

## ***ProSim's thermodynamic models library***

The use of a process simulator rests on the knowledge of pure component properties and binaries. These properties serve as a basis for the determination of the thermodynamic properties, transfer properties and fluid phase equilibria. The results accuracy is thus directly linked to the pure components properties and binaries and to the thermodynamic model that has been chosen to represent the thermodynamic behavior of the system.

The choice of the thermodynamic model is lead by a concern of rigor, reliability and validity in the considered operating range.

Two kinds of methods exist in order to compute fluid phase equilibria:

- The first consists in applying a different model to each phase: fugacities in liquid phase are calculated from a reference state which is characterized by the pure component in the same conditions of physical state, temperature and pressure, ideal laws being corrected by using a Gibbs free energy model or an activity coefficients model (NRTL, UNIQUAC, UNIFAC...). Fugacities in vapor phase are calculated by using an Equation of State (ideal gases, SRK, PR...). These methods are used in order to represent the heterogeneity of the system and are classically called **heterogeneous methods**. Their use covers the low pressure field and it should be noted that they do not satisfy the continuity in the critical zone between vapor phase and liquid phase.
- The second consists in **homogeneous methods**, which apply the same model, usually an Equation of State, to the two phases, allowing thus to ensure continuity at the critical point. Equations of State with their classical mixing rules (SRK, PR, LKP...) are included in this second category. However, the field of application of these models is limited to non polar or few polar systems.

By integrating Gibbs free energy models in the mixing rules for Cubic Equations of State, some authors succeeded in merging both approaches. These models are often called **combined approach**. It has to be noted that some **specific models** have been developed for some particular fields of application, like electrolyte solutions, strong acids...

Thermodynamic calculations in computer aided process simulation require defining a "thermodynamic profile", which is fully configurable for software using ProSim's thermodynamic library. The following table shows the list of available models for each option of the thermodynamic profile.

Option of the thermodynamic profile	Available models
<b>Thermodynamic approach</b>	<ul style="list-style-type: none"> <li>▪ Equation of State: <math>K_i = \frac{\Phi_i^L}{\Phi_i^V}</math></li> <li>▪ Gamma-Phi approach: <math>K_i = \frac{\gamma_i f_i^{OL}}{\Phi_i^V P}</math></li> </ul>
<b>Equations of State (EoS)</b>	<ul style="list-style-type: none"> <li>▪ Ideal Gas</li> <li>▪ Equations of State derived from Virial EoS: <ul style="list-style-type: none"> <li>○ REDLICH-KWONG</li> <li>○ SOAVE-REDLICH-KWONG</li> <li>○ SOAVE-REDLICH-KWONG BOSTON MATHIAS</li> <li>○ SOAVE-REDLICH-KWONG KABADI DANNER (1985)</li> <li>○ SOAVE-REDLICH-KWONG KABADI DANNER (1988)</li> <li>○ PENG-ROBINSON</li> <li>○ PENG-ROBINSON BOSTON MATHIAS</li> <li>○ PENG-ROBINSON 78</li> <li>○ PENG-ROBINSON 78 BOSTON MATHIAS</li> <li>○ Predictive PENG-ROBINSON 78</li> </ul> </li> <li>▪ Equations of State derived from Van der Waals EoS: <ul style="list-style-type: none"> <li>○ LEE-KESLER-PLOCKER</li> <li>○ BENEDICT-WEBB-RUBBIN-STARLING</li> </ul> </li> <li>▪ Others: <ul style="list-style-type: none"> <li>○ PC-SAFT</li> <li>○ ASSOCIATION (carboxylic acids)</li> <li>○ NAKAMURA (hard sphere EoS)</li> <li>○ PURE WATER (NBS/NRC steam tables (IAPS, 1984))</li> </ul> </li> </ul>
<b>Mixing rules for Cubic Equation of State (CEoS)</b> <i>Mixing rules for Cubic Equations of State used in the combined approach are particularly powerful since they allow to model, with an homogeneous approach, systems containing polar and non polar compounds, with no discontinuity at the critical point. Complex mixing rules implemented in the ProSim's thermodynamic library are the following:</i> <ul style="list-style-type: none"> <li>▪ HURON-VIDAL mixing rules modified by MICHELSEN (MHV1 and MHV2)</li> <li>▪ PSRK mixing rules proposed by GMEHLING and al.</li> </ul>	<ul style="list-style-type: none"> <li>▪ STANDARD (CEoS with their own mixing rules)</li> <li>▪ MHV2</li> <li>▪ MHV1</li> <li>▪ PSRK</li> </ul>
<b>Activity coefficients</b> <i>It has to be noted that Liquid – Liquid – Vapor equilibria lead to some difficulties (appearance, disappearance of phases,...) and needs the implementation of some specific unit operation modules (Flash, Column,...). In order to get round these drawbacks, a strategy is used in ProSim's thermodynamic library for the fluid phase equilibrium constant calculation of such systems: the possible liquid phase splitting is taken into account at the thermodynamic level, allowing thus to calculate a fluid phase equilibrium constant between a global liquid phase and the vapor phase. Users of this library can thus access some models called "VLL" (e.g. VLL</i>	<ul style="list-style-type: none"> <li>▪ Ideal</li> <li>▪ MARGULES</li> <li>▪ SCATCHARD-HILDEBRAND</li> <li>▪ WILSON</li> <li>▪ WILSON Dechema compliant</li> <li>▪ NRTL</li> <li>▪ UNIQUAC</li> <li>▪ Predictive models (based on group contribution) <ul style="list-style-type: none"> <li>○ UNIFAC original</li> <li>○ UNIFAC modified Dortmund</li> <li>○ UNIFAC modified LARSEN</li> <li>○ UNIFAC PSRK</li> </ul> </li> </ul>

<p><i>NRTL or VLL UNIQUAC). Mathematical formula of these models are the same as for liquid - vapor models, only the equations relating to the possible liquid phase splitting are added.</i></p>	<ul style="list-style-type: none"> <li>○ UNIFAC LLE</li> <li>▪ Electrolytic systems : <ul style="list-style-type: none"> <li>○ EDWARDS</li> <li>○ UNIQUAC Electrolyte SOUR WATER</li> <li>○ UNIQUAC Electrolyte MULTISOLVENT</li> <li>○ ULPDHS</li> <li>○ Engels (strong acids)</li> </ul> </li> </ul>
<p><b>Standard state pure liquid fugacity</b></p>	<ul style="list-style-type: none"> <li>▪ <math>f_i^{0L} = \Phi_i^{0V} P_i^0</math> (standard)</li> <li>▪ <math>f_i^{0L} = \Phi_i^{0V} P_i^0 \Pi</math> (<math>\Pi</math> : Poynting factor)</li> <li>▪ CHAO-SEADER</li> <li>▪ <math>f_i^{0L} = P_i^0</math> (vapor pressure)</li> <li>▪ CHAO-SEADER modified GRAYSON-STREED</li> <li>▪ ENGELS</li> <li>▪ Henry's law with Poynting factor</li> </ul>
<p><b>Transport properties</b></p>	<ul style="list-style-type: none"> <li>▪ PURE methods</li> <li>▪ Classic methods</li> <li>▪ ELY-HANLEY model (TRAPP model)</li> <li>▪ PETRO methods</li> </ul>
<p><b>Liquid molar volume</b></p>	<ul style="list-style-type: none"> <li>▪ IDEAL</li> <li>▪ RACKETT</li> <li>▪ API 6A2.22</li> <li>▪ COSTALD</li> <li>▪ LEE-KESLER-PLOCKER</li> <li>▪ LEE-KESLER</li> <li>▪ BENEDIC-WEBB-RUBBIN-STARLING</li> <li>▪ HELGESON</li> <li>▪ NOVOTNY et SÖHNEL</li> <li>▪ SOAVE-REDLICH-KWONG</li> <li>▪ PENG-ROBINSON</li> <li>▪ REDLICH-KWONG</li> <li>▪ PC-SAFT</li> </ul>
<p><b>Enthalpy calculation</b></p>	<ul style="list-style-type: none"> <li>▪ Enthalpy basis: H=0, ideal gas state, 25°C, 1 atm and liquid enthalpy calculation from liquid specific heat</li> <li>▪ Enthalpy basis: H=0, liquid state at 25°C, 1 atm</li> <li>▪ Enthalpy basis: H=0, ideal gas state, 25°C, 1 atm and enthalpy calculated with LKP model</li> <li>▪ Enthalpy basis: H=0, ideal gas state, 25°C, 1 atm and enthalpy calculated with LK model</li> <li>▪ Enthalpy basis: H= 0, ideal gas state, 25°C, 1 atm and liquid enthalpy calculation with heat of vaporization for each component</li> <li>▪ Enthalpy basis: <math>H = \Delta H_f^0</math>, ideal gas state, 25°C, 1 atm</li> </ul>

### **Pure component properties estimation**

ProSim's software are delivered with a pure components database, an enriched version of DIPPR database with properties for over 2 000 components. Simulis Thermodynamics is embedded in most ProSim software and is used as a property server and to manage private database. For pure components temperature dependant properties, besides the possibility to regress from experimental data coefficients of mathematical formulations required by each of these properties, some predictive methods have been implemented for estimation of missing properties:

- *Vapor pressure :*
  - Lee-Kesler
  - Riedel-Planck-Miller
  - Gomez-Nieto-Thodos for non polar compounds
  - Gomez-Nieto-Thodos for polar compounds
  - Gomez-Nieto-Thodos for non polar compounds with hydrogen bound
- *Liquid specific heat:*
  - Yuan-Stiel for non polar compounds
  - Yuan-Stiel for polar compounds
- *Ideal gas heat capacity:*
  - Harrison-Seaton
- *Heat of vaporization:*
  - Clausius-Clapeyron
  - Watson (simplified)
  - Watson (extended)
  - Watson improved by Visvanath-Kuloor
- *Liquid density:*
  - Rackett (simplified)
  - Rackett-Gunn-Yamada
  - Gunn-Yamada
  - API 6A2.22
- *Surface tension:*
  - MacLeod-Sudgen
  - Brock-Bird
  - Hakim
  - API 10A3.1
- *Liquid viscosity:*
  - Letsou-Stiel-Gambill
  - Gambill
  - Twu
- *Gas viscosity:*
  - Chapman-Enskog
  - Stiel-Thodos for polar compounds
  - Stiel-Thodos for polar compounds with hydrogen bound
  - Lucas
  - Chung
- *Liquid thermal conductivity:*
  - Sato-Riedel
  - Missenard
- *Gas thermal conductivity:*
  - Stiel-Thodos
  - Roy-Thodos
  - Riazi-Faghri

### **Treatment of petroleum cut – Generation of pseudo-components**

It is not always possible to precisely analyze the characteristics of petroleum cut type complex mixtures in order to determine their nature and the composition of each component. The notion of pseudo-component was introduced to represent such mixtures. It plays, in a petroleum cut, the same role as a pure component in a defined mixture. For each thermodynamic calculation, it is necessary to know the physical properties of these pseudo-components. These calculations are made possible with the use of specific correlations which do not require the knowledge of the chemical structure of the pseudo-component. The cutting of a petroleum fraction in pseudo-components can be done by supplying for each pseudo-component the basic data. The correlations used all require the knowledge of at least two characteristic properties among the following ones:

- boiling point at 1 atm,
- specific gravity or API degree,
- WATSON characterization factor,
- molar weight.

The “generated” properties and the various available correlations are the following one:

- Molar weight:
  - TWU,
  - LEE-KESLER,
  - WINN,
  - RIAZI-DAUBERT,
  - CAVETT.
- Critical temperature:
  - TWU,
  - LEE-KESLER,
  - WINN,
  - RIAZI-DAUBERT,
  - CAVETT,
  - WATANASIRI – OWENS – STARLING.
- Critical volume:
  - TWU,
  - RIEDEL,
  - WATANASIRI – OWENS – STARLING.
- Acentric factor:
  - LEE-KESLER,
  - EDMINSTER,
  - WATANASIRI – OWENS – STARLING.
- Constants for the ideal gas heat capacity:
  - API Data Books,
  - LEE-KESLER with use of the acentric factor,
  - LEE-KESLER without use of the acentric factor,
  - CAVETT.
- Latent heat of vaporization:
  - RIAZI-DAUBERT (default correlation),
  - KISTIAKOWSKY.



# ProSim

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