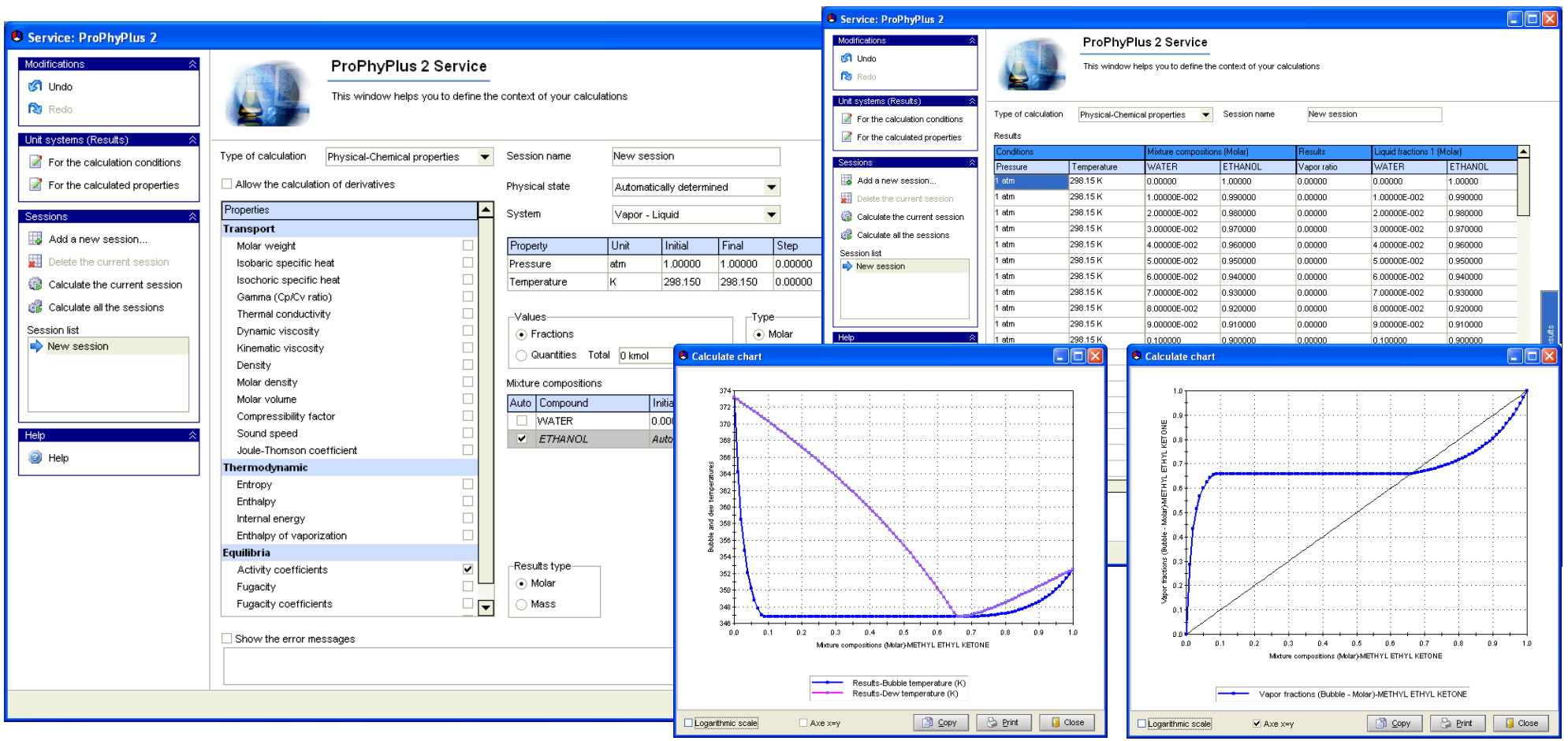
$$P \to 0 \qquad G^{ex}_0 \to \text{mod}\, G^e_\gamma$$

$$\alpha = \sum x_i\alpha_i + \frac{1}{q_1}\left[\frac{G^e_\gamma\left(T, P=0, x_i\right)}{RT} + \sum x_i \ln\frac{b}{b_i}\right] \quad (\text{MHV1, PSRK})$$

$$q_1\left(\alpha - \sum x_i\alpha_i\right) + q_2\left(\alpha^2 - \sum x_i\alpha_i^2\right) = \frac{G^e_\gamma\left(T, P=0, x_i\right)}{RT} + \sum x_i \ln\frac{b}{b_i} \quad (\text{MHV2})$$

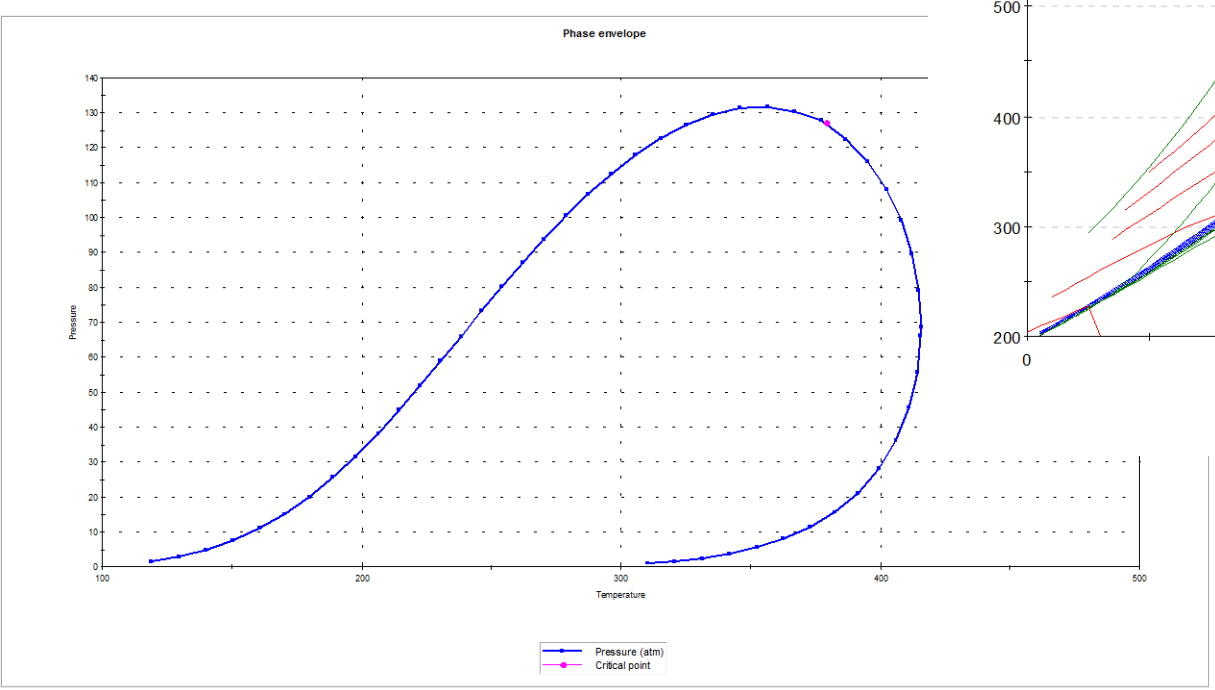
A Range of Services Available

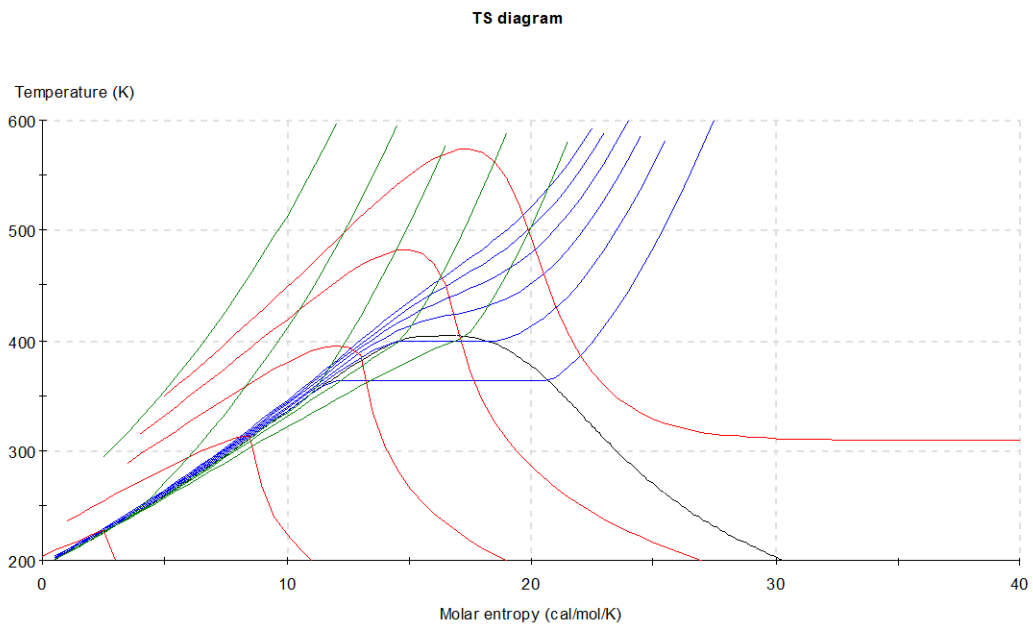
An interactive calculation service



A Range of Services Available

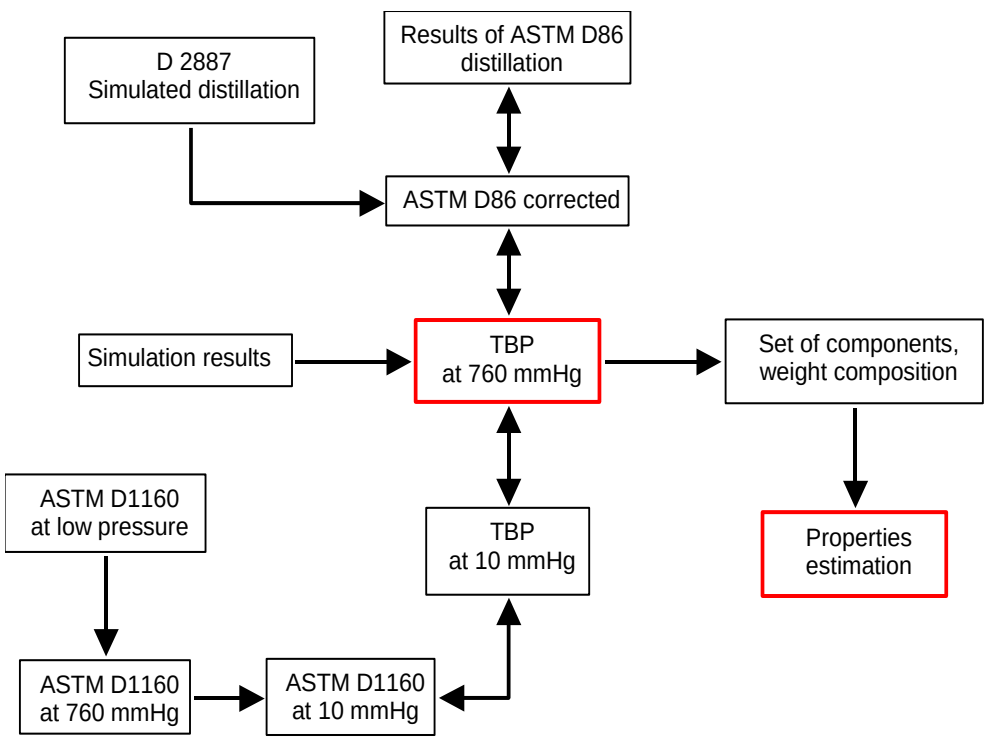
- An interactive calculation service
- **Graphical display of properties on temperature, pressure or composition ranges**





A Range of Services Available

- An interactive calculation service
- Graphical display of properties on temperature, pressure or composition ranges
- **Calculation of petroleum fractions properties**



A Range of Services Available

- An interactive calculation service
- Graphical display of properties on temperature, pressure or composition ranges
- Calculation of petroleum fractions properties
- **Management of group contribution methods versions**
  - **Several versions are supported:**
    - UNIFAC original
    - UNIFAC (Dortmund) modified
    - UNIFAC (Dortmund) LL
    - UNIFAC (Lyngby) modified Larsen
    - UNIFAC formaldehyde
    - PPR78
    - NRTL-PR
  - **A group contribution models editor is supplied**

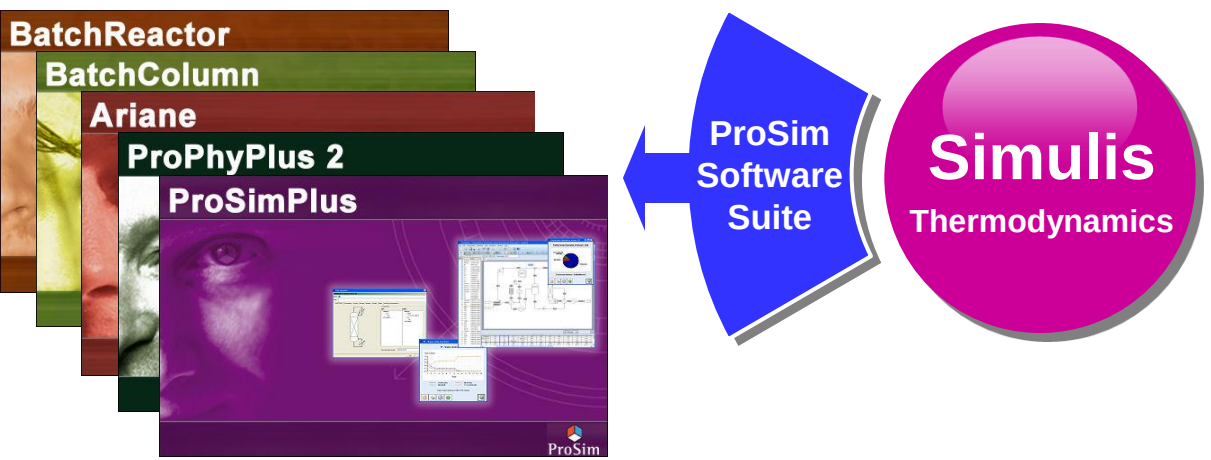
A Range of Services Available

- An interactive calculation service
- Graphical display of properties on temperature, pressure or composition ranges
- Calculation of petroleum fractions properties
- Management of UNIFAC versions
- **Estimation of pure component properties**
- **Data regression of pure components experimental properties**
- **Unit conversions management tool**
- **etc…**

⇨**Provide user with quite all tools required for thermodynamics analysis**

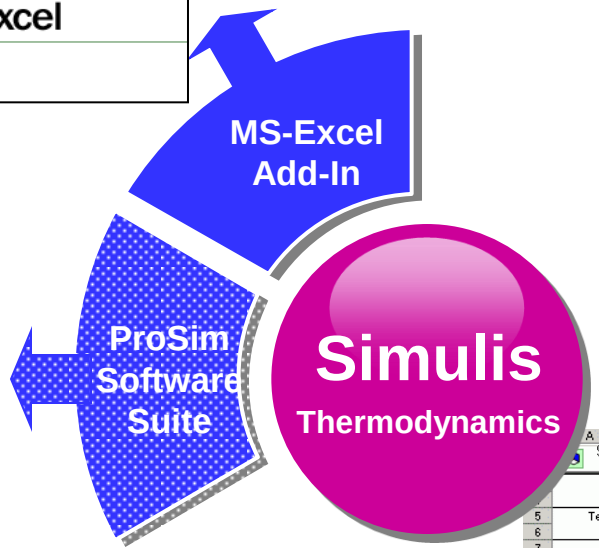
Simulis® Thermodynamics Can Be Used in ProSim Software Suite

- **Since Simulis® Thermodynamics is a software component it must be embedded in another application**

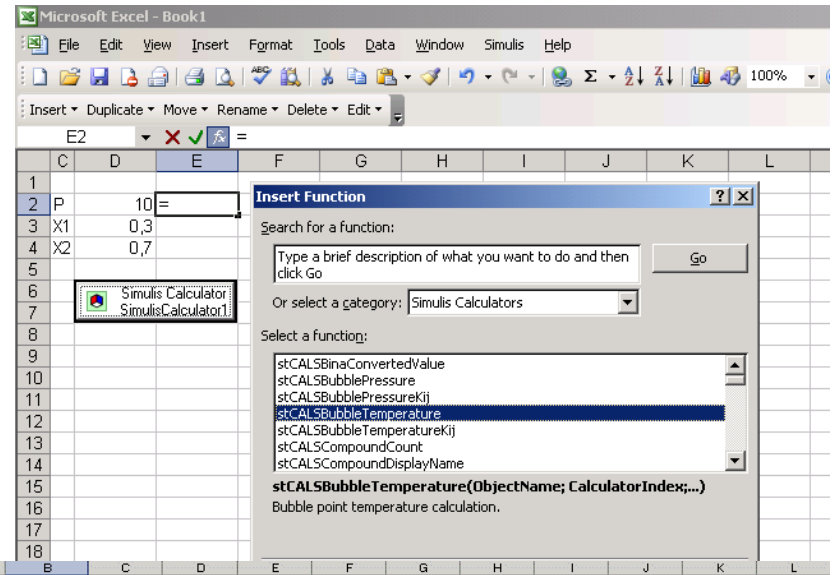


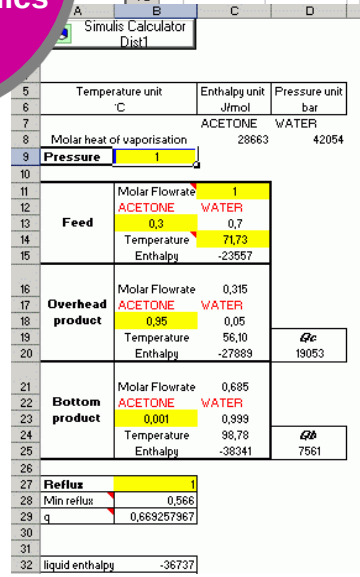
⇨ ***Simulis® Thermodynamics is the thermodynamic "heart" of all ProSim software suite***

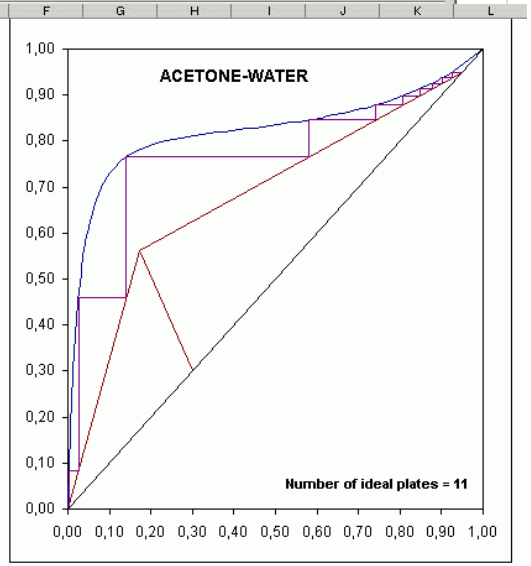
Simulis® Thermodynamics Can Be Used Within MS-Excel®



- **Thermodynamic functions are added to Microsoft® Excel**
- **…and used in spreadsheets as native functions…**
- **…to perform more or less complex engineering calculations (with rigorous thermodynamics)…**
- **… to fit BIP of models**

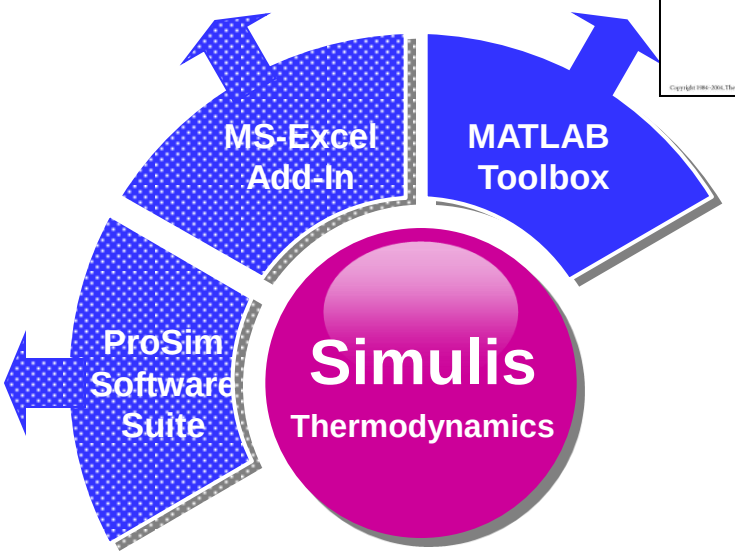






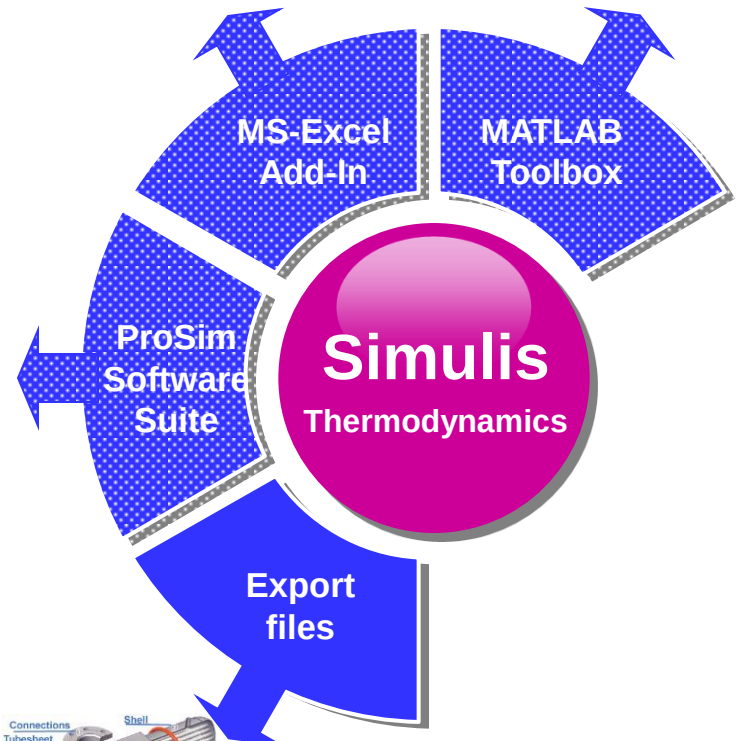
Simulis® Thermodynamics Can Be Used Within MATLAB®

- **Simulis® Thermodynamics is provided as a toolbox in MATLAB®**



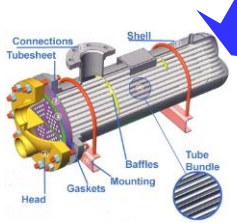
⇨ ***Rigorous thermodynamics become available in MATLAB® without further programming effort***

Simulis® Thermodynamics Can Export Result Files to Other Packages



Tabulated results to :

- **MS-Excel**
- **Aspen TASC** (PSF file)

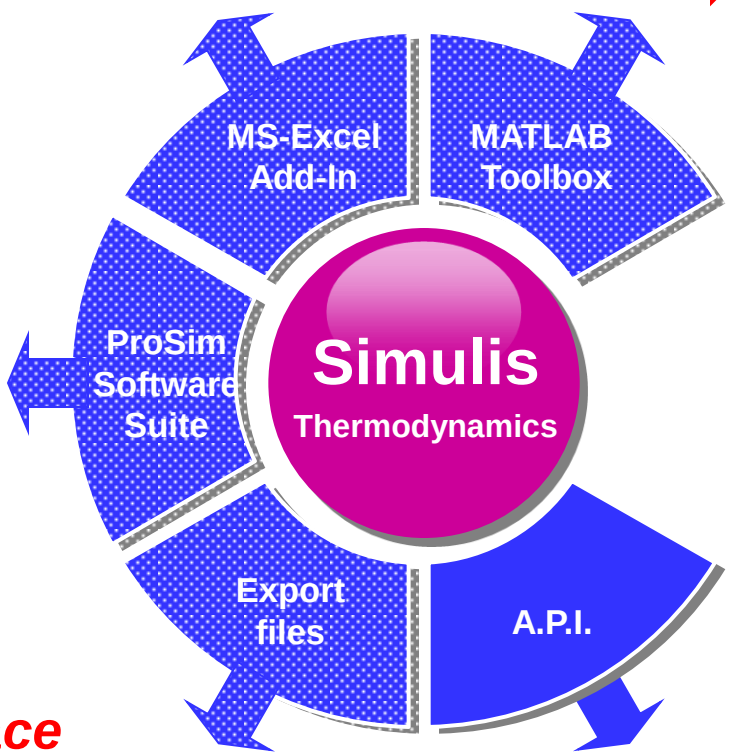


- **OLGA** (PVT file) SPT GROUP

Simulis® Thermodynamics Can Be Used Within Your Software

A complete Application Programming Interface (API) is also provided

- ✓ Visual Basic
- ✓ C++
- ✓ Delphi
- ✓ FORTRAN
- ✓ C#
- ✓ etc…



⇨ ***Simulis® Thermodynamics can be easily embedded in any application supporting the COM/DCOM technology***

⇨ ***However, the interface between the embedding application and Simulis® Thermodynamics must be coded***

Your software
(C++, VB, FORTRAN,…)

Simulis® Thermodynamics Can Be Used Within CO Compliant Packages