

# Select a thermodynamic model for process simulation: a practical guide to a three-steps methodology

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# Objectif

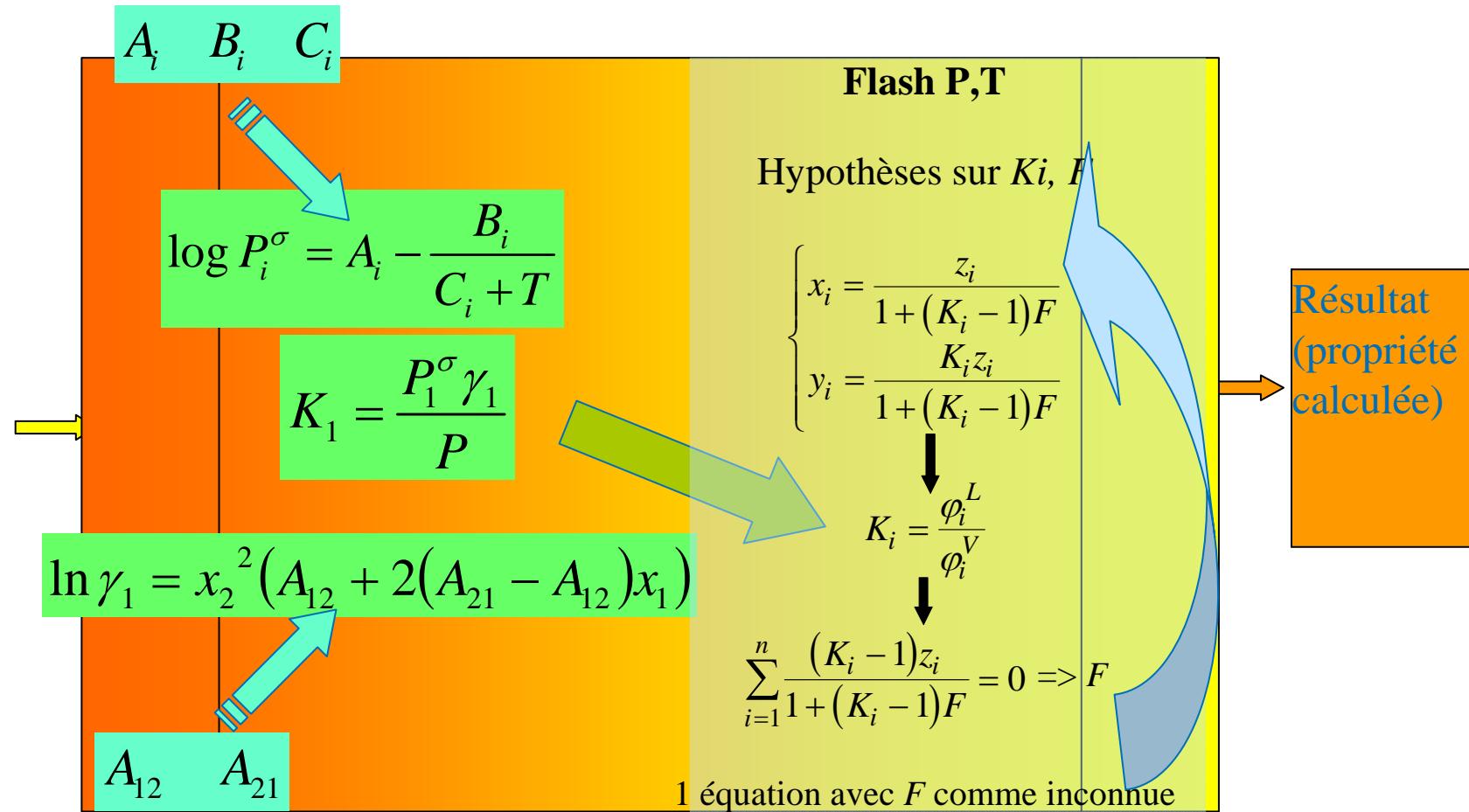
- Ouvrage de référence contenant les outils (formulaires, équations de base, ...)
- pour qu'un ingénieur procédé puisse se débrouiller seul, et connaître ses limites
  
- Non un ouvrage de cours
- Non un ouvrage pour experts

# Les chapitres

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- Introduction: Philosophie générale
- 'From Fundamentals to Properties'
- 'From Components to Models'
- 'From phases to method (models) selection'
- Case studies

# La philosophie: Qu'est-ce qu'une méthode thermo?



# Se poser les bonnes questions

- Qu'est-ce que j'ai / qu'est-ce que je cherche?
  - -> comprendre les principes
  - -> propriétés intermédiaires?
- Quels fluides  $\Leftrightarrow$  comment paramétrier les modèles ?
  - Constituants
  - Les données
  - Les modèles
- Où se situe le procédé dans le diagramme de phases?

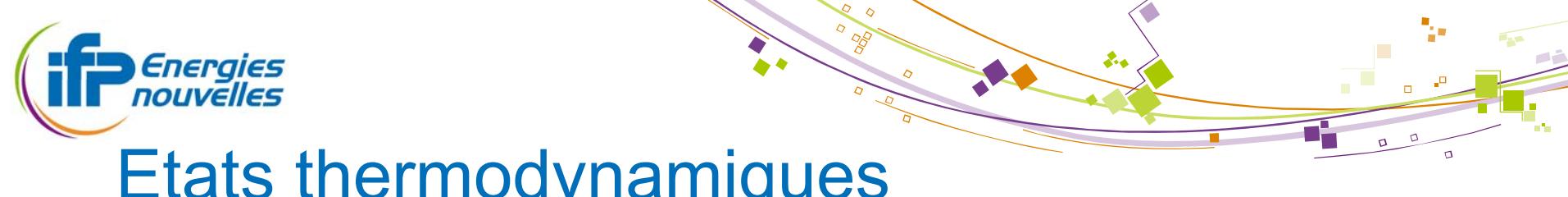
# From fundamentals to properties

## ■ Définitions

- Les propriétés
- Les états thermodynamiques
- Les règles de phases

## ■ Modes de calcul

- Relations entre propriétés
- Approches résiduelle et excès
- Les équilibres de phase
- Les équilibres chimiques



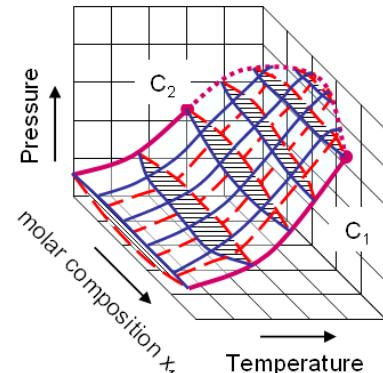
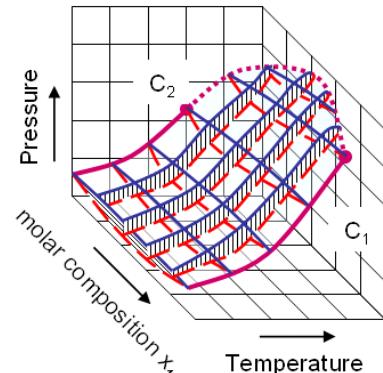
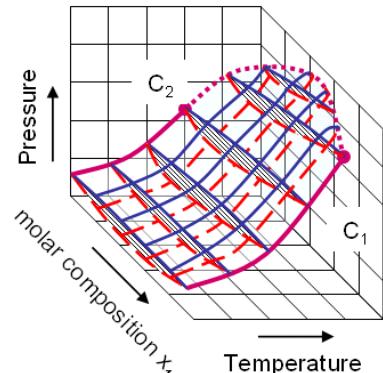
# Etats thermodynamiques

<b>Temper (K)</b>	<b>Pressure (kPa)</b>	<b>Used by</b>	<b>Known as</b>	<b>(L/mol)</b>
273.15 (0 °C)	101.325 (1 atm)	IUPAC (before 1982), NIST	Standard conditions, Normal cubic meter, DIN 1343	22.414
273.15 (0 °C)	100	IUPAC (since 1982)	Standard temperature and pressure (STP), Standard conditions, ISO 13443	22.711
288.15 (15 °C)	101.325 (1 atm)	European gas companies	International standard atmosphere (ISA), Normal cubic meter, ISO 2533	23.645
293.15 (20 °C)	101.325 (1 atm)	NIST [10]	Ambient, Room	24.055
298.056 (60 °F)	101.325 (14.696 psi)	American gas companies, SPE	Standard cubic feet	24.458
298.056 (60 °F)	101.5598 (14.73 psi)	American gas companies, OPEC	Standard cubic feet	24.401
298.15 (25 °C)	101.325 (1 atm)		Ambient, Room	24.465
298.15	100	NBS [11]		24.790

# Règles de phases

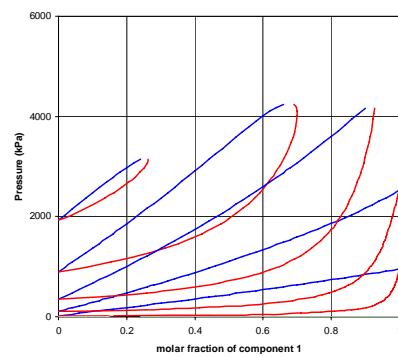
## Généralités

Thermodynamique  
pour la simulation

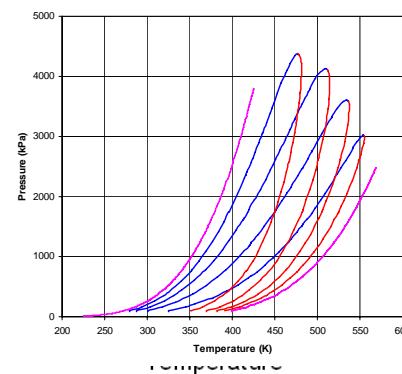


## Géométrie

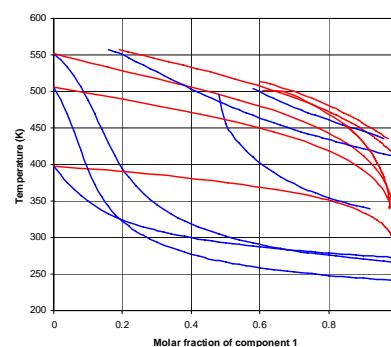
iso-temperatures



iso-compositions



iso-pressures



# Les règles de phase

**Table 2-7: Duhem's phase rule: most frequently encountered combinations of data types given**

<i>Flash type</i>	<i>Meaning</i>	<i>Applications</i>
<i>PT</i>	<i>pressure and temperature given</i>	<i>Basic case</i> <i>Used in all calculations</i>
<i>Tθ or Pθ</i>	<i>temperature or pressure and vapour fraction given</i>	<i>Bubble point</i> <i>Dew point</i> <i>Partially vaporised flash</i>
<i>TV</i>	<i>temperature and volume given</i>	<i>closed vessel at known temperature</i>
<i>PH</i>	<i>pressure and enthalpy given</i>	<i>adiabatic distillation columns</i> <i>adiabatic expansions</i>
<i>PS</i>	<i>pressure and entropy given</i>	<i>ideal adiabatic compressors</i> <i>pumps</i> <i>turbines</i>

# Liens entre propriétés (Maxwell)

## Premier et second principes donnent:

Table 2-1: Definition of the fundamental energy properties

Table 2.13 Molar residual properties as a function of temperature and pressure

$$u^{\text{res}}(T, P) = \int_0^P \left( v - T \frac{\partial v}{\partial T} \Big|_P \right) dP + RT - Pv = \int_{\infty}^v \left( T \frac{\partial P}{\partial T} \Big|_v - P \right) dv \quad (2.65)$$

$$H^{\text{res}}(T, P) = \int_0^P \left( v - T \frac{\partial v}{\partial T} \Big|_P \right) dP = \int_{\infty}^v \left( T \frac{\partial P}{\partial T} \Big|_v - P \right) dv + Pv - RT \quad (2.66)$$

$$d^{\text{res}}(T, P) = \int_0^P \left( v - \frac{RT}{P} \right) dP + RT - Pv = \int_{\infty}^v \left( -P + \frac{RT}{v} \right) dv - RT \ln \frac{Pv}{RT} \quad (2.67)$$

$$g^{\text{res}}(T, P) = \int_0^P \left( v - \frac{RT}{P} \right) dP = \int_{\infty}^v \left( -P + \frac{RT}{v} \right) dv - RT \ln \frac{Pv}{RT} + Pv - RT \quad (2.68)$$

$$s^{\text{res}}(T, P) = \int_0^P \left( -\frac{\partial v}{\partial T} \Big|_P + \frac{R}{P} \right) dP = \int_{\infty}^v \left( \frac{\partial P}{\partial T} \Big|_v - \frac{R}{v} \right) dv + R \ln \frac{Pv}{RT} \quad (2.69)$$

# L'approche résiduelle

Table 2.14 Total properties from a residual approach

Real mixture				
Ideal mixture				
Ideal gas state ( $P_0, T_0$ )	Ideal gas state change to ( $P, T_0$ )	Ideal gas state change to ( $P, T$ )	Residual property at ( $P, T$ )	
$U = U^\#(T_0, P_0, N) + 0 + \int_{T_0}^T C_V^\#(T, N) dT$			$+ U^{res}(T, P, N)$	(2.73)
$H = H^\#(T_0, P_0, N) + 0 + \int_{T_0}^T C_P^\#(T, N) dT$			$+ H^{res}(T, P, N)$	(2.74)
$A = A^\#(T_0, P_0, N) + NRT_0 \ln\left(\frac{P}{P_0}\right) - \int_{T_0}^T (S^\#(T, P, N) + NR) dT$			$+ A^{res}(T, P, N)$	(2.75)
$G = G^\#(T_0, P_0, N) + NRT_0 \ln\left(\frac{P}{P_0}\right) - \int_{T_0}^T s^\#(T, P, N) dT$			$+ G^{res}(T, P, N)$	(2.76)
$S = S^\#(T_0, P_0, N) - NR \ln\left(\frac{P}{P_0}\right) - \int_{T_0}^T \frac{C_P^\#(T, N)}{T} dT$			$+ S^{res}(T, P, N)$	(2.77)

# L'approche excès

Table 2.15 Properties from an excess approach

	Real mixture					
	Ideal mixture					
	Pure component		Mixing contribution		Excess property	
$V$	$= \sum_{i=1}^{\mathcal{N}} N_i v_i^*$	+	0	+	$V^E$	(2.104)
$U$	$= \sum_{i=1}^{\mathcal{N}} N_i u_i^*$	+	0	+	$U^E$	(2.105)
$H$	$= \sum_{i=1}^{\mathcal{N}} N_i h_i^*$	+	0	+	$H^E$	(2.106)
$A$	$= \sum_{i=1}^{\mathcal{N}} N_i a_i^*$	+	$RT \sum_{i=1}^{\mathcal{N}} N_i \ln(x_i)$	+	$A^E$	(2.107)
$G$	$= \sum_{i=1}^{\mathcal{N}} N_i g_i^*$	+	$RT \sum_{i=1}^{\mathcal{N}} N_i \ln(x_i)$	+	$G^E$	(2.108)
$S$	$= \sum_{i=1}^{\mathcal{N}} N_i s_i^*$	-	$R \sum_{i=1}^{\mathcal{N}} N_i \ln(x_i)$	+	$S^E$	(2.109)

# L'équilibre de phases

- Le coefficient de partage
  - Approche homogène – hétérogène
  - Approche symétrique – asymétrique
- Types de flash et méthode Rachford-Rice

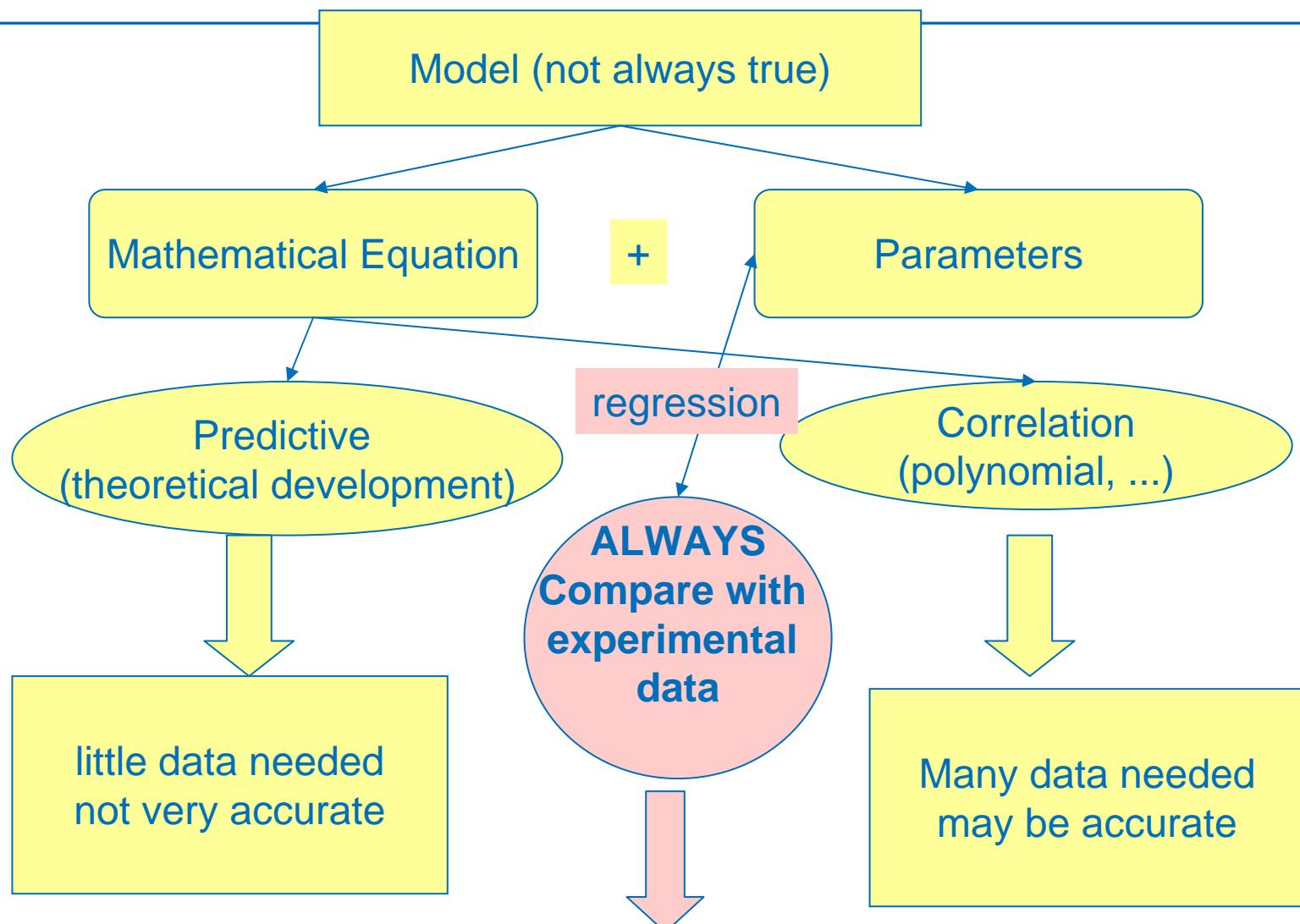
Summing up, the unknowns in a **PTflash** are  $K_i$  and  $\theta$  (i.e.  $\mathcal{N} + 1$  unknowns), and the equations to be solved are:

$$\begin{cases} K_i = \frac{\varphi_i^L}{\varphi_i^V} \\ \sum_{i=1}^{\mathcal{N}} \frac{(K_i - 1)z_i}{1 + \theta(K_i - 1)} = 0 \end{cases} \quad (2.1)$$

One possible procedure to solve the equations (known as successive substitution) is as follows:

1. Estimate the missing piece of information,  $\theta$
2. Estimate the distribution coefficients  $K_i$
3. Use (2.143) to calculate  $x_i$  and  $y_i$
4. Improve the evaluation of  $K_i$  using equations (2.127), (2.128) or (2.129)
5. Evaluate a better  $\theta$  from (2.144)
6. If  $\theta$  is different from its previous value, return to 3, otherwise the answer is reached.

# 'From Components to Models'



# 'From Components to Models'

- Les corps purs: comment caractériser?
- Les mélanges: quelles données?
- La régression: son fonctionnement
- Les modèles et leurs paramètres
- Composants clés et domaines de concentration

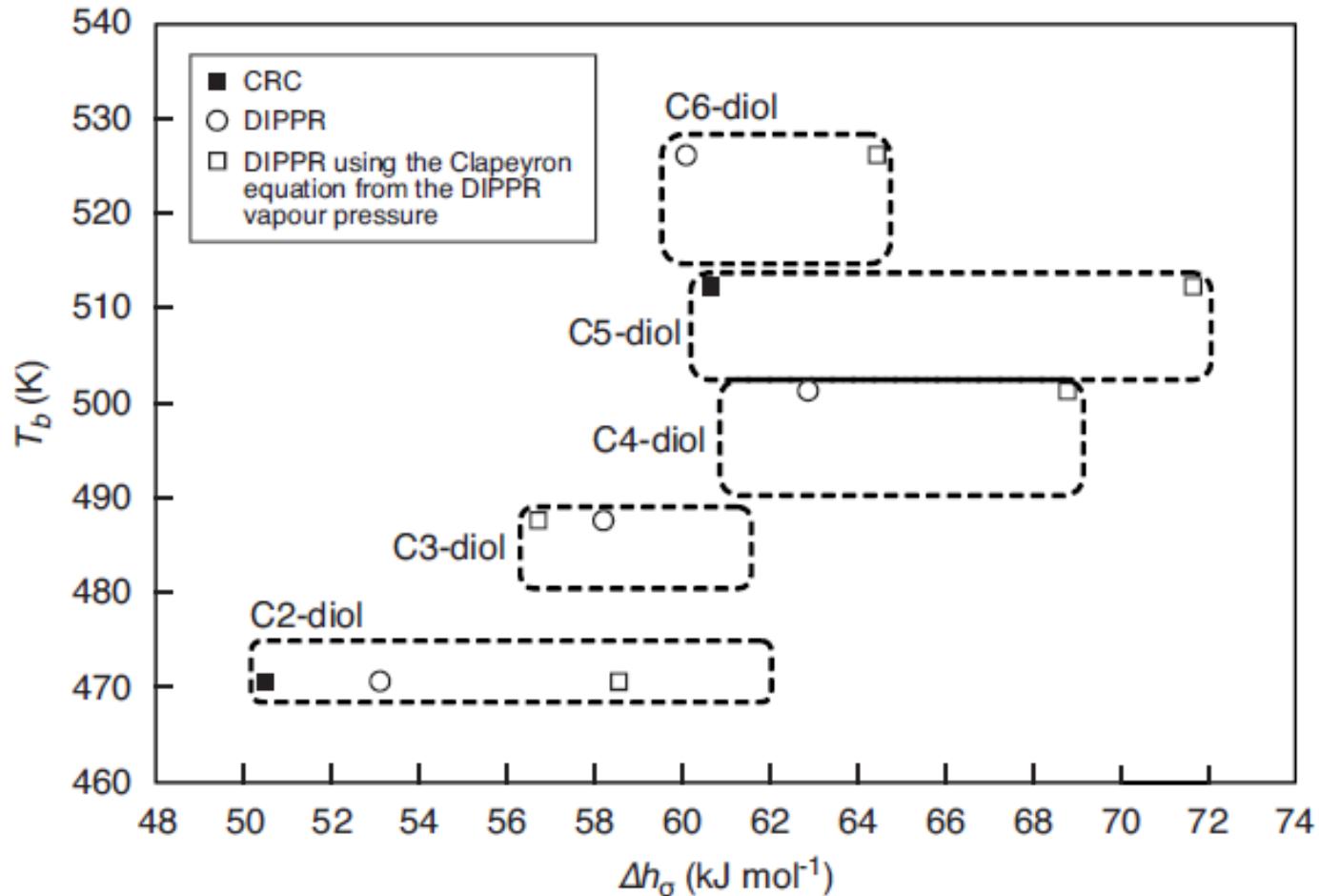
# Les corps purs

- Propriétés et paramètres
  - Constantes caractéristiques
  - Fonctions de la température
- Le type de corps
  - Issus de base de données
  - Complexes (par contribution de groupes)
  - Pseudo-constituants pétroliers: courbes de distillation et regroupements
- Quelques astuces pour évaluer la qualité des données

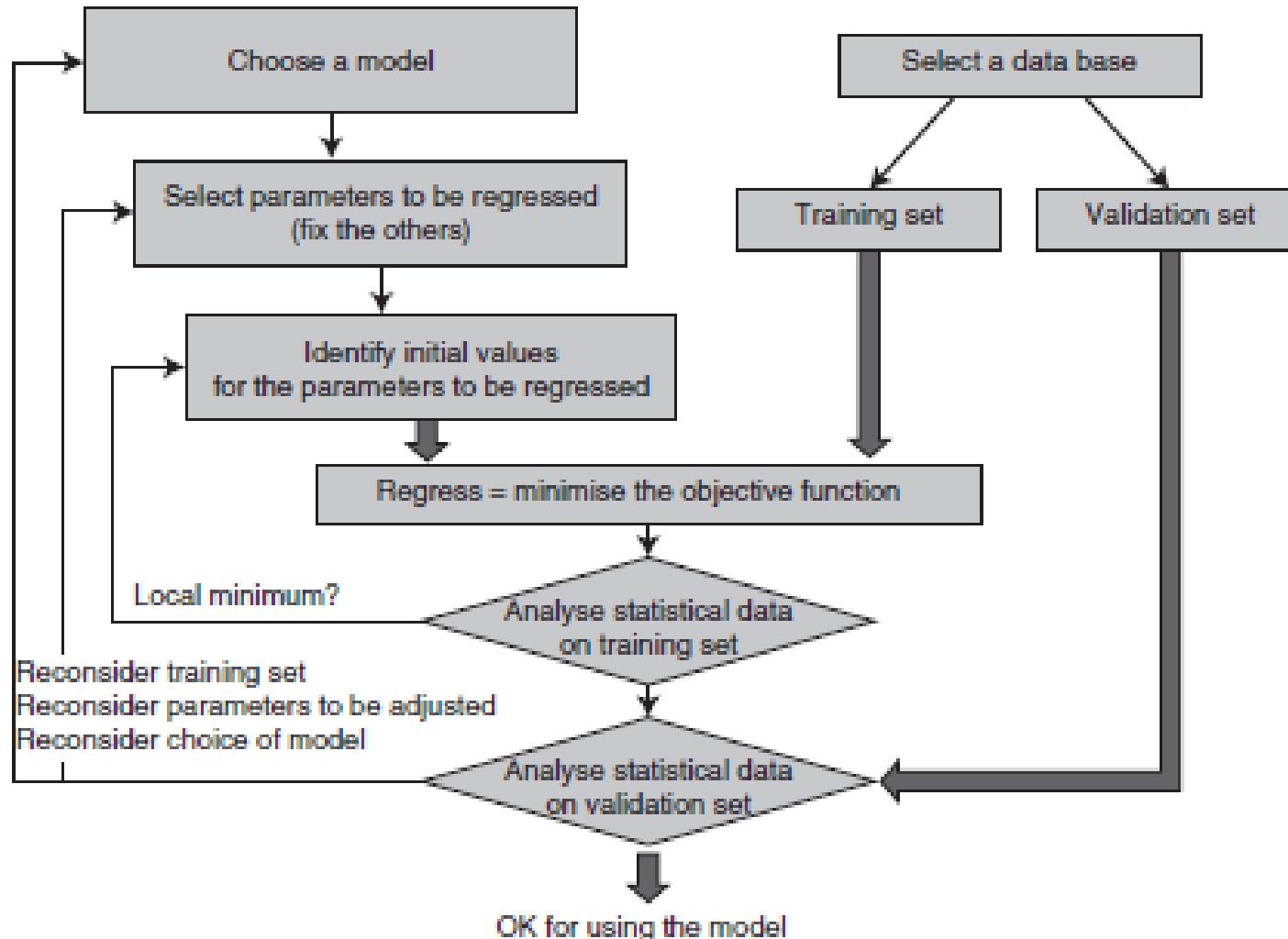
# Types de corps

- **Les corps issus de base de données**
  - Des paramètres sont disponibles et
  - des données existent le long de la courbe de saturation
- **Les corps lourds**
  - les données sont indisponibles, mais la structure chimique est connue
- **Les pseudo-composants**
  - mélanges de corps se comportant de manière semblable du point de vue thermo, et qu'on considère comme si c'était un corps pur

# Intérêt de diagrammes pour évaluer la qualité des données



# Régression de paramètres



# Les modèles pour les mélanges

## ■ Modèles de coefficient d'activité

	<i>"Predictive"</i>	<i>"Correlative"</i>
<i>Enthalpic</i>	<i>Hildebrand</i>	<i>NRTL</i> <i>Margules</i> <i>Van Laar</i>
<i>Entropic</i>	<i>Flory</i> <i>Staverman-Guggenheim</i>	<i>Wilson</i>
<i>Enthalpic + entropic</i>	<i>UNIFAC</i> <i>Flory-Huggins</i>	<i>UNIQUAC</i> <i>(Flory-Huggins)*</i>

\* The Flory Huggins model is presented here as predictive, but it is very often used with a correlated parameter for solvent-polymer mixtures.

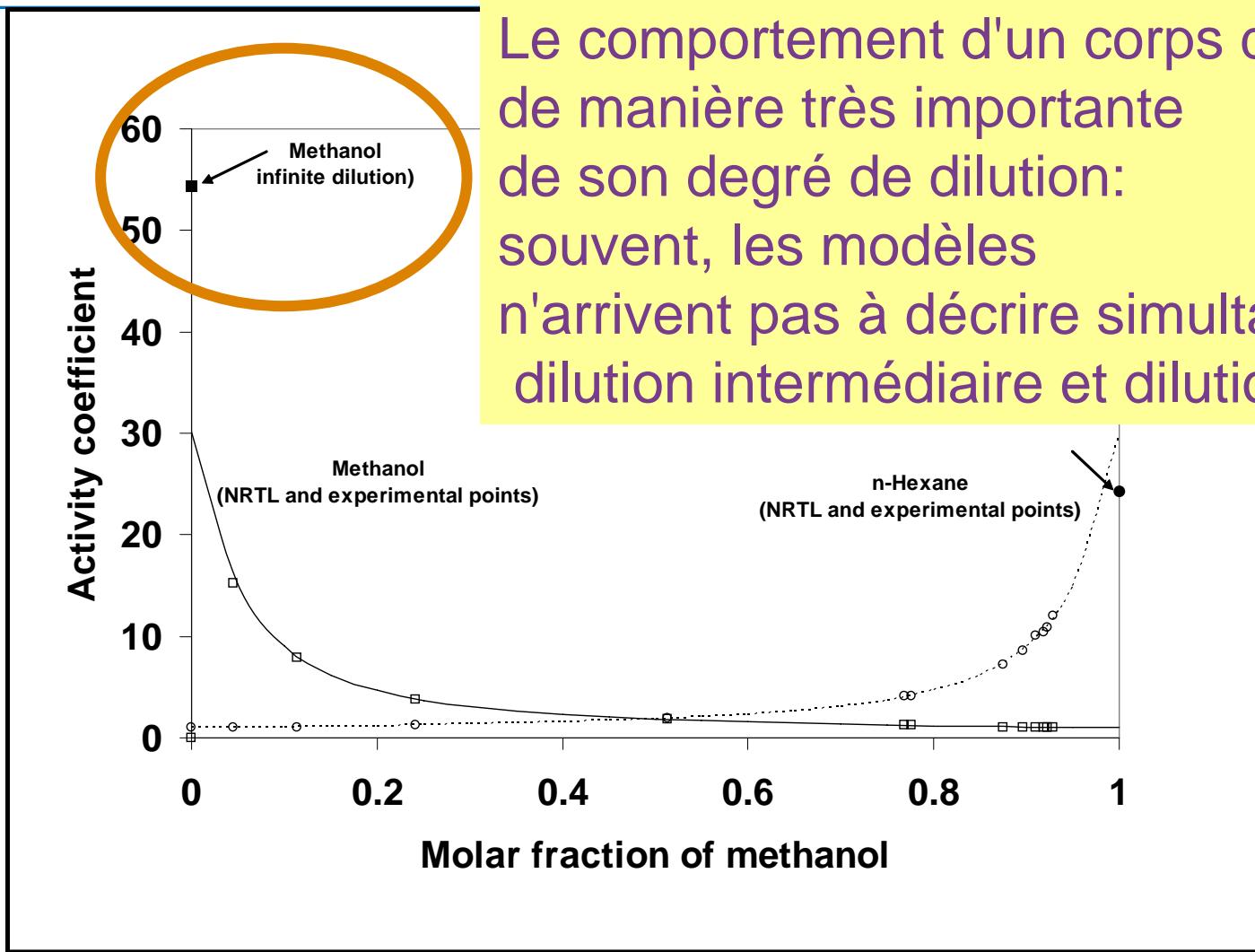
## ■ Les équations d'état

# Les modèles pour les mélanges

- Modèles de coefficient d'activité
- Les équations d'état

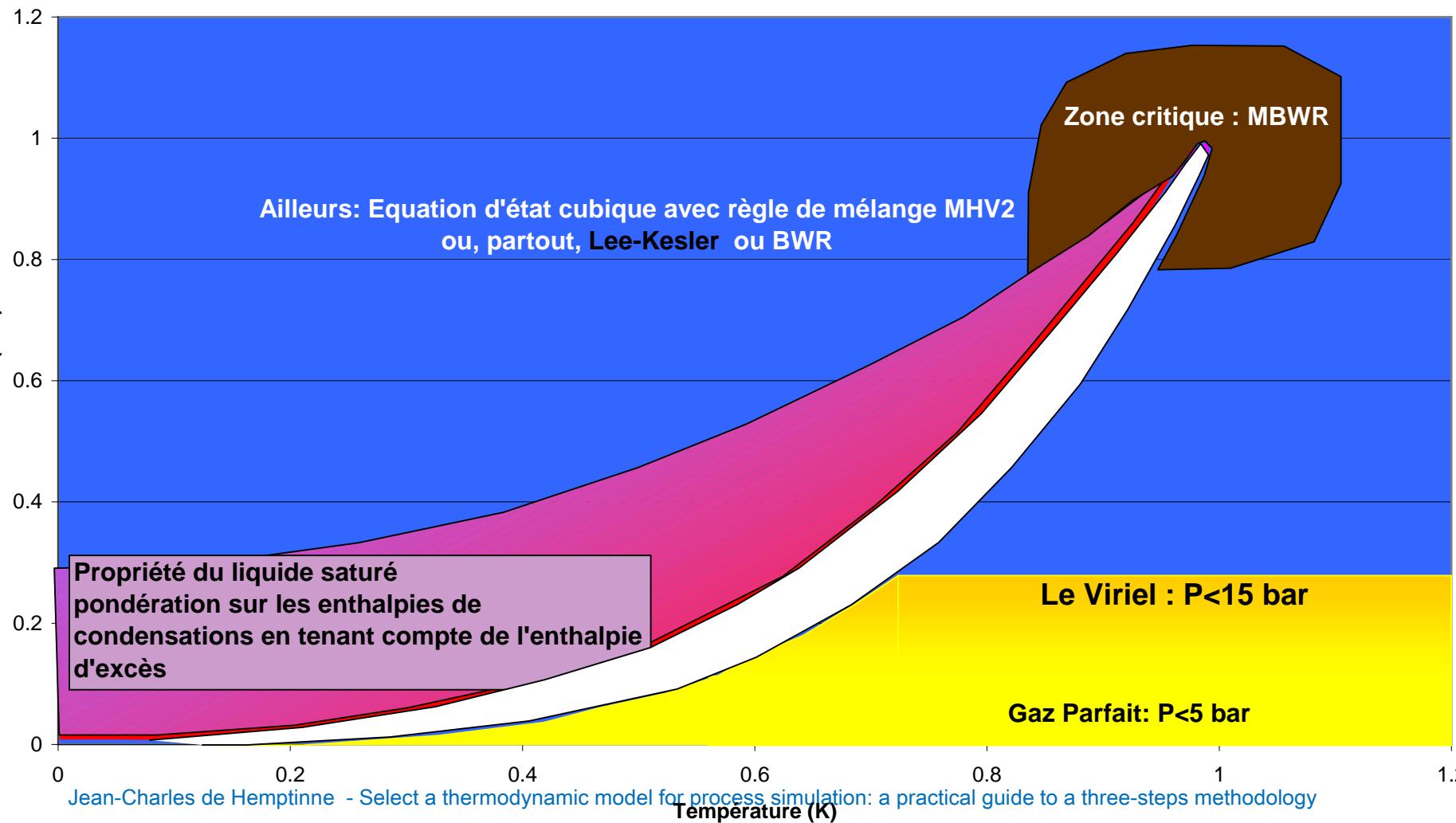
	correlative	corresponding states	group contribution
Phase equilibria		cubic + $\alpha(T)$	
Hydrocarbons slightly non-ideal (enthalpic)	cubic + $k_{ij}$ mixing rule		cubic + Jaubert $k_{ij}$ PC-SAFT (Tihic)
strongly non-ideal (enthalpic)	cubic + GE-type mixing rule CPA (water, alcohols, gases)		GC-PPC-SAFT (Passarello)
enthalpic + entropic non- ideality	NRHB		VR- $\gamma$ -SAFT (Lymeriadis) GCA (bio-applications)
phase properties	VR-SAFT	Lee Kesler	GC-Lattice Fluid
		Starling - BWR	

# Effet de la dilution sur le comportement du modèle



# From phases to method<sup>o</sup>d (models) selection

Enveloppe de phase

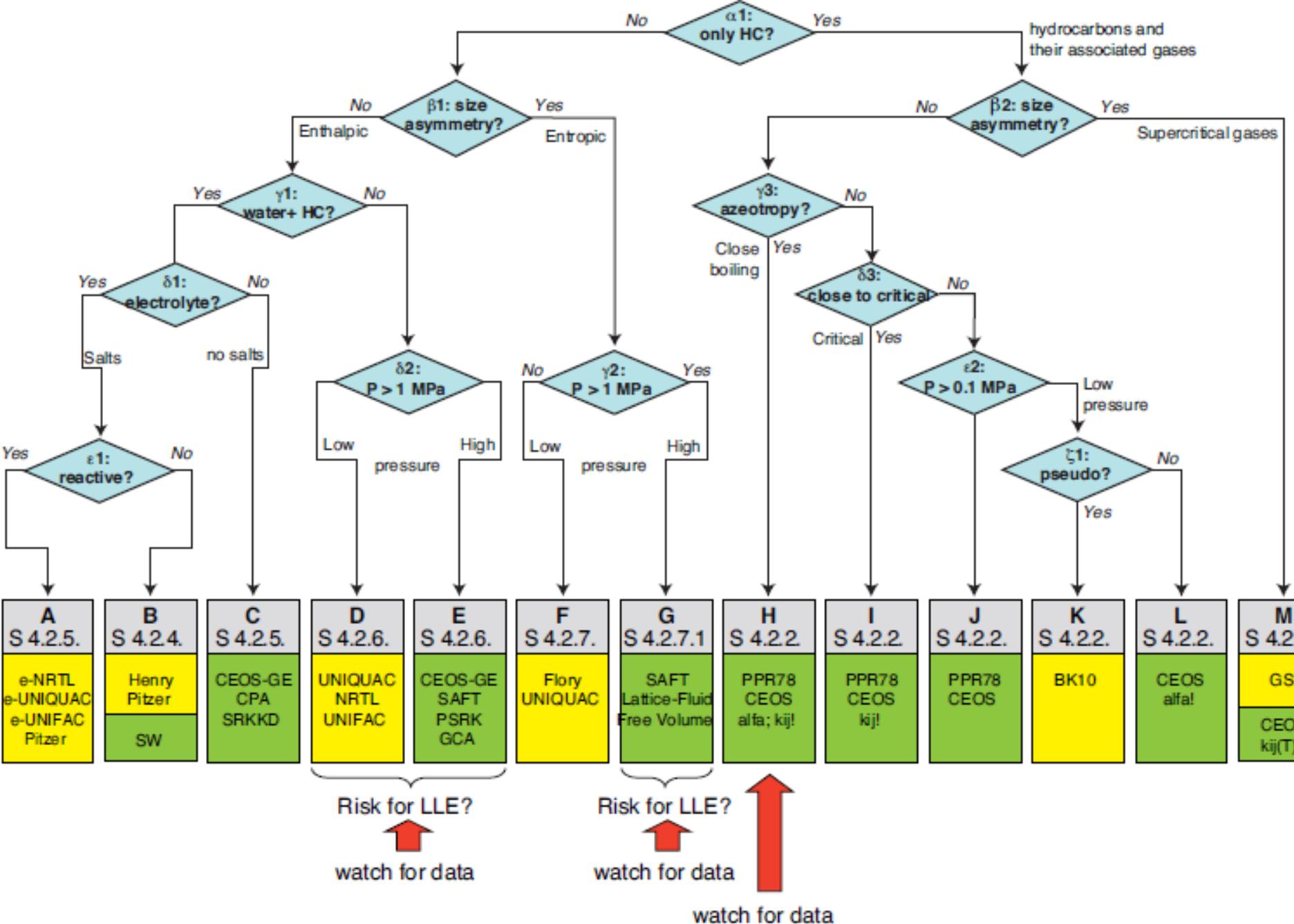


# Les systèmes d'intérêt industriel

- Les fluides organiques
  - ELV, ELLV
  - Asphaltènes
  - Crystallisation de Paraffines
- Les mélanges avec gaz sustances volatiles
  - ELV
- Les mélanges avec de l'eau
  - ELV
  - Phases solides (glace, hydrates)
- Les mélanges avec gaz acides
  - En présence d'eau
  - Solvants physiques
  - Solvants chimiques
- Les mélanges de fluides polaires (bio-molécules)



Pour chaque cas,  
proposition de modèles  
-points importants



# Arbre de décision

Question	Label	Explanation
	D	In the presence of a mixture of very polar components (as for example discussed in section 4.2.6, page 316), it is generally recommended to use an activity coefficient model, with well-documented binary interaction parameters, on the condition that pressure is not too high. UNIQUAC and NRTL are often used indifferently, and UNIFAC (section 3.4.2.4.C, p. 184; the Dortmund version is considered better) is preferred when no parameters are available. Note that it is often possible to fill automatically the UNIQUAC or NRTL parameter matrix using UNIFAC. In case of risk of liquid-liquid phase split, it is essential to validate the model with experimental data, because a slight change in conditions may have a great effect on LLE. The vapour phase is often considered ideal, but the Hayden-O'Connell virial coefficient can be needed for hydrogen-bonding systems. Sometimes, special approaches are required (hexamer forming of HF, for example). The equations of state discussed under label E are increasingly used for low pressure calculations.
	E	In the presence of a mixture of very polar components (as for example discussed in section 4.2.6, page 316), the activity coefficient models are limited in pressure. At pressures higher than 1 MPa, an equation of state should be used. A cubic EoS can do the job if an appropriate activity coefficient model is included in the GE-type mixing rule (as in the case of the PSRK EoS). The SAFT model is increasingly used in this context.
	I	The process may be focusing on components that are close to their critical points (either gases, as CO <sub>2</sub> or H <sub>2</sub> S, or light hydrocarbons). Only a homogeneous method with an equation of state can be used. Cubic EoS are particularly well-suited because their very construction makes that the pure component critical point is exact. For mixtures, the prediction should be used with caution. The PPR78 EoS has been designed for this type of problems. The other properties (enthalpic or density), require a high quality virial EoS (as recommended by NIST, see also section 3.4.3.3, page 199).
	A	In some cases, chemical reactions in the aqueous phase strongly affect the vapour-liquid equilibrium (e.g. amine treatment). Specific packages (that include simultaneous phase and chemical equilibrium calculations) must be used for these reacting systems. They very often use the electrolyte version of NRTL or UNIQUAC as discussed in section 3.4.2.5. Some simulators propose a special "sour gas" package for acid gas + water mixtures.
	J	If pressure is larger than 0.1 MPa, and no specific azeotropic condition is feared, the traditional cubic EoS can be used without great danger. This is the case for stabilization columns, for example.
	K	In some cases, very low pressure calculations are needed, which means that the liquid is a heavy component. Very often, petroleum pseudocomponents are used (typically for vacuum distillation). In this case, the automated API nomograph BK10 (which is nothing but an improved Raoult's law) is traditionally recommended.
	L	In the case the heavy end is paraffinic, for example (wax treatment), it is rather recommended to use a cubic EoS, for which the validity of the alpha function has been extended to heavy components (as in PR78).

# Case studies

- Sélectionner le modèle (la méthode)
  - Choisir en fonction des propriétés recherchées, le mélange et les conditions opératoires
- Evaluer les données les plus adaptées
  - Pour régression (si nécessaire)
  - Pour évaluation
- Comparer le modèles aux données
  - Repérer les déviations moyennes par rapport aux incertitudes des données
  - Repérer les tendances de ces déviations pour estimer les risques en extrapolation

## + site web

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- On y retrouvera:
- Les chapitres + résumé + références
- Les exercices + fichiers excel à télécharger

# remerciements

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Energies Nouvelles)

# SELECT THERMODYNAMIC MODELS FOR PROCESS SIMULATION

A Practical Guide using a  
Three Steps Methodology

Jean-Charles de Hemptinne, Jean-Marie Ledanois,  
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Editions TECHNIP

