Conceptual Engineering Product™ 2004

COMThermo Reference Guide

aspentech
driving process profitability

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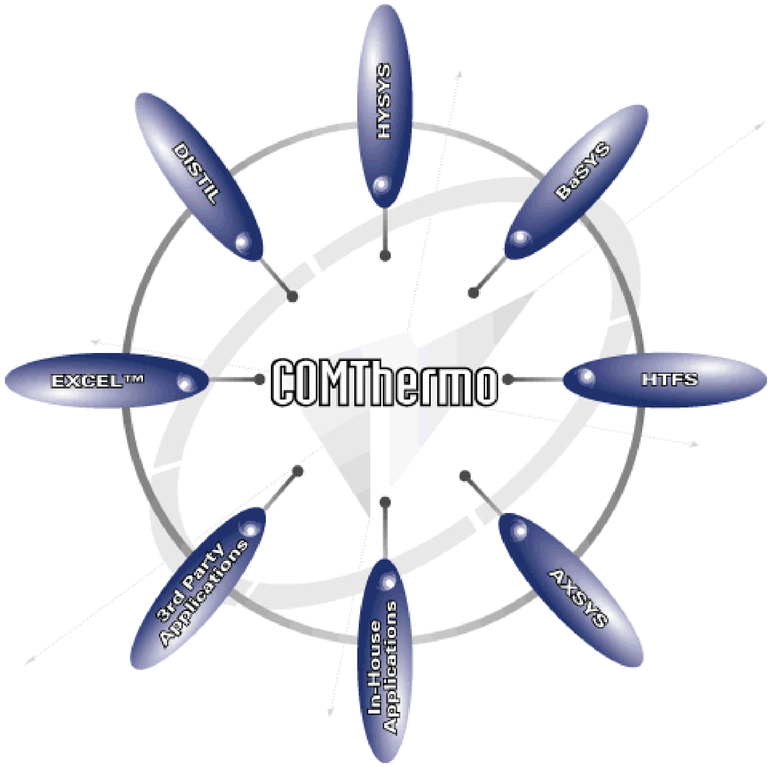
1 Introducing COMThermo

1.1 Introduction

The use of process simulation has expanded from its origins in engineering design to applications in real time optimization, dynamic simulation and control studies, performance monitoring, operator training systems, and others. At every stage of the lifecycle there is a need for consistent results such that the modeling efforts can be leveraged in those many applications.

Accurate thermophysical properties of fluids are essential for design and operation in the chemical process industries. The need of having a good thermophysical model is widely recognized in this context. All process models rely on physical properties to represent the behavior of unit operations, and the transformations that process streams undergo in a process. Properties are calculated from models created and fine-tuned to mimic the behaviour of the process substances at the operating conditions

COMThermo is a complete thermodynamics package that encompasses property methods, flash calculations, property databases, and property estimation. The package is fully componentized, and therefore fully extensible to the level of detail that allows the user to utilize, supplement, or replace any of the components. The objective of this package is to improve the engineering workflow by providing an open structure that can be used in many different software applications and obtain consistent results.



The main benefit of COMThermo is delivered via consistent and rigorous thermodynamic calculations across engineering applications.

COMThermo enables the provision of specialized thermodynamic capabilities to the HYSYS Environment and to other third party applications including internal legacy tools. It also allows the user to support development of internal thermo capabilities. COMThermo Interfaces are written to specifically support thermodynamics.

The COMThermo reference guide details information on relevant equations, models, and the thermodynamic calculation engine. The calculation engine encompasses a wide variety of thermodynamic property calculations, flash methods, and databases used in the COMThermo framework.

2 Thermodynamic Principles

2.1 Introduction

To determine the actual state of a mixture defined by its components and two intensive variables (usually pressure and temperature), a unique set of conditions and equations defining equilibrium is required.

Consider a closed, multi-component, and multi-phase system whose phases are in thermal, mechanical, and mass transfer equilibrium. At this state, the internal energy of the system is at a minimum, and any variation in *U* at constant entropy and volume vanishes ([1]Prausnitz et al, 1986):

$$dU = TdS - PdV \tag{2.1}$$

$$(dU)_{S,\ V} = 0 \tag{2.2}$$

The total differential for the internal energy is:

$$dU = \sum_{j=1}^{\pi} T^j dS^j - \sum_{j=1}^{\pi} P^j dV^j + \sum_{j=1}^{\pi} \sum_{i=1}^{nc} \mu_i^j dn_i^j \tag{2.3}$$

where: *j = Phase (from 1 to π)*

i = Component (from 1 to nc)

μ_i^j *= Chemical potential of component i in phase j, defined as*

$$\mu_i^j = \left(\frac{\partial U}{\partial n_i}\right)_{S,\ V,\ n^j_{k \neq 1}} \tag{2.4}$$

Since the system is closed, the differentials in number of moles, volume, and entropy are not all independent, but are instead constrained as follows:

$$dS = \sum_{j=1}^{\pi} dS^j = 0 \tag{2.5}$$

$$dV = \sum_{j=1}^{\pi} dV^j = 0 \tag{2.6}$$

$$\sum_{j=1}^{\pi} dn_i^j = 0 \qquad i = 1, ..., nc \tag{2.7}$$

Therefore, a system of equations with $\pi(nc+2)$ variables and $nc + 2$ constraints (**Equations (2.5)**, **(2.6)** and **(2.7)**) is defined. The constraints can be used to eliminate some variables and reduce the system to a set of $(\pi - 1)(nc + 2)$ independent equations.

The variables can be eliminated in the following way:

$$dS^1 = -\sum_{j=2}^{\pi} dS^j \tag{2.8}$$

$$dV^1 = -\sum_{j=2}^{\pi} dV^j \tag{2.9}$$

$$dn_i^1 = \sum_{j=2}^{\pi} dn_i^j \tag{2.10}$$

The result is as follows:

$$dU = \sum_{j>1}^{\pi} (T^j - T^1)\,dS^j - \sum_{j>1}^{\pi} (P^j - P^1)\,dV^j + \sum_{j>1}^{\pi} \sum_{i=1}^{nc} (\mu_i^j - \mu_i^1)\,dn_i^j \qquad (2.11)$$

where: the differentials on the right side of ***Equation (2.11)*** *are independent.*

Setting all of the independent variables constant except one, at equilibrium you have:

$$\frac{\partial U}{\partial S} = 0 \qquad \frac{\partial U}{\partial V} = 0 \qquad \frac{\partial U}{\partial n_i} = 0 \qquad \frac{\partial^2 U}{\partial S^2} = 0 \qquad (2.12)$$

Therefore:

$$T^1 = T^j \qquad j = 2, \ldots, \pi \qquad (2.13)$$

Repeating the same argument for all of the independent variables, the general conditions necessary for thermodynamic equilibrium between heterogeneous phases are established (for all *i*):

$T^1 = T^2 = \ldots = T^{\pi}$	*Thermal Equilibrium - no heat flux across phases*	(2.14)
$P^1 = P^2 = \ldots = P^{\pi}$	*Mechanical Equilibrium - no phase displacement*	(2.15)
$\mu_i^1 = \mu_i^2 = \ldots = \mu_i^{\pi}$	*Mass Transfer Equilibrium - no mass transfer for component i between phases*	(2.16)

From now on, it is assumed that **Equations (2.14)** and **(2.15)** are always satisfied. The equilibrium condition established in **Equation (2.16)** will be discussed in more detail. Note that the description of equilibrium according to **Equations (2.13)**, **(2.14)**, **(2.15)**, and **(2.16)** is at best incomplete, since other intensive variables could be important in the process being analysed. For example, the electric or magnetic fields in the equations, or area affects are not being considered.

Nevertheless, **Equations (2.13)**, **(2.14)**, **(2.15)** and **(2.16)** are important in chemical engineering thermodynamic calculations, and will be assumed to always apply. Provided that a reasonable physical model is available for the property calculations, virtually all chemical engineering problems that involve phase equilibria can be represented by the above equations and constraints.

The following will relate the chemical potential in **Equation (2.16)** with measurable system properties.

2.2 Chemical Potential & Fugacity

The concept of chemical potential was introduced by J. Willard Gibbs to explain phase and chemical equilibria. Since chemical potential cannot be directly related with any directly measured property, G.N. Lewis introduced the concept of fugacity in 1902. Using a series of elegant transformations, Lewis found a way to change the representation using chemical potential by representing the equilibrium conditions with an equivalent property directly related to composition, temperature and pressure. He named this property "fugacity." It can be seen as a "thermodynamic pressure" or, in simpler terms, the effective partial pressure that one compound exerts in a mixture.

2.3 Chemical Potential for Ideal Gas

You start by finding an equivalent to **Equation (2.5)** which allows us to work with a better set of independent variables, namely pressure and temperature. This brings us to the Gibbs free energy, which is expressed as a function of P and T:

$$dG = -SdT + VdP + \sum_{i=1}^{nc} \mu_i dn_i \tag{2.17}$$

where:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_{k \neq 1}} \tag{2.18}$$

The chemical potential is the partial molar Gibbs free energy, since partial molar properties are defined at constant *P* and *T*. Note that the chemical potential is not the partial molar internal energy, enthalpy or Helmholtz energy. Since a partial molar property is used, the following holds:

$$d\overline{G}_i = -\overline{S}_i dT + \overline{V}_i dP \tag{2.19}$$

where:

$$\overline{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,\ P,\ n_{k \neq 1}} \tag{2.20}$$

Now assuming the system to be at constant temperature:

$$d\mu_i = d\overline{G}_i = \overline{V}_i dP \tag{2.21}$$

2.4 Chemical Potential & Fugacity for a Real Gas

Although **Equation (2.21)** has only limited interest, its basic form can still be used. Pressure, *P*, can be replaced by another thermodynamic quantity which represents a real gas. This quantity is called fugacity, and it is a function of pressure, temperature, and composition:

$$\mu_i = C_i + RT\ln f_i \tag{2.22}$$

It is interesting to note that the combination of **Equations (2.22)** and **(2.16)** results in a simple set of equations for the multi-phase, multi-component phase equilibria:

$$f_i^1 = f_i^2 = \ldots = f_i^\pi \tag{2.23}$$

Assuming again that the system is at constant temperature, **Equations (2.21)** and **(2.22)** can be combined, resulting in a working definition for fugacity:

$$\left(\frac{\partial}{\partial P}(\ln f_i)\right)_T = \frac{\bar{V}_i}{RT} \tag{2.24}$$

In principle, if the behaviour of the partial molar volume is known, the fugacity can be computed, and the phase equilibria is defined. In reality, the engineering solution to this problem lies in the creation of models for the fluid's equation of state—from those models, the fugacity is calculated.

2.5 Fugacity & Activity Coefficients

Writing the fugacity expressions for a real and ideal gas:

$$RTd\ln f = VdP \tag{2.25}$$

$$RTd\ln P = V^{ideal}dP \tag{2.26}$$

Subtracting and rearranging **Equation (2.26)** from **Equation (2.25)** yields:

$$RTd\ln\frac{f}{P} = (V - V^{ideal})dP \tag{2.27}$$

You integrate from 0 to P, noting that the behaviour of any real gas approaches the behaviour of an ideal gas at sufficiently low pressures (the limit of f/P as $P \rightarrow 0 = 1$):

$$\ln\frac{f}{P} = \int_0^P \left(\frac{V}{RT} - \frac{V^{ideal}}{RT}\right)dP \tag{2.28}$$

Using the definition of compressibility factor ($PV = ZRT$), **Equation (2.28)** can be expressed in a more familiar format:

$$\ln\frac{f}{P} = \int_0^P \frac{(Z-1)}{P}dP \tag{2.29}$$

The ratio f/P measures the deviation of a real gas from ideal gas behaviour, and is called the fugacity coefficient:

$$\phi = \frac{f}{P} \tag{2.30}$$

These results are easily generalized for multi-component mixtures:

$$\ln\frac{f_i}{Px_i} = \int_0^P \frac{(\bar{Z}_i - 1)}{P}dP \tag{2.31}$$

The partial molar compressibility factor is calculated:

$$\bar{Z}_i = \left(\frac{\partial Z}{\partial n_i}\right)_{T,\ P,\ n^j_{k\neq i}} = \frac{P}{RT}\left(\frac{\partial V}{\partial n_i}\right)_{T,\ P,\ n^j_{k\neq i}} = \frac{P\bar{V}_i}{RT} \tag{2.32}$$

substituting **Equation (2.32)** into **Equation (2.31)** and rearranging:

$$\ln\frac{f_i}{Px_i} = \frac{1}{RT}\int_0^P \left(\bar{V}_i - \frac{RT}{P}\right)dP \tag{2.33}$$

The quantity f_i / Px_i measures the deviation behaviour of component *i* in a mixture as a real gas from the behaviour of an ideal gas, and is called the *fugacity coefficient of component i in the mixture:*

$$\phi_i = \frac{f_i}{Px_i} \tag{2.34}$$

For mixtures in the liquid state, an ideal mixing condition can be defined. Usually this is done using the Lewis-Randall concept of ideal solution, in which an ideal solution is defined as:

$$f_i^V = y_i f_i^{V,\ pure} \tag{2.35}$$

$$f_i^L = x_i f_i^{L,\ pure} \tag{2.36}$$

where: $f_i^{,\ pure}$ *refers to the fugacity of pure component i in the vapour or liquid phase, at the mixture pressure and temperature.*

The definition used by Lewis and Randall defines an ideal solution, not the ideal gas behaviour for the fugacities. Therefore, the fugacities of each pure component may be given by an accurate equation of state, while the mixture assumes that different molecules do not interact. Although very few mixtures actually obey ideal solution behaviour, approximate equilibrium charts (nomographs) using the Lewis-Randall rule were calculated in the 1940s and 50s, and were successfully used in the design of hydrocarbon distillation towers.

Generalizing **Equation (2.36)** for an arbitrary standard state, the activity coefficient for component *i* can written as:

$$\gamma_i = \frac{f_i^L}{f_i^{L,\ pure} x_i} \tag{2.37}$$

It is important to properly define the normalization condition (the way in which ideal solution behaviour is defined (i.e., when the activity coefficient approaches one), so that supercritical components are handled correctly, and the Gibbs-Duhem equation is satisfied.

2.6 Henry's Law

The normalized condition is the state where the activity coefficient is equal to 1. For ordinary mixtures of condensable components (i.e., components at a temperature below the critical temperature), the normalization condition is defined as ([2]Prausnitz et al, 1980):

$$\lim_{x_i \to 1} \frac{f_i^L}{f_i^{L,\ pure} x_i} = \lim_{x_i \to 1} \gamma_i = 1 \tag{2.38}$$

However, the definition does not apply for components that cannot exist as pure liquids at the conditions of the system. Sometimes, for components like carbon dioxide at near ambient conditions, a reasonably correct hypothetical liquid fugacity can be extrapolated. But for components like hydrogen and nitrogen, this extrapolated liquid behaviour has little physical significance.

For solutions of light gases in condensable solvents, a different normalization convention can be defined than the (other than the one in **Equation (2.38)**):

$$\lim_{x_i \to 0} \frac{f_i^L}{f_i^{ref} x_i} = \lim_{x_i \to 0} \gamma_i{}^* = 1 \tag{2.39}$$

This equation implies that the fugacity of component i in a multi-component mixture approaches the product of the mole fraction and standard state fugacity in very dilute solutions of component i. Using the definition of $\gamma_i{}^*$ it can be shown that:

$$f_i^{ref} = \lim_{x_i \to 0} \frac{f_i^L}{x_i} = H_{ij} \tag{2.40}$$

where: H_{ij} *is called Henry's Constant of component i in solvent j.*

Therefore, the Henry's constant is the standard state fugacity for a non-condensable component in a specific solvent. Usually the Henry's constant is a rather strong function of temperature, but a weak function of the pressure and composition. The extension of Henry's law into more concentrated solutions and at higher pressures is represented by the Kritchevsky-Ilinskaya equation:

$$\ln H_{ij} = \ln H_{ij}^{P_j^{Sat}} + \frac{A_{ij}}{RT}(x_j^2 - 1) + \frac{\overline{V}_i^{\infty}(P - P_j^{sat})}{RT} \tag{2.41}$$

where: P_j^{sat} *= Solvent saturation pressure at mixture temperature*

H_{ij}^{sat} *= Henry's law calculated at the saturation pressure of the solvent*

A_{ij} *= Margules interaction parameter for molecular interactions between the solute and solvent*

$\overline{V}_i^{\infty}$ *= Infinite dilution partial molar volume of solute i in solvent j*

2.6.1 Non-Condensable Components

Non-condensable components are treated using Henry's constants as defined by **Equation (2.40)**. The temperature dependency of the Henry's law for a binary pair *ij* is represented by an Antoine-type of equation with four parameters per binary pair:

$$\ln H_{ij} = A_{ij} + \frac{B_{ij}}{T} + C_{ij} \ln T + D_{ij} T \tag{2.42}$$

The Henry's constant of component *i* in a multi-component mixture is estimated neglecting the solvent-solvent interactions.

A mixing rule for the Henry's constant of a non-condensable component in a mixture of condensable components must be defined. There are several alternatives, but the following formulation works reasonably well:

$$\ln H_{i,\ mixture} = \frac{\sum_{j=1,\ j \neq i}^{nc} \ln H_{ij} x_j V_{c,\ j}^{\frac{2}{3}}}{\sum_{j=1,\ j \neq i}^{nc} x_j V_{c,\ j}^{\frac{2}{3}}} \tag{2.43}$$

2.6.2 Estimation of Henry's constants

A rigorous estimation of gas solubilities in condensable solvents depends on the existence of a rigorous theory of solutions, which currently does not exist. On the other hand, corresponding states and regular solution theory give us a correlative tool which allows us to estimate gas solubilities. The use of regular solution theory assumes that there is no volume change on mixing. Therefore consider a process in which the pure gas, *i*, is condensed to a liquid-like state, corresponding to the partial molar volume of the gas in the solvent. At this point, "liquid" gas is dissolved in the solvent (Prausnitz et al, 1986):

$$\Delta g = \Delta g^{I} + \Delta g^{II} \tag{2.44}$$

$$\Delta g^{I} = RT\ln\frac{f_i^{L,\ pure}}{f_i^{G}} \tag{2.45}$$

$$\Delta g^{II} = RT\ln\gamma_i x_i \tag{2.46}$$

Since the gas dissolved in the liquid is in equilibrium with the gas in the gas phase:

$$f_i^{G} = \gamma_i x_i f_i^{L,\ pure} \tag{2.47}$$

and therefore:

$$\Delta g = 0 \tag{2.48}$$

Using regular solution theory to estimate the activity coefficient of the gas in the solvent:

$$RT\ln\gamma_i = \nu_i^{L}(\delta_j - \delta_i)^2\phi_j^2 \tag{2.49}$$

and finally the expression for the Henry's constant is:

$$H_{ij} = \frac{f_i^{G}}{x_i} = f_i^{L,\ pure}\exp\left[\frac{\nu_i^{L}(\delta_j - \delta_i)^2\phi_j^2}{RT}\right] \tag{2.50}$$

Since regular solution theory assumes that the activity coefficient is proportional to the inverse of temperature, the term $\nu_i^L(\delta_j - \delta_i)\phi_j^2$ is temperature independent, and any convenient temperature (usually 25 °C) can be used for the calculation of ν_i^L, ν_j^L, δ_i, and δ_j. Note also that as a first approximation, ϕ_j is very close to 1, and **Equation (2.50)** simplifies to:

$$H_{ij} = \frac{f_i^{G}}{x_i} = f_i^{L,\ pure}\exp\left[\frac{\nu_i^{L}(\delta_i - \delta_j)^2}{RT}\right] \tag{2.51}$$

This is the equation used when estimating Henry's constants. The Henry's constants are calculated constants at 270.0, 300.0, 330.0, 360.0, 390.0, 420.0, 450.0 K and fits the results using Equation (2.42), for each non-condensable/condensable pair present in the fluid package.

The interaction between two non-condensable components are not taken into account.

2.7 Gibbs-Duhem Equation

At constant temperature and pressure, the Gibbs-Duhem equation states that:

$$\sum_{i=1}^{nc} x_i d\ln\gamma_i = 0 \tag{2.52}$$

This equation applies to condensable and non-condensable components and only when integrating the Gibbs-Duhem equation should normalization conditions be considered. A more general form of the Gibbs-Duhem is also available, which is applicable to non-isothermal and non-isobaric cases. These forms are difficult to integrate, and do little to help in the definition of the standard state fugacity.

If the liquid composition of a binary mixture was varied from $x_i = 0$ to $x_i = 1$ at constant temperature, the equilibrium pressure would change. Therefore, if the integrated form of Equation (2.52) is used to correlate isothermal activity coefficients, all of the activity coefficients will have to be corrected to some constant reference pressure. This is easily done if the dependency of fugacity on pressure is known:

$$\gamma_i^{P^{ref}} = \gamma_i^P \exp\left(\int_P^{P^{ref}} \frac{\overline{V}_i}{RT} dP\right) \tag{2.53}$$

Now if the fugacity equation is written using activity coefficients:

$$f_i^L = \gamma_i^P x_i f_i^{ref} \qquad \text{or} \qquad f_i^L = \gamma_i^{P^{ref}} x_i f_i^{ref} \exp\left(\int_{P^{ref}}^{P} \frac{\overline{V}_i}{RT} dP \right) \tag{2.54}$$

The definition of the standard state fugacity now comes directly from the Gibbs-Duhem equation using the normalization condition for a condensable component; i.e., f_i^{ref} is the fugacity of component *i* in the pure state at the mixture temperature and reference pressure preference. The standard state fugacity can be conveniently represented as a departure from the saturated conditions:

$$f_i^{ref} = P_i^{vap} \phi_i^{sat} \exp\left(\int_{P_i^{vap}}^{P^{ref}} \frac{V_i}{RT} dP \right) \tag{2.55}$$

Combining **Equations (2.54)** and **(2.55)**:

$$f_i^L = P_i^{vap} \phi_i^{sat} \exp\left[\int_{P_i^{vap}}^{P^{ref}} \frac{\overline{V}_i}{RT} + \frac{V_i}{RT} dP \right] \tag{2.56}$$

This equation is the basis for practically all low to moderate pressure engineering equilibrium calculations using activity coefficients. The exponential correction in **Equations (2.54)** and **(2.55)** is often called the *Poynting correction*, and takes into account the fact that the liquid is at a different pressure than the saturation pressure. The *Poynting correction* at low to moderate pressures is very close to unity.

2.7.1 Simplifications on Liquid Fugacity using Activity Coeff

There are many traditional simplifications involving **Equation (2.56)** which are currently used in engineering applications.

Ideal Gas

When ideal gas behaviour is assumed, this usually implies that the Poynting correction is dropped. Also, since the gas is ideal, $\phi_i^{sat} = 1$:

$$f_i^L = \gamma_i x_i P_i^{vap} \tag{2.57}$$

$$f_i^{ref} = P_i^{vap} \tag{2.58}$$

Low Pressures & Conditions Away from the Critical Point

For conditions away from the critical point and at low to moderate pressures, the activity coefficients are virtually independent of pressure. For these conditions, it is common to set $P^{ref} = P_i^{vap}$ giving us the familiar equation:

$$f_i^L = \gamma_i x_i P_i^{vap} \phi_i^{sat} \exp\left[\int_{P_i^{vap}}^{P} \left(\frac{\bar{V}_i}{RT}\right) dP\right] \tag{2.59}$$

It is common to assume that the partial molar volume is approximately the same as the molar volume of the pure liquid *i* at *P* and *T*, and equation simplifies even further:

$$f_i^L = \gamma_i x_i P_i^{vap} \phi_i^{sat} \exp\left[\int_{P_i^{vap}}^{P} \left(\frac{V_i}{RT}\right) dP\right] \tag{2.60}$$

Since fluids are usually incompressible at conditions removed from the critical point, V_i can be considered constant and the integration of **Equation (2.60)** leads to:

$$f_i^L = \gamma_i x_i P_i^{vap} \phi_i^{sat} \exp\left[\frac{V_i(P - P_i^{vap})}{RT}\right] \tag{2.61}$$

$$f_i^{ref} = P_i^{vap} \phi_i^{sat} \exp\left[\frac{V_i(P - P_i^{vap})}{RT}\right] \tag{2.62}$$

This is the equation used when taking into account vapour phase non-ideality. Sometimes, **Equation (2.60)** is simplified even further, assuming that the Poynting correction is equal to 1:

$$f_i^L = \gamma_i x_i P_i^{vap} \phi_i^{sat} \tag{2.63}$$

$$f_i^{ref} = P_i^{vap} \phi_i^{sat} \tag{2.64}$$

Equations (2.57), **(2.60)** and **(2.61)** form the basis used to name several of the activity coefficient based property packages.

2.8 Association in Vapour Phase - Ideal Gas

For some types of mixtures (especially carboxylic acids), there is a strong tendency for association in the vapour phase, where the associating component can dimerize, forming a reasonably stable "associated" component. Effectively, a simple chemical reaction in the vapour phase takes place, and even at modest pressures a strong deviation from the vapour phase behaviour predicted by the ideal gas law may be observed. This happens because an additional "component" is present in the mixture (Walas, 1985).

$$2A \leftrightarrow A_2 \tag{2.65}$$

where: A is the associating component in the mixture (assumed binary for simplicity).

the equilibrium constant for the chemical reaction can be written as:

$$K = \frac{[A_2]}{[A]^2} \tag{2.66}$$

Assuming that the species in the vapour phase behave like ideal gases:

$$K = \frac{[P_d]}{[P_m]^2} \tag{2.67}$$

where: P_d *is the dimer partial pressure*

P_m *is the monomer partial pressure*

At equilibrium, the molar concentrations of monomer and dimer are:

$$y_m = \frac{2-2e}{2-e} \tag{2.68}$$

$$y_d = \frac{e}{2-e} \tag{2.69}$$

where: e is the extent of dimerization

The expression for the dimerization extent in terms of the equilibrium constant can be written as follows:

$$K = \frac{P_d}{P_m^2} = \frac{P_A^{vap} y_d}{(P_A^{vap} y_m)^2} = \frac{e(2-e)}{(2-2e)^2 P_A^{vap}} = \frac{e(2-e)}{4P_A^{vap}(1-e)^2} \tag{2.70}$$

Solving for e the following:

$$e = \sqrt{\frac{1}{1+4KP_A^{vap}}} \tag{2.71}$$

The vapour pressure of the associating substance at a given temperature is the sum of the monomer and dimer partial pressures:

$$P_A^{vap} = P_m^\circ + P_d = P_m^\circ + K[P_m^\circ]^2 \tag{2.72}$$

The hypothetical monomer vapour pressure $P^o{}_m$ can be solved for:

$$P_m^\circ = \frac{\sqrt{1+4KP_A^{vap}} - 1}{2K} \tag{2.73}$$

The partial pressure of the monomer can be written as a function of a hypothetical monomer vapour pressure and the activity coefficient of the associated substance in the liquid mixture:

$$P_m = \gamma_A x_A P_m^\circ \tag{2.74}$$

Note that in the working equations the mole fraction of dimer is not included. The associating substance is used when calculating the number of moles in the vapour phase:

$$w_A = n_m M_m + 2 n_d M_m \tag{2.75}$$

where: w_A = *Weight of associating substance*

n_m, n_d = *Number of moles of monomer and dimer*

M_m = *Molecular weight of monomer*

Dividing by M_m:

$$n_A = n_m + 2 n_d \tag{2.76}$$

Since there are n_t total number of moles in the vapour phase, the mass balance is expressed as:

$$x_m + 2x_d + x_2 = 1 \tag{2.77}$$

where: *the index 2 represents the non-associating component in the mixture.*

Since it is assumed that the components in the mixture behave like an ideal gas:

$$P_A = P_m + 2P_d + P_2 \tag{2.78}$$

where: P_A *is the total pressure using* ***Equation (2.77)***.

Knowing that:

$$P = P_m + P_d + P_2 \tag{2.79}$$

You have:

$$y_A = \frac{P_m + 2P_d}{P_m + 2P_d + P_2} = \frac{P_m + 2P_d}{P + P_d} \tag{2.80}$$

$$y_2 = \frac{P_2}{P_m + 2P_d + P_2} = \frac{P_2}{P + P_d} = \frac{\gamma_2 x_2 P_2^{vap}}{P + P_d} \tag{2.81}$$

The usage of **Equations (2.80)** and **(2.81)** can be easily accomodated by defining a new standard state fugacity for systems with dimerization:

$$f^L_{dimerizing} = \left(\frac{P}{P+P_d}\right) P^{\circ}_m \ (1 + 2KP_m) \tag{2.82}$$

$$f^L_{non-dimerizing} = \left(\frac{P}{P+P_d}\right) P^{vap}_{non-dimerizing} \tag{2.83}$$

Several property packages in DISTIL support ideal gas dimerization. The standard nomenclature is:

[Activity Coefficient Model] + [Dimer] = Property Package Name

For example, NRTL-Dimer is the property package which uses NRTL for the activity coefficient calculations and the carboxylic acid dimer assuming ideal gas phase behaviour. The following carboxylic acids are supported:

- Formic Acid
- Acetic Acid
- Acrylic Acid
- Propionic Acid
- Butyric Acid
- IsoButyric Acid
- Valeric Acid
- Hexanoic Acid

2.9 Equilibrium Calculations

When performing flash calculations, K-values are usually calculated. K-values are defined as follows:

$$K_i = \frac{y_i}{x_i} \tag{2.84}$$

where: y_i *is the composition of one phase (usually the vapour)*

x_i *is the composition of another phase (usually the liquid)*

When using equations of state to represent the vapour and liquid behaviour, you have:

$$f_i^V = \phi_i^V y_i P \tag{2.85}$$

$$f_i^L = \phi_i^L x_i P \tag{2.86}$$

and therefore:

$$K_i = \frac{\phi_i^L}{\phi_i^V} \tag{2.87}$$

Activity coefficient based models can easily be expressed in this format:

$$f_i^L = \phi_i^L x_i P = \gamma_i x_i f_i^{ref} \tag{2.88}$$

and therefore:

$$\phi_i^L = \frac{\gamma_i f_i^{ref}}{P} \tag{2.89}$$

where the standard state reference fugacity is calculated by **Equations (2.58)**, **(2.62)** or **(2.64)** depending on the desired property package.

2.10 Basic Models for VLE & LLE

2.10.1 Symmetric Phase Representation

Symmetric phase representation is the use of only one thermodynamic model to represent the behaviour of the vapour and liquid phases. Examples are the Peng-Robinson and SRK models.

The advantages of symmetric phase representation are as follows:

- Consistent representation for both liquid and vapour phases.
- Other thermodynamic properties like enthalpies, entropies and densities can be readily obtained.

The disadvantages of symmetric phase representation are as follows:

- It is not always accurate enough to represent the behaviour of the liquid and vapour phase for polar components. Unless empirical modifications are made on the equations, the representation of the vapour pressures for polar components is not accurate.
- The simple composition dependence usually shown by standard cubic equations of state is inadequate to represent the phase behaviour of polar mixtures.

2.10.2 Asymmetric Phase Representation

Asymmetric phase representation is the use of one model to represent the behaviour of the vapour phase and a separate model to represent the behaviour of the liquid phase (such as Ideal Gas/UNIQUAC, or RK/Van Laar).

The advantages of asymmetric phase representation are:

- The vapour pressure representation is limited only by the accuracy of the vapour pressure correlation.
- There are more adjustable parameters to represent the liquid mixture behaviour.
- There is the possibility of reasonable liquid-liquid representation.

The disadvantages of asymmetric phase representation are:

- The necessity of an arbitrary reference state.
- There are potential problems representing supercritical components.
- There are problems when approaching the mixture critical point.
- Enthalpies, entropies and densities must be computed using a separate model.

2.10.3 Interaction Parameters

The phase behaviour of mixtures is generally not well represented using only pure component properties. When working with either the symmetric or asymmetric approach, it will often be necessary to use some experimental data to "help" the semi-theoretical equations represent reality. If you are using an equation of state, this experimental parameter is usually called "k_{ij}", and is commonly used to correct the quadratic mixture term in cubic equations of state, roughly representing the energies of interaction between components present in the mixture.

If you are using an activity model, the experimental parameters are usually called “a_{ij}” and “a_{ji}”. Several different approaches create different equations with different interpretations of what interaction parameters are. As a rough comparison, the Margules and Van Laar equations are polynomial expansions of the Gibbs free energy of mixture, and the Wilson, NRTL and UNIQUAC methods are statistical mechanics equations based on the Local Composition Concept.

2.10.4 Selecting Property Methods

The various property packages available allow you to predict properties of mixtures ranging from well defined light hydrocarbon systems to highly non-ideal (non-electrolyte) chemical systems. Enhanced equations of state (PR and PRSV) are provided for rigorous treatment of hydrocarbon systems and activity coefficient models for chemical systems. All of these equations have their own inherent limitations and you are encouraged to become more familiar with the application of each equation. This section contains a description of each property package as well as listings of referenced literature.

The range of applicability in many cases is more indicative of the availability of good data rather than on the actual limitations of the Equation of State.

For oil, gas and petrochemical applications, the Peng-Robinson EOS (PR) is generally the recommended property package. The enhancements to this equation of state enable it to be accurate for a variety of systems over a wide range of conditions. It rigorously solves any single, two-phase or three-phase system with a high degree of efficiency and reliability, and is applicable over a wide range of conditions, as shown in the following table.

Method	Temperature, F	Pressure, psia
PR	> -456 (-271 C)	< 15,000 (100,000 kPa)
SRK	> -225 (-143 C)	< 5,000 (35,000 kPa)

The PR equation of state has been enhanced to yield accurate phase equilibrium calculations for systems ranging from low temperature cryogenic systems to high temperature, high pressure reservoir systems. The same equation of state satisfactorily predicts component distributions for heavy oil systems, aqueous glycol and methanol systems, and acid gas/sour water systems.

Although the Soave-Redlich-Kwong (SRK) equation will also provide comparable results to the PR in many cases, it has been observed that its range of application is significantly more limited and this method is not as reliable for non-ideal systems. For example, it should not be used for systems with methanol or glycols.

As an alternative, the PRSV equation of state should be considered. It can handle the same systems as the PR equation with equivalent, or better accuracy, plus it is more suitable for handling non-ideal systems.

The advantage of the PRSV equation is that not only does it have the potential to more accurately predict the phase behaviour of hydrocarbon systems, particularly for systems composed of dissimilar components, but it can also be extended to handle non-ideal systems with accuracies that rival traditional activity coefficient models. The only compromise is increased computational time and an additional interaction parameter which is required for the equation.

The PR and PRSV equations of state can be used to perform rigorous three-phase flash calculations for aqueous systems containing water, methanol or glycols, as well as systems containing other hydrocarbons or non-hydrocarbons in the second liquid phase. The same is true for SRK, but only for aqueous systems.

The PR can also be used for crude systems, which have traditionally been modeled with dual model thermodynamic packages (an activity model representing the liquid phase behaviour, and an equation of state or the ideal gas law for the vapour phase properties). These earlier models become less accurate for systems with large amounts of light ends or when approaching critical regions. Also, the dual model system leads to internal inconsistencies. The proprietary enhancements to the PR and SRK methods allow these Equations of State to correctly represent vacuum conditions and heavy components (a problem with traditional EOS methods), and handle the light-end components and high-pressure systems.

The table below lists some typical systems and the recommended correlations. However, when in doubt of the accuracy or application of one of the property packages, call Technical Support. They will try to either provide you with additional validation material or give the best estimate of its accuracy.

Type of System	Recommended Property Method
TEG Dehydration	PR
Cryogenic Gas Processing	PR, PRSV
Air Separation	PR, PRSV
Reservoir Systems	PR, PR Options
Highly Polar and non-hydrocarbon systems	Activity Models, PRSV
Hydrocarbon systems where H_2O solubility in HC is important	Kabadi Danner

The Property Package methods are divided into eight basic categories, as shown in the following table. Listed with each of the property methods are the available methods for VLE and Enthalpy/Entropy calculations.

Property Method	VLE Calculation	Enthalpy/Entropy Calculation
Equations of State		
PR	PR	PR
SRK	SRK	SRK
Equation of State Options		
PRSV	PRSV	PRSV
Kabadi Danner	Kabadi Danner	SRK
RK-Zudekevitch-Joffee	RK-Zudekevitch-Joffee	RK-Zudekevitch-Joffee
Activity Models		
Liquid		
Margules	Margules	Cavett
Van Laar	Van Laar	Cavett
Wilson	Wilson	Cavett
NRTL	NRTL	Cavett
UNIQUAC	UNIQUAC	Cavett
Chien Null	Chien Null	Cavett
Vapour		
Ideal Gas	Ideal Gas	Ideal Gas
Ideal Gas/Dimer	Ideal Gas/Dimer	Ideal Gas
RK	RK	RK
Peng Robinson	Peng Robinson	Peng Robinson
Virial	Virial	Virial

2.10.5 Vapour Phase Options for Activity Models

There are several models available for calculating the vapour phase in conjunction with the selected activity model. The choice will depend on specific considerations of your system. However, in cases when you are operating at moderate pressures (less than 5 atm), choosing Ideal Gas should be satisfactory.

Ideal

The ideal gas law will be used to model the vapour phase. This model is appropriate for low pressures and for a vapour phase with little intermolecular interaction.

Peng Robinson and SRK

These two options have been provided to allow for better representation of unit operations (such as compressor loops).

Henry's Law

For systems containing non-condensable components, you can supply Henry's law information via the extended Henry's law equations.

The program considers the following components as "non-condensable":

Component	Simulation Name
C1	Methane
C2	Ethane
C2=	Ethylene
C2#	Acetylene
H2	Hydrogen
He	Helium
Argon	Argon
N2	Nitrogen
O2	Oxygen

Component	Simulation Name
NitricOxide	Nitric Oxide
CO	Carbon Monoxide
CO2	Carbon Dioxide
H2S	Hydrogen Sulfide

Refer to **Section 2.6.1 - Non-Condensable Components** and **Section 2.6 - Henry's Law** for the use of Henry's Law.

This information is used to model dilute solute/solvent interactions. Non-condensable components are defined as those components that have critical temperatures below the system temperature you are modeling.

The equation has the following form:

$$\ln H_{ij} = A + \frac{B}{T} + C\ln(T) + DT \tag{2.90}$$

where: i = *Solute or non-condensable component*

j = *Solvent or condensable component*

H_{ij} = *Henry's constant between i and j in kPa, Temperature in degrees K*

A = *A coefficient entered as* a_{ij} *in the parameter matrix*

B = *B coefficient entered as* a_{ji} *in the parameter matrix*

C = *C coefficient entered as* b_{ij} *in the parameter matrix*

D = *D coefficient entered as* b_{ji} *in the parameter matrix*

T = *temperature in degrees K*

Only components listed in the table will be treated as Henry's Law components. If the program does not contain pre-fitted Henry's coefficients, it will estimate the missing coefficients. To supply your own coefficients, you must enter them directly into the a_{ij} and b_{ij} matrices according to **Equation (2.90)**.

No interaction between "non-condensable" component pairs is taken into account in the VLE calculations.

2.11 Phase Stability

So far, the equality of fugacities on the phases for each individual component has been used as the criteria for phase equilibria. Although the equality of fugacities is a necessary criteria, it is not sufficient to ensure that the system is at equilibrium. A necessary and sufficient criteria for thermodynamic equilibrium is that the fugacities of the individual components are the same and the Gibbs Free Energy of the system is at its minimum.

Mathematically:

$$f_i^I = f_i^{II} = f_i^{III} \ldots \tag{2.91}$$

and $G_{system} = minimum$.

The problem of phase stability is not a trivial one, since the number of phases that constitute a system is not known initially, and the creation (or deletion) of new phases during the search for the minimum is a blend of physics, empiricism and art.

2.11.1 Gibbs Free Energy for Binary Systems

According to the definitions, the excess Gibbs energy is given by:

$$G^E = G - G^{ID} = RT \sum_{i=1}^{nc} x_i \ln\gamma_i = RT\sum x_i \ln\frac{f_i}{x_i f_i^{ref}} \tag{2.92}$$

From the previous discussion on partial molar properties, $G^E = \sum x_i \overline{G^E}_i$; thus, if you find a condition such that:

$$G^E = \sum_{j=1}^{np} \sum_{i}^{nc} x_i^P \overline{G_i^{P,\ E}} \tag{2.93}$$

is smaller than:

$$G^E = \sum_{j=1}^{np-1} \sum_{i}^{nc} x_i^P \overline{G_i^{P,\ E}} \tag{2.94}$$

where: np = number of phases

The former condition is more stable than the latter one. If G^E for two phases is smaller than G^E for one phase, then a solution with two phases is more stable than the solution with one. This is represented graphically as shown in the following figures.

Figure 2.1

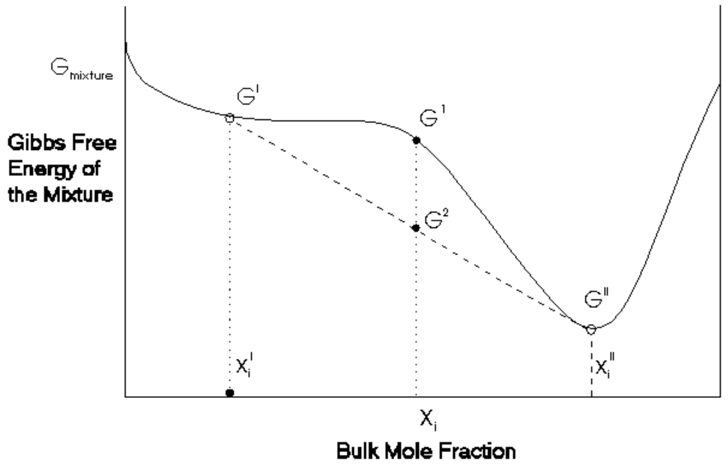
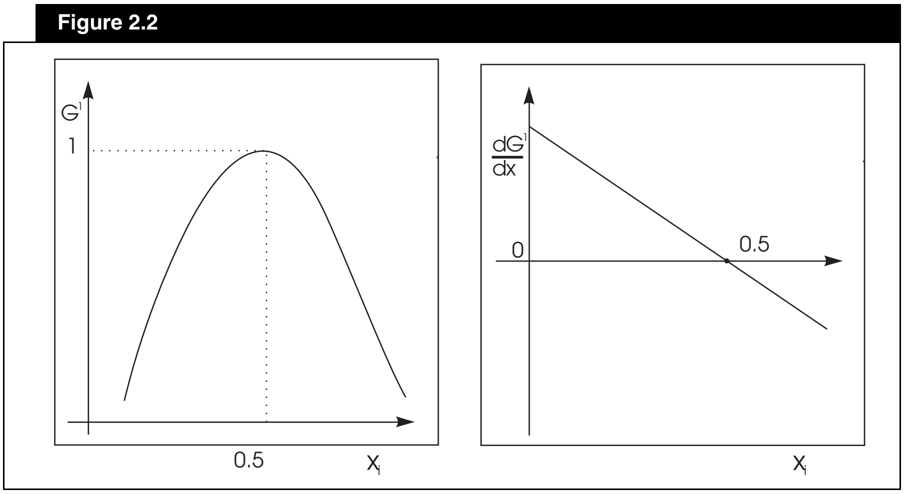


Figure 2.2



If you have a binary mixture of bulk composition x_i, the Gibbs Free Energy of the mixture will be $\overline{G}_1 = \overline{G}_i x_i + \overline{G}_j x_j$. If you consider that two phases can exist, the mass and energy balance tells us that:

$$\beta = \frac{x_i - x_i^I}{x_i^{II} - x_i^I} \qquad and \qquad \beta = \frac{G^2 - G^I}{G^{II} - G^I} \tag{2.95}$$

where: β *is the phase fraction*

Therefore, (G^2, x_i), (G^I, x_i^I) and (G^{II}, x_i^{II}) are co-linear points and you can calculate $G^2 = \beta G^I + (1\text{-}\beta) G^{II}$.

where:

$$G^I = G^I(x_i^I,\ x_j^I,\ P,\ T) \qquad G^{II} = G^{II}(x_i^{II},\ x_j^{II},\ P,\ T) \tag{2.96}$$

Thus, the conditions for phase splitting can be mathematically expressed as requiring that the function G^1 has a local maximum and is convex. This is conveniently expressed using derivatives:

$$\left(\frac{\partial G^1}{\partial x_i}\right)_{T,\ P} = 0 \qquad and \qquad \left(\frac{\partial^2 G^1}{\partial x_i^2}\right)_{T,\ P} = 0 \tag{2.97}$$

If you use

$$G^E = G - G^{ID} = RT\sum_{i=1}^{nc} x_i \ln\gamma_i \tag{2.98}$$

and you use the simple Margules one-parameter expression, you have:

$$\begin{aligned} G &= G^{ID} + G^E = G^{ID} + Ax_ix_j \\ G^{ID} &= \sum x_iG_i + RTx_i\ln x_i + RTx_j\ln x_j \end{aligned} \tag{2.99}$$

and

$$\begin{aligned} G &= \sum x_iG_i + RT(x_i\ln x_i + x_j\ln x_j) + Ax_ix_j \\ \left(\frac{\partial G}{\partial x_i}\right)_{T,\ P} &= A - 2Ax_i + RT\ln\frac{x_i}{x_j} + G_i - G_j \\ \left(\frac{\partial^2 G}{\partial x_i}\right)_{T,\ P} &= -2A + R\frac{T}{x_jx_i} \end{aligned} \tag{2.100}$$

And you want to verify the condition:

$$\left(\frac{\partial^2 G}{\partial x_i}\right)_{T,\ P} = -2A + \frac{RT}{x_jx_i} < 0 \tag{2.101}$$

The minimum of $\frac{RT}{x_jx_i}$ is at $x_i = x_j = 0.5$ and is equal to $4RT$. Thus, the minimum value of A for which phase splitting occurs is $\frac{A}{RT} > 2$. A similar analysis can be performed for the other activity coefficient models for the binary case. The multi-component problem is more complex and useful discussions can be found in the book by [3]Modell and Reid (1983) and in the works of [4]Michelsen (1982) and [5]Seider (1979).

2.12 Enthalpy/Cp Departure Functions

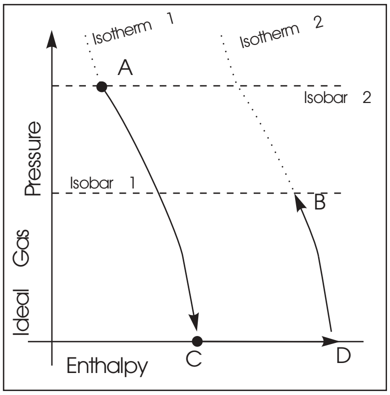
Let *Prop* be any thermodynamic property. If you define the difference of *Prop-Prop*^{0} to be the residual of that property (its value minus the value it would have at a reference state) and call this reference state the ideal gas at the system temperature and composition, you have:

$$P^\circ V^\circ = RT \qquad or \qquad V^\circ = \frac{RT}{P^\circ} \tag{2.102}$$

where: P is an arbitrary pressure, usually 1 atm.

If you have an equation of state defined in terms of *V* and *T* (explicit in pressure), the Helmholtz free energy is the most convenient to work with (*dA* = -*SdT* -*PdV*).

Figure 2.3



At constant temperature you have $dA = -PdV$ and if you integrate from the reference state, you have:

$$A - A° = -\int_{V°}^{V} PdV \tag{2.103}$$

You can divide the integral into two parts:

$$A - A° = -\int_{\infty}^{V} PdV - \int_{V°}^{\infty} PdV \tag{2.104}$$

The second integral refers to the ideal gas, and can be immediately evaluated:

$$P = \frac{RT}{V} \qquad and \qquad \int_{V°}^{\infty} PdV = \int_{V°}^{\infty} \frac{RT}{V} dV \tag{2.105}$$

It is interesting to note that A-A^o for an ideal gas is not zero. The A-A^o term can be rearranged by adding and subtracting $\int_{\infty}^{V} \frac{RT}{V} dV$ and the final result is:

$$A - A° = -\int_{\infty}^{V} \left(P - \frac{RT}{V}\right) dV - RT \ln \frac{V}{V°} \tag{2.106}$$

(Notice that (P-RT/V) goes to zero when the limit $V \rightarrow \infty$ is approached).

The other energy-related thermodynamic functions are immediately derived from the Helmholtz energy:

$$S - S° = -\frac{\partial}{\partial T}(A - A°)_V = \int_{\infty}^{V} \left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{R}{V}\right] dV + R \ln \frac{V}{V°} \tag{2.107}$$

$$H - H° = (A - A°) + T(S - S°) + RT(Z - 1)$$

By the definition of C_p, you have:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \qquad and \qquad \left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$
$$dC_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P dP \tag{2.108}$$

and integrating at constant temperature you have:

$$C_p - C_p{}^\circ = -T\int_{P^\circ}^{P}\left(\frac{\partial^2 V}{\partial T^2}\right)_P dP$$
$$or$$
$$C_p - C_p{}^\circ = T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV - \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial T}\right)_T} - R \tag{2.109}$$

A more complete table of thermodynamic relations and a very convenient derivation for cubic equations of state is given by [6]Reid, Prausnitz and Poling (1987). The only missing derivations are the ideal gas properties. Recalling the previous section, if you were to call *I* an ideal gas property:

$$I^{mix} = \sum_{i=1}^{nc} x_i I_i \tag{2.110}$$

2.12.1 Alternative Formulation for Low Pressure Systems

For chemical systems, where the non-idealities in the liquid phase may be severe even at relatively low pressures, alternate formulations for the thermal properties are as follows:

$$H_i^L = \int_{T,\ ref}^{T} Cp_i dT \qquad and \qquad H^L = \sum_{i=1}^{nc} x_i H_i^L + \Delta H_{mix}^L \tag{2.111}$$

The vapour properties can be calculated as:

$$H_{mix}^V = H_{mix}^L + \Delta H^V + \Delta H_P^V + \Delta H_{mix}^V \tag{2.112}$$

It is assumed that H_i^L at the reference temperature is zero.

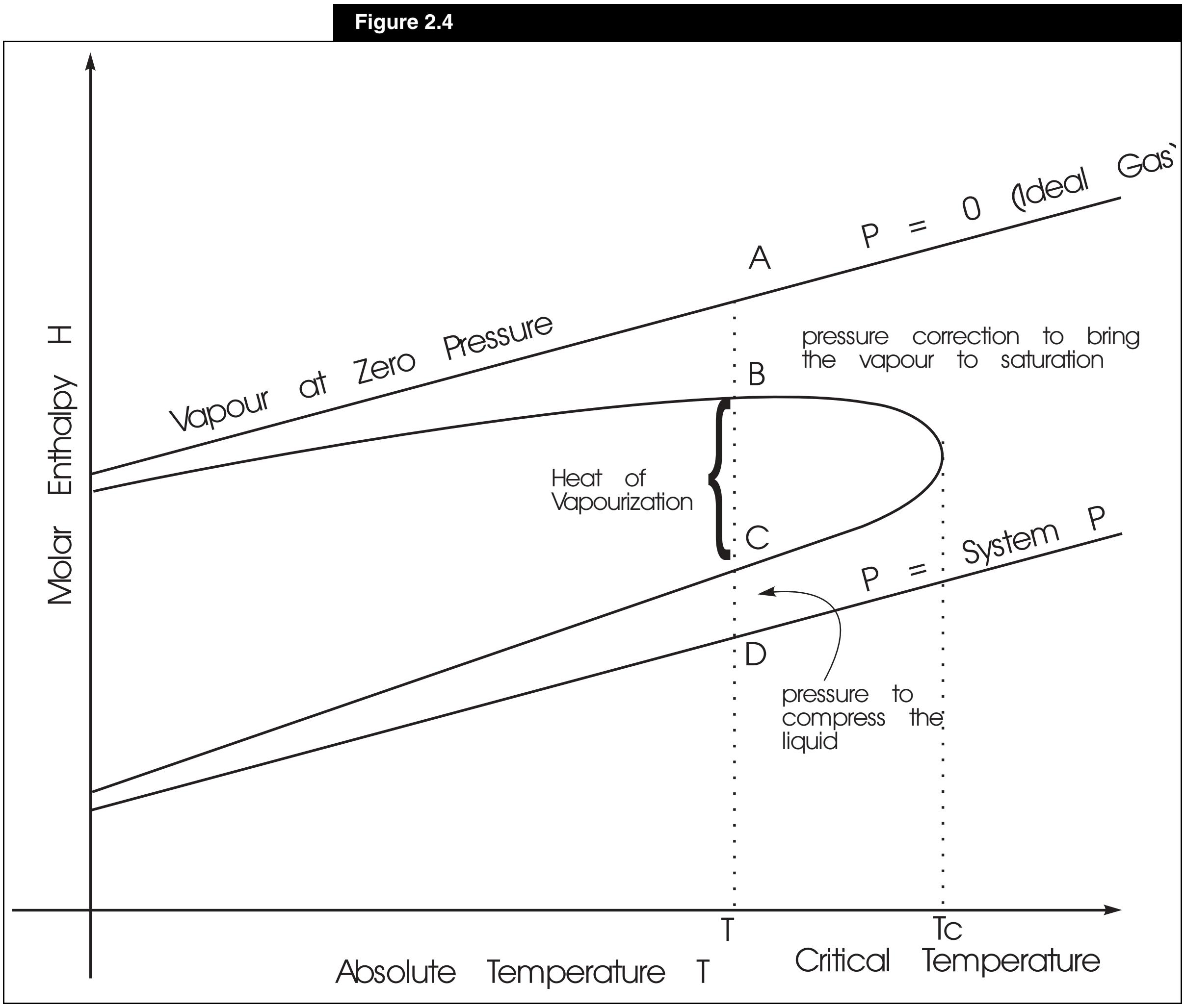
where: ΔH^V *is the enthalpy of vapourization of the mixture at the system pressure*

Usually the ΔH_{mix}^V term is ignored (although it can be computed in a fairly straight forward way for systems where association in the vapour phase is important ([2]Prausnitz et al., (1980)).

The term ΔH_P^V is the contribution to the enthalpy due to compression or expansion, and is zero for an ideal gas. The calculation of this term depends on what model was selected for the vapour phase—Ideal Gas, Redlich Kwong or Virial.

All contribution to the enthalpy at constant temperature can be summarized as follows ([7]Henley and Seader, 1981):

Figure 2.4



3 Thermodynamic Calculation Models

3.1 Equations of State

The program currently offers the enhanced Peng-Robinson (PR), and Soave-Redlich-Kwong (SRK) equations of state. In addition, several methods are offered which are modifications of these property packages, including PRSV, Zudkevitch Joffee and Kabadi Danner. Of these, the Peng-Robinson equation of state supports the widest range of operating conditions and the greatest variety of systems. The Peng-Robinson and Soave-Redlich-Kwong equations of state (EOS) generate all required equilibrium and thermodynamic properties directly. Although the forms of these EOS methods are common with other commercial simulators, they have been significantly enhanced to extend their range of applicability.

The PR and SRK packages contain enhanced binary interaction parameters for all library hydrocarbon-hydrocarbon pairs (a combination of fitted and generated interaction parameters), as well as for most hydrocarbon-non-hydrocarbon binaries.

The PR or SRK EOS should not be used for non-ideal chemicals such as alcohols, acids or other components. These systems are more accurately handled by the Activity Models or the PRSV EOS.

For non-library or hydrocarbon hypocomponents, HC-HC interaction parameters can be generated automatically for improved VLE property predictions.

The PR equation of state applies a functionality to some specific component-component interaction parameters. Key components receiving special treatment include He, H_2, N_2, CO_2, H_2S, H_2O, CH_3OH, EG, and TEG.

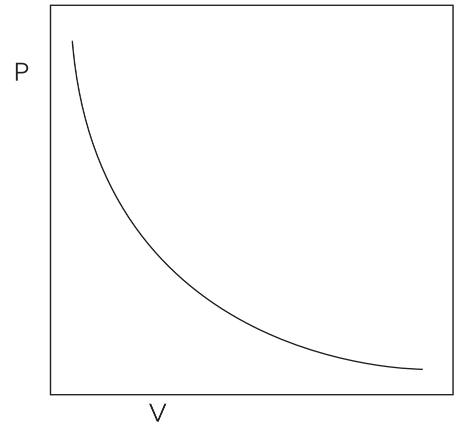
3.1.1 Ideal Gas Equation of State

To use the fugacity coefficient approach, a functional form relating P, V, and T is required. These functional relationships are called equations of state, and their development dates from the 17th century when Boyle first discovered the functionality between pressure and volume. The experimental results obtained from Boyle, Charles, Gay-Lussac, Dalton and Avogadro can be summarized in the Ideal Gas law:

$$PV = RT \tag{3.1}$$

The Ideal Gas equation, while very useful in some applications and as a limiting case, is restricted from the practical point of view. The primary drawbacks of the ideal gas equation stem from the fact that in its derivation two major simplifications are assumed:

Figure 3.1



1. The molecules do not have a physical dimension; they are points in a geometrical sense.
2. There are no electrostatic interactions between molecules.

Usually the Ideal Gas equation is adequate when working with distillation systems without association at low pressures (less than 5 bar).

For further information on the derivation of the Ideal Gas law from first principles, see [8]Feynman (1966).

Property Methods

A quick reference of calculation methods is shown in the table below for Ideal Gas.

Calculation Method	Applicable Phase	Property Class Name
Molar Volume	Vapour	**COTHIGVolume Class**
Enthalpy	Vapour	**COTHIGEnthalpy Class**
Entropy	Vapour	**COTHIGEntropy Class**
Isobaric heat capacity	Vapour	**COTHIGCp Class**
Fugacity coefficient calculation	Vapour	**COTHIGLnFugacityCoeff Class**
Fugacity calculation	Vapour	**COTHIGLnFugacity Class**

The calculation methods from the table are described in the following sections.

IG Molar Volume

The following relation calculates the Molar Volume for a specific phase.

$$V = \frac{RT}{P} \tag{3.2}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIGVolume Class	Vapour

IG Enthalpy

The following relation calculates enthalpy.

$$H = \sum x_i H_i^{IG} \tag{3.3}$$

where: H_i^{IG} *is the pure compound ideal gas enthalpy*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIGEnthalpy Class	Vapour

IG Entropy

The following relation calculates entropy.

$$S = \sum x_i S_i^{IG} - R \sum x_i \ln x_i \tag{3.4}$$

where: S_i^{IG} *is the pure compound ideal gas entropy*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIGEntropy Class	Vapour

IG Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p = \sum x_i C_{p_i}^{IG} \tag{3.5}$$

where: Cp_i^{IG} *is the pure compound ideal gas Cp*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIGCp Class	Vapour

IG Fugacity Coefficient

The following relation calculates the fugacity coefficient.

$$\ln \phi_i = 0 \tag{3.6}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIGLnFugacityCoeff Class	Vapour

IG Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = y_i P \tag{3.7}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIGLnFugacity Class	Vapour

3.1.2 Peng-Robinson Equation of State

The [9]Peng Robinson (1976) equation of state (EOS) is a modification of the RK equation to better represent VLE calculations. The densities for the liquid phase in the SRK did not accurately represent the experimental values due to a high universal critical compressibility factor of 0.3333. The PR is a modification of the RK equation of state which corresponds to a lower critical compressibility of about 0.307 thus representing the VLE of natural gas systems accurately. The PR equation is represented by:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{3.8}$$

where:

$$\begin{aligned} a &= a_c \alpha \\ a_c &= 0.45724 \frac{R^2 T_c^2}{P_c} \\ b &= 0.077480 \frac{R T_c}{P_c} \end{aligned} \tag{3.9}$$

Equations of state in general - attractive and repulsion parts

Simplest cubic EOS - van der Waals

Principle of corresponding states

First successful modification for engineering - RK

The property that is usually required for engineering calculations is vapour pressure.

The SRK and RK EOS propose modifications which improve the vapour pressure calculations for relatively simple gases and hydrocarbons.

The functional dependency of the "*a*" term is shown in the following relation.

$$\begin{aligned} \sqrt{\alpha} &= 1 + \kappa(1 - T_r^{0.5}) \\ \kappa &= 0.37464 + 1.5422\omega - 0.26992\omega^2 \end{aligned} \tag{3.10}$$

The accuracy of the PR and SRK equations of state are approximately the same. However, the PR EOS represents the density of the liquid phase more accurately due to the lower critical compressibility factor.

These equations were originally developed for pure components. To apply the PR EOS to mixtures, mixing rules are required for the "*a*" and "*b*" terms in **Equation (3.2)**. Refer to the **Mixing Rules** section on the mixing rules available.

Property Methods

A quick reference of calculation methods is shown in the table below for the PR EOS.

Calculation Method	Applicable Phase	Property Class Name
Z Factor	Vapour and Liquid	**COTHPRZFactor Class**
Molar Volume	Vapour and Liquid	**COTHPRVolume Class**
Enthalpy	Vapour and Liquid	**COTHPREnthalpy Class**
Entropy	Vapour and Liquid	**COTHPREntropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTHPRCp Class**
Fugacity coefficient calculation	Vapour and Liquid	**COTHPRLnFugacityCoeff Class**
Fugacity calculation	Vapour and Liquid	**COTHPRLnFugacity Class**
Isochoric heat capacity	Vapour and Liquid	**COTHPRCv Class**
Mixing Rule 1	Vapour and Liquid	**COTHPRab_1 Class**
Mixing Rule 2	Vapour and Liquid	**COTHPRab_2 Class**
Mixing Rule 3	Vapour and Liquid	**COTHPRab_3 Class**
Mixing Rule 4	Vapour and Liquid	**COTHPRab_4 Class**
Mixing Rule 5	Vapour and Liquid	**COTHPRab_5 Class**
Mixing Rule 6	Vapour and Liquid	**COTHPRab_6 Class**

The calculation methods from the table are described in the following sections.

PR Z Factor

The compressibility factor, Z, is calculated as the root for the following equation:

$$Z^3 - (1 - B)Z^2 + Z(A - 3B^2 - 2B) - (AB - B^2 - B^3) = 0 \tag{3.11}$$

$$A = \frac{aP}{R^2T^2} \tag{3.12}$$

$$B = \frac{bP}{RT} \tag{3.13}$$

There are three roots for the above equation. It is considered that the smallest root is for the liquid phase and the largest root is for the vapour phase. The third root has no physical meaning.

PR Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{ZRT}{P} \tag{3.14}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRVolume Class	Vapour and Liquid

The compressibility factor, Z, is calculated using PR Z Factor. For consistency, the PR molar volume always calls the PR Z Factor for the calculation of Z.

PR Enthalpy

The following relation calculates the enthalpy.

$$H - H^{IG} = PV - RT - \left(a - \left(\frac{da}{dT}\right)T\right)\frac{1}{2\sqrt{2}b}\ln\frac{V + b(1+\sqrt{2})}{V + b(1-\sqrt{2})} \qquad (3.15)$$

where: H^{IG} *is the ideal gas enthalpy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPREnthalpy Class	Vapour and Liquid

The volume, V, is calculated using PR Molar Volume. For consistency, the PR Enthalpy always calls the PR Volume for the calculation of V.

PR Entropy

The following relation calculates the entropy.

$$S - S^{IG} = R\ln\left(\frac{V - b}{RT}\right) - \frac{1}{2b\sqrt{2}}\ln\left(\frac{V + b(1+\sqrt{2})}{V + b(1-\sqrt{2})}\right)\frac{da}{dT} \qquad (3.16)$$

where: S^{IG} *is the ideal gas entropy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPREntropy Class	Vapour and Liquid

The volume, V, is calculated using PR Molar Volume. For consistency, the PR Entropy always calls the PR Volume for the calculation of V.

PR Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{3.17}$$

where: Cp^{IG} *is the ideal gas heat capacity calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRCp Class	Vapour and Liquid

The volume, V, is calculated using PR Molar Volume. For consistency, the PR Entropy always calls the PR Volume for the calculation of V.

PR Fugacity Coefficient

The following relation calculates the fugacity coefficient.

$$\ln\phi_i = -\ln(V-b) + \frac{\bar{b}}{V-b} + \frac{a}{2\sqrt{2}b}\ln\left(\frac{V+b(1+\sqrt{2})}{V+b(1-\sqrt{2})}\right)\left(-1+\frac{\bar{a}}{a}+\frac{\bar{b}}{b}\right) \tag{3.18}$$

$$\bar{a} = \frac{\partial n^2 a}{\partial n} \tag{3.19}$$

$$\bar{b} = \frac{\partial nb}{\partial n} \tag{3.20}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRLnFugacityCoeff Class	Vapour and Liquid

The volume, V, is calculated using PR Molar Volume. For consistency, the PR Fugacity Coefficient always calls the PR Volume for the calculation of V. The parameters *a* and *b* are calculated from the Mixing Rules.

PR Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.21}$$

Property Class Name and Applicable Phase

Property Class Name	Applicable Phase
COTHPRLnFugacity Class	Vapour and Liquid

PR Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v = C_p + \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{3.22}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRCv Class	Vapour and Liquid

Mixing Rules

The mixing rules available for the PR EOS state are shown below.

$$a = \sum_{i=1}^{nc}\sum_{j=1}^{nc}(x_i x_j a_{ij}) \tag{3.23}$$

$$b = \sum_{i=1}^{nc} b_i x_i \tag{3.24}$$

$$a_{ij} = \xi_{ij}\sqrt{a_{ci}a_{cj}\alpha_i\alpha_j} \tag{3.25}$$

$$\sqrt{\alpha_i} = (1 - \kappa_i)(1 - T_{ri}^{0.5}) \tag{3.26}$$

$$a_{ci} = \frac{0.45724R^2T_{ci}^2}{P_{ci}} \tag{3.27}$$

$$b_i = \frac{0.07780RT_{ci}}{P_{ci}} \tag{3.28}$$

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \qquad \omega_i < 0.49 \tag{3.29}$$

Mixing Rule 1

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + C_{ij}T^2 \tag{3.30}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 2

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + \frac{C_{ij}}{T} \tag{3.31}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 3

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as

$$\xi_{ij} = 1 - x_i(A_{ij} + B_{ij} + C_{ij}T^2) - x_j(A_{ji} + B_{ji}T + C_{ji}T^2) \tag{3.32}$$

Mixing Rule 4

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) - x_j\left(A_{ji} + B_{ji} + \frac{C_{ji}}{T}\right) \tag{3.33}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 5

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{(A_{ij} + B_{ij}T + C_{ij}T^2)(A_{ji} + B_{ji}T + C_{ij}T^2)}{x_i(A_{ij} + B_{ij}T + C_{ij}T^2) + x_j(A_{ji} + B_{ji}T + C_{ji}T^2)} \tag{3.34}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 6

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right)\left(A_{ji} + B_{ji}T + \frac{C_{ij}}{T}\right)}{x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) + x_j\left(A_{ji} + B_{ji}T + \frac{C_{ji}}{T}\right)} \qquad (3.35)$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

3.1.3 HysysPR Equation of State

The HysysPR EOS is similar to the PR EOS with several enhancements to the original PR equation. It extends its range of applicability and better represents the VLE of complex systems. The HysysPR equation is represented by:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \qquad (3.36)$$

where:

$$\begin{aligned} a &= a_c\alpha \\ a_c &= 0.45724\frac{R^2T_c^2}{P_c} \\ b &= 0.077480\frac{RT_c}{P_c} \end{aligned} \qquad (3.37)$$

The functional dependency of the *"a"* term is shown in the following relation as Soave:

$$\sqrt{\alpha} = 1 + S(1 - T_r^{0.5})$$
$$S = 0.37464 + 1.5422\omega - 0.26992\omega^2 \tag{3.38}$$

Property Methods

A quick reference of calculation methods is shown in the table below for the HysysPR EOS.

Calculation Method	Applicable Phase	Property Class Name
Z Factor	Vapour and Liquid	**COTH_HYSYS_ZFactor Class**
Molar Volume	Vapour and Liquid	**COTH_HYSYS_Volume Class**
Enthalpy	Vapour and Liquid	**COTH_HYSYS_PREnthalpy Class**
Entropy	Vapour and Liquid	**COTH_HYSYS_Entropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTH_HYSYS_Cp Class**
Fugacity coefficient calculation	Vapour and Liquid	**COTH_HYSYS_LnFugacityCoeff Class**
Fugacity calculation	Vapour and Liquid	**COTH_HYSYS_LnFugacity Class**
Isochoric heat capacity	Vapour and Liquid	**COTH_HYSYS_Cv Class**

The calculation methods from the table are described in the following sections.

HysysPR Z Factor

The compressibility factor, Z, is calculated as the root for the following equation:

$$Z^3 - (1 - B)Z^2 + Z(A - 3B^2 - 2B) - (AB - B^2 - B^3) = 0 \tag{3.39}$$

$$A = \frac{aP}{R^2T^2} \tag{3.40}$$

$$B = \frac{bP}{RT} \tag{3.41}$$

There are three roots for the above equation. It is considered that the smallest root is for the liquid phase and the largest root is for the vapour phase. The third root has no physical meaning.

HysysPR Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{ZRT}{P} \tag{3.42}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTH_HYSYS_Volume Class	Vapour and Liquid

The compressibility factor, Z, is calculated using HysysPR Z Factor. For consistency, the HysysPR molar volume always calls the HysysPR Z Factor for the calculation of Z.

HysysPR Enthalpy

The following relation calculates the enthalpy.

$$H - H^{IG} = PV - RT - \left(a - \left(\frac{da}{dT}\right)T\right)\frac{1}{2\sqrt{2}b}\ln\frac{V + b(1 + \sqrt{2})}{V + b(1 - \sqrt{2})} \qquad (3.43)$$

where: H^{IG} *is the ideal gas enthalpy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTH_HYSYS_Enthalpy Class	Vapour and Liquid

The volume, V, is calculated using HysysPR Molar Volume. For consistency, the PR Enthalpy always calls the PR Volume for the calculation of V.

HysysPR Entropy

The following relation calculates the entropy.

$$S - S^{IG} = R\ln\left(\frac{V-b}{RT}\right) - \frac{1}{2b\sqrt{2}}\ln\left(\frac{V+b(1+\sqrt{2})}{V+b(1-\sqrt{2})}\right)\frac{da}{dT} \tag{3.44}$$

where: S^{IG} *is the ideal gas entropy calculated at temperature,* T

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTH_HYSYS_Entropy Class	Vapour and Liquid

The volume, V, is calculated using HysysPR Molar Volume. For consistency, the HysysPR Entropy always calls the HysysPR Volume for the calculation of V.

HysysPR Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{3.45}$$

where: Cp^{IG} *is the ideal gas heat capacity calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTH_HYSYS_Cp Class	Vapour and Liquid

HysysPR Fugacity Coefficient

The following relation calculates the fugacity coefficient.

$$\ln\phi_i = -\ln(V-b) + \frac{\bar{b}}{V-b} + \frac{a}{2\sqrt{2}b}\ln\left(\frac{V+b(1+\sqrt{2})}{V+b(1-\sqrt{2})}\right)\left(-1+\frac{\bar{a}}{a}+\frac{\bar{b}}{b}\right) \tag{3.46}$$

$$\bar{a} = \frac{\partial n^2 a}{\partial n} \tag{3.47}$$

$$\bar{b} = \frac{\partial nb}{\partial n} \tag{3.48}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTH_HYSYS_LnFugacityCoeff Class	Vapour and Liquid

The volume, V, is calculated using HysysPR Molar Volume. For consistency, the HysysPR Fugacity Coefficient always calls the HysysPR Volume for the calculation of V. The parameters *a* and *b* are calculated from the Mixing Rules.

HysysPR Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.49}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTH_HYSYS_LnFugacity Class	Vapour and Liquid

HysysPR Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v = C_p + \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{3.50}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTH_HYSYS_Cv Class	Vapour and Liquid

Mixing Rules

The mixing rules available for the HysysPR EOS state are shown below.

$$a = \sum_{i=1}^{nc}\sum_{j=1}^{nc}(x_i x_j a_{ij}) \tag{3.51}$$

$$b = \sum_{i=1}^{nc} b_i x_i \tag{3.52}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_{ci}a_{cj}\alpha_i\alpha_j} \tag{3.53}$$

$$\sqrt{\alpha_i} = (1 - \kappa_i)(1 - T_{ri}^{0.5}) \tag{3.54}$$

$$a_{ci} = \frac{0.45724R^2T_{ci}^2}{P_{ci}} \tag{3.55}$$

$$b_i = \frac{0.07780RT_{ci}}{P_{ci}} \tag{3.56}$$

$$\kappa_i = \begin{cases} 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 & \omega_i < 0.49 \\ 0.37964 + 1.48503\omega_i - 0.16442\omega_i^2 + 0.016666\omega_i^3 & \omega_i \geq 0.49 \end{cases} \tag{3.57}$$

where: κij = asymmetric binary interaction parameter

3.1.4 Peng-Robinson Stryjek-Vera

The Peng-Robinson [10]Stryjek-Vera PRSV, 1986) equation of state is a two-fold modification of the PR equation of state that extends the application of the original PR method for highly non-ideal systems. It has been shown to match vapour pressures curves of pure components and mixtures more accurately, especially at low vapour pressures.

It has been extended to handle non-ideal systems providing results similar to those obtained using excess Gibbs energy functions like the Wilson, NRTL or UNIQUAC equations.

The PRSV equation of state is defined as:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{3.58}$$

where:

$$\begin{aligned} a &= a_c\alpha \\ a_c &= 0.45724\frac{R^2T_c^2}{P_c} \\ b &= 0.077480\frac{RT_c}{P_c} \end{aligned} \tag{3.59}$$

One of the proposed modifications to the PR equation of state by Stryjek and Vera was an expanded alpha, "α", term that became a function of acentricity and an empirical parameter, κ_i, used for fitting pure component vapour pressures.

$$\begin{aligned}\alpha_i &= [1 + \kappa_i(1 - T_r^{0.5})]^2 \\ \kappa_i &= \kappa_{0i} + \kappa_1(1 + T_{ri}^{0.5})(0.7 - T_{ri}) \\ \kappa_{0i} &= 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3\end{aligned} \tag{3.60}$$

where: κ_1 = *Characteristic pure component parameter*

ω_i = *Acentric factor*

The adjustable κ_1 parameter allows for a much better fit of the pure component vapour pressure curves. This parameter has been regressed against the pure component vapour pressure for all library components.

For hypocomponents that have been generated to represent oil fractions, the κ_1 term for each hypocomponent will be automatically regressed against the Lee-Kesler vapour pressure curves. For individual user-added hypothetical components, κ_1 terms can either be entered or they will automatically be regressed against the Lee-Kesler, Gomez-Thodos or Reidel correlations.

The second modification consists of a new set of mixing rules for mixtures. To apply the PRSV EOS to mixtures, mixing rules are required for the "*a*" and "*b*" terms in **Equation (3.46)**. Refer to the **Mixing Rules** section for the set of mixing rules applicable.

Property Methods

A quick reference of calculation methods is shown in the table below for the PRSV EOS.

Calculation Method	Applicable Phase	Property Class Name
Z Factor	Vapour and Liquid	**COTHPRSVZFactor Class**
Molar Volume	Vapour and Liquid	**COTHPRSVVolume Class**
Enthalpy	Vapour and Liquid	**COTHPRSVEnthalpy Class**
Entropy	Vapour and Liquid	**COTHPRSVEntropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTHPRSVCp Class**
Fugacity coefficient calculation	Vapour and Liquid	**COTHPRSVLnFugacityCoeff Class**
Fugacity calculation	Vapour and Liquid	**COTHPRSVLnFugacity Class**
Isochoric heat capacity	Vapour and Liquid	**COTHPRSVCv Class**
Mixing Rule 1	Vapour and Liquid	**COTHPRSVab_1 Class**
Mixing Rule 2	Vapour and Liquid	**COTHPRSVab_2 Class**
Mixing Rule 3	Vapour and Liquid	**COTHPRSVab_3 Class**
Mixing Rule 4	Vapour and Liquid	**COTHPRSVab_4 Class**
Mixing Rule 5	Vapour and Liquid	**COTHPRSVab_5 Class**
Mixing Rule 6	Vapour and Liquid	**COTHPRSVab_6 Class**

The calculation methods from the table are described in the following sections.

PRSV Z Factor

The compressibility factor, Z, is calculated as the root for the following equation:

$$Z^3 - (1 - B)Z^2 + Z(A - 3B^2 - 2B) - (AB - B^2 - B^3) = 0 \tag{3.61}$$

$$A = \frac{aP}{R^2T^2} \tag{3.62}$$

$$B = \frac{bP}{RT} \tag{3.63}$$

There are three roots for the above equation. It is considered that the smallest root is for the liquid phase and the largest root is for the vapour phase. The third root has no physical meaning.

PRSV Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{ZRT}{P} \tag{3.64}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRSVVolume Class	Vapour and Liquid

The compressibility factor, Z, is calculated using PRSV Z Factor. For consistency, the PRSV molar volume always calls the PRSV Z factor for the calculation of Z.

PRSV Enthalpy

The following relation calculates the enthalpy

$$H - H^{IG} = PV - RT - \left(a - \left(\frac{da}{dT}\right)T\right)\frac{1}{2\sqrt{2}b}\ln\frac{V + b(1+\sqrt{2})}{V + b(1-\sqrt{2})} \qquad (3.65)$$

where: H^{IG} *is the ideal gas enthalpy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRSVEnthalpy Class	Vapour and Liquid

The volume, V, is calculated using PRSV Molar Volume. For consistency, the PRSV Enthalpy always calls the PRSV Volume for the calculation of V.

PRSV Entropy

The following relation calculates the entropy.

$$S - S^{IG} = R\ln\left(\frac{V-b}{RT}\right) - \frac{1}{2b\sqrt{2}}\ln\left(\frac{V+b(1+\sqrt{2})}{V+b(1-\sqrt{2})}\right)\frac{da}{dT} \tag{3.66}$$

where: S^{IG} *is the ideal gas entropy calculated at temperature,* T

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRSVEntropy Class	Vapour and Liquid

The volume, V, is calculated using PRSV Molar Volume. For consistency, the PRSV Entropy always calls the PRSV Volume for the calculation of V.

PRSV Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{3.67}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRSVCp Class	Vapour and Liquid

PRSV Fugacity Coefficient

The following relation calculates the fugacity Coefficient.

$$\ln\phi_i = -\ln(V-b) + \frac{\bar{b}}{V-b} + \frac{a}{2\sqrt{2}b}\ln\left(\frac{V+b(1+\sqrt{2})}{V+b(1-\sqrt{2})}\right)\left(-1+\frac{\bar{a}}{a}+\frac{\bar{b}}{b}\right) \tag{3.68}$$

$$\bar{a} = \frac{\partial n^2 a}{\partial n} \tag{3.69}$$

$$\bar{b} = \frac{\partial nb}{\partial n} \tag{3.70}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRSVLnFugacityCoeff Class	Vapour and Liquid

The volume, V, is calculated using PRSV Molar Volume. For consistency, the PRSV Fugacity Coefficient always calls the PRSV Volume for the calculation of V. The parameters a and b are calculated from the Mixing Rules.

PRSV Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.71}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRSVLnFugacity Class	Vapour and Liquid

PRSV Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v = C_p + \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{3.72}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHPRSVCv Class	Vapour and Liquid

Mixing Rules

The mixing rules available for the PRSV equation are shown below.

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} (x_i x_j a_{ij}) \tag{3.73}$$

$$b = \sum_{i=1}^{nc} b_i x_i \tag{3.74}$$

$$a_{ij} = (a_{ii}a_{jj})^{0.5}\xi_{ij} \tag{3.75}$$

$$\sqrt{\alpha_i} = (1-\kappa_i)(1-T_{ri}^{0.5}) \tag{3.76}$$

$$a_i = \frac{0.45724R^2T_{ci}^2}{P_{ci}} \tag{3.77}$$

$$b_i = \frac{0.07780RT_{ci}}{P_{ci}} \tag{3.78}$$

$$\kappa_i = \kappa_{i0} + \kappa_{i1}(1+T_{ri}^{0.5})(0.7-T_{ri}) \tag{3.79}$$

$$\kappa_{i0} = 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3 \tag{3.80}$$

Mixing Rule 1

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + C_{ij}T^2 \tag{3.81}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 2

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + \frac{C_{ij}}{T} \tag{3.82}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 3

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i(A_{ij} + B_{ij} + C_{ij}T^2) - x_j(A_{ji} + B_{ji}T + C_{ji}T^2) \tag{3.83}$$

Mixing Rule 4

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) - x_j\left(A_{ji} + B_{ji} + \frac{C_{ji}}{T}\right) \tag{3.84}$$

where: *A_{ij}, B_{ij}, and C_{ij} are asymmetric binary interaction parameters*

Mixing Rule 5

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{(A_{ij} + B_{ij}T + C_{ij}T^2)(A_{ji} + B_{ji}T + C_{ij}T^2)}{x_i(A_{ij} + B_{ij}T + C_{ij}T^2) + x_j(A_{ji} + B_{ji}T + C_{ji}T^2)} \tag{3.85}$$

where: *A_{ij}, B_{ij}, and C_{ij} are asymmetric binary interaction parameters*

Mixing Rule 6

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right)\left(A_{ji} + B_{ji}T + \frac{C_{ij}}{T}\right)}{x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) + x_j\left(A_{ji} + B_{ji}T + \frac{C_{ji}}{T}\right)} \tag{3.86}$$

where: *A_{ij}, B_{ij}, and C_{ij} are asymmetric binary interaction parameters*

3.1.5 Soave-Redlich-Kwong Equation of State

Wilson (1965, 1966) noted that the main drawback of the RK equation of state was its inability of accurately reproducing the vapour pressures of pure component constituents of a given mixture. He proposed a modification to the RK equation of state using the acentricity as a correlating parameter, but this approach was widely ignored until 1972, when [11]Soave (1972) proposed a modification of the RK equation of this form:

$$P = \frac{RT}{V-b} - \frac{a(T,\ T_c,\ \omega)}{V(V+b)} \tag{3.87}$$

The *"a"* term was fitted to reproduce the vapour pressure of hydrocarbons using the acentric factor as a correlating parameter. This led to the following development:

$$\begin{aligned} P &= \frac{RT}{V-b} - \frac{a_c\alpha}{V(V+b)} \\ a_c &= \Omega_a \frac{R^2 T_c^2}{P_c} \\ \sqrt{\alpha} &= 1 + S(1 - T_r^{0.5}) \\ S &= 0.480 + 1.574\omega - 0.176\omega^2 \end{aligned} \tag{3.88}$$

Empirical modifications for the "*a*" term for specific substances like hydrogen were proposed by [12]Graboski and Daubert (1976), and different, substance specific forms for the "*a*" term with several adjusted parameters are proposed up to the present, varying from 1 to 3 adjustable parameters. The SRK equation of state can represent the behaviour of hydrocarbon systems for separation operations with accuracy. Since, it is readily converted into computer code, its usage has been intense in the last twenty years. Other derived thermodynamic properties, like enthalpies and entropies, are reasonably accurate for engineering work, and the SRK equation has wide acceptance in the engineering community today.

Refer to the **Mixing Rules** section for the applicable set of mixing rules.

To apply the SRK EOS to mixtures, mixing rules are required for the "*a*" and "*b*" terms in Equation (3.270).

Property Methods

A quick reference of calculation methods is shown in the table below for the SRK EOS.

Calculation Method	Applicable Phase	Property Class Name
Z Factor	Vapour and Liquid	**COTHSRKZFactor Class**
Molar Volume	Vapour and Liquid	**COTHSRKVolume Class**
Enthalpy	Vapour and Liquid	**COTHSRKEnthalpy Class**
Entropy	Vapour and Liquid	**COTHSRKEntropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTHSRKCp Class**
Fugacity coefficient calculation	Vapour and Liquid	**COTHSRKLnFugacityCoeff Class**
Fugacity calculation	Vapour and Liquid	**COTHSRKLnFugacity Class**
Isochoric heat capacity	Vapour and Liquid	**COTHSRKCv Class**
Mixing Rule 1	Vapour and Liquid	**COTHSRKab_1 Class**
Mixing Rule 2	Vapour and Liquid	**COTHSRKab_2 Class**
Mixing Rule 3	Vapour and Liquid	**COTHSRKab_3 Class**
Mixing Rule 4	Vapour and Liquid	**COTHSRKab_4 Class**
Mixing Rule 5	Vapour and Liquid	**COTHSRKab_5 Class**
Mixing Rule 6	Vapour and Liquid	**COTHSRKab_6 Class**

The calculation methods from the table are described in the following sections.

SRK Z Factor

The compressibility factor is calculated as the root for the following equation:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \tag{3.89}$$

$$A = \frac{aP}{R^2T^2} \tag{3.90}$$

$$B = \frac{bP}{RT} \tag{3.91}$$

There are three roots for the above equation.

It is considered that the smallest root is for the liquid phase and the largest root is for the vapour phase. The third root has no physical meaning.

SRK Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{ZRT}{P} \tag{3.92}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHSRKVolume Class	Vapour and Liquid

The compressibility factor, Z, is calculated using SRK Z Factor. For consistency, the SRK molar volume always calls the SRK Z Factor for the calculation of Z

SRK Enthalpy

The following relation calculates the enthalpy.

$$H - H^{IG} = PV - RT + \frac{1}{b}\left(a - T\frac{\partial a}{\partial T}\right)\ln\frac{V}{V+b} \tag{3.93}$$

where: H^{IG} *is the ideal gas enthalpy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHSRKEnthalpy Class	Vapour and Liquid

The volume, V, is calculated using SRK Molar Volume. For consistency, the SRK Enthalpy always calls the SRK Volume for the calculation of V.

SRK Entropy

The following relation calculates the entropy.

$$S - S^{IG} = R\ln\left(\frac{V-b}{RT}\right) - \frac{1}{b}\left(\frac{\partial a}{\partial T}\right)\ln\left(\frac{V+b}{V}\right) \tag{3.94}$$

where: S^{IG} *is the ideal gas entropy calculated at temperature, T.*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHSRKEntropy Class	Vapour and Liquid

The volume, V, is calculated using SRK Molar Volume. For consistency, the SRK Entropy always calls the SRK Volume for the calculation of V.

SRK Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{3.95}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHSRKCp Class	Vapour and Liquid

SRK Fugacity Coefficient

The following relation calculates the fugacity coefficient.

$$\ln\phi_i = \ln(V-b) + \frac{\bar{b}}{V-b} + \frac{a}{RTb}\left(\frac{\bar{b}}{b} - \frac{\bar{a}}{a} - 1\right)\ln\left(\frac{V+b}{V}\right) \tag{3.96}$$

$$\bar{a} = \frac{\partial n^2 a}{\partial n} \tag{3.97}$$

$$\bar{b} = \frac{\partial nb}{\partial n_i} \tag{3.98}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHSRKLnFugacityCoeff Class	Vapour and Liquid

The volume, V, is calculated using SRK Molar Volume. For consistency, the SRK Fugacity Coefficient always calls the SRK Volume for the calculation of V. The parameters *a* and *b* are calculated from the Mixing Rules.

SRK Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.99}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHSRKLnFugacity Class	Vapour and Liquid

SRK Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v = C_p + \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{3.100}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHSRKCv Class	Vapour and Liquid

Mixing Rules

The mixing rules available for the SRK EOS state are shown below.

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} (x_i x_j a_{ij}) \tag{3.101}$$

$$b = \sum_{i=1}^{nc} b_i x_i \tag{3.102}$$

$$a_{ij} = \xi_{ij} \sqrt{a_{ci} a_{cj} \alpha_i \alpha_j} \tag{3.103}$$

$$\sqrt{\alpha_i} = 1 - \kappa_{ij}(1 - T_{ri}^{0.5}) \tag{3.104}$$

$$a_{ci} = \frac{0.42748 R^2 T_{ci}^2}{P_{ci}} \tag{3.105}$$

$$b_i = \frac{0.08664 R T_{ci}}{P_{ci}} \tag{3.106}$$

$$\kappa_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \tag{3.107}$$

Mixing Rule 1

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij} T + C_{ij} T^2 \tag{3.108}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 2

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + \frac{C_{ij}}{T} \tag{3.109}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 3

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i(A_{ij} + B_{ij} + C_{ij}T^2) - x_j(A_{ji} + B_{ji}T + C_{ji}T^2) \tag{3.110}$$

Mixing Rule 4

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) - x_j\left(A_{ji} + B_{ji} + \frac{C_{ji}}{T}\right) \tag{3.111}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 5

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{(A_{ij} + B_{ij}T + C_{ij}T^2)(A_{ji} + B_{ji}T + C_{ij}T^2)}{x_i(A_{ij} + B_{ij}T + C_{ij}T^2) + x_j(A_{ji} + B_{ji}T + C_{ji}T^2)} \tag{3.112}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 6

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right)\left(A_{ji} + B_{ji}T + \frac{C_{ij}}{T}\right)}{x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) + x_j\left(A_{ji} + B_{ji}T + \frac{C_{ji}}{T}\right)} \tag{3.113}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

3.1.6 Redlich-Kwong Equation of State

In 1949, Redlich and Kwong proposed a modification of the van der Waals equation where the universal critical compressibility was reduced to a more reasonable number (i.e., 0.3333). This modification, known as the Redlich-Kwong (RK) equation of state, was very successful, and for the first time, a simple cubic equation of state would be used for engineering calculations with acceptable accuracy. Previous equations used for engineering calculations were modifications of the virial equation of state, notably the Beatie-Bridgeman and the Benedict-Webb-Rubin (BWR).

These other equations, although capable of accurately representing the behaviour of pure fluids, had many adjustable constants to be determined through empirical fitting of PVT properties, and received limited use. On the other hand, the RK equation required only T_c and P_c, and (fortunately) the principles of corresponding states using T_c and P_c applies with fair accuracy for simple hydrocarbon systems. This combination of simplicity and relative accuracy made the RK equation of state a very useful tool for engineering calculations in hydrocarbon systems. The Redlich-Kwong equation of state is represented by the following equation:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)}\frac{1}{\sqrt{T}} \tag{3.114}$$

and the reduced form is represented by:

$$\begin{aligned}
P_r &= \frac{3T_r}{V_r - 3\Omega_b} - \frac{9\Omega_a}{T_r^{0.5}V_r(V_r + 3\Omega_b)} \\
\Omega_a &= 0.42748 \\
\Omega_b &= 0.08664 \\
a &= \Omega_a R^2 \frac{T_c^{2.5}}{P_c} \\
b &= \Omega_b R \frac{T_c}{P_c}
\end{aligned} \tag{3.115}$$

Pitzer's definition is based on an empirical study in which it was verified that noble gases have a reduced pressure of about 0.1 at $T_r = 0.7$.

Although simple systems approximately obey the corresponding states law as expressed by the RK equation, further improvements were required, especially when using the equation to predict the vapour pressure of pure substances. It was noted by several researchers, notably Pitzer, that the corresponding states principle could be extended by the use of a third corresponding state parameter, in addition to T_c and P_c. The two most widely used third parameters are the critical compressibility (Z_c) and the acentric factor (ω). The acentric factor has a special appeal for equations of state based on the van der Waals ideas, since it is related to the lack of sphericity of a given substance. Pitzer defined the acentric factor as:

$$\omega = -1 - \log P_r \qquad when\ T_r = 0.7 \tag{3.116}$$

In this way, one may consider developing an equation of state using T_c, P_c, and ωas correlating parameters.

To apply the RK EOS to mixtures, mixing rules are required for the “*a*” and “*b*” terms in **Equation (3.64)**. Refer to the **Mixing Rules** section for the set of mixing rules applicable.

Property Methods

A quick reference of calculation methods is shown in the table below for the RK EOS.

Calculation Method	Applicable Phase	Property Class Name
Z Factor	Vapour and Liquid	**COTHRKZFactor Class**
Molar Volume	Vapour and Liquid	**COTHRKVolume Class**
Enthalpy	Vapour and Liquid	**COTHRKEnthalpy Class**
Entropy	Vapour and Liquid	**COTHRKEntropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTHRKCp Class**
Fugacity coefficient calculation	Vapour and Liquid	**COTHRKLnFugacityCoeff Class**
Fugacity calculation	Vapour and Liquid	**COTHRKLnFugacity Class**
Isochoric heat capacity	Vapour and Liquid	**COTHRKCv Class**
Mixing Rule 1	Vapour and Liquid	**COTHRKab_1 Class**
Mixing Rule 2	Vapour and Liquid	**COTHRKab_2 Class**
Mixing Rule 3	Vapour and Liquid	**COTHRKab_3 Class**
Mixing Rule 4	Vapour and Liquid	**COTHRKab_4 Class**
Mixing Rule 5	Vapour and Liquid	**COTHRKab_5 Class**
Mixing Rule 6	Vapour and Liquid	**COTHRKab_6 Class**

The calculation methods from the table are described in the following sections.

RK Z Factor

The compressibility factor is calculated as the root for the following equation:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \tag{3.117}$$

$$A = \frac{aP}{R^2T^2} \tag{3.118}$$

$$B = \frac{bP}{RT} \tag{3.119}$$

There are three roots for the above equation. It is considered that the smallest root is for the liquid phase and the largest root is for the vapour phase. The third root has no physical meaning.

RK Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{ZRT}{P} \tag{3.120}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRKVolume Class	Vapour and Liquid

The compressibility factor, Z, is calculated using RK Z Factor. For consistency, the RK molar volume always calls the RK Z Factor for the calculation of Z

RK Enthalpy

The following relation calculates the enthalpy.

$$H - H^{IG} = PV - RT + \frac{1}{b}\left(a - T\frac{\partial a}{\partial T}\right)\ln\frac{V}{V+b} \tag{3.121}$$

where: H^{IG} *is the ideal gas enthalpy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRKEnthalpy Class	Vapour and Liquid

The volume, V, is calculated using RK Molar Volume. For consistency, the RK Enthalpy always calls the RK Volume for the calculation of V.

RK Entropy

The following relation calculates the entropy.

$$S - S^{IG} = R \ln\left(\frac{V-b}{RT}\right) - \frac{1}{b}\left(\frac{\partial a}{\partial T}\right) \ln\left(\frac{V+b}{V}\right) \tag{3.122}$$

where: S^{IG} *is the ideal gas entropy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRKEntropy Class	Vapour and Liquid

The volume, V, is calculated using RK Molar Volume. For consistency, the RK Entropy always calls the RK Volume for the calculation of V.

RK Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V} \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{3.123}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRKCp Class	Vapour and Liquid

RK Fugacity Coefficient

The following relation calculates the fugacity coefficient.

$$\ln\phi_i = \ln(V-b) + \frac{\bar{b}}{V-b} + \frac{a}{RTb}\left(\frac{\bar{b}}{b} - \frac{\bar{a}}{a} - 1\right)\ln\left(\frac{V+b}{V}\right) \tag{3.124}$$

$$\bar{a} = \frac{\partial n^2 a}{\partial n} \tag{3.125}$$

$$\bar{b} = \frac{\partial nb}{\partial n_i} \tag{3.126}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRKLnFugacityCoeff Class	Vapour and Liquid

The volume, V, is calculated using RK Molar Volume. For consistency, the RK Fugacity Coefficient always calls the RK Volume for the calculation of V. The parameters a and b are calculated from the Mixing Rules.

RK Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.127}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRKLnFugacity Class	Vapour and Liquid

RK Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v = C_p + \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{3.128}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRKCv Class	Vapour and Liquid

Mixing Rules

The mixing rules available for the RK EOS state are shown below.

$$a = \sum_{i=1}^{nc}\sum_{j=1}^{nc}(x_i x_j a_{ij}) \tag{3.129}$$

$$b = \sum_{i=1}^{nc} b_i x_i \tag{3.130}$$

$$a_{ij} = \xi_{ij}\sqrt{a_i a_j} \tag{3.131}$$

$$a_i = \frac{0.42748 R^2 T_{ci}^{2.5}}{P_{ci}\sqrt{T}} \tag{3.132}$$

$$b_i = \frac{0.08664 R T_{ci}}{P_{ci}} \tag{3.133}$$

Mixing Rule 1

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + C_{ij}T^2 \tag{3.134}$$

where: A_{ij}*,* B_{ij}*, and* C_{ij} *are asymmetric binary interaction parameters.*

Mixing Rule 2

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + \frac{C_{ij}}{T} \tag{3.135}$$

where: A_{ij}*,* B_{ij}*, and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 3

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i(A_{ij} + B_{ij} + C_{ij}T^2) - x_j(A_{ji} + B_{ji}T + C_{ji}T^2) \tag{3.136}$$

Mixing Rule 4

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) - x_j\left(A_{ji} + B_{ji} + \frac{C_{ji}}{T}\right) \tag{3.137}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 5

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{(A_{ij} + B_{ij}T + C_{ij}T^2)(A_{ji} + B_{ji}T + C_{ij}T^2)}{x_i(A_{ij} + B_{ij}T + C_{ij}T^2) + x_j(A_{ji} + B_{ji}T + C_{ji}T^2)} \tag{3.138}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 6

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right)\left(A_{ji} + B_{ji}T + \frac{C_{ij}}{T}\right)}{x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) + x_j\left(A_{ji} + B_{ji}T + \frac{C_{ji}}{T}\right)} \tag{3.139}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

3.1.7 Zudkevitch-Joffee Equation of State

The [13]Zudkevitch-Joffee (ZJ, 1970) model is a modification of the Redlich- Kwong equation of state. This model has been enhanced for better prediction of vapour-liquid equilibria for hydrocarbon systems, and systems containing Hydrogen. The major advantage of this model over previous versions of the RK equation is the improved capability of predicting pure compound vapour pressure and the simplification of the method for determining the required coefficients for the equation.

Enthalpy calculations for this model are performed using the Lee-Kesler method.

The Zudkevitch-Joffe EOS is represented by the following equation:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{3.140}$$

To apply the ZJ EOS to mixtures, mixing rules are required for the “*a*” and “*b*” terms in **Equation (3.84)**. Refer to the **Mixing Rules** section for the set of mixing rules applicable.

Property Methods

A quick reference of calculation methods is shown in the table below for the ZJ EOS.

Calculation Method	Applicable Phase	Property Class Name
Z Factor	Vapour and Liquid	**COTHZJZFactor Class**
Molar Volume	Vapour and Liquid	**COTHZJVolume Class**
Enthalpy	Vapour and Liquid	**COTHZJEnthalpy Class**
Entropy	Vapour and Liquid	**COTHZJEntropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTHZJCp Class**
Fugacity coefficient calculation	Vapour and Liquid	**COTHZJLnFugacityCoeff Class**
Fugacity calculation	Vapour and Liquid	**COTHZJLnFugacity Class**
Isochoric heat capacity	Vapour and Liquid	**COTHZJCv Class**
Mixing Rule 1	Vapour and Liquid	**COTHZJab_1 Class**
Mixing Rule 2	Vapour and Liquid	**COTHZJab_2 Class**
Mixing Rule 3	Vapour and Liquid	**COTHZJab_3 Class**

Calculation Method	Applicable Phase	Property Class Name
Mixing Rule 4	Vapour and Liquid	**COTHZJab_4 Class**
Mixing Rule 5	Vapour and Liquid	**COTHZJab_5 Class**
Mixing Rule 6	Vapour and Liquid	**COTHZJab_6 Class**

The calculation methods from the table are described in the following sections.

ZJ Z Factor

The compressibility factor is calculated as the root for the following equation:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \tag{3.141}$$

$$A = \frac{aP}{R^2T^2} \tag{3.142}$$

$$B = \frac{bP}{RT} \tag{3.143}$$

There are three roots for the above equation. It is considered that the smallest root is for the liquid phase and the largest root is for the vapour phase. The third root has no physical meaning.

ZJ Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{ZRT}{P} \tag{3.144}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHZJVolume Class	Vapour and Liquid

The compressibility factor, Z, is calculated using ZJ Z Factor. For consistency, the ZJ molar volume always calls the ZJ Z Factor for the calculation of Z.

ZJ Enthalpy

The following relation calculates the enthalpy.

$$H - H^{IG} = PV - RT + \frac{1}{b}\left(a - T\frac{\partial a}{\partial T}\right)\ln\frac{V}{V+b} \qquad (3.145)$$

where: H^{IG} *is the ideal gas enthalpy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHLeeKeslerEnthalpy Class	Vapour and Liquid

The volume, V, is calculated using ZJ Molar Volume. For consistency, the ZJ Enthalpy always calls the ZJ Volume for the calculation of V.

ZJ Entropy

The following relation calculates the entropy.

$$S - S^{IG} = R\ln\left(\frac{V-b}{RT}\right) - \frac{1}{b}\left(\frac{\partial a}{\partial T}\right)\ln\left(\frac{V+b}{V}\right) \qquad (3.146)$$

where: S^{IG} *is the ideal gas entropy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHLeeKeslerEntropy Class	Vapour and Liquid

The volume, V, is calculated using ZJ Molar Volume. For consistency, the ZJ Entropy always calls the ZJ Volume for the calculation of V.

ZJ Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{3.147}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHLeeKeslerCp Class	Vapour and Liquid

ZJ Fugacity Coefficient

The following relation calculates the fugacity coefficient:

$$\ln\phi_i = \ln(V-b) + \frac{\bar{b}}{V-b} + \frac{a}{RTb}\left(\frac{\bar{b}}{b} - \frac{\bar{a}}{a} - 1\right)\ln\left(\frac{V+b}{V}\right) \tag{3.148}$$

$$\bar{a} = \frac{\partial n^2 a}{\partial n} \tag{3.149}$$

$$\bar{b} = \frac{\partial nb}{\partial n_i} \tag{3.150}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHZJLnFugacityCoeff Class	Vapour and Liquid

The volume, V, is calculated using ZJ Molar Volume. For consistency, the ZJ Fugacity Coefficient always calls the ZJ Volume for the calculation of V. The parameters a and b are calculated from the Mixing Rules.

ZJ Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.151}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHZJLnFugacity Class	Vapour and Liquid

ZJ Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v = C_p + \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{3.152}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHZJCv Class	Vapour and Liquid

Mixing Rules

The mixing rules available for the ZJ EOS state are shown below.

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} (x_i x_j a_{ij}) \tag{3.153}$$

$$b = \sum_{i=1}^{nc} b_i x_i \tag{3.154}$$

$$a_{ij} = \xi_{ij} \sqrt{a_i a_j \alpha_i \alpha_j} \tag{3.155}$$

$$\sqrt{\alpha}_{i_{sub-critical}} = 1 + \sum_{k=1}^{2} D_k \left[-\ln\frac{P_r}{T_r} - \ln 10\right]^{\frac{k+1}{2}} + \sum_{k=3}^{10} D_k \left[-\ln\frac{P_r}{T_r} - \ln 10\right]^{k-1} \tag{3.156}$$

$$P_r = P_i^{sat} / P_{ci} \tag{3.157}$$

(for $T_r < 0.9$) ([41]Soave, 1986)

$$\ln\alpha_{super-critical} = 2M_1(1 - T_r^{M_2}) \tag{3.158}$$

With M_1 and M_2 determined at $0.9T_c$ to match the value and slope of the vapour pressure curve ([14]Mathias, 1983):

$$M_1 M_2 = -\frac{1}{2}\left(\frac{d\alpha}{dT_r}\right)_{0.9T_c} \tag{3.159}$$

$$M_2 = \frac{M_1 - 1}{M_1} \tag{3.160}$$

$$a_{ci} = \frac{0.42748 R^2 T_{ci}^2}{P_{ci}} \tag{3.161}$$

$$b_i = \frac{0.08664 R T_{ci}}{P_{ci}} \tag{3.162}$$

$$\kappa_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \tag{3.163}$$

Mixing Rule 1

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij} T + C_{ij} T^2 \tag{3.164}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 2

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij} T + \frac{C_{ij}}{T} \tag{3.165}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 3

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i(A_{ij} + B_{ij} + C_{ij}T^2) - x_j(A_{ji} + B_{ji}T + C_{ji}T^2) \tag{3.166}$$

Mixing Rule 4

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) - x_j\left(A_{ji} + B_{ji} + \frac{C_{ji}}{T}\right) \tag{3.167}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 5

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{(A_{ij} + B_{ij}T + C_{ij}T^2)(A_{ji} + B_{ji}T + C_{ij}T^2)}{x_i(A_{ij} + B_{ij}T + C_{ij}T^2) + x_j(A_{ji} + B_{ji}T + C_{ji}T^2)} \tag{3.168}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 6

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right)\left(A_{ji} + B_{ji}T + \frac{C_{ij}}{T}\right)}{x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) + x_j\left(A_{ji} + B_{ji}T + \frac{C_{ji}}{T}\right)} \tag{3.169}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

3.1.8 Kabadi-Danner Equation of State

The [16]Kabadi-Danner (KD, 1985) model is a modification of the SRK equation of State. It is enhanced to improve the vapour-liquid-liquid equilibria calculations for water-hydrocarbon systems, particularly in the dilute regions.

The model is an improvement over previous attempts which were limited in the region of validity. The modification is based on an asymmetric mixing rule, whereby the interaction in the water phase (with its strong hydrogen bonding) is calculated. It is based on both the interaction between the hydrocarbon and the water, and on the perturbation by the hydrocarbon on the water-water interaction due to its structure.

The Kabadi-Danner equation of state is written as:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{3.170}$$

The KD equation of state is similar to the SRK equation of state, with the following modifications:

- Inclusion of a second energy parameter. The a_i' secondary energy parameter is a function of the hydrocarbon structure expressed as a group factor G_i. The G_i factor is assumed to be zero for all non-hydrocarbons, including water.
- Different alpha function for water ([16]Kabadi and Danner, 1985).

The interaction parameters between water and hydrocarbon were generalized by Twu and Bluck, based on the k_{ij} values given by Kabadi and Danner:

$$k_{iw} = \begin{cases} 0.315 & Watson < 10.5 \\ -0.3325 + 0.061667\,Watson & 10.5 \le Watson \le 13.5 \\ 0.5 & Watson > 13.5 \end{cases} \tag{3.171}$$

where: Watson is the hydrocarbon characterization factor, defined as:

$$Watson = \frac{\sqrt[3]{T_b}}{SG} \tag{3.172}$$

The group factors G_i are expressed as a perturbation from normal alcane values as generalized by [17]Twu and Bluck (1988):

$$\ln G = \ln G^\circ \left(\frac{1+2f}{1-2f}\right)^2 \tag{3.173}$$

$$f = |f_1| \Delta SG + f_2 \Delta SG^2 \tag{3.174}$$

$$f_1 = C_1 + C_2 / \ln T_b(R) \tag{3.175}$$

$$f_2 = C_3 + C_4 / \ln T_b(R) \tag{3.176}$$

$$\Delta SG = e^{5(SG^\circ - SG)} - 1 \tag{3.177}$$

$$\left(\frac{G^\circ - 1.358}{426 - 1.358}\right)^{a_5} = \frac{1}{a_4} \ln\left(\frac{N_{gv} + a_6 F^\circ}{N_{gv} - F^\circ}\right) \tag{3.178}$$

$$N_{gv} = \frac{1 + a_6 e^{-a4}}{1 - e^{-a4}} \tag{3.179}$$

$$F^{\circ} = \frac{1 + a_3 e^{-a_1}}{1 - e^{-a_1}} \frac{1 - e^{-a_1 \tau}}{1 + a_3 e^{-a_1 \tau}} \tag{3.180}$$

$$\tau = \left(\frac{T_b - 200.99}{2000 - 200.99}\right)^{a_2} \tag{3.181}$$

Coefficients	
a$_1$ = 0.405040	***a$_6$*** = -0.958481
a$_2$ = 1.99638	***c$_1$*** = -0.178530
a$_3$ = 34.9349	***c$_2$*** = 1.41110
a$_4$ = 0.507059	***c$_3$*** = 0.237806
a$_5$ = 1.2589	***c$_4$*** = -1.97726

The alcane group factor G^o is calculated as:

$$SG^{\circ} = 0.843593 - 0.128624\beta - 3.36159\beta^3 - 13749.5\beta^{12} \tag{3.182}$$

$$\beta = 1 - \frac{T_b}{T_c} \tag{3.183}$$

$$\frac{T_b}{T_c^{\circ}} = 0.533272 + 0.191017 \times 10^{-3} T_b + 0.779681 \times 10^{-7} T_b^2 - 0.284376 \times 10^{-10} T_b^3 + 95.9468 \left(\frac{T_b}{100}\right)^{-1} \tag{3.184}$$

To apply the KD EOS to mixtures, mixing rules are required for the "*a*" and "*b*" terms in Equation (3.170). Refer to the Mixing Rules section for the applicable set of mixing rules.

Property Methods

A quick reference of calculation methods is shown in the table below for the KD EOS.

Calculation Method	Applicable Phase	Property Class Name
Z Factor	Vapour and Liquid	**COTHKDZFactor Class**
Molar Volume	Vapour and Liquid	**COTHKDVolume Class**
Enthalpy	Vapour and Liquid	**COTHKDEnthalpy Class**
Entropy	Vapour and Liquid	**COTHKDEntropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTHKDCp Class**
Fugacity coefficient calculation	Vapour and Liquid	**COTHKDLnFugacityCoeff Class**
Fugacity calculation	Vapour and Liquid	**COTHKDLnFugacity Class**
Isochoric heat capacity	Vapour and Liquid	**COTHKDCv Class**
Mixing Rule 1	Vapour and Liquid	**COTHKDab_1 Class**
Mixing Rule 2	Vapour and Liquid	**COTHKDab_2 Class**
Mixing Rule 3	Vapour and Liquid	**COTHKDab_3 Class**
Mixing Rule 4	Vapour and Liquid	**COTHKDab_4 Class**
Mixing Rule 5	Vapour and Liquid	**COTHKDab_5 Class**
Mixing Rule 6	Vapour and Liquid	**COTHKDab_6 Class**

The calculation methods from the table are described in the following sections.

KD Z Factor

The compressibility factor is calculated as the root for the following equation:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \tag{3.185}$$

$$A = \frac{aP}{R^2T^2} \tag{3.186}$$

$$B = \frac{bP}{RT} \tag{3.187}$$

There are three roots for the above equation. It is considered that the smallest root is for the liquid phase and the largest root is for the vapour phase. The third root has no physical meaning.

KD Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{ZRT}{P} \tag{3.188}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHKDVolume Class	Vapour and Liquid

The compressibility factor, Z, is calculated using KD Z Factor. For consistency, the KD molar volume always calls the KD Z Factor for the calculation of Z.

KD Enthalpy

The following relation calculates the enthalpy.

$$H - H^{IG} = PV - RT + \frac{1}{b}\left(a - T\frac{\partial a}{\partial T}\right)\ln\frac{V}{V+b} \tag{3.189}$$

where: H^{IG} *is the ideal gas enthalpy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHKDEnthalpy Class	Vapour and Liquid

The volume, V, is calculated using KD Molar Volume. For consistency, the KD Enthalpy always calls the KD Volume for the calculation of V.

KD Entropy

The following relation calculates the entropy.

$$S - S^{IG} = R\ln\left(\frac{V-b}{RT}\right) - \frac{1}{b}\left(\frac{\partial a}{\partial T}\right)\ln\left(\frac{V+b}{V}\right) \tag{3.190}$$

where: S^{IG} *is the ideal gas entropy calculated at temperature, T*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHKDEntropy Class	Vapour and Liquid

The volume, V, is calculated using KD Molar Volume. For consistency, the KD Entropy always calls the KD Volume for the calculation of V.

KD Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \tag{3.191}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHKDCp Class	Vapour and Liquid

KD Fugacity Coefficient

The following relation calculates the Fugacity Coefficient:

$$\ln\phi_i = \ln(V-b) + \frac{\bar{b}}{V-b} + \frac{a}{RTb}\left(\frac{\bar{b}}{b} - \frac{\bar{a}}{a} - 1\right)\ln\left(\frac{V+b}{V}\right) \tag{3.192}$$

$$\bar{a} = \frac{\partial n^2 a}{\partial n} \tag{3.193}$$

$$\bar{b} = \frac{\partial nb}{\partial n_i} \tag{3.194}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHKDLnFugacityCoeff Class	Vapour and Liquid

The volume, V, is calculated using KD Molar Volume. For consistency, the KD Fugacity Coefficient always calls the KD Volume for the calculation of V.

KD Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.195}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHKDLnFugacity Class	Vapour and Liquid

KD Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v = C_p + \frac{T\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T} \tag{3.196}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHKDCv Class	Vapour and Liquid

Mixing Rules

The mixing rules available for the KD EOS state are shown below.

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} (x_i x_j a_{ij}) + \sum_{i=1}^{nc} (x_i x_w^2 a_i') \tag{3.197}$$

$$b = \sum_{i=1}^{nc} b_i x_i \tag{3.198}$$

$$a_{ij} = \xi_{ij} \sqrt{a_i a_j \alpha_i \alpha_j} \tag{3.199}$$

$$\sqrt{\alpha_i} = \begin{cases} (1 + \kappa_i)(1 - T_{ri}^{0.5}) & i \neq w \\ 1 + 0.662(1 - T_{rw}^{0.8}) & i = w \end{cases} \tag{3.200}$$

$$a_i = \frac{0.42747 R^2 T_{ci}^2}{P_{ci}} \tag{3.201}$$

$$b_i = \frac{0.08664 R T_{ci}}{P_{ci}} \tag{3.202}$$

$$\kappa_i = 0.480 + 1.57\omega_i - 0.176\omega_i^2 \tag{3.203}$$

$$a_i' = \begin{cases} G_i 1 - T_{rw}^{0.8} & T < T_{cw} \\ 0.0 & T \geq T_{cw} \end{cases} \tag{3.204}$$

Mixing Rule 1

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + C_{ij}T^2 \tag{3.205}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 2

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - A_{ij} + B_{ij}T + \frac{C_{ij}}{T} \tag{3.206}$$

where: A_{ij}, B_{ij}, *and* C_{ij} *are asymmetric binary interaction parameters*

Mixing Rule 3

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i(A_{ij} + B_{ij} + C_{ij}T^2) - x_j(A_{ji} + B_{ji}T + C_{ji}T^2) \tag{3.207}$$

Mixing Rule 4

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) - x_j\left(A_{ji} + B_{ji} + \frac{C_{ji}}{T}\right) \tag{3.208}$$

where: A_{ij}, B_{ij}, and C_{ij} are asymmetric binary interaction parameters

Mixing Rule 5

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{(A_{ij} + B_{ij}T + C_{ij}T^2)(A_{ji} + B_{ji}T + C_{ij}T^2)}{x_i(A_{ij} + B_{ij}T + C_{ij}T^2) + x_j(A_{ji} + B_{ji}T + C_{ji}T^2)} \tag{3.209}$$

where: A_{ij}, B_{ij}, and C_{ij} are asymmetric binary interaction parameters

Mixing Rule 6

The definition of terms *a* and *b* are the same for all **Mixing Rules**. The only difference between the mixing rules is the temperature dependent binary interaction parameter, ξ ij, which is defined as:

$$\xi_{ij} = 1 - \frac{\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right)\left(A_{ji} + B_{ji}T + \frac{C_{ij}}{T}\right)}{x_i\left(A_{ij} + B_{ij}T + \frac{C_{ij}}{T}\right) + x_j\left(A_{ji} + B_{ji}T + \frac{C_{ji}}{T}\right)} \tag{3.210}$$

where: A_{ij}, B_{ij}, and C_{ij} are asymmetric binary interaction parameters

3.1.9 The Virial Equation of State

The term Virial comes from the Latin *vis* (force) and refers to the interaction forces between 2, 3 or more molecules.

The Virial equation of state has theoretical importance since it can be derived from rigorous statistical mechanical arguments. It is represented as an infinite sum of power series in the inverse of the molar volume:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \tag{3.211}$$

where: B is the second virial coefficient, C the third, etc.

The above equation may be rewritten as a series in molar density:

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots \tag{3.212}$$

and pressure:

$$Z = 1 + B'P + C'P^2 + D'P^3 + \ldots \tag{3.213}$$

The last format is not widely used since it gives an inferior representation of Z over a range of densities or pressures ([6]Reid, Prausnitz and Poling, 1987). It is clear that B can be calculated as:

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots \tag{3.214}$$

$$\left(\frac{\partial Z}{\partial \rho}\right)_T = B + 2C\rho + 3D\rho^2 + \ldots \tag{3.215}$$

and taking the limit where ρ -> 0, B can be expressed as:

$$B = \lim_{\rho \to 0}\left(\frac{\partial Z}{\partial \rho}\right)_T \tag{3.216}$$

Similarly, the following can be obtained:

$$C = \lim_{\rho \to 0}\left(\frac{\partial^2 Z}{\partial \rho^2}\right)_T \qquad D = \lim_{\rho \to 0}\left(\frac{\partial^3 Z}{\partial \rho^3}\right)_T \tag{3.217}$$

This approach can easily be extended to higher terms.

It is experimentally verified that the Virial equation, when truncated after the second Virial coefficient, gives reasonable vapour phase density predictions provided that the density is smaller than half of the critical density. The Virial EOS truncated after the second Virial coefficient is:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} \tag{3.218}$$

Calculating the Second Virial Coefficient

There are several ways of estimating the second virial coefficient for pure components and mixtures. If accurate volumetric data is available, the procedure is straightforward, but tedious. In your applications, it is better to estimate the second virial coefficient similar to the way in which the cubic equation of state parameters were determined. That is, it is desired to express the second virial coefficient as a function of T_c, P_c and the acentric factor. Pitzer attempted to do this, proposing a simple corresponding states approach:

$$B = B^{(0)} + \omega B^{(1)} \tag{3.219}$$

where: $B^{(0)}$ *is a simple fluid term depending only on* T_c

$B^{(1)}$ *is a correction term for the real fluid, which is a function of* T_c *and* P_c

Note that this three-parameter corresponding states relation displays in many different forms, such as in the Soave, Peng-Robinson, Lee-Kesler and BWR-Starling equations of state.

Pitzer proposed several modifications to this simple form. Pitzer was motivated mainly because polar fluids do not obey a simple three-parameter corresponding states theory. [18]Tsonopoulos (1974) suggested that the problem can (at least partially) be solved by the inclusion of a third term in the previous expression:

$$B = B^{(0)} + \omega B^{(1)} + B^{(2)} \qquad (3.220)$$

where: $B^{(2)}$ *is a function of* T_c *and one (or more) empirical constants*

It was found that this empirical function can sometimes be generalized in terms of the reduced dipole moment:

$$\mu_R = \frac{10^5 \mu^2 P_c}{T_c} \times 0.9869 \qquad (3.221)$$

where: P_c *is in bar and* μ_R *is in debyes*

The method of [19]Hayden and O'Connell (1975) is used, where they define:

$$\begin{aligned} B_{ij} &= B_{ij}^F + B_{ij}^D \\ B_{ij}^F &= (B_{ij}^F,\ _{non-polar}) + (B_{ij}^F,\ _{polar}) \\ B_{ij}^D &= (B_{ij}^D,\ _{metastable}) + (B_{ij}^D,\ _{bound}) + (B_{ij}^D,\ _{chemical}) \end{aligned} \qquad (3.222)$$

where: B_{ij}^F*, non-polar = Second virial coefficient contribution from the non-polar part due to physical interactions*

B_{ij}^F*, polar = Second virial coefficient contribution from the polar part due to physical interactions*

B_{ij}^D*, metastable = Second virial coefficient contribution due to the formation of metastable compounds due to the "chemical" (dimerization) reaction*

B_{ij}^D*, bound = Second virial coefficient contribution due to the formation of chemical bonds*

B_{ij}^D*, chemical = Second virial coefficient contribution due to the chemical reaction*

The several contributions to the second Virial coefficient are calculated as follows:

$$B^F_{ij},\ _{non-polar} = b^0_{ij}\left(0.94 - \frac{1.47}{T^{*'}_{ij}} + \frac{0.85}{T^{*'2}_{ij}} - \frac{1.015}{T^{*'3}_{ij}}\right) \tag{3.223}$$

$$B^F_{ij},\ _{polar} = -b^0_{ij}\mu^{*'}_{ij}\left(0.74 - \frac{3.0}{T^{*'}_{ij}} + \frac{2.1}{T^{*'2}_{ij}} + \frac{2.1}{T^{*'3}_{ij}}\right) \tag{3.224}$$

$$(B^D_{ij},\ _{metastable}) + (B^D_{ij},\ _{bound}) = b^0_{ij}A_{ij}\exp\left(\frac{\Delta H_{ij}}{T^*_{ij}}\right) \tag{3.225}$$

$$(B^D_{ij},\ _{chemical}) = b^0_{ij}E_{ij}\left(1 - \exp\left(\frac{1500\eta_{ij}}{T}\right)\right) \tag{3.226}$$

where:

$$\frac{1}{T_{ij}^{*'}} = \frac{1}{T_{ij}^{*}} - 1.6\omega_{ij}$$

$$T_{ij}^{*} = \frac{T}{(\varepsilon_{ij}/k)}$$

$$b_{ij}^{0} = 1.26184\sigma_{ij}^{3} \quad (cm^3/gmol)$$

$$\mu_{ij}^{*'} = \mu_{ij}^{*} \qquad if\ \mu_{ij}^{*} < 0.04$$

$$\mu_{ij}^{*'} = 0 \qquad if\ 0.04 \le \mu_{ij}^{*} < 0.25$$

$$\mu_{ij}^{*'} = \mu_{ij}^{*} - 0.25 \qquad if\ \mu_{ij}^{*} \ge 0.25$$

$$A_{ij} = -0.3 - 0.05\mu_{ij}^{*}$$

$$\Delta H_{ij} = 1.99 + 0.2\mu_{ij}^{*2}$$

$$\mu_{ij}^{*} = \left[\frac{7243.8\mu_i\mu_j}{\left(\frac{\varepsilon_{ij}}{k}\right)\sigma_{ij}^{3}}\right]$$

$$E_{ij} = \exp\left\{\eta_j\left(\frac{650}{\left(\frac{\varepsilon_{ij}}{k}\right) + 300} - 4.27\right)\right\} \qquad if\ \eta_j < 4.5$$

$$E_{ij} = \exp\left\{\eta_j\left(\frac{42800}{\left(\frac{\varepsilon_{ij}}{k}\right) + 22400} - 4.27\right)\right\} \qquad if\ \eta_j \ge 4.5$$

For pure components:

$$\begin{aligned}
\omega_i &= 0.006026R_{Di} + 0.02096R_{Di}^{2} - 0.001366R_{Di}^{3} \\
\frac{\varepsilon_{ij}}{k} &= \left(\frac{\varepsilon_{ij}}{k}\right)'\left(1 - \xi C_1\left(1 - \xi\left(1 + \frac{C_1}{2}\right)\right)\right) \\
\sigma_i &= \sigma_i'(1 + \xi C_2)^{1/3} \\
\left(\frac{\varepsilon_i}{k}\right)' &= T_{c,\,i}\left(0.748 + 0.91\omega_i - 0.4\frac{\eta_i}{2 + 20\omega_i}\right)
\end{aligned} \qquad (3.227)$$

and

$$\sigma_i' = (2.44 - \omega_i)\left(1.0133\frac{T_{c,\ i}}{P_{c,\ i}}\right)^{1/\ 3}$$

$$\begin{gathered}
\xi = 0 \qquad \text{if } \mu_i < 1.45 \\
\textit{or} \\
\xi = \left(\frac{1.7941\times 10^7 \mu_i^4}{\left[\left(2.882 - \dfrac{1.882\omega_i}{0.03+\omega_i}\right)T_{c,\ i}\sigma_i'^6\left(\dfrac{\varepsilon_i}{k}\right)'\right]}\right) \quad \text{if } \mu_i \ge 1.45
\end{gathered} \tag{3.228}$$

$$C_1 = \frac{16+400\omega_i}{10+400\omega_i} \quad \textit{and} \quad C_2 = \frac{3}{10+400\omega_i} \tag{3.229}$$

For the cross parameters:

$$\begin{gathered}
\omega_{ij} = \frac{1}{2}(\omega_i + \omega_j) \\
\left(\frac{\varepsilon_{ij}}{k}\right) = \left(\frac{\varepsilon_{ij}}{k}\right)' (1 + \xi' C_1') \\
\sigma_{ij} = \sigma_{ij}' (1 - \xi' C_2') \\
\left(\frac{\varepsilon_{ij}}{k}\right)' = 0.7\left[\left(\frac{\varepsilon_{ii}}{k}\right)\left(\frac{\varepsilon_{jj}}{k}\right)\right]^{\frac{1}{2}} + \frac{0.6}{\left[\dfrac{1}{\varepsilon_{ii}/\ k} + \dfrac{1}{\varepsilon_{jj}/\ k}\right]}
\end{gathered} \tag{3.230}$$

$$\begin{gathered}
\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{\frac{1}{2}} \\
\xi' = \frac{u_i^2\left(\dfrac{\varepsilon_{jj}}{k}\right)^{2/\ 3}\sigma_{jj}^4}{\left(\dfrac{\varepsilon_{ij}}{k}\right)'\sigma_{ij}^6} \qquad \text{if } \mu_i \ge 2 \text{ and } \mu_j = 0 \\
\xi' = \frac{u^2\left(\dfrac{\varepsilon_{ii}}{k}\right)^2\sigma_{ii}^4}{\left(\dfrac{\varepsilon_{ij}}{k}\right)'\acute{\sigma}_{ij}^6} \qquad \text{if } \mu_j \ge 2 \text{ and } \mu_i = 0 \\
\xi' = 0 \textit{ for all other values of } \mu_i \text{ and } \mu_j
\end{gathered} \tag{3.231}$$

$$C_1' = \frac{16 + 400\omega_{ij}}{10 + 400\omega_{ij}} \quad and \quad C_2' = \frac{3}{10 + 400\omega_{ij}} \tag{3.232}$$

Thus, Hayden-O'Connell models the behaviour of a mixture subject to physical (polarity) and chemical (associative and solvation) forces as a function of T_c, P_c, R_D (radius of gyration), μ (dipole moment) and two empirical constants that describe the "chemical" behaviour of the gas:

η_i = *association parameter*

η_{ij} = *solvation parameter*

This is discussed in more detail in the next section.

Mixing Rules

For a multi-component mixture, it can be shown that B_{mix} is rigorously calculated by:

$$B_{mix} = \sum_i \sum_j y_i y_j B_{ij} \tag{3.233}$$

and the fugacity coefficient for a component *i* in the mixture comes from:

$$\ln\phi_i = \left(2\sum_j y_i B_{ij} - B_{mix}\right)\frac{P}{RT} \tag{3.234}$$

Vapour Phase Chemical Association using the Virial Equation

Although it was suggested many years ago that the non-ideality in mixtures could be explained by pseudo-chemical reactions and formation of complexes, there is evidence that this is true only in a few special cases. Of special practical importance are mixtures which contain carboxylic acids. Carboxylic acids tend to dimerize through strong hydrogen bonding.

This is not limited to carboxylic acids alone; hydrofluoric acid forms polymers (usually hexamers) and the hydrogen bonding can happen with dissimilar molecules.

Usually, hydrogen bonding between similar molecules is called association, while bonding between dissimilar molecules is called solvation.

The hydrogen bonding process can be observed as a chemical reaction:

$$i + j \leftrightarrow ij \tag{3.235}$$

where: i and j are monomer molecules and ij is the complex formed by hydrogen bonding

The following may be written to describe the chemical reaction:

$$k_{ij} = \frac{f_{ij}}{f_i f_j} = \frac{Z_{ij}\phi^{\#}{}_{ij}}{Z_i Z_j \phi_i^{\#} \phi^{\#}{}_j P} \tag{3.236}$$

where: Z is the true mole fraction of the species in equilibrium

$\phi^{\#}$ *is the fugacity coefficient of the true species*

P is the system pressure

k_{ij} *is the reaction equilibrium constant*

If y_{i} is defined as the mole fraction of component *i* in the vapour phase, disregarding dimerization, it can be shown that:

$$\phi^{\#}{}_i Z_i = \phi_i y_i \qquad or \qquad \phi_i = \frac{\phi_i^{\#} Z_i}{y_i} \tag{3.237}$$

where: ϕ_i *denotes the apparent fugacity coefficient of component i*

If it is assumed that the vapour solution behaves like an ideal solution (Lewis), the following may be written:

$$\ln \phi_i^{\#} = \frac{B_i^F P}{RT} \tag{3.238}$$

where: B_i^F *is the contribution to the second virial coefficient from physical forces*

If the Lewis ideal solution is carried all the way:

$$k_{ij} = \frac{\phi_{ij} Z_{ij} P}{\phi_i Z_i P \phi_j Z_j P} \tag{3.239}$$

and finally:

$$k_{ij} = \frac{Z_{ij}}{Z_i Z_j} \frac{1}{P} \times \frac{\exp\left(B_{ij}^F \frac{P}{RT}\right)}{\exp\left(B_{ii}^F \frac{P}{RT}\right) \exp\left(B_{jj}^F \frac{P}{RT}\right)} \tag{3.240}$$

The chemical equilibrium constant is also found from the relation:

$$\begin{gathered} k_{ij} = \frac{-B_{ij}^D (2 - \delta_{ij})}{RT} \\ \delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} \end{gathered} \tag{3.241}$$

where: B_{ij}^D *is the contribution of dimerization to the second virial coefficient*

Therefore:

$$k_{ij} = \frac{Z_{ij}}{Z_i Z_j} \frac{1}{P} \times \frac{\exp\left(B^F_{ij} \frac{P}{RT}\right)}{\exp\left(B^F_{ii} \frac{P}{RT}\right) \exp\left(B^F_{jj} \frac{P}{RT}\right)} \tag{3.242}$$

$$= \frac{-B^D_{ij}(2 - \delta_{ij})}{RT}$$

The calculation of the fugacity coefficient for species *i* and *j* is accomplished by solving the previous chemical equilibrium constant equation combined with the restriction that the sum of Z_i, Z_j and Z_{ij} is equal to 1.

Application of the Virial Equation

The equation enables you to better model vapour phase fugacities of systems displaying strong vapour phase interactions. Typically this occurs in systems containing carboxylic acids, or compounds that have the tendency to form stable hydrogen bonds in the vapour phase. In these cases, the fugacity coefficient shows large deviations from ideality, even at low or moderate pressures.

The regression module contains temperature dependent coefficients for carboxylic acids. You can overwrite these by changing the Association *(ij)* or Solvation *(ii)* coefficients from the default values.

If the virial coefficients need to be calculated, the software contains correlations utilizing the following pure component properties:

- critical temperature
- critical pressure
- dipole moment
- mean radius of gyration
- association parameter
- association parameter for each binary pair

The equation is restricted to systems where the density is moderate, typically less than *one-half* the critical density. The *Virial* equation used is valid for the following range:

$$P \leq \frac{T}{2} \frac{\sum_{i=1}^{m} y_i P_{c_i}}{\sum_{i=1}^{m} y_i T_{c_i}} \tag{3.243}$$

Property Methods

A quick reference of calculation methods is shown in the table below for the Virial EOS.

Calculation Method	Applicable Phase	Property Class Name
Molar Volume	Vapour	**COTHVirial_Volume Class**
Enthalpy	Vapour	**COTHVirial_Enthalpy Class**
Entropy	Vapour	**COTHVirial_Entropy Class**
Isobaric heat capacity	Vapour	**COTHVirial_Cp Class**
Fugacity coefficient calculation	Vapour	**COTHVirial_LnFugacityCoeff Class**
Fugacity calculation	Vapour	**COTHVirial_LnFugacity Class**
Density	Vapour	**COTHVirial_Density Class**
Isochoric Heat Capacity	Vapour	**COTHVirial_Cv Class**
Gibbs Energy	Vapour	**COTHVirial_GibbsEnergy Class**
Helmholtz Energy	Vapour	**COTHVirial_HelmholtzEnergy Class**
Z Factor	Vapour	**COTHVirial_ZFactor Class**

The calculation methods from the table are described in the following sections.

Virial Molar Volume

The following relation calculates the molar volume for a specific phase.

$$V = \frac{B}{Z-1} \tag{3.244}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_Volume Class	Vapour

Virial Enthalpy

The following relation calculates the enthalpy.

$$H - H^{\circ} = A - A^{\circ} + T(S - S^{\circ}) + RT(Z-1) \tag{3.245}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_Enthalpy Class	Vapour

Virial Entropy

The following relation calculates the entropy.

$$S - S^{o} = -RT\frac{(\mathrm{dB}/\ dT)}{V-B} - R\ln\frac{V}{V-B} + R\ln\frac{V}{V_o} \tag{3.246}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_Entropy Class	Vapour

Virial Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^\circ = T\int_\infty^V \left(\frac{\partial^2 P}{\partial T^2}\right) dV - T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial T}\right)_T} - R \tag{3.247}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_Cp Class	Vapour

Virial Fugacity Coefficient

The following relation calculates the fugacity coefficient:

$$\ln\phi_i = \left(2\sum_j y_i B_{ij} - B_{mix}\right)\frac{P}{RT} \tag{3.248}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_LnFugacityCoeff Class	Vapour

Virial Fugacity

The following relation calculates the fugacity for a specific phase.

$$f_i = \phi_i y_i P \tag{3.249}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_LnFugacity Class	Vapour and Liquid

Virial Density

The following relation calculates the molar density for a specific phase.

$$\rho = \frac{P}{ZRT} \tag{3.250}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_Density Class	Vapour and Liquid

Virial Cv (isochoric)

The following relation calculates the isochoric heat capacity.

$$C_v - C_v{}^\circ = T\int_{\infty}^{V} \left(\frac{\partial^2 P}{\partial T^2}\right) dV \tag{3.251}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_Cv Class	Vapour and Liquid

Virial Gibbs Energy

The following relation calculates the Gibbs energy.

$$G = A + RT(Z - 1) \tag{3.252}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_GibbsEnergy Class	Vapour

Virial Helmholtz Energy

The following relation calculates the Helmholtz energy.

$$A - A_o = RT\ln\frac{V}{V - B} - RT\ln\frac{V}{V_o} \tag{3.253}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_HelmholtzEnergy Class	Vapour

Virial Z Factor

The following relation calculates the Z Factor.

$$Z = 1 + \frac{B}{V} \tag{3.254}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVirial_ZFactor Class	Vapour

3.1.10 Lee-Kesler Equation of State

The [50]Lee-Kesler (LK, 1975) method is an effort to extend the method originally proposed by Pitzer to temperatures lower than 0.8 T_r. Lee and Kesler expanded Pitzer's method expressing the compressibility factor as:

$$Z = Z^{\circ} + \frac{\omega}{\omega^{r}}(Z^{r} - Z^{\circ}) \tag{3.255}$$

where: Z^{o} *= the compressibility factor of a simple fluid*

Z^{r} *= the compressibility factor of a reference fluid*

They chose the reduced form of the BWR EOS to represent both Z^{o} and Z^{r}:

$$Z = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{D}{T_r^3 V_r^3}\left(\beta - \frac{\gamma}{V_r^2}\right) e^{-\left(\frac{\gamma}{V_r^2}\right)} \tag{3.256}$$

where:

$$V_r = \frac{VP_c}{RT_c}$$

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^4}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3}$$

$$D = d_1 + \frac{d_2}{T_r}$$

The constants in these equations were determined using experimental compressibility and enthalpy data. Two sets of constants, one for the simple fluid ($\omega^o = 0$) and one for the reference fluid (ω^r=0.3978, n-C_8) were determined.

Property Methods

A quick reference of calculation methods is shown in the table below for the LK EOS.

Calculation Method	Applicable Phase	Property Class Name
Enthalpy	Vapour and Liquid	**COTHLeeKeslerEnthalpy Class**
Entropy	Vapour and Liquid	**COTHLeeKeslerEntropy Class**
Isobaric heat capacity	Vapour and Liquid	**COTHLeeKeslerCp Class**

The calculation methods from the table are described in the following sections.

LK Enthalpy

The following relation calculates the enthalpy departure.

$$\frac{H - H^{IG}}{RT_c} = T_r\left\{Z - 1 - \frac{b_2 + 2\frac{b_3}{T_r} + 3\frac{b_4}{T_r^2}}{T_rV_r} - \frac{c_2 - 3\frac{c_3}{T_r^2}}{2T_rV_r^2} - \frac{d_2}{5T_rV_r^5} + 3E\right\} \tag{3.257}$$

where:

$$T_r = \frac{T}{T_c} \tag{3.258}$$

$$V_r = \frac{V}{V_c} \tag{3.259}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHLeeKeslerEnthalpy Class	Vapour and Liquid

The values of T_c and V_c are calculated from the Mixing Rules.

LK Entropy

The following relation calculates the entropy departure.

$$\frac{S - S_\circ{}^{IG}}{R} = \ln Z - \ln\left(\frac{P}{P^\circ}\right) - \frac{b_1 + \frac{b_3}{T_r^2} + 2\frac{b_4}{T_r^3}}{V_r} - \frac{c_1 - 3\frac{c_3}{T_r^2}}{2V_r^2} - \frac{d_1}{5V_r^2} + 2E \tag{3.260}$$

where:

$$T_r = \frac{T}{T_c} \tag{3.261}$$

$$V_r = \frac{V}{V_c} \tag{3.262}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHLeeKeslerEntropy Class	Vapour and Liquid

The values of T_c and V_c are calculated from the Mixing Rules.

LK Cp (Heat Capacity)

The following relation calculates the isobaric heat capacity.

$$C_p - C_p^{IG} = -T\int_{\infty}^{V}\left(\frac{\partial^2 P}{\partial T^2}\right)_V dV + R + \frac{T\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T} \qquad (3.263)$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHLeeKeslerCp Class	Vapour and Liquid

Mixing Rules

For mixtures, the Critical properties for the LK EOS state are defined as follows.

$$\omega = \sum_{i=1}^{N} x_i \omega_i$$

$$z_{c_i} = 0.2905 - 0.0851\omega_i$$

$$V_{c_i} = \frac{Z_{c_i} R T_{c_i}}{P_{c_i}}$$

$$V_c = \frac{1}{8} \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \left(V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}} \right)^3$$

$$T_c = \frac{1}{8V_c} \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \left(V_{c_i}^{\frac{1}{3}} + V_{c_j}^{\frac{1}{3}} \right)^3 (T_{c_i} T_{c_j})^{0.5}$$

$$P_c = (0.2905 - 0.085\omega)\frac{RT_c}{V_c}$$

3.1.11 Lee-Kesler-Plöcker

The Lee-Kesler-Plöcker equation does not use the COSTALD correlation in computing liquid density. This may result in differences when comparing results between equation of states.

The Lee-Kesler-Plöcker equation is an accurate general method for non-polar substances and mixtures. [3]Plöcker et al, applied the Lee-Kesler equation to mixtures, which itself was modified from the **BWR** equation.

$$z = z^{(o)} + \frac{\omega}{\omega^{(r)}}(z^{(r)} - z^{(o)}) \tag{3.264}$$

The compressibility factors are determined as follows:

$$z = \frac{pv}{RT} = \frac{p_r v_r}{T_r} = z(T_r,\ v_r,\ A_k) \tag{3.265}$$

$$z = 1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^5} + \frac{C_4}{T_r^3 v_r^2}\left[\beta + \frac{\gamma}{v_r^2}\right]\exp\left[\frac{-\gamma}{v_r^2}\right] \tag{3.266}$$

where:

$$v_r = \frac{p_c v}{RT_c} \qquad B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^2} \qquad D = d_1 - \frac{d_2}{T_r}$$

$$\omega^{(o)} = 0 \qquad \omega^{(r)} = 0.3978$$

Mixing rules for pseudocritical properties are as follows:

$$T_{cm} = \left(\frac{1}{V_{cm}^{\eta}}\right)\sum_i\sum_j x_i x_j v_{c_{ij}} \tag{3.267}$$

where:

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{1/2} \qquad T_{c_{ii}} = T_{c_i} \qquad T_{c_{jj}} = T_{c_j}$$

$$v_{c_m} = \sum_i\sum_j x_i x_j v_{c_{ij}} \qquad v_{c_{ij}} = \frac{1}{8}(v_{c_i}^{1/3} + v_{c_j}^{1/3})^3$$

$$v_{c_i} = z_{c_i}\frac{RT_{c_i}}{p_{c_i}} \qquad z_{c_i} = 0.2905 - 0.085\omega_i$$

$$p_{c_m} = z_{c_m}\frac{RT_{c_m}}{v_{c_m}} \qquad z_{c_m} = 0.2905 - 0.085\omega_m$$

$$\omega_m = \sum_i x_i \omega_i$$

3.2 Activity Models

Although equation of state models have proven to be very reliable in predicting properties of most hydrocarbon-based fluids over a large range of operating conditions, their application has been limited to primarily non-polar or slightly polar components. Polar or non-ideal chemical systems have traditionally been handled using dual model approaches. In this approach, an equation of state is used for predicting the vapour fugacity coefficients (normally ideal gas or the Redlich-Kwong, Peng-Robinson or SRK equations of state) and an activity coefficient model is used for the liquid phase. Although there is considerable research being conducted to extend equation of state applications into the chemical arena (e.g., the PRSV equation), the state of the art of property predictions for chemical systems is still governed mainly by activity models.

Activity models generate the best results when they are applied in the operating region in which the interaction parameters were generated.

Activity models are much more empirical in nature when compared to the property predictions in the hydrocarbon industry. For this reason, they cannot be used as reliably as the equations of state for generalized application or extrapolated into untested operating conditions. Their adjustable parameters should be fitted against a representative sample of experimental data and their application should be limited to moderate pressures. Consequently, caution should be exercised when selecting these models for your simulation.

The phase separation or equilibrium ratio K_i for component i (defined in terms of the vapour phase fugacity coefficient and the liquid phase activity coefficient), is calculated from the following expression:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i f_i^{\circ}}{P\phi_i} \qquad (3.268)$$

where: γ_i = *Liquid phase activity coefficient of component i*

f_i^o = *Standard state fugacity of component i*

P = *System pressure*

f_i = *Vapour phase fugacity coefficient of component i*

Although for ideal solutions the activity coefficient is unity, for most chemical (non-ideal) systems this approximation is incorrect. Dissimilar chemicals normally exhibit not only large deviations from an ideal solution, but the deviation is also found to be a strong function of the composition. To account for this non-ideality, activity models were developed to predict the activity coefficients of the components in the liquid phase. The derived correlations were based on the excess Gibbs energy function, which is defined as the observed Gibbs energy of a mixture in excess of what it would be if the solution behaved ideally, at the same temperature and pressure.

For a multi-component mixture consisting of n_i moles of component i, the total excess Gibbs free energy is represented by the following expression:

$$G^E = RT\sum(n_i \ln\gamma_i) \tag{3.269}$$

where: γ_i *is the activity coefficient for component i*

The individual activity coefficients for any system can be obtained from a derived expression for excess Gibbs energy function coupled with the Gibbs-Duhem equation. The early models (Margules, van Laar) provide an empirical representation of the excess function that limits their application. The newer models such as Wilson, NRTL and UNIQUAC use the local composition concept and provide an improvement in their general application and reliability. All of these models involve the concept of binary interaction parameters and require that they be fitted to experimental data.

Since the Margules and van Laar models are less complex than the Wilson, NRTL and UNIQUAC models, they require less CPU time for solving flash calculations. However, these are older and more empirically based models and generally give poorer results for strongly non-ideal mixtures such as alcohol-hydrocarbon systems, particularly for dilute regions.

The following table briefly summarizes recommended models for different applications.

Application	Margules	van Laar	Wilson	NRTL	UNIQUAC
Binary Systems	A	A	A	A	A
multi-component Systems	LA	LA	A	A	A
Azeotropic Systems	A	A	A	A	A
Liquid-Liquid Equilibria	A	A	N/A	A	A
Dilute Systems	?	?	A	A	A
Self-Associating Systems	?	?	A	A	A
Polymers	N/A	N/A	N/A	N/A	A
Extrapolation	?	?	G	G	G

A = Applicable; N/A = Not Applicable;? = Questionable; G = Good; LA = Limited Application

Vapour phase non-ideality can be taken into account for each activity model by selecting the Redlich-Kwong, Peng-Robinson or SRK equations of state as the vapour phase model. When one of the equations of state is used for the vapour phase, the standard form of the Poynting correction factor is always used for liquid phase correction.

The binary parameters required for the activity models have been regressed based on the VLE data collected from DECHEMA, Chemistry Data Series. There are over 16,000 fitted binary pairs in the library. The structures of all library components applicable for the UNIFAC VLE estimation have been stored. The Poynting correction for the liquid phase is ignored if ideal solution behaviour is assumed.

All of the binary parameters stored in the properties library have been regressed using an ideal gas model for the vapour phase.

If you are using the built-in binary parameters, the ideal gas model should be used. All activity models, with the exception of the Wilson equation, automatically calculate three phases given the correct set of energy parameters. The vapour pressures used in the calculation of the standard state fugacity are based on the pure component library coefficients using the modified form of the Antoine equation.

The internally stored binary parameters have NOT been regressed against three-phase equilibrium data.

3.2.1 Ideal Solution Model

The ideal solution model is the simplest activity model that ignores all non-idealities in a liquid solution. Although this model is very simple, it is incapable of representing complex systems such as those with azeotropes.

Property Methods

A quick reference of calculation methods is shown in the table below for the Ideal Solution model.

Calculation Method	Applicable Phase	Property Class Name
Activity coefficient	Liquid	**COTHIdealSolLnActivityCoeff Class**
Fugacity coefficient	Liquid	**COTHIdealSolLnFugacityCoeff Class**
Fugacity	Liquid	**COTHIdealSolLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHIdealSolLnActivityCoeffDT Class**
Enthalpy	Liquid	**COTHIdealSolEnthalpy Class**
Gibbs energy	Liquid	**COTHIdealSolGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

Ideal Solution Ln Activity Coefficient

This method calculates the activity coefficient of components, *i*, using the Ideal Solution model. The extended, multi-component form of the Ideal Solution is shown in the following relation:

$$\ln\gamma_i = 0 \tag{3.270}$$

where: γ_i *= activity coefficient of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIdealSolLnActivityCoeff Class	Liquid

Ideal Solution Ln Fugacity Coefficient

This method calculates the fugacity coefficient of components using the Ideal Solution activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\frac{f_i^{std}}{P}\right) \tag{3.271}$$

where: $\gamma_i = 1$

P = *pressure*

f_i = *standard state fugacity*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIdealSolLnFugacityCoeff Class	Liquid

For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Ideal Solution Ln Fugacity

This method calculates the fugacity of components using the Ideal Solution activity model. The fugacity of component *i*, f_i, is calculated from the following relation.

$$\ln f_i = \ln (x_i f_i^{std}) \tag{3.272}$$

where: $\gamma_i = 1$

f_i^{std} = *standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIdealSolLnFugacity Class	Liquid

For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Ideal Solution Activity Coefficient Differential wrt Temperature

This method calculates the activity coefficient differential wrt to temperature using the Ideal Solution model from the following relation.

$$\frac{\partial \ln \gamma_i}{\partial T} = 0 \tag{3.273}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIdealSolLnActivityCoeffDT Class	Liquid

Ideal Solution Gibbs Energy

This method calculates the Gibbs free energy using the Ideal Solution activity model from the following relation.

$$\mathrm{G} = \sum_{i}^{n} x_i G_i + RT \sum_{i}^{n} x_i \ln x_i \tag{3.274}$$

where: x_i *= mole fraction of component i*

G_i *= Gibbs energy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIdealSolGibbsEnergy Class	Liquid

Ideal Solution Enthalpy

This method calculates the enthalpy using the Ideal Solution activity model from the following relation.

$$H = \sum_{i}^{n} x_i H_i \tag{3.275}$$

where: x_i *= mole fraction of component i*

H_i *= enthalpy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHIdealSolEnthalpy Class	Liquid

3.2.2 Regular Solution Model

The Regular Solution model as defined by [40]Hildebrand (1970) is one in which the excess entropy is eliminated when a solution is mixed at constant temperature and volume. The model is recommended for non-polar components in which the molecules do not differ greatly in size. By the attraction of intermolecular forces, the excess Gibbs energy may be determined. Scatchard and Hildebrand assumed that the activity coefficients are a function of pure component properties only relating mixture interactions to those in pure fluids. The solubility parameter is a required and important pure component property which is related to the energy required to vaporize a liquid component to an ideal gas state. This method should not be used for highly non-ideal mixtures, especially if they contain polar components.

Property Methods

A quick reference of calculation methods is shown in the table below for the Regular Solution activity model.

Calculation Method	Applicable Phase	Property Class Name
Fugacity coefficient	Liquid	**COTHRegSolLnFugacityCoeff Class**
Activity coefficient	Liquid	**COTHRegSolLnActivityCoeff Class**
Fugacity	Liquid	**COTHRegSolLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHRegSolLnActivityCoeffDT Class**
Standard Fugacity	Liquid	**COTHIdealStdFug Class**
Excess Gibbs Energy	Liquid	**COTHRegSolExcessGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

Regular Solution Ln Activity Coefficient

This method calculates the activity coefficient of components, *i*, using the Regular Solution model as shown in the expression below.

$$\ln\gamma_i = \frac{V_i}{RT}\left[\delta_i - \sum_j \varphi_j \delta_i\right]^2 \tag{3.276}$$

$$\varphi_j = \frac{x_j V_j}{\sum_k x_k V_k} \tag{3.277}$$

where: γ_i = *activity coefficient of component i*

V_i = *liquid molar volume of component i*

δi = *solubility parameter of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRegSolLnActivityCoeff Class	Liquid

Regular Solution Ln Fugacity Coefficient

This method calculates the fugacity coefficient of components using the Regular Solution activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\gamma_i \frac{f_i^{std}}{P}\right) \tag{3.278}$$

where: γ_i = *activity coefficient of component i*

P = *pressure*

f_i^{std} = *standard state fugacity*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRegSolLnFugacityCoeff Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the Regular Solution Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Regular Solution Ln Fugacity

This method calculates the fugacity of components using the Regular Solution activity model. The fugacity of component i, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \tag{3.279}$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRegSolLnFugacity Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the Regular Solution Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Regular Solution Activity Coefficient Differential wrt Temperature

This method calculates the activity coefficient differential wrt to temperature using the Regular Solution model from the following relation.

$$\frac{d\ln\gamma_i}{dT} \tag{3.280}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarLnActivityCoeffDT Class	Liquid

Regular Solution Excess Gibbs Energy

This method calculates the excess Gibbs energy using the Regular Solution activity model from the following relation.

$$G^E = RT\sum_i^n x_i \ln\gamma_i \tag{3.281}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

T = *temperature*

R = *universal gas constant*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHRegSolLnActivityCoeffDT Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the Regular Solution Ln Activity Coefficient.

3.2.3 van Laar Model

In the Van Laar ([2]Prausnitz et al., 1986) activity model, it is assumed that, if two pure liquids are mixed at constant pressure and temperature, no volume expansion or contraction would happen ($V^E = 0$) and that the entropy of mixing would be zero. Thus the following relation:

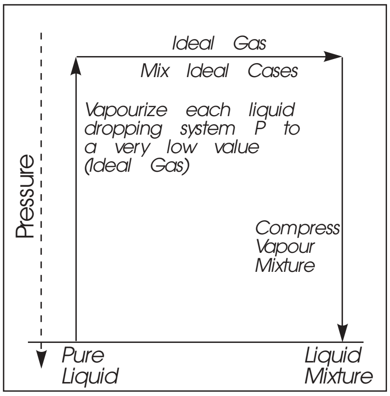
$$G^E = U^E + PV^E - TS^E \tag{3.282}$$

simplifies to:

$$G^E = H^E = U^E \tag{3.283}$$

To calculate the Gibbs free energy of mixing, the simple Van Laar thermodynamic cycle is shown below:

Figure 3.2



Since U is a point function, the value of U^E is:

$$U^E = U_I + U_{II} + U_{III} \tag{3.284}$$

The expression for ΔU_I is:

$$\Delta U_I = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{3.285}$$

The expression $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ can be derived from fundamental thermodynamic relationships.

The following is true:

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T - P\\ \left(\frac{\partial P}{\partial T}\right)_V &= -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T\end{aligned} \tag{3.286}$$

Therefore:

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left(P + T\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}\right) \tag{3.287}$$

In the van Laar model, it is assumed that the volumetric properties of the pure fluids could be represented by the van der Waals equation. This leads to:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \tag{3.288}$$

Assuming that there are x_1 moles of component 1 and x_2 of component 2 and $x_1 + x_2 = 1$ mole of mixture:

$$\begin{aligned} x_1(U^{id} - U)_1 &= \int_{V_1^L}^{\infty} \frac{a_1 x_1}{V^2} dV = \frac{a_1 x_1}{V_1^L} \\ x_2(U^{id} - U)_2 &= \int_{V_2^L}^{\infty} \frac{a_1 x_1}{V^2} dV = \frac{a_2 x_2}{V_1^L} \end{aligned} \tag{3.289}$$

thus:

$$\Delta U_I = x_1(U^{id} - U)_1 + x_2(U^{id} - U)_2 \tag{3.290}$$

and:

$$\Delta U_I = \frac{a_1 x_1}{V_2^L} + \frac{a_2 x_2}{V_1^L} \tag{3.291}$$

Using the van der Waals equation:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} \tag{3.292}$$

and for a real fluid well below its critical point, $\left(\frac{\partial P}{\partial V}\right)_T$ should be a large negative number (since liquids exhibit low compressibility) and consequently:

$$V - b \cong 0 \quad or \quad V \cong b \tag{3.293}$$

Therefore,

$$\Delta U_I = \frac{a_1 x_1}{b_1} + \frac{a_2 x_2}{b_2} \tag{3.294}$$

It follows that:

$$\Delta U_{II} = 0 \tag{3.295}$$

And since two ideal gases are being mixed,

$$\Delta U_{III} = -\frac{a_{mix}}{b_{mix}} \tag{3.296}$$

Again, it is assumed that the van der Waals equation applies.

Using the simple mixing rules for the van der Waals equation:

$$a_{mix} = \sum\sum x_i x_j \sqrt{a_i a_j} = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 \sqrt{a_1 a_2} \tag{3.297}$$

$$b_{mix} = \sum_{i=1}^{nc} x_i b_i = x_1 b_1 + x_2 b_2 \tag{3.298}$$

Finally, after some manipulation:

$$G^E = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 + x_2 b_2}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)^2 \tag{3.299}$$

and:

$$\begin{aligned} \ln\gamma_1 &= \frac{A}{\left[1 + \frac{Ax_1}{Bx_2}\right]^2} \\ \ln\gamma_2 &= \frac{B}{\left[1 + \frac{Bx_2}{Ax_1}\right]^2} \end{aligned} \tag{3.300}$$

where:

$$A = \frac{b_1}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right)$$
$$B = \frac{b_2}{RT}\left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2}\right) \tag{3.301}$$

Ethanol: T_c=513.9 K
P_c=6147 kPa
a=1252.5 l^2/gmol^2
b=0.087 l^2/gmol^2

Water: T_c=647.3 K
P_c=22120 kPa
a=552.2 l^2/gmol^2
b=0.030 l^2/gmol^2

System: T = 25 C
A_{ij} = 4.976
A_{ij} = 1.716

Two important features that are evident from the activity coefficient equations are that the log of the activity coefficient is proportional to the inverse of the absolute temperature, and that the activity coefficient of a component in a mixture is always greater than one. The quantitative agreement of the van Laar equation is not good, mainly due to the use of the van der Waals equation to represent the behaviour of the condensed phase, and the poor mixing rules for the mixture.

If one uses the van Laar equation to correlate experimental data (regarding the A and B parameters as purely empirical), good results are obtained even for highly non-ideal systems. One well-known exception is when one uses the van Laar equation to correlate data for self-associating mixtures like alcohol-hydrocarbon.

Application of the van Laar Equation

The van Laar equation was the first Gibbs excess energy representation with physical significance. The van Laar equation is a modified form of that described in "Phase Equilibrium in Process Design" by Null. This equation fits many systems quite well, particularly for LLE component distributions. It can be used for systems that exhibit positive or negative deviations from Raoult's Law, however, it cannot predict maximas or minimas in the activity coefficient. Therefore, it generally performs poorly for systems with halogenated hydrocarbons and alcohols. Due to the empirical nature of the equation, caution should be exercised in analyzing multi-component systems. It also has a tendency to predict two liquid phases when they do not exist.

The Van Laar equation also performs poorly for dilute systems and cannot represent many common systems, such as alcohol-hydrocarbon mixtures, with acceptable accuracy.

The van Laar equation has some advantages over the other activity models in that it requires less CPU time and can represent limited miscibility as well as three-phase equilibrium.

Property Methods

A quick reference of calculation methods is shown in the table below for the van Laar model.

Calculation Method	Applicable Phase	Property Class Name
Activity coefficient	Liquid	**COTHVanLaarLnActivityCoeff Class**
Fugacity coefficient	Liquid	**COTHVanLaarLnFugacityCoeff Class**
Fugacity	Liquid	**COTHVanLaarLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHVanLaarLnActivityCoeffDT Class**
Excess Gibbs	Liquid	**COTHVanLaarExcessGibbsEnergy Class**
Excess enthalpy	Liquid	**COTHVanLaarExcessEnthalpy Class**
Enthalpy	Liquid	**COTHVanLaarEnthalpy Class**
Gibbs energy	Liquid	**COTHVanLaarGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

van Laar Ln Activity Coefficient

This method calculates the activity coefficient of components, *i*, using the van Laar activity model. The extended, multi-component form of the van Laar equation is shown in the following relation:

$$\ln\gamma_i = A_i[1.0 - z_i]^2(1.0 + E_i z_i) \tag{3.302}$$

where: γ_i *= activity coefficient of component i*

x_i *= mole fraction of component i*

$$A_i = \sum_{j=1}^{n}\left[x_j\frac{(a_{ij} + b_{ij}T)}{(1.0 - x_i)}\right] \tag{3.303}$$

$$B_i = \sum_{j=1}^{n}\left[x_j\frac{(a_{ji} + b_{ji}T)}{(1.0 - x_i)}\right] \tag{3.304}$$

E_i = -4.0 if A_iB_i < 0.0, otherwise 0.0

$$z_i = \frac{A_i x_i}{[A_i x_i + B_i(1.0 - x_i)]} \tag{3.305}$$

The four adjustable parameters for the Van Laar equation are the a_{ij}, a_{ji}, b_{ij}, and b_{ji} terms. The equation will use stored parameter values stored or any user-supplied value for further fitting the equation to a given set of data.

where: T = *temperature (K)*

n = *total number of components*

a_{ij} = *non-temperature-dependent energy parameter between components i and j*

b_{ij} = *temperature-dependent energy parameter between components i and j [1/K]*

a_{ji} = *non-temperature-dependent energy parameter between components j and i*

b_{ji} = *temperature-dependent energy parameter between components j and i [1/K]*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarLnActivityCoeff Class	Liquid

van Laar Ln Fugacity Coefficient

This method calculates the fugacity coefficient of components using the van Laar activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln \phi_i = \ln\left(\gamma_i \frac{f_i^{std}}{P}\right) \tag{3.306}$$

where: γ_i = *activity coefficient of component i*

P = *pressure*

f_i = *standard state fugacity*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarLnFugacityCoeff Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the van Laar Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

van Laar Ln Fugacity

This method calculates the fugacity of components using the van Laar activity model. The fugacity of component *i*, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \tag{3.307}$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarLnFugacity Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the van Laar Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

van Laar Activity Coefficient Differential wrt Temperature

This method calculates the activity coefficient differential wrt to temperature using the van Laar model from the following relation.

$$\frac{d\ln\gamma_i}{dT} = (1-z_i)^2(1+E_i zi)\frac{dA_i}{dT} - 2A_i(1-z_i)(1+Ez_i)\frac{dz_i}{dT} + A(1-z_i)^2E_i\frac{dz_i}{dT} \qquad (3.308)$$

where:

$$\frac{dB_i}{dT} = \sum_{j=1}^{n}\frac{x_j b_{ji}}{1-x_i}$$

$$\frac{dZ_i}{dT} = \frac{x_i(1-x_i)\left(\frac{dA_i}{dT}B_i - \frac{dB_i}{dT}A_i\right)}{[A_i x_i + B_i(1-x_i)]^2}$$

$$\frac{dA_i}{dT} = \sum_{j=1}^{n}\frac{x_j b_{ij}}{1-x_i}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarLnActivityCoeffDT Class	Liquid

van Laar Excess Gibbs Energy

This method calculates the excess Gibbs energy using the van Laar activity model from the following relation.

$$G^E = RT\sum_i^n x_i \ln\gamma_i \tag{3.309}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarExcessGibbsEnergy Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the van Laar Ln Activity Coefficient.

van Laar Gibbs Energy

This method calculates the Gibbs free energy using the van Laar activity model from the following relation.

$$G = \sum_i^n x_i G_i + RT\sum_i^n x_i \ln x_i + G^E \tag{3.310}$$

where: G^E = *excess Gibbs energy*

x_i = *mole fraction of component i*

G_i = *Gibbs energy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarGibbsEnergy Class	Liquid

The term, *G*^{E}, in the above equation is exclusively calculated using the van Laar Excess Gibbs Energy.

van Laar Excess Enthalpy

This method calculates the excess enthalpy using the van Laar activity model from the following relation.

$$H^E = -RT^2\sum_i^n x_i\frac{d\ln\gamma_i}{dT} \qquad (3.311)$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarExcessEnthalpy Class	Liquid

The term, $\frac{d\ln\gamma_i}{dT}$, in the above equation is exclusively calculated using the van Laar Activity Coefficient Differential wrt Temperature.

van Laar Enthalpy

This method calculates the enthalpy using the van Laar activity model from the following relation.

$$H = \sum_{i}^{n} x_i H_i + H^E \tag{3.312}$$

where: H^E = *excess enthalpy*

x_i = *mole fraction of component i*

H_i = *enthalpy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHVanLaarEnthalpy Class	Liquid

The term, H^E, in the above equation is exclusively calculated using the van Laar Ln Activity Coefficient.

3.2.4 Margules Model

This equation should not be used for extrapolation beyond the range over which the energy parameters have been fitted.

The Margules equation was the first Gibbs excess energy representation developed. The equation does not have any theoretical basis, but is useful for quick estimates and data interpolation. The software has an extended multi-component Margules equation with up to four adjustable parameters per binary.

The four adjustable parameters for the Margules equation are the a_{ij} and a_{ji} (temperature independent) and the b_{ij} and b_{ji} terms (temperature dependent). The equation will use stored parameter values or any user-supplied value for further fitting the equation to a given set of data.

Property Methods

A quick reference of calculation methods is shown in the table below for the Margules property model.

Calculation Method	Applicable Phase	Property Class Name
Activity Coefficient	Liquid	**COTHMargulesLnActivityCoeff Class**
Fugacity coefficient calculation	Liquid	**COTHMargulesLnFugacityCoeff Class**
Fugacity calculation	Liquid	**COTHMargulesLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHMargulesLnActivityCoeffDT Class**
Excess Gibbs	Liquid	**COTHMargulesExcessGibbsEnergy Class**
Excess enthalpy	Liquid	**COTHMargulesExcessEnthalpy Class**
Enthalpy	Liquid	**COTHMargulesEnthalpy Class**
Gibbs energy	Liquid	**COTHMargulesGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

Margules Ln Activity Coefficient

This method calculates the activity coefficient for components, *i*, using the Margules activity model from the following relation:

$$\ln\gamma_i = [1.0 - x_i]^2[A_i + 2x_i(B_i - A_i)] \tag{3.313}$$

where: γ_i *= activity Coefficient of component i*

x_i *= mole fraction of component i*

$$A_i = \sum_{j=1}^{n}\left[x_j\frac{(a_{ij} + b_{ij}T)}{(1.0 - x_i)}\right] \tag{3.314}$$

$$B_i = \sum_{j=1}^{n}\left[x_j\frac{(a_{ji}+b_{ji}T)}{(1.0-x_i)}\right] \tag{3.315}$$

where: T = temperature (K)

n = total number of components

a_{ij} = non-temperature-dependent energy parameter between components i and j

b_{ij} = temperature-dependent energy parameter between components i and j [1/K]

a_{ji} = non-temperature-dependent energy parameter between components j and i

b_{ji} = temperature-dependent energy parameter between components j and i [1/K]

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesLnActivityCoeff Class	Liquid

Margules Ln Fugacity Coefficient

This method calculates the fugacity coefficient of components using the Margules activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\gamma_i\frac{f_i^{std}}{P}\right) \tag{3.316}$$

where: γ_i = activity coefficient of component i

f_i = standard state fugacity

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesLnFugacityCoeff Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the Margules Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Margules Fugacity

This method calculates the fugacity logarithm of components using Margules activity model. The fugacity of component *i*, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \tag{3.317}$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *Standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesLnFugacity Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the Margules Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Margules Activity Coefficient Differential wrt Temperature

This method calculates the activity coefficient wrt to temperature from the following relation.

$$\frac{\partial \ln\gamma_i}{\partial T} \tag{3.318}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesLnActivityCoeffDT Class	Liquid

Margules Excess Gibbs Energy

This method calculates the excess Gibbs energy using the Margules activity model from the following relation.

$$G^E = RT\sum_i^n x_i \ln\gamma_i \tag{3.319}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesExcessGibbsEnergy Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the Margules Ln Activity Coefficient.

Margules Gibbs Energy

This method calculates the Gibbs free energy using the Margules activity model from the following relation.

$$G = \sum_{i}^{n} x_i G_i + RT\sum_{i}^{n} x_i \ln x_i + G^E \tag{3.320}$$

where: G^E = *excess Gibbs energy*

x_i = *mole fraction of component i*

G_i = *Gibbs energy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesGibbsEnergy Class	Liquid

The term, G^E, in the above equation is exclusively calculated using the Margules Excess Gibbs Energy.

Margules Excess Enthalpy

This method calculates the excess enthalpy using the Margules activity model from the following relation.

$$\mathrm{H}^E = -RT^2\sum_i^n x_i \frac{d\ln\gamma_i}{dT} \tag{3.321}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesExcessEnthalpy Class	Liquid

The term, $\frac{d\ln\gamma_i}{dT}$, in the above equation is exclusively calculated using the Margules Activity Coefficient Differential wrt Temperature.

Margules Enthalpy

This method calculates the enthalpy using the Margules activity model from the following relation.

$$H = \sum_i^n x_i H_i + H^E \tag{3.322}$$

where: H^E = *excess enthalpy*

x_i = *mole fraction of component i*

H_i = *enthalpy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHMargulesEnthalpy Class	Liquid

The term, *H*^{E}, in the above equation is exclusively calculated using the Margules Excess Enthalpy.

3.2.5 Wilson Model

The [20]Wilson (1964) equation is based on the Flory-Huggins theory, assuming that intermolecular interactions are negligible. First, imagine that the liquid mixture can be magnified to a point where molecules of type 1 and type 2 in a binary mixture can be visualized. Consider molecules of type 1, and determine the ratio of the probability of finding a molecule of type 2 over the probability of finding a molecule of type 1 in the surrounding of this particular molecule of type 1.

Wilson proposed that:

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp\left(-\frac{a_{21}}{RT}\right)}{x_1 \exp\left(-\frac{a_{11}}{RT}\right)} \tag{3.323}$$

The parameters a_{21} and a_{11} are related to the potential energies of the 1-1 and 1-2 pairs of molecules. Similarly, to see what is happening in the region of a specific molecule of type 2, you have:

$$\frac{x_{12}}{x_{22}} = \frac{x_1 \exp\left(-\frac{a_{12}}{RT}\right)}{x_2 \exp\left(-\frac{a_{22}}{RT}\right)} \tag{3.324}$$

Wilson defined the local volume fractions based on the two equations above, using the pure component molar volumes as weights:

$$\phi_1 = \frac{V_1 x_{11}}{V_1 x_{11} + V_2 x_{21}} \qquad \phi_2 = \frac{V_2 x_{22}}{V_1 x_{12} + V_2 x_{22}} \tag{3.325}$$

ϕ_i is the volume fraction of component i.

When the above relations for ϕ are substituted into the Flory-Huggins equation:

$$\frac{G^E}{RT} = \sum x_i \ln\left(\frac{\phi_i}{x_i}\right)$$

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \tag{3.326}$$

where:

$$\begin{aligned} \Lambda_{12} &= \frac{V_2}{V_1}\exp\left(-\frac{\lambda_{12}}{RT}\right) \\ \Lambda_{21} &= \frac{V_1}{V_2}\exp\left(-\frac{\lambda_{21}}{RT}\right) \end{aligned} \tag{3.327}$$

and:

$$\begin{aligned} \ln\gamma_1 &= -\ln(x_1 + \Lambda_{12} x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1}\right] \\ \ln\gamma_2 &= -\ln(x_2 + \Lambda_{21} x_1) + x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} x_1}\right] \end{aligned} \tag{3.328}$$

The Wilson equation, although fundamentally empirical, provides a fair description of how real liquid systems behave. Also, it is a powerful framework for regression and extension of experimental data. Of primary importance, the Wilson equation can be extended to multi-component mixtures without the use of simplifications (as in the case of van Laar and Margules) or ternary or higher parameters. In other words, if one has the λ_{ij} - λ_{ii} parameters for all binaries in a multi-component mixture, the Wilson equation can be used to model the multi-component behaviour.

This is very important, since multi-component data are rather scarce and tedious to collect and correlate. In the same way that the CS correlation opened the doors for VLE modeling of fairly complex hydrocarbon systems, the Wilson equation enabled the systematic modeling of fairly complex non-ideal systems. However, one still has to measure the VLE behaviour to obtain the binary parameters. Only in very specific situations can the parameters be generalized ([30]Orye and Prausnitz, 1965).

Perhaps more importantly, the Wilson equation can not predict phase splitting, thus it cannot be used for LLE calculations. An empirical additional parameter proposed by Wilson to account for phase splitting did not find wide acceptance, since it cannot be easily extended for multi-component mixtures. An interesting modification of the Wilson equation to account for phase splitting is the one by Tsuboka and Katayama, as described in the [21]Walas (1985).

To extend the applicability of the Wilson equation

$$a_{ij} = \Lambda_{ij} - \Lambda_{ji} \tag{3.329}$$

It is modeled as a simple linear function of temperature:

$$a_{ij} = b_{ij} + c_{ij}T \tag{3.330}$$

Application of Wilson Equation

The Wilson equation was the first activity coefficient equation that used the local composition model to derive the excess Gibbs energy expression. It offers a thermodynamically consistent approach to predicting multi-component behaviour from regressed binary equilibrium data. Experience also shows that the Wilson equation can be extrapolated with reasonable confidence to other operating regions with the same set of regressed energy parameters.

Although the Wilson equation is more complex and requires more CPU time than either the van Laar or Margules equations, it can represent almost all non-ideal liquid solutions satisfactorily, except electrolytes and solutions exhibiting limited miscibility (LLE or VLLE). It provides an excellent prediction of ternary equilibrium using parameters regressed from binary data only. The Wilson equation will give similar results as the Margules and van Laar equations for weak non-ideal systems, but consistently outperforms them for increasingly non-ideal systems.

Setting all four parameters to zero does not reduce the binary to an ideal solution, but maintains a small effect due to molecular size differences represented by the ratio of molar volumes.

The Wilson equation used in this program requires two to four adjustable parameters per binary. The four adjustable parameters for the Wilson equation are the a_{ij} and a_{ji} (temperature independent) terms, and the b_{ij} and b_{ji} terms (temperature dependent). Depending upon the available information, the temperature dependent parameters may be set to zero. Although the Wilson equation contains terms for temperature dependency, caution should be exercised when extrapolating.

Property Methods

A quick reference of calculation methods is shown in the table below for the Wilson property model.

Calculation Method	Applicable Phase	Property Class Name
Activity Coefficient	Liquid	**COTHWilsonLnActivityCoeff Class**
Fugacity coefficient calculation	Liquid	**COTHWilsonLnFugacityCoeff Class**
Fugacity calculation	Liquid	**COTHWilsonLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHWilsonLnActivityCoeffDT Class**
Excess Gibbs	Liquid	**COTHWilsonExcessGibbsEnergy Class**
Excess enthalpy	Liquid	**COTHWilsonExcessEnthalpy Class**
Enthalpy	Liquid	**COTHWilsonEnthalpy Class**
Gibbs energy	Liquid	**COTHWilsonGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

Wilson Ln Activity Coefficient

This method calculates the activity coefficient for components, *i*, using the Wilson activity model from the following relation.

$$\ln\gamma_i = 1.0 - \ln \sum_{j=1}^{n} x_j \Lambda_{ij} - \sum_{k=1}^{n} \left[\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{n} x_k \Lambda_{kj}} \right] \tag{3.331}$$

where: γ_i = *Activity coefficient of component i*

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left[-\frac{(a_{ij} + b_{ij}T)}{RT}\right]$$

x_i = *Mole fraction of component i*

T = *Temperature (K)*

n = *Total number of components*

a_{ij} = *Non-temperature dependent energy parameter between components i and j (cal/gmol)*

b_{ij} = *Temperature dependent energy parameter between components i and j (cal/gmol-K)*

V_i = *Molar volume of pure liquid component i in m3/kgmol (litres/gmol)*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonLnActivityCoeff Class	Liquid

This method uses the Henry's convention for non-condensable components.

Wilson Fugacity Coefficient

This method calculates the fugacity coefficient of components using the Wilson activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\gamma_i \frac{f_i^{std}}{P}\right) \tag{3.332}$$

where: γ_i = activity coefficient of component i

P = Pressure

f_i = Standard state fugacity

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonLnFugacityCoeff Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the Wilson Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Wilson Fugacity

This method calculates the fugacity of components using the Wilson activity model. The fugacity of component *i*, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \tag{3.333}$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *Standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonLnFugacity Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the Wilson Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Wilson Activity Coefficient Differential wrt Temperature

This method calculates the activity coefficient wrt to temperature from the following relation.

$$\frac{d\ln\gamma_i}{dT} = -\frac{\sum\limits_{j=1}^{n}\frac{x_j d\Lambda_{ij}}{dT}}{\sum\limits_{j=1}^{n} x_j\Lambda_{ij}} - \sum_{k=1}^{n}\frac{x_k\frac{d\Lambda_{ki}}{dT}\left(\sum\limits_{j=1}^{n} x_j\Lambda_{kj}\right) - x_k\Lambda_{ij}\left(\sum\limits_{j=1}^{n} x_j\frac{d\Lambda_{kj}}{dT}\right)}{\left(\sum\limits_{j=1}^{n} x_j\Lambda_{kj}\right)^2} \tag{3.334}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonLnActivityCoeffDT Class	Liquid

Wilson Excess Gibbs Energy

This method calculates the excess Gibbs energy using the Wilson activity model from the following relation.

$$G^E = RT\sum_i^n x_i \ln\gamma_i \tag{3.335}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

T = *temperature*

R = *universal gas constant*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonExcessGibbsEnergy Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the Wilson Ln Activity Coefficient.

Wilson Gibbs Energy

This method calculates the Gibbs free energy using the Wilson activity model from the following relation.

$$G = \sum_{i}^{n} x_i G_i + RT \sum_{i}^{n} x_i \ln x_i + G^E \tag{3.336}$$

where: G^E = *excess Gibbs energy*

x_i = *mole fraction of component i*

G_i = *Gibbs energy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonGibbsEnergy Class	Liquid

The term, G^E, in the above equation is exclusively calculated using the Wilson Excess Gibbs Energy.

Wilson Excess Enthalpy

This method calculates the excess enthalpy using the Wilson activity model from the following relation.

$$\mathrm{H}^E = -RT^2\sum_i^n x_i \frac{d\ln\gamma_i}{dT} \tag{3.337}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonExcessEnthalpy Class	Liquid

The term, $\frac{d\ln\gamma_i}{dT}$, in the above equation is exclusively calculated using the Wilson Activity Coefficient Differential wrt Temperature.

Wilson Enthalpy

This method calculates the enthalpy using the Wilson activity model from the following relation.

$$H = \sum_i^n x_i H_i + H^E \tag{3.338}$$

where: H^E = *excess enthalpy*

x_i = *mole fraction of component i*

H_i = *enthalpy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHWilsonEnthalpy Class	Liquid

The term, H^E, in the above equation is exclusively calculated using the Wilson Excess Enthalpy.

3.2.6 NRTL Model

The Wilson equation is very successful in the representation of VLE behaviour of completely miscible systems, but is not theoretically capable of predicting VLE and LLE. [22]Renon and Prausnitz (1968) developed the **Non-Random Two-Liquid Equation** (NRTL). In developing the NRTL, they used the quasi-chemical theory of Guggenheim and the two-liquid theory from Scott. To take into account the "structure" of the liquid generated by the electrostatic force fields of individual molecules, the local composition expression suggested by Wilson is modified:

$$\frac{x_{21}}{x_{11}} = \frac{x_2}{x_1}\left[\frac{\exp\left(\frac{-\alpha_{12}g_{21}}{RT}\right)}{\exp\left(\frac{-\alpha_{12}g_{11}}{RT}\right)}\right] \tag{3.339}$$

$$\frac{x_{21}}{x_{22}} = \frac{x_1}{x_2}\left[\frac{\exp\left(\frac{-\alpha_{12}g_{12}}{RT}\right)}{\exp\left(\frac{-\alpha_{12}g_{22}}{RT}\right)}\right] \tag{3.340}$$

where: α_{12} = *is a parameter which characterizes the non-randomness of the mixture.*

x = *is mole fraction of component*

g = *is free energies for mixture*

The local model fractions are restricted by material balance to $x_{12} + x_{22} = 1$ and $x_{21} + x_{11} = 1$. If the ratios $\frac{x_{21}}{x_{11}}$ and $\frac{x_{12}}{x_{22}}$ are multiplied:

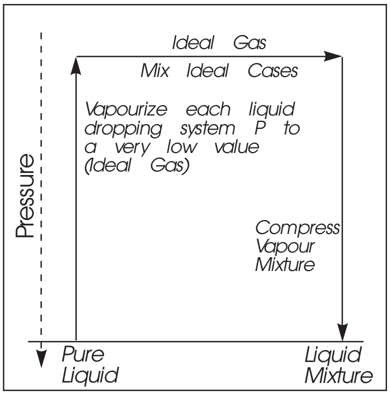
$$\frac{x_{21}}{x_{11}} \times \frac{x_{12}}{x_{22}} = \exp\left(-\alpha_{12}\frac{(2g_{12} - g_{11} - g_{22})}{RT}\right) \tag{3.341}$$

When the material balance equations are substituted:

$$(1 - x_{21})(1 - x_{12})\exp\left(-\alpha_{12}\frac{(2g_{12} - g_{11} - g_{22})}{RT}\right) = x_{21}x_{12} \tag{3.342}$$

Scotts Two Liquid Theory

Figure 3.3



The quasi-chemical theory of Guggenheim with the non-random assumption can be written as:

$$(1 - x_{21})(1 - x_{12})\exp\left(-\frac{1}{Z}\frac{(2\omega_{12} - \omega_{11} - \omega_{22})}{RT}\right) = x_{21}x_{12} \tag{3.343}$$

where: Z = *is the coordination number*

ω= *is the energy of interaction between pairs*

x = *is mole fraction of components*

This gives a physical interpretation of the α_{ij} parameter. Since the coordination number represents the number of neighbour molecules a given molecule may have, the usual value is somewhere between 6 and 12, giving an α value in the order of positive 0.1 to 0.3. The significance of α is somewhat ambiguous when its value is greater than 0.3, where a hypothetical fluid mixture in which a molecule with very few neighbours should exist. The following equations for the local compositions exist:

$$x_{21} = \frac{x_2 \exp\left[-\alpha_{12}\frac{(g_{21}-g_{11})}{RT}\right]}{x_1 + x_2 \exp\left[-\alpha_{12}\frac{(g_{21}-g_{11})}{RT}\right]} \tag{3.344}$$

and

$$x_{12} = \frac{x_1 \exp\left[-\alpha_{12}\frac{(g_{12}-g_{22})}{RT}\right]}{x_1 + x_2 \exp\left[-\alpha_{12}\frac{(g_{12}-g_{22})}{RT}\right]} \tag{3.345}$$

Renon and Prausnitz used the above equations in the two-liquid theory of Scott. Scott assumed that a liquid mixture can be idealized as a set of cells, in which there are cells with molecules of type 1 and type 2 in the centre. "For cells with molecules of type 1 in the centre, the residual Gibbs free energy (the Gibbs free energy when compared with that of an ideal gas at the same temperature, pressure and composition) is the sum of all the residual Gibbs free energies for two body interactions experienced by centre molecule of type 1" ([22]Renon and Prausnitz, 1968). Thus:

$$\begin{aligned} g^{(1)} &= x_{11}g_{11} + x_{21}g_{21} \\ g^{(1)}_{pure} &= g_{11} \end{aligned} \tag{3.346}$$

A molecule of type 2 in the centre can be:

$$\begin{aligned} g^{(2)} &= x_{22}g_{22} + x_{12}g_{12} \\ g^{(2)}_{pure} &= g_{22} \end{aligned} \tag{3.347}$$

The Gibbs excess energy is the sum of the changes where molecules of type 1 from a cell of pure component 1 are transferred into the centre of a cell of liquid 2; the same reasoning applies for molecule 2.

Consequently:

$$g^E = x_1(g^{(1)} - g^{(1)}_{pure}) + x_2(g^{(2)} - g^{(2)}_{pure}) \tag{3.348}$$

substituting and finally:

$$g^E = x_1x_{21}(g_{21} - g_{11}) + x_2x_{12}(g_{12} - g_{22}) \tag{3.349}$$

where: g^E is the excess Gibbs free energy

g is Gibbs free energy for interaction between components

and the activity coefficients are:

$$\ln\gamma_1 = x_2^2\left(\tau_{21}\frac{\exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2\exp(-\alpha_{12}\tau_{21})]^2} + \tau_{12}\frac{\exp(-2\alpha_{12}\tau_{12})}{[x_2 + x_1\exp(-\alpha_{12}\tau_{12})]^2}\right) \tag{3.350}$$

$$\ln\gamma_2 = x_1^2\left(\tau_{12}\frac{\exp(-2\alpha_{12}\tau_{12})}{[x_2 + x_1\exp(-\alpha_{12}\tau_{12})]^2} + \tau_{21}\frac{\exp(-2\alpha_{12}\tau_{21})}{[x_1 + x_2\exp(-\alpha_{12}\tau_{21})]^2}\right) \tag{3.351}$$

where:

$$\begin{aligned} \tau_{12} &= \frac{g_{12} - g_{22}}{RT} \\ \tau_{21} &= \frac{g_{21} - g_{11}}{RT} \qquad (3.352) \\ g_{12} &= \exp(-\alpha_{12}\tau_{12}) \\ g_{21} &= \exp(-\alpha_{12}\tau_{21}) \end{aligned}$$

The NRTL equation offers little advantage over Wilson for systems that are completely miscible. On the other hand, the NRTL equation can be used for systems that will phase split. When the g_{ij} - g_{ji} parameters are temperature dependent, the NRTL equation is very flexible and can be used to model a wide variety of chemical systems. Although the α_{ij} term has a physical meaning and [22]Renon and Prausnitz (1968) suggested a series of rules to fix its value depending on the mixture type, it is better treated as an empirical parameter to be determined through regression of experimental data. That is, if there is enough data to justify the use of 3 parameters.

The NRTL equation is an extension of the original Wilson equation. It uses statistical mechanics and the liquid cell theory to represent the liquid structure. These concepts, combined with Wilson's local composition model, produce an equation capable of representing VLE, LLE and VLLE phase behaviour. Like the Wilson equation, the NRTL is thermodynamically consistent and can be applied to ternary and higher order systems using parameters regressed from binary equilibrium data. It has an accuracy comparable to the Wilson equation for VLE systems.

The NRTL combines the advantages of the Wilson and van Laar equations, and, like the van Laar equation, it is not extremely CPU intensive and can represent LLE quite well. It is important to note that because of the mathematical structure of the NRTL equation, it can produce erroneous multiple miscibility gaps. Unlike the van Laar equation, NRTL can be used for dilute systems and hydrocarbon-alcohol mixtures, although it may not be as good for alcohol-hydrocarbon systems as the Wilson equation.

Property Methods

A quick reference of calculation methods is shown in the table below for the NRTL property model.

Calculation Method	Applicable Phase	Property Class Name
Activity Coefficient	Liquid	**COTHNRTLLnActivityCoeff Class**
Fugacity coefficient calculation	Liquid	**COTHNRTLLnFugacityCoeff Class**
Fugacity calculation	Liquid	**COTHNRTLLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHNRTLLnActivityCoeffDT Class**
NRTL temperature dependent binary interaction parameters	Liquid	**COTHNRTLTempDep Class**
Excess Gibbs	Liquid	**COTHNRTLExcessGibbsEnergy Class**
Excess enthalpy	Liquid	**COTHNRTLExcessEnthalpy Class**
Enthalpy	Liquid	**COTHNRTLEnthalpy Class**
Gibbs energy	Liquid	**COTHNRTLGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

NRTL Ln Activity Coefficient

This method calculates the activity coefficient for components, *i,* using the NRTL activity model from the following relation:

$$\ln\gamma_i = \frac{\sum_{j=1}^{n}\tau_{ji}x_jG_{ji}}{\sum_{k=1}^{n}x_kG_{ki}} + \sum_{j=1}^{n}\frac{x_jG_{ij}}{x_kG_{kj}}\left(\tau_{ij} - \frac{\sum_{m=1}^{n}\tau_{mi}x_mG_{mi}}{\sum_{k=1}^{n}x_kG_{kj}}\right) \tag{3.353}$$

where: γ_i = *Activity coefficient of component i*

x_i = *Mole fraction of component i*

n = *Total number of components*

τ_{ij} = *Temperature-dependent energy parameter between components i and j (cal/gmol-K)*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLLnActivityCoeff Class	Liquid

This method uses Henry's convention for non-condensable components.

The values G_{ij} and τ_{ij} are calculated from the temperature dependent binary interaction parameters.

NRTL Fugacity Coefficient

This method calculates the fugacity coefficient of components using the NRTL activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\gamma_i \frac{f_i^{std}}{P}\right) \tag{3.354}$$

where: γ_i = *activity coefficient of component i*

P = *Pressure*

f_i = *Standard state fugacity*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLLnFugacityCoeff Class	Liquid

The term, $\ln\gamma_i$, in the above equation is exclusively calculated using the NRTL Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

NRTL Fugacity

This method calculates the fugacity of components using the NRTL activity model. The fugacity of component, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \qquad (3.355)$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *Standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLLnFugacity Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the NRTL Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

NRTL Activity Coefficient Differential wrt Temperature

This method analytically calculates the differential activity coefficient with respect to temperature from the following relation.

$$\frac{d\ln\gamma_i}{dT} \qquad (3.356)$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLLnActivityCoeffDT Class	Liquid

Temperature Dependent Binary Interaction Parameters

This method calculates the temperature dependent binary interaction parameters for the NRTL model from the following relation.

$$\tau_{ij} = \left(a_{ij} + \frac{b_{ij}}{T} + c_{ij}\ln T + d_{ij}T + \frac{e_{ij}}{T^2}\right) \tag{3.357}$$

$$G_{ij} = EXP(-\alpha\tau_{ij}) \tag{3.358}$$

where:

$$\alpha = \alpha_0 + \alpha_1 T$$

$$a_{ij} = 0;\ \mathrm{b}_{ij} = 0;\ \mathrm{c}_{ij} = 0;\ \mathrm{d}_{ij} = 0;\ \mathrm{e}_{ij} = 0$$
$$\tau_{ij} = 0$$

where: a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij}, = *Temperature-dependent energy parameter between components i and j (cal/gmol-K)*

α_{ij} = *NRTL non-randomness parameters for binary interaction (note that* $a_{ij} = a_{ji}$ *for all binaries)*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLTempDep Class	Liquid

NRTL Excess Gibbs Energy

This method calculates the excess Gibbs energy using the NRTL activity model from the following relation.

$$G^E = RT\sum_i^n x_i \ln\gamma_i \tag{3.359}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLExcessGibbsEnergy Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the NRTL Ln Activity Coefficient.

NRTL Gibbs Energy

This method calculates the Gibbs free energy NRTL activity model from the following relation.

$$\mathrm{G} = \sum_i^n x_i G_i + RT\sum_i^n x_i \ln x_i + G^E \tag{3.360}$$

where: G^E = *excess Gibbs energy*

x_i = *mole fraction of component i*

G_i = *Gibbs energy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLGibbsEnergy Class	Liquid

The term, G^E, in the above equation is exclusively calculated using the NRTL Gibbs Energy.

NRTL Excess Enthalpy

This method calculates the excess enthalpy using the NRTL activity model from the following relation.

$$\mathrm{H}^E = -RT^2\sum_i^n x_i \frac{d\ln\gamma_i}{dT} \tag{3.361}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLExcessEnthalpy Class	Liquid

The term, $\frac{d\ln\gamma_i}{dT}$, in the above equation is exclusively calculated using the NRTL Activity Coefficient Differential wrt Temperature.

NRTL Enthalpy

This method calculates the enthalpy using the NRTL activity model from the following relation.

$$H = \sum_{i}^{n} x_i H_i + H^E \qquad (3.362)$$

where: H^E = *excess enthalpy*

x_i = *mole fraction of component i*

H_i = *enthalpy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHNRTLEnthalpy Class	Liquid

The term, H^E, in the above equation is exclusively calculated using the NRTL Excess Enthalpy.

3.2.7 HypNRTL Model

The methods in the HypNRTL model are same as the **Section 3.2.6 - NRTL Model** explained in the previous section. The difference between the models is that the HypNRTL does not offer a flexible temperature dependence for τ ij. The HypNRTL is represented by the following relation:

$$G_{ij} = \exp[-\tau_{ij}\alpha_{ij}] \tag{3.363}$$

$$\tau_{ij} = \frac{a_{ij} + b_{ij}T}{RT} \tag{3.364}$$

x_i = *Mole fraction of component i*

T = *Temperature (K)*

n = *Total number of components*

a_{ij} = *Non-temperature-dependent energy parameter between components i and j (cal/gmol)**

b_{ij} = *Temperature-dependent energy parameter between components i and j (cal/gmol-K)**

α_{ij} = *NRTL non-randomness parameters for binary interaction (note that* $a_{ij} = a_{ji}$ *for all binaries)*

Property Methods

A quick reference of calculation methods is shown in the table below for the HYPNRTL property model.

Calculation Method	Applicable Phase	Property Class Name
Activity Coefficient	Liquid	**COTHHYPNRTLLnActivityCoeff Class**
Fugacity coefficient calculation	Liquid	**COTHHYPNRTLLnFugacityCoeff Class**
Fugacity calculation	Liquid	**COTHHYPNRTLLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHHYPNRTLLnActivityCoeffDT Class**
Excess Gibbs	Liquid	**COTHHYPNRTLExcessGibbsEnergy Class**
Excess enthalpy	Liquid	**COTHHYPNRTLExcessEnthalpy Class**
Enthalpy	Liquid	**COTHHYPNRTLEnthalpy Class**
Gibbs energy	Liquid	**COTHHYPNRTLGibbsEnergy Class**

3.2.8 The General NRTL Model

The General NRTL model is a variation of the NRTL model. More binary interaction parameters are used in defining the component activity coefficients. You may apply either model to systems:

- with a wide boiling point range between components.
- where you require simultaneous solution of VLE and LLE, and there exists a wide boiling point range or concentration range between components.

The equations options can be viewed in the Display Form drop down list on the **Binary Coeffs** tab of the **Fluid Package** property view.

With the General NRTL model, you can specify the format for the equations of τ_{ij} and a_{ij} to be any of the following:

τ_{ij} and α_{ij} Options
$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} + \frac{C_{ij}}{T^2} + F_{ij}T + G_{ij}\ln(T)$ $\alpha_{ij} = Alp1_{ij} + Alp2_{ij}T$
$\tau_{ij} = \frac{A_{ij} + \frac{B_{ij}}{T}}{RT}$ $\alpha_{ij} = Alp1_{ij}$
$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T} + F_{ij}T + G_{ij}\ln(T)$ $\alpha_{ij} = Alp1_{ij} + Alp2_{ij}T$
$\tau_{ij} = A_{ij} + B_{ij}t + \frac{C_{ij}}{T}$ $\alpha_{ij} = Alp1_{ij} + Alp2_{ij}T$ *where: T is in K and t is °C*
$\tau_{ij} = A_{ij} + \frac{B_{ij}}{T}$ $\alpha_{ij} = Alp1_{ij}$

Depending on the form of the equations that you choose, you can specify values for the different component energy parameters. The General NRTL model provides radio buttons on the *Binary Coeffs* tab which access the matrices for the A_{ij}, B_{ij}, C_{ij}, F_{ij}, G_{ij}, $Alp1_{ij}$ and $Alp2_{ij}$ energy parameters.

3.2.9 HYSYS - General NRTL

Method	Description	Equation
HYSIMStdLiquidVolume	Standard Liquid Volume	$V = \sum_{i=1}^{nc} \frac{MW_i}{\rho_i} x_i$
HYSIMLiqDensity	Density	Hankinson, R.W. and Thompson, G.H., A.I.Ch.E. Journal 25, No.4, P. 653, (1979).
HYSIMLiqVolume	Volume	Hankinson, R.W. and Thompson, G.H., A.I.Ch.E. Journal 25, No.4, P. 653, (1979).
GenLiquid1Fug Coefficient	Fugacity Coefficient	$\phi_i = \gamma_i \left(\frac{f_i^{std}}{P} \right)$
NRTLActCoeff	Activity Coefficient	$\ln\gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} x_j G_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{n} \tau_{mi} x_m G_{mi}}{\sum_{k=1}^{n} x_k G_{kj}} \right)$
ActivityLiquid1Fugacity	Fugacity	$f_i = \gamma_i x_i f_i^{std}$
CavettEnthalpy	Enthalpy	$H^l = x_{water} H_{water}^{steam67} + \sum_i x_i \left(H_i^\circ + \Delta H_i^{Cavett} \right)$
CavettEntropy	Entropy	$S^l = x_{water} S_{water}^{steam67} + \sum_i x_i \left(S^\circ + \Delta S_i^{Cavett} \right)$
CavettGibbs	Gibbs Free Energy	$G = G^\circ + (A - A^\circ) + RT(Z - 1)$
CavettHelmholtz	Helmholtz Energy	$A = A^\circ + (H - H^\circ) + T(S - S^\circ) - RT(Z - 1)$
CavettInternal	Internal Energy	$U = U^\circ + (A - A^\circ) + T(S - S^\circ)$
CavettCp	Cp	$Cp^l = x_{water} Cp_{water}^{steam67} + \sum_i x_i \left(Cp_i^\circ + \Delta Cp_i^{Cavett} \right)$
CavettCv	Cv	$C_v = C_p - R$

Method	Description	Equation
NRTLGe	Excess Gibbs free energy	$G^E = RT\sum_{i=1}^{nc} x_i \ln\gamma_i$
MRTLHe	Excess enthalpy	$H^E = G^E - T\left(\frac{\partial G^E}{\partial T}\right)$
HYSIMLiquidViscosity*	Viscosity	Light Hydrocarbons (NBP<155 F) - Modified Ely & Hanley (1983) Heavy Hydrocarbons (NVP>155 F) - Twu (1984) Non-Ideal Chemicals - Modified Letsou-Stiel (see Reid, Prausnitz and Poling, 1987).
HYSIMVapourThermalK*	Thermal Conductivity	Misic and Thodos; Chung et al. methods (see Reid, Prausnitz and Poling, 1987).
HYSIMSurfaceTension	Surface Tension	$\sigma = P_c^{\frac{2}{3}} T_c^{\frac{1}{3}} Q(1 - T_R)^a b$

3.2.10 UNIQUAC Model

[23]Abrams and Prausnitz (1975) derived an equation with a semi-theoretical basis like NRTL, but using only two adjustable parameters per binary pair. Their approach is heavily dependent on some statistical mechanics concepts which are outside the scope of this guide. Only a few highlights from their work will be presented here.

"Guggenheim proposed that a liquid mixture can be seen as a set of tri-dimensional lattice sites, the volume in the immediate vicinity of a site is called a cell. Each molecule in the liquid is divided in segments such that each segment occupies one cell" ([23]Abrams and Prausnitz, 1975). Using the configurational partition function, it can be shown that:

$$g^E \cong a^E = \frac{\Delta A}{n_1 + n_2} - RT(x_1 \ln x_1 + x_2 \ln x_2) \tag{3.365}$$

where: A = *Helmholtz function*

n = *number of moles*

x = *mole fraction*

In the original work of Guggenheim, he assumed that the liquid was composed of molecules with relatively the same size; thus the number of neighbours of type 2 to a molecule of type 1 was a reasonable measure of the local composition.

Since Prausnitz and Abrams proposed to handle molecules of different sizes and shapes, they developed a different measurement of the local composition, i.e., a local area fraction. Using this idea, coupled with some arguments based on statistical thermodynamics, they reached the following expression for the Gibbs free energy:

$$G^E = G^E_{combinational} + G^E_{resdiual} \tag{3.366}$$

and:

Combinational refers to the non-ideality caused by differences in size and shape (entropic effects).

Residual refers to non-idealities due to energetic interactions between molecules (temperature or energy dependent).

$$G^E_{combinational} = x_1 \ln\left(\frac{\phi_1}{x_1}\right) + x_2 \ln\left(\frac{\phi_2}{x_2}\right) + \frac{Z}{2}\left(q_1 x_1 \ln\left(\frac{\theta_1}{\phi_1}\right) + q_2 x_2 \ln\left(\frac{\theta_2}{\phi_2}\right)\right) \tag{3.367}$$

$$G^E_{resdiual} = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \tag{3.368}$$

$$\begin{aligned} \tau_{21} &= \exp\left(-\frac{u_{21} - u_{11}}{RT}\right) \\ \tau_{12} &= \exp\left(-\frac{u_{12} - u_{22}}{RT}\right) \end{aligned} \tag{3.369}$$

where:

$$\begin{aligned} \theta_1 &= \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \qquad \theta_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} \\ \phi_1 &= \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} \qquad \phi_2 = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} \end{aligned} \tag{3.370}$$

q = parameter proportional to the area

r = parameter proportional to the volume of the individual molecules.

And finally, the expressions for the activity coefficients are:

$$\ln\gamma_1 = \ln\left(\frac{\phi_1}{x_1}\right) + \frac{Z}{2}q_1\ln\left(\frac{\theta_1}{\phi_1}\right) + \phi_2\left(l_1 - \frac{r_1}{r_2}l_2\right) - q_1\ln(\theta_1 + \theta_2\tau_{21}) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{21}}\right) \tag{3.371}$$

$$l_1 = \frac{Z}{2}(r_1 - q_1) - (r_1 - 1)$$

and $\ln\gamma_2$ can be found by interchanging the subscripts.

As with the Wilson and NRTL equations, the UNIQUAC equation is readily expanded for a multi-component system without the need for ternary or higher data. Like NRTL, it is capable of predicting two liquid phases, but unlike NRTL, it needs only two parameters per binary pair.

One interesting theoretical result from the UNIQUAC equation is that it is an equation for which the entropy contributions to the Gibbs free energy are separated from the temperature (energy) contributions. The idea of looking at the entropy portion based on segments of molecules suggests that one can divide a molecule into atomic groups and compute the activity coefficient as a function of the group. This idea was explored in full by [24]Fredenslund et al (1975, [25]1977) and is implemented in the UNIFAC method.

The UNIQUAC equation has been successfully used to predict VLE and LLE behaviour of highly non-ideal systems.

Application of UNIQUAC

The UNIQUAC (UNIversal QUASI-Chemical) equation uses statistical mechanics and the quasi-chemical theory of Guggenhiem to represent the liquid structure. The equation is capable of representing LLE, VLE and VLLE with accuracy comparable to the NRTL equation, but without the need for a non-randomness factor. The UNIQUAC equation is significantly more detailed and sophisticated than any of the other activity models. Its main advantage is that a good representation of both VLE and LLE can be obtained for a large range of non-electrolyte mixtures using only two adjustable parameters per binary. The fitted parameters usually exhibit a smaller temperature dependence which makes them more valid for extrapolation purposes.

The UNIQUAC equation uses the concept of local composition as proposed by Wilson. Since the primary concentration variable is a surface fraction as opposed to a mole fraction, it is applicable to systems containing molecules of very different sizes and shapes, such as polymers. The UNIQUAC equation can be applied to a wide range of mixtures containing water, alcohols, nitriles, amines, esters, ketones, aldehydes, halogenated hydrocarbons and hydrocarbons.

This software uses the following four-parameter extended form of the UNIQUAC equation. The four adjustable parameters for the UNIQUAC equation are the a_{ij} and a_{ji} terms (temperature independent), and the b_{ij} and b_{ji} terms (temperature dependent).

The equation uses stored parameter values or any user-supplied value for further fitting the equation to a given set of data.

Property Methods

A quick reference of calculation methods is shown in the table below for the UNIQUAC property model.

Calculation Method	Applicable Phase	Property Class Name
Activity Coefficient	Liquid	**COTHUNIQUACLnActivityCoeff Class**
Fugacity coefficient calculation	Liquid	**COTHUNIQUACLnFugacityCoeff Class**
Fugacity calculation	Liquid	**COTHUNIQUACLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHUNIQUACLnActivityCoeffDT Class**
Excess Gibbs	Liquid	**COTHUNIQUACExcessGibbsEnergy Class**
Excess enthalpy	Liquid	**COTHUNIQUACExcessEnthalpy Class**
Enthalpy	Liquid	**COTHUNIQUACEnthalpy Class**
Gibbs energy	Liquid	**COTHUNIQUACGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

UNIQUAC Ln Activity Coefficient

This method calculates the activity coefficient for components, *i*, using the UNIQUAC activity model from the following relation.

$$\ln\gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + 0.5Zq_i\ln\left(\frac{\theta_i}{\Phi_i}\right) + L_i - \left(\frac{\Phi_i}{x_i}\right)\sum_{j=1}^{n}L_jx_j + q_i\left(1.0 - \ln\sum_{j=1}^{n}\theta_j\tau_{ji}\right) - q_i\sum_{j=1}^{n}\left(\frac{\theta_j\tau_{ji}}{\sum_{k=1}^{n}\theta_k\tau_{kj}}\right) \tag{3.372}$$

where: γ_i = *Activity coefficient of component i*

x_i = *Mole fraction of component i*

T = *Temperature (K)*

n = *Total number of components*

$$L_j = 0.5Z(r_j - q_j) - r_j + 1 \tag{3.373}$$

$$\theta_i = \frac{q_ix_i}{\sum q_jx_j} \tag{3.374}$$

$$\tau_{ij} = \exp-\left[\frac{a_{ij} + b_{ij}T}{RT}\right] \tag{3.375}$$

Z = 10.0 *(coordination number)*

a_{ij} = *Non-temperature-dependent energy parameter between components i and j (cal/gmol)*

b_{ij} = *Temperature-dependent energy parameter between components i and j (cal/gmol-K)*

q_i = *van der Waals area parameter -* $Aw_i/(2.5\text{x}10^9)$

A_w = *van der Waals area*

r_i = *van der Waals volume parameter -* $Vw_i/(15.17)$

V_w = *van der Waals volume*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIQUACLnActivityCoeff Class	Liquid

UNIQUAC Fugacity Coefficient

This method calculates the fugacity coefficient of components using the UNIQUAC activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\gamma_i \frac{f_i^{std}}{P}\right) \tag{3.376}$$

where: γ_i = *activity coefficient of component i*

f_i = *Standard state fugacity*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIQUACLnFugacityCoeff Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the UNIQUAC Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

UNIQUAC Fugacity

This method calculates the fugacity of components using the UNIQUAC activity model. The fugacity of component *i*, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \tag{3.377}$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *Standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIQUACLnFugacity Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the UNIQUAC Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

UNIQUAC Activity Coefficient Differential wrt Temperature

This method analytically calculates the differential activity coefficient wrt to temperature from the following relation.

$$\frac{d\ln\gamma_i}{dT} \tag{3.378}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIQUACLnActivityCoeffDT Class	Liquid

UNIQUAC Excess Gibbs Energy

This method calculates the excess Gibbs energy using the UNIQUAC activity model from the following relation.

$$G^E = RT\sum_{i}^{n} x_i \ln\gamma_i \tag{3.379}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIQUACExcessGibbsEnergy Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the UNIQUAC Ln Activity Coefficient.

UNIQUAC Gibbs Energy

This method calculates the Gibbs free energy using the UNIQUAC activity model from the following relation.

$$\mathrm{G} = \sum_{i}^{n} x_i G_i + RT \sum_{i}^{n} x_i \ln x_i + G^E \tag{3.380}$$

where: G^E = *excess Gibbs energy*

x_i = *mole fraction of component i*

G_i = *Gibbs energy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIQUACGibbsEnergy Class	Liquid

The term, G^E, in the above equation is exclusively calculated using the UNIQUAC Excess Gibbs Energy.

UNIQUAC Excess Enthalpy

This method calculates the excess enthalpy using the UNIQUAC activity model from the following relation.

$$\mathrm{H}^E = -RT^2 \sum_{i}^{n} x_i \frac{d \ln \gamma_i}{dT} \tag{3.381}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIQUACExcessEnthalpy Class	Liquid

The term, $\frac{d\ln\gamma_i}{dT}$, in the above equation is exclusively calculated using the UNIQUAC Activity Coefficient Differential wrt Temperature.

UNIQUAC Enthalpy

This method calculates the enthalpy using the UNIQUAC activity model from the following relation.

$$H = \sum_{i}^{n} x_i H_i + H^E \tag{3.382}$$

where: H^E = excess enthalpy

x_i = mole fraction of component i

H_i = enthalpy of component i

Property Class Name and Applicable Phases

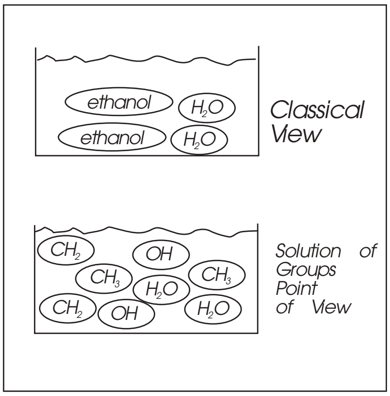
Property Class Name	Applicable Phase
COTHUNIQUACEnthalpy Class	Liquid

The term, H^E, in the above equation is exclusively calculated using the UNIQUAC Excess Enthalpy.

3.2.11 UNIFAC Model

For more complex mixtures, [26]Wilson and Deal (1962), and [27]Derr and Deal (1969), proposed a group contribution method in which the mixture was treated as a solution of atomic groups instead of a solution of molecules. The concept of atomic group activity, although not new in chemical engineering ([28]Le Bas, 1915), was shown to be applicable to the prediction of mixture behaviour, thus increasing its utility many times. The Wilson, Deal and Derr approach was based on the athermal Flory-Huggins equation and it found acceptance, especially in Japan where it modified to a computer method called ASOG (Analytical Solution of Groups) by [29]Kojima and Toguichi (1979).

Figure 3.4



In 1975, [24]Fredenslund et al presented the UNIFAC (1975) method (UNIQUAC Functional Group Activity Coefficients), in which he used the UNIQUAC equation as the basis for the atomic group method. In 1977, the UNIFAC group was published in a book (1977), which included a thorough description of the method by which the atomic group contributions were calculated, plus the computer code which performed the activity coefficient calculations (including fugacity coefficients using the virial equation, vapour phase association and a distillation column program). The method found wide acceptance in the engineering community and revisions are continuously being published to update and extend the original group interaction parameter matrix for VLE calculations.

Also, there are specially-developed UNIFAC interaction parameter matrices for LLE calculations ([31]Magnussen et al, 1981), vapour pressure estimation ([32]Jensen et al, 1981), gas solubility estimation ([33]Dahl et al, 1991) and polymer properties ([34]Elbro, 1991).

The UNIFAC method has several interesting features:

- Coefficients are based on a data reduction using the Dortmund Data Bank (DDB) as a source for VLE data points.
- Parameters are approximately independent of temperature.
- Area and volume group parameters are readily available.
- Group interaction parameters are available for many group combinations.
- The group interaction parameter matrix is being continuously updated.
- Gives reasonable predictions between 0 and 150°C, and pressures up to a few atmospheres.
- Extensive comparisons against experimental data are available, often permitting a rough estimate of errors in the predictions.

The original UNIFAC method also has several shortcomings that stem from the assumptions used to make it a useful engineering tool. Perhaps the most important one is that the group activity concept is not correct, since the group area and volume should be a function of the position in the molecule, as well as the other groups present in the molecule. Also, [35]Sandler suggested that the original choice of groups might not be optimal (1991a, [36]1991b) and sometimes wrong results are predicted.

Also, the original UNIFAC VLE produces wrong LLE predictions (which is not surprising). This was remedied by [31]Magnussen (1981) with the publication of interaction parameter tables for LLE calculations. This area has received considerably less attention than the VLE, and hopefully new revisions for the LLE interaction parameter matrix will appear.

One more interesting point is that the a_{mk} interaction parameter term is not, in reality, temperature independent. Thus, serious errors can be expected when predicting excess enthalpies. There is work being done to extend the applicability and reliability of the UNIFAC method, especially in Denmark (1984) and Germany (1987).

The main idea is to modify the a_{mk} term to include a temperature dependency, in a form such as:

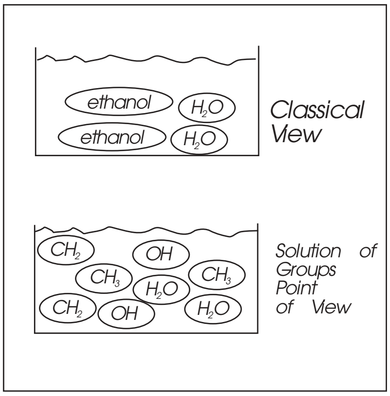
$$a_{mk} = a_{mk}^{(0)} + \frac{a_{mk}^{(1)}}{T} + a_{mk}^{(2)} \ln T \qquad (3.383)$$

These refinements will probably continue for several years and UNIFAC will be continuously updated.

For more complex mixtures, [26]Wilson and Deal (1962), and [27]Derr and Deal (1969), proposed a group contribution method in which the mixture was treated as a solution of atomic groups instead of a solution of molecules. The concept of atomic group activity, although not new in chemical engineering ([28]Le Bas, 1915), was shown to be applicable to the prediction of mixture behaviour, thus increasing its utility many times.

The Wilson, Deal and Derr approach was based on the athermal Flory-Huggins equation and it found acceptance, especially in Japan where it modified to a computer method called ASOG (Analytical Solution of Groups) by [29]Kojima and Toguichi (1979).

Figure 3.5



Property Methods

A quick reference of calculation methods is shown in the table below for the UNIFAC property model.

Calculation Method	Applicable Phase	Property Class Name
Activity Coefficient (VLE)	Liquid	**COTHUNIFAC1_VLELnActivityCoeff Class**
Fugacity coefficient calculation (VLE)	Liquid	**COTHUNIFAC1_VLELnFugacityCoeff Class**
Fugacity calculation (VLE)	Liquid	**COTHUNIFAC1_VLELnFugacity Class**
Activity coefficient differential wrt temperature (VLE)	Liquid	**COTHUNIFAC1_VLELnActivityCoeffDT Class**
Enthalpy (VLE)	Liquid	**COTHUNIFAC1_VLEEnthalpy Class**
Gibbs energy (VLE)	Liquid	**COTHUNIFAC1_VLEGibbsEnergy Class**
Activity Coefficient (LLE)	Liquid	**COTHUNIFAC1_LLELnActivityCoeff Class**
Fugacity coefficient calculation (LLE)	Liquid	**COTHUNIFAC1_LLELnFugacityCoeff Class**
Fugacity calculation (LLE)	Liquid	**COTHUNIFAC1_LLELnFugacity Class**
Activity coefficient differential wrt temperature (LLE)	Liquid	**COTHUNIFAC1_LLELnActivityCoeffDT Class**
Enthalpy (LLE)	Liquid	**COTHUNIFAC1_LLEEnthalpy Class**
Gibbs energy (LLE)	Liquid	**COTHUNIFAC1_LLEGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

UNIFAC Ln Activity Coefficient

This method calculates the activity coefficient for components, *i*, using the UNIFAC activity model from the following relation.

This relation is from the UNIQUAC method

$$\ln\gamma_i = \ln\gamma_i^c + \ln\gamma_i^e \qquad (3.384)$$

In γ_i^c is calculated in the same way as for the UNIQUAC equation, but the residual part is calculated as follows:

$$\ln\gamma_i^e = \sum_k v_k^{(i)} \ln(\Gamma_k - \ln\Gamma_k^{(i)}) \qquad (3.385)$$

Notice that normalization is required to avoid the spurious prediction of an activity coefficient different than one for a pure component liquid.

where: *k = functional group in the mixture*

ν_k^i *= number of atomic groups of type k in molecule i*

Γ_k *= residual activity coefficient of the functional group k in the actual mixture*

$\Gamma_k^{(i)}$ *= residual activity coefficient of the functional group k in a mixture that contains only molecules i (this is necessary to ensure the prediction of* $\gamma_i = 1$ *for a pure liquid)*

The summation is extended over all the groups present in the mixture. Γ_k is calculated in a similar manner as γ_i^R in the UNIQUAC equation:

$$\ln\Gamma_k = Q_k\left[1 - \ln\left(\sum_m \theta_m \tau_{mk}\right) - \sum_m\left(\frac{\theta_m \tau_{mk}}{\sum_n \theta_n \tau_{nm}}\right)\right] \qquad (3.386)$$

where: θ_m *= area function of group m defined as:*

$$\theta_m = \frac{x_m Q_k}{\sum_n \theta_n \tau_{nm}} \tag{3.387}$$

where: x_m *= mole fraction of component m in the mixture:*

$$x_m = \frac{\sum_j x_m Q_m}{\sum_n \theta_n \tau_{nm}} \tag{3.388}$$

where: τ_{mk} *= group interaction parameter similar to the one defined in UNIQUAC:*

$$\tau_{mk} = \frac{v_m^{(j)} x_j}{\sum_j \sum_n v_m^{(j)} x_j} \tag{3.389}$$

In which $a_{mk} = 0$ when $m = k$. Also, the area and volume for the molecules are computed by:

$$r_i = \sum_k v_k^{(i)} R_k \qquad q_i = \sum_k v_k^{(i)} Q_k \tag{3.390}$$

where: R_k *= van der Waals volume of group k*

Q_k *= van der Waals area of group k*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIFAC1_VLELnActivityCoeff Class	Liquid
COTHUNIFAC1_LLELnActivityCoeff Class	Liquid

The UNIFAC VLE model uses the interaction parameters which have been calculated from the experimental VLE data, whereas, the UNIFAC LLE uses the interaction parameters calculated from LLE experimental data.

UNIFAC Fugacity Coefficient

This method calculates the fugacity coefficient of components using the UNIFAC activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\gamma_i \frac{f_i^{std}}{P}\right) \tag{3.391}$$

where: γ_i = *activity coefficient of component i*

P = *Pressure*

f_i = *Standard state fugacity*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIFAC1_VLELnFugacityCoeff Class	Liquid
COTHUNIFAC1_LLELnFugacityCoeff Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the UNIFAC Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

The UNIFAC VLE model uses the interaction parameters which have been calculated from the experimental VLE data, whereas, the UNIFAC LLE uses the interaction parameters calculated from LLE experimental data.

UNIFAC Fugacity

This method calculates the fugacity of components using the UNIFAC activity model. The fugacity of component *i*, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \qquad (3.392)$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *Standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIFAC1_VLELnFugacity Class	Liquid
COTHUNIFAC1_LLELnFugacity Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the UNIFAC Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

The UNIFAC VLE model uses the interaction parameters which have been calculated from the experimental VLE data, whereas, the UNIFAC LLE uses the interaction parameters calculated from LLE experimental data.

UNIFAC Activity Coefficient Differential wrt Temperature

This method calculates the activity coefficient wrt to temperature from the following relation.

$$\frac{d\ln\gamma_i}{dT} \tag{3.393}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIFAC1_VLELnActivityCoeffDT Class	Liquid
COTHUNIFA1_LLECLnActivityCoeffDT Class	Liquid

The UNIFAC VLE model uses the interaction parameters which have been calculated from the experimental VLE data, whereas, the UNIFAC LLE uses the interaction parameters calculated from LLE experimental data.

UNIFAC Gibbs Energy

This method calculates the Gibbs free energy using the UNIFAC activity model from the following relation.

$$G = \sum_{i}^{n} x_i G_i + RT \sum_{i}^{n} x_i \ln x_i + G^E \tag{3.394}$$

where: G^E = excess Gibbs energy

x_i = mole fraction of component i

G_i = Gibbs energy of component i

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIFAC1_VLEGibbsEnergy Class	Liquid
COTHUNIFAC1_LLEGibbsEnergy Class	Liquid

The term, G^E, in the above equation is exclusively calculated by the UNIQUAC Excess Gibbs Energy.

The UNIFAC VLE model uses the interaction parameters which have been calculated from the experimental VLE data, whereas, the UNIFAC LLE uses the interaction parameters calculated from LLE experimental data.

UNIFAC Enthalpy

This method calculates the enthalpy using the UNIFAC activity model from the following relation.

$$H = \sum_{i}^{n} x_i H_i + H^E \tag{3.395}$$

where: H^E = *excess enthalpy*

x_i = *mole fraction of component i*

H_i = *enthalpy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHUNIFAC1_VLEEnthalpy Class	Liquid
COTHUNIFAC1_LLEEnthalpy Class	Liquid

The term, H^E, in the above equation is exclusively calculated by the UNIQUAC Excess Enthalpy.

The UNIFAC VLE model uses the interaction parameters which have been calculated from the experimental VLE data, whereas, the UNIFAC LLE uses the interaction parameters calculated from LLE experimental data.

3.2.12 Chien-Null Model

The Chien-Null (CN) model provides a consistent framework for applying existing activity models on a binary by binary basis. In this manner, the Chien-Null model allows you to select the best activity model for each pair in the case.

The Chien-Null model allows three sets of coefficients for each component pair, accessible via the **A**, **B** and **C** coefficient matrices. Refer to the following sections for an explanation of the terms for each of the models.

Chien-Null Form

The Chien-Null generalized multi-component equation can be expressed as:

$$2\ln\Gamma_i^L = \frac{\left(\sum_j A_{j,i}x_j\right)\left(\sum_j R_{j,i}x_j\right)}{\left(\sum_j S_{j,i}x_j\right)\left(\sum_j V_{j,i}x_j\right)} + \sum_k x_k \frac{\left(\sum_j A_{j,k}x_j\right)\left(\sum_j R_{j,k}x_j\right)}{\left(\sum_j S_{j,k}x_j\right)\left(\sum_j V_{j,i}x_j\right)} \cdot \left[\frac{A_{i,k}}{\sum_j A_{j,k}x_j} + \frac{R_{i,k}}{\sum_j R_{j,k}x_j} - \frac{S_{i,k}}{\sum_j S_{j,k}x_j} - \frac{V_{i,k}}{\sum_j V_{j,k}x_j}\right] \tag{3.396}$$

Each of the parameters in this equation are defined specifically for each of the applicable activity methods.

Description of Terms

The **Regular Solution** equation uses the following:

$$A_{i,j} = \frac{v_i^L(\delta_i - \delta_j)^2}{RT} \qquad R_{i,j} = \frac{A_{i,j}}{A_{j,i}} \qquad V_{i,j} = |R_{i,j}| \qquad S_{i,j} = |R_{i,j} \tag{3.397}$$

δ_i is the solubility parameter in $(\text{cal/cm}^3)^{1/2}$ and v_i^L is the saturated liquid volume in cm^3/mol calculated from:

$$v_i^L = v_{\omega,i}(5.7 + 3T_{r,i}) \tag{3.398}$$

The **van Laar**, **Margules** and **Scatchard Hamer** use the following:

Model	**$A_{i,j}$**	**$R_{i,j}$**	**$S_{i,j}$**	**$V_{i,j}$**
van Laar	$\ln\gamma_{i,j}^{\infty}$	$\frac{A_{i,j}}{A_{j,i}}$	$\|R_{i,j}\|$	$\|R_{i,j}\|$
Margules	$\frac{2\ln\gamma_{i,j}^{\infty}}{1+\left(\frac{\ln\gamma_{i,j}^{\infty}}{\ln\gamma_{j,i}^{\infty}}\right)}$	$\frac{A_{i,j}}{A_{j,i}}$	1	1
Scatchard Hamer	$\frac{2\ln\gamma_{i,j}^{\infty}}{1+\left(\frac{\ln\gamma_{i,j}^{\infty}}{\ln\gamma_{j,i}^{\infty}}\right)}$	$\frac{A_{i,j}}{A_{j,i}}$	$\frac{v_i^{\infty}}{v_j^{\infty}}$	$\frac{v_i^{\infty}}{v_j^{\infty}}$

For the van Laar, Margules and Scatchard Hamer equations:

$$\ln\gamma_{i,j}^{\infty} = a_{i,j} + \frac{b_{i,j}}{T} + c_{ij}T \tag{3.399}$$

where: *T must be in K*

This equation is of a different form than the original van Laar and Margules equations in HYSY S, which used an ***a* + *bT*** relationship. However, since HYSYS only contains $\boldsymbol{a_{ij}}$ values, the difference should not cause problems.

The NRTL form for the Chien-Null uses:

$$A_{i,\,j} = 2\tau_{i,\,j}V_{i,\,j} \qquad R_{i,\,j} = 1 \qquad V_{i,\,j} = \exp(-c_{i,\,j}\tau_{i,\,j}) \qquad S_{i,\,j} = 1 \qquad \tau_{i,\,j} = a_{i,\,j} + \frac{b_{i,}}{T(} \tag{3.400}$$

The expression for the τ term under the Chien-Null incorporates the R term of NRTL into the values for a_{ij} and b_{ij}. As such, the values initialized for NRTL under Chien-Null will not be the same as for the regular NRTL. When you select NRTL for a binary pair, a_{ij} will be empty (essentially equivalent to the regular NRTL b_{ij} term), b_{ij} will be initialized and c_{ij} will be the α term for the original NRTL, and will be assumed to be symmetric.

The General Chien-Null equation is:

$$A_{i,\,j} = a_{i,\,j} + \frac{b_{i,\,j}}{T(K)} \qquad R_{i,\,j} = \frac{A_{i,\,j}}{A_{j,\,i}} \qquad V_{i,\,j} = C_{i,\,j} \qquad S_{i,\,j} = C_{i,\,j} \tag{3.401}$$

In all cases:

$$A_{i,\,i} = 0 \qquad R_{i,\,i} = S_{i,\,i} = V_{i,\,i} = 1 \tag{3.402}$$

With the exception of the Regular Solution option, all models can use six constants, $a_{i,j}$, $a_{j,i}$, $b_{i,j}$, $b_{j,i}$, $c_{i,j}$ and $c_{j,i}$ for each component pair. For all models, if the constants are unknown they can be estimated from the UNIFAC VLE or LLE methods, the Insoluble option, or using Henry's Law coefficients for appropriate components. For the general Chien-Null model, the c_{ij} values are assumed to be 1.

Property Methods

A quick reference of calculation methods is shown in the table below for the Chien-Null (CN) property model.

Calculation Method	Applicable Phase	Property Class Name
Activity Coefficient	Liquid	**COTHCNLnActivityCoeff Class**
Fugacity coefficient calculation	Liquid	**COTHCNLnFugacityCoeff Class**
Fugacity calculation	Liquid	**COTHCNLnFugacity Class**
Activity coefficient differential wrt temperature	Liquid	**COTHCNLnActivityCoeffDT Class**
NRTL temperature dependent properties	Liquid	**COTHNRTLTempDep Class**
Excess Gibbs	Liquid	**COTHCNExcessGibbsEnergy Class**
Excess enthalpy	Liquid	**COTHCNExcessEnthalpy Class**
Enthalpy	Liquid	**COTHCNEnthalpy Class**
Gibbs energy	Liquid	**COTHCNGibbsEnergy Class**

The calculation methods from the table are described in the following sections.

Chien-Null Ln Activity Coefficient

Refer to Equation (3.379) to Equation (3.385) for methods on calculating the activity coefficient for components, *i*, using the CN activity model.

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNLnActivityCoeff Class	Liquid

Chien-Null Fugacity Coefficient

This method calculates the fugacity coefficient of components using the CN activity model. The fugacity coefficient of component *i*, ϕ_i, is calculated from the following relation.

$$\ln\phi_i = \ln\left(\gamma_i \frac{f_i^{std}}{P}\right) \tag{3.403}$$

where: γ_i = *activity coefficient of component i*

f_i = *Standard state fugacity*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNLnFugacityCoeff Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the Chien-Null Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Chien-Null Fugacity

This method calculates the fugacity of components using the UNIFAC activity model. The fugacity of component *i*, f_i, is calculated from the following relation.

$$\ln f_i = \ln(\gamma_i x_i f_i^{std}) \tag{3.404}$$

where: γ_i = *activity coefficient of component i*

f_i^{std} = *Standard state fugacity*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNLnFugacity Class	Liquid

The term, lnγ_i, in the above equation is exclusively calculated using the Chien-Null Ln Activity Coefficient. For the standard fugacity, f_i^{std}, refer to Section 5.4 - Standard State Fugacity.

Chien-Null Activity Coefficient Differential wrt Temperature

This method analytically calculates the activity coefficient differential wrt to temperature from the following relation.

$$\frac{\partial \ln \gamma_i}{\partial T} \tag{3.405}$$

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNLnActivityCoeffDT Class	Liquid

Chien-Null Excess Gibbs Energy

This method calculates the excess Gibbs energy using the CN activity model from the following relation.

$$G^E = RT\sum_i^n x_i \ln\gamma_i \tag{3.406}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNExcessGibbsEnergy Class	Liquid

The term, ln γ_i, in the above equation is exclusively calculated using the Chien-Null Ln Activity Coefficient.

Chien-Null Gibbs Energy

This method calculates the Gibbs free energy using the CN activity model from the following relation.

$$G = \sum_i^n x_i G_i + RT\sum_i^n x_i \ln x_i + G^E \tag{3.407}$$

where: G^E = *excess Gibbs energy*

x_i = *mole fraction of component i*

G_i = *Gibbs energy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNGibbsEnergy Class	Liquid

The term, G^E, in the above equation is exclusively calculated using the Chien-Null Excess Gibbs Energy.

Chien-Null Excess Enthalpy

This method calculates the excess enthalpy using the CN activity model from the following relation.

$$\mathrm{H}^E = -RT^2 \sum_i^n x_i \frac{d\ln\gamma_i}{dT} \tag{3.408}$$

where: γ_i = *activity coefficient of component i*

x_i = *mole fraction of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNExcessEnthalpy Class	Liquid

The term, $\frac{d\ln\gamma_i}{dT}$, in the above equation is exclusively calculated using the Chien-Null Activity Coefficient Differential wrt Temperature.

Chien-Null Enthalpy

This method calculates the enthalpy using the CN activity model from the following relation.

$$H = \sum_{i}^{n} x_i H_i + H^E \tag{3.409}$$

where: H^E = *excess enthalpy*

x_i = *mole fraction of component i*

H_i = *enthalpy of component i*

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHCNEnthalpy Class	Liquid

The term, H^E, in the above equation is exclusively calculated using the Chien-Null Excess Enthalpy.

3.3 Chao-Seader Model

The [47]Chao-Seader (CS, 1961) method is an older and semi-empirical method. This method has also been adopted by and is recommended for use in the API Technical Data Book.

Model	Description
Chao-Seader	Use this method for heavy hydrocarbons, where the pressure is less than 10342 kPa (1500 psia), and temperatures range between -17.78 and 260°C (0-500°F).

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHChaoSeaderLnFugacityCoeff Class	Liquid
COTHChaoSeaderLnFugacity Class	Liquid

The following table gives an approximate range of applicability for this method, and under what conditions it is applicable.

Method	Temp. (°C)	Temp. (°C)	Press. (psia)	Press. (kPa)
CS	0 to 500	18 to 260	< 1,500	< 10,000

Conditions of Applicability	
For all hydrocarbons (except CH4):	$0.5 < Tr_i < 1.3$ and $Pr_{mixture} < 0.8$
If CH4 or H2 is present:	• molal average Tr < 0.93 • CH4 mole fraction < 0.3 • mole fraction dissolved gases < 0.2
When predicting K values for:	
Paraffinic or Olefinic Mixtures	liquid phase aromatic mole fraction < 0.5
Aromatic Mixtures	liquid phase aromatic mole fraction > 0.5

3.4 Grayson-Streed Model

The Grayson-Streed (GS) method is an older, semi-empirical method. The GS correlation is an extension of the Chao-Seader method with special emphasis on hydrogen. This method has also been adopted by and is recommended for use in the API Technical Data Book.

Grayson-Streed Model	Description
Grayson-Streed	Recommended for simulating heavy hydrocarbon systems with a high hydrogen content.

Property Class Name and Applicable Phases

Property Class Name	Applicable Phase
COTHGraysonStreedLnFugacityCoeff Class	Liquid
COTHGraysonStreedLnFugacity Class	Liquid

The following table gives an approximate range of applicability for this method, and under what conditions it is applicable.

Method	Temp. (°C)	Temp. (°C)	Press. (psia)	Press. (kPa)
GS	0 to 800	18 to 425	< 3,000	< 20,000

Conditions of Applicability	
For all hydrocarbons (except CH4):	$0.5 < Tr_i < 1.3$ and $Pr_{mixture} < 0.8$
If CH4 or H2 is present:	• molal average Tr < 0.93 • CH4 mole fraction < 0.3 • mole fraction dissolved gases < 0.2
When predicting K values for:	
Paraffinic or Olefinic Mixtures	liquid phase aromatic mole fraction < 0.5
Aromatic Mixtures	liquid phase aromatic mole fraction > 0.5

The GS correlation is recommended for simulating heavy hydrocarbon systems with a high H_2 content, such as hydrotreating units. The **GS** correlation can also be used for simulating topping units and heavy ends vacuum applications. The vapour phase fugacity coefficients are calculated with the Redlich Kwong equation of state. The pure liquid fugacity coefficients are calculated via the principle of corresponding states. Modified acentric factors are included in the library for most components. Special functions have been incorporated for the calculation of liquid phase fugacities for N_2, CO_2 and H_2S. These functions are restricted to hydrocarbon mixtures with less than five percent of each of the above components. As with the Vapour Pressure models, H_2O is treated using a combination of the steam tables and the kerosene solubility charts from the API data book. This method of handling H_2O is not very accurate for gas systems. Although three phase calculations are performed for all systems, it is important to note that the aqueous phase is always treated as pure H_2O with these correlations.

4 Physical Property Calculation Methods

4.1 Cavett Method

COMThermo uses the three-parameter corresponding states method to represent the enthalpy of a liquid when working with the activity models. Water is the only exception which uses the 1967 formulation for steam ([37]McClintock and Silvestri, 1967). For the Cavett method, a generalized slope for the liquid enthalpy is correlated using P_c, T_c and the Cavett parameter (an empirical constant fitted to match the heat of vapourization at the normal boiling point). The Cavett parameter may be approximated by the critical compressibility factor of a component if no heat of vapourization data is available.

Property Methods

A quick reference of calculation methods is shown in the table below for the Cavett method.

Calculation Method	Phase Applicable	Property Class Name
Enthalpy	Liquid	**COTHCavettEnthalpy Class**
Entropy	Liquid	**COTHCavettEntropy Class**
Isobaric heat capacity	Liquid	**COTHNCavettCp Class**
Helmholtz energy	Liquid	**COTHCavettHelmholtz Class**
Gibbs energy	Liquid	**COTHCavettGibbs Class**
Internal energy	Liquid	**COTHCavettInternalEnergy Class**

The calculation methods from the table are described in the following sections.

Cavett Enthalpy

This method calculates the liquid enthalpy using the Cavett model from the following relation.

$$H^l = x_{water} H_{water}^{steam67} + \sum_i x_i (H_i^\circ + \Delta H_i^{Cavett}) \tag{4.1}$$

where: the calculation of the change in Cavett enthalpy is shown below

$$\Delta H_{non-aqueous}^{cavett} = \sum_{i=1; i \neq 1}^{nc} min(\Delta H_i^{cavett}) x_i \tag{4.2}$$

$$\Delta H_i^1 = T_{c,\ i}(a1 + a2(1 - T_{r,\ i})^{e1}) \tag{4.3}$$

$$a1 = b1 + b2\chi_i + b3\chi_i^2 + b4\chi_i^3 \tag{4.4}$$

$$a2 = b5 + b6\chi_i + b7\chi_i^2 + b8\chi_i^3 \tag{4.5}$$

$$a9 = b9 + b10\chi_i + b11\chi_i^2 + b12\chi_i^3 \tag{4.6}$$

$$e1 = 1 - a3(T_{r,\ i} - 0.1) \tag{4.7}$$

$$\Delta H_i^2 = T_{c,\ i}(max(c1 + c2T_{r,\ i}^2 + c3T_{r,\ i}^3 + c4T_{r,\ i}^4 + c5T_{r,\ i}^2,\ 0)) \tag{4.8}$$

where: *i = non-aqueous components*

x_i *= mole fraction of component i*

For subcritical, non-hydrocarbon components, the change in enthalpy is:

$$\Delta H_i^{cavett} = \Delta H_i^1 \tag{4.9}$$

For subcritical, hydrocarbon components, the change in enthalpy is:

$$\Delta H_i^{cavett} = min(\Delta H_i^1,\ \Delta H_i^2) \tag{4.10}$$

For supercritical components, the change in enthalpy is:

$$\Delta H_i^{cavett} = \Delta H_i^2 \tag{4.11}$$

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCavettEnthalpy Class	Liquid

Cavett Entropy

This method calculates the liquid entropy using the Cavett model from the following relation:

$$S^l = x_{water}S_{water}^{steam67} + \sum_i x_i(S_i^\circ + \Delta S_i^{Cavett}) \tag{4.12}$$

For subcritical, non-hydrocarbon components, the change in entropy is:

$$\Delta S_i^{cavett} = \frac{\Delta H_i^1}{T} \tag{4.13}$$

For subcritical, hydrocarbon components, the change in entropy is:

$$\Delta S_i^{cavett} = \frac{min(\Delta H_i^1,\ \Delta H_i^2)}{T} \tag{4.14}$$

For supercritical components, the change in entropy is:

$$\Delta S_i^{cavett} = \frac{\Delta H_i^2}{T} \tag{4.15}$$

where: *i = non-aqueous components*

x_i = mole fraction of component i

T = Temperature (K)

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCavettEntropy Class	Liquid

Cavett Cp (Isobaric)

This method calculates the liquid isobaric heat capacity using the Cavett model from the following relation.

$$Cp^l = x_{water} Cp_{water}^{steam67} + \sum_i x_i (Cp_i^\circ + \Delta Cp_i^{Cavett}) \tag{4.16}$$

where: *i = non-aqueous components*

For subcritical hydrocarbons with $\Delta H_i^1 > \Delta H_i^2$, the change in heat capacity is:

$$\Delta Cp_i^{cavett} = T_{r,\,i}(2(c2 + c5P_{r,\,i}) + T_{r,\,i}(3c3 + T_{r,\,i}(4c4))) \tag{4.17}$$

For other subcritical components, the change in heat capacity is:

$$\Delta Cp_i^{cavett} = \left(a_1 - \frac{\Delta H_i^1}{T_{c,\,i}}\right)\left(a_3 \log\left((1 - T_{r,\,i}) + \frac{e_1}{1 - T_{r,\,i}}\right)\right) \tag{4.18}$$

For supercritical components with ΔH_i^2 equal to zero, the change in heat capacity is:

$$\Delta Cp_i^{cavett} = 0 \tag{4.19}$$

For supercritical components with ΔH_i^2 different than zero, the change in heat capacity is:

$$\Delta Cp_i^{cavett} = T_{r,\,i}(2(c_2 + c_5 P_{r,\,i}) + T_{r,\,i}(3c_3 + T_{r,\,i}(4c_4))) \tag{4.20}$$

where:

b1 = -67.022001
b2 = 644.81654
b3 = -1613.1584
b4 = 844.13728
b5 = -270.43935
b6 = 4944.9795

b7 = -23612.5670
b8 = 34152.870
b9 = 8.9994977
b10 = -78.472151
b11 = 212.61128
b12 = -143.59393

c1 = 10.273695
c2 = -1.5594238
c3 = 0.019399
c4 = -0.03060833
c5 = -0.168872

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCavettCp Class	Liquid

The term, ΔH_i^1, in the above equation is exclusively calculated using the Cavett Enthalpy.

Cavett Helmholtz Energy

This method calculates the liquid Helmholtz energy using the Cavett model from the following relation.

$$A = G - PV \tag{4.21}$$

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCavettHelmholtz Class	Liquid

The term, *G*, in the above equation is exclusively calculated using the Cavett Gibbs Energy.

Cavett Gibbs Energy

This method calculates the liquid Gibbs free energy using the Cavett model from the following relation.

$$G = H - TS \tag{4.22}$$

where: H = *Cavett enthalpy*

S = *Cavett entropy*

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCavettGibbs Class	Liquid

The terms, *H* and *S*, in the above equation are exclusively calculated using the Cavett Enthalpy and Cavett Entropy, respectively.

Cavett Internal Energy

This method calculates the liquid internal energy using the Cavett model from the following relation.

$$U = H - PV \tag{4.23}$$

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCavettInternal Class	Liquid

The term, *H*, in the above equation is exclusively calculated using the Cavett Enthalpy.

4.2 Rackett Method

Property Packages with this option currently available:

NRTL-Ideal-Zra

Peng-Robinson-Rackett Liq Density

Liquid densities and molar volumes can be calculated by generalized cubic equations of state, although they are often inaccurate and often provide incorrect estimations. COMThermo allows for alternate methods of calculating the saturated liquid volumes including the Rackett Liquid Density correlations. This method was developed by Rackett (1970) and later modified by Spencer and Danner.

The Rackett Equation has been found to produce slightly more accurate estimations for chemical groups such as acetylenes, cycloparaffins, aromatics, flurocarbons, cryogenic liquids, and sulfides.

Property Methods

A quick reference of liquid density and volume calculations are shown in the table below for the Rackett method.

Calculation Method	Phase Applicable	Property Class Name
Liquid Volume	Liquid	**COTHRackettVolume Class**
Liquid Density	Liquid	**COTHRackettDensity Class**

The calculation methods from the table are described in the following sections.

Rackett Liquid Volume

This method calculates the liquid volume using the Rackett method from the following relation.

$$V_s = \frac{RT_c}{P_c} Z_{RA}^{1 + (1 - T_r)^{\frac{2}{7}}} \tag{4.24}$$

where: V_s = *saturated liquid volume*

R = *ideal gas constant*

T_c & P_c = *critical constants for each compound*

Z_{RA} = *Rackett compressibility factor*

T_r = *reduced temperature,* T/T_c

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHRackettVolume Class	Liquid

The Rackett Compressibility factor (Z_{RA}) is a unique constant for each compound and is usually determined from experimental data, however if no data is available, Z_c can be used as an estimate of Z_{RA}.

Rackett Liquid Density

This method calculates the liquid density using the Rackett method from the following relation.

$$\rho_s = \left(1 \Big/ \left(\frac{RT_c}{P_c}\right)\right) Z_{RA}^{1+(1-T_r)^{\frac{2}{7}}} \tag{4.25}$$

where: V_s = *saturated liquid volume*

R = *ideal gas constant*

T_c & P_c = *critical constants for each compound*

Z_{RA} = *Rackett compressibility factor*

T_r = *reduced temperature,* T/T_c

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHRackettDensity Class	Liquid

4.3 COSTALD Method

Saturated liquid volumes are obtained using a corresponding states equation developed by [38]R.W. Hankinson and G.H. Thompson which explicitly relates the liquid volume of a pure component to its reduced temperature and a second parameter termed the characteristic volume. This method has been adopted as an API standard.

The pure compound parameters needed in the corresponding states liquid density (COSTALD) calculations are taken from the original tables published by Hankinson and Thompson, and the API data book for components contained in the HYSYS library. The parameters for hypothetical components are based on the API gravity and the generalized Lu equation.

Although the COSTALD method was developed for saturated liquid densities, it can be applied to sub-cooled liquid densities (i.e., at pressures greater than the vapour pressure), using the Chueh and Prausnitz correction factor for compressed fluids. It is used to predict the density for all systems whose pseudo-reduced temperature is below 1.0. Above this temperature, the equation of state compressibility factor is used to calculate the liquid density.

[38]R.W. Hankinson and G.H. Thompson (1979) published a new method of correlating saturated densities of liquids and their mixtures. This method was superior to its predecessors in that it overcame the mathematical discontinuities presented in methods by Yen and Woods (1966) and was not limited to pure compounds. COSTALD was later successfully applied to compressed liquids and liquid mixtures.

Property Methods

A quick reference of liquid density and volume calculations are shown in the table below for the Rackett method.

Calculation Method	Phase Applicable	Property Class Name
Liquid Volume	Liquid	**COTHCOSTALDVolume Class**
Liquid Density	Liquid	**COTHCOSTALDDensity Class**

The calculation methods from the table are described in the following sections.

COSTALD Liquid Volume

This method calculates the liquid volume using the COSTALD method for pure compounds:

$$\begin{aligned} V_s/V^* &= V_r^{(o)}[1-\omega_{SRK}V_r^{(\delta)}] \\ V_r^{(o)} &= 1+\sum_{k=1}^{4}A_k(1-T_r)^{k/3} \qquad 0.25 < T_r < 0.95 \\ V_r^{(\delta)} &= \left[\sum_{k=0}^{3}B_kT_r^k\right]/(T_r-1.00001) \qquad 0.25 < T_r < 1.0 \end{aligned} \tag{4.26}$$

and for mixtures:

$$T_{cm} = \left(\sum_i \sum_j x_i x_j V_{ij}^* T_{c_{ij}}\right) / \ V_m^*$$

$$V_m^* = 1/\ 4\left[\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*\frac{2}{3}}\right)\left(\sum_i x_i V_i^{*\frac{1}{3}}\right)\right] \tag{4.27}$$

$$V_{ij}^* T_{c_{ij}} = (V_i^* T_{c_i} V_j^* T_{c_j})^{\frac{1}{2}}$$

$$\omega_{SRK_m} = \sum_i x_i \omega_{SRK_i}$$

where: A_k *and* B_k *are constants*

V^* = *the characteristic volume*

ω_{SRK} = *SRK acentric factor*

T_c = *critical temperature for each compound*

T_r = *reduced temperature,* T/T_c

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCOSTALDVolume Class	Liquid

COSTALD Liquid Density

This method calculates the liquid density using the COSTALD method from the following relation.

$$\rho = \frac{1}{V_s} \tag{4.28}$$

where: V_s = *saturated liquid volume*

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHCOSTALDDensity Class	Liquid

The saturated liquid volume, V_s, is calculated from Equations (4.26) and (4.27).

4.4 Viscosity

This method will automatically select the model best suited for predicting the phase viscosities of the system under study. The model selected will be from one of the three available in this method: a modification of the NBS method ([39]Ely and Hanley), Twu's model, or a modification of the Letsou-Stiel correlation. This method will select the appropriate model using the following criteria:

Chemical System	Vapour Phase	Liquid Phase
Lt Hydrocarbons (NBP < 155°F)	Mod Ely & Hanley	Mod Ely & Hanley
Hvy Hydrocarbons (NBP > 155°F)	Mod Ely & Hanley	Twu
Non-Ideal Chemicals	Mod Ely & Hanley	Mod Letsou-Stiel

All of the models are based on corresponding states principles and have been modified for more reliable application. Internal validation showed that these models yielded the most reliable results for the chemical systems shown. Viscosity predictions for light hydrocarbon liquid phases and vapour phases were found to be handled more reliably by an in-house modification of the original Ely and Hanley model, heavier hydrocarbon liquids were more effectively handled by Twu's model, and chemical systems were more accurately handled by an in-house modification of the original Letsou-Stiel model.

A complete description of the original corresponding states (NBS) model used for viscosity predictions is presented by Ely and Hanley in their NBS publication. The original model has been modified to eliminate the iterative procedure for calculating the system shape factors. The generalized Leech-Leland shape factor models have been replaced by component specific models. This method constructs a PVT map for each component using the COSTALD for the liquid region. The shape factors are adjusted such that the PVT map can be reproduced using the reference fluid.

The shape factors for all the library components have already been regressed and are included in the Pure Component Library. Hypocomponent shape factors are regressed using estimated viscosities. These viscosity estimations are functions of the hypocomponent Base Properties and Critical Properties.

Hypocomponents generated in the Oil Characterization Environment have the additional ability of having their shape factors regressed to match kinematic or dynamic viscosity assays.

The general model employs CH_4 as a reference fluid and is applicable to the entire range of non-polar fluid mixtures in the hydrocarbon industry. Accuracy for highly aromatic or naphthenic crudes will be increased by supplying viscosity curves when available, since the pure component property generators were developed for average crude oils. The model also handles H_2O and acid gases as well as quantum gases.

Although the modified NBS model handles these systems very well, the Twu method was found to do a better job of predicting the viscosities of heavier hydrocarbon liquids. The Twu model is also based on corresponding states principles, but has implemented a viscosity correlation for n-alkanes as its reference fluid instead of CH_4. A complete description of this model is given in the paper entitled "[42]Internally Consistent Correlation for Predicting Liquid Viscosities of Petroleum Fractions".

For chemical systems, the modified NBS model of Ely and Hanley is used for predicting vapour phase viscosities, whereas a modified form of the Letsou-Stiel model is used for predicting the liquid viscosities. This method is also based on corresponding states principles and was found to perform satisfactorily for the components tested.

The shape factors contained within this methods Pure Component Library have been fit to match experimental viscosity data over a broad operating range.

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHViscosity Class	Liquid and vapour

Liquid Phase Mixing Rules for Viscosity

The estimates of the apparent liquid phase viscosity of immiscible Hydrocarbon Liquid - Aqueous mixtures are calculated using the following "mixing rules":

- If the volume fraction of the hydrocarbon phase is greater than or equal to 0.5, the following equation is used[51]:

$$\mu_{eff} = \mu_{oil} e^{3.6(1 - \nu_{oil})} \tag{4.29}$$

where: μ_{eff} = *apparent viscosity*

μ_{oil} = *viscosity of Hydrocarbon phase*

ν_{oil} = *volume fraction Hydrocarbon phase*

- If the volume fraction of the hydrocarbon phase is less than 0.33, the following equation is used[52]:

$$\mu_{eff} = \left[1 + 2.5\nu_{oil}\left(\frac{\mu_{oil} + 0.4\mu_{H_2O}}{\mu_{oil} + \mu_{H_2O}}\right)\right]\mu_{H_2O} \tag{4.30}$$

where: μ_{eff} = *apparent viscosity*

μ_{oil} = *viscosity of Hydrocarbon phase*

μ_{H2O}= *viscosity of Aqueous phase*

ν_{oil} = *volume fraction Hydrocarbon phase*

- If the volume of the hydrocarbon phase is between 0.33 and 0.5, the effective viscosity for combined liquid phase is calculated using a weighted average between **Equation (4.29)** and **Equation (4.30)**.

The remaining properties of the pseudo phase are calculated as follows:

$$MW_{eff} = \sum x_i MW_i \qquad \text{(molecular weight)}$$

$$\rho_{eff} = \frac{1}{\sum\left(\frac{x_i}{\rho_i}\right)} \qquad \text{(mixture density)} \tag{4.31}$$

$$C_{p_{eff}} = \sum x_i C_{p_i} \qquad \text{(mixture specific heat)}$$

4.5 Thermal Conductivity

As in viscosity predictions, a number of different models and component specific correlations are implemented for prediction of liquid and vapour phase thermal conductivities. The text by Reid, Prausnitz and Poling[6] was used as a general guideline in determining which model was best suited for each class of components. For hydrocarbon systems, the corresponding states method proposed by Ely and Hanley[39] is generally used. The method requires molecular weight, acentric factor and ideal heat capacity for each component. These parameters are tabulated for all library components and may either be input or calculated for hypothetical components. It is recommended that all of these parameters be supplied for non-hydrocarbon hypotheticals to ensure reliable thermal conductivity coefficients and enthalpy departures.

The modifications to the method are identical to those for the viscosity calculations. Shape factors calculated in the viscosity routines are used directly in the thermal conductivity equations. The accuracy of the method will depend on the consistency of the original PVT map.

The Sato-Reidel method is used for liquid phase thermal conductivity predictions of glycols and acids, the Latini et al method is used for esters, alcohols and light hydrocarbons in the range of C_3-C_7, and the Missenard and Reidel method is used for the remaining components.

For vapour phase thermal conductivity predictions, the Misic and Thodos, and Chung et al methods are used. The effect of higher pressure on thermal conductivities is taken into account by the Chung et al method.

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHThermCond Class	Liquid and vapour

As with viscosity, the thermal conductivity for two liquid phases is approximated by using empirical mixing rules for generating a single pseudo liquid phase property. The thermal conductivity for an immiscible binary of liquid phases is calculated by the following equation[53]:

$$\lambda_{L_{mix}} = \phi_1^2\lambda_{L_1} + 2\phi_1\phi_2\lambda_{12} + \phi_2^2\lambda_{L_2} \tag{4.32}$$

where: λ_{Lmix} = *mixture liquid thermal conductivity at temperature T (K)*

$$\lambda_{Lmix} = \sum_i\sum_j \phi_i\phi_j k_{ij}$$

κ_{ij} = *liquid thermal conductivity of pure component i or j at temperature T*

$$k_{ij} = \frac{2}{(1/\ k_i) + (1/\ k_j)}$$

λ_{L1} = *liquid thermal conductivity of liquid phase 1*

λ_{L2} = *liquid thermal conductivity of liquid phase 2*

$$\phi_1 = \frac{x_1V_1}{\sum_{i=1}^{2} x_iV_i}$$

$$\phi_2 = \frac{x_2V_2}{\sum_{i=1}^{2} x_iV_i}$$

x_i = *mole fraction of component i*

V_i = *molar volume of component i*

4.6 Surface Tension

Surface tensions for hydrocarbon systems are calculated using a modified form of the Brock and Bird equation.

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHSurfaceTension Class	Liquid and vapour

The equation expresses the surface tension, σ, as a function of the reduced and critical properties of the component. The basic form of the equation was used to regress parameters for each family of components.

$$\sigma = P_c^{2/3} T_c^{1/3} Q(1 - T_R)^a \times b \tag{4.33}$$

where: σ = *surface tension (dynes/cm^2)*

$Q = 0.1207[1.0 + T_{BR} \ln P_c /(1.0 - T_{BR})] - 0.281$

T_{BR} = *reduced boiling point temperature* (T_b/T_c)

a = *parameter fitted for each chemical class*

$b = c_0 + c_1\,\omega + c_2\,\omega_2 + c_3\,\omega_3$ *(parameter fitted for each chemical class, expanded as a polynomial in acentricity)*

For aqueous systems, HYSYS employs a polynomial to predict the surface tension. It is important to note that HYSYS predicts only liquid-vapour surface tensions.

4.7 Insoluble Solids

An insoluble solid is identified from its pure compound "family" classification.

Property Methods

A quick reference of calculation methods for insoluble solids is shown in the table below.

Calculation Method	Phase Applicable	Property Class Name
MolarDensity	xptInsolubleSolid	**COTHSolidDensity Class**
MolarVolume	xptInsolubleSolid	**COTHSolidVolume Class**
Enthalpy	xptInsolubleSolid	**COTHSolidEnthalpy Class**
Entropy	xptInsolubleSolid	**COTHSolidEntropy Class**
Cp	xptInsolubleSolid	**COTHSolidCp Class**

The calculation methods from the table are described in the following sections.

Insoluble Solid Molar Density

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHSolidDensity Class	xptInsolubleSolid

Insoluble Solid MolarVolume

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHSolidVolume Class	xptInsolubleSolid

Insoluble Solid Enthalpy

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHSolidEnthalpy Class	xptInsolubleSolid

Insoluble Solid Entropy

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHSolidEnthalpy Class	xptInsolubleSolid

Insoluble Solid Cp

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHSolidCp Class	xptInsolubleSolid

5 References & Standard States

5.1 Enthalpy Reference States

All enthalpy calculations are determined with respect to a reference enthalpy which are defined in the following methods.

Property Methods

The enthalpy reference state calculation methods are shown in the table below.

Calculation Method	Phase Applicable	Property Class Name
Ideal Gas Enthalpy Offset	Vapour & Liquid	**COTHOffsetIGH Class**
Enthalpy Offset	Vapour & Liquid	**COTHOffsetH Class**

5.1.1 Ideal Gas Enthalpy Offset

The Ideal Gas enthalpy calculates and returns an array of:

$$H_i^{ig} + \text{offset H}_i \tag{5.1}$$

for all components.

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHOffsetIGH Class	Vapour & Liquid

The term, offset H_i, is calculated by Section 5.1.2 - Enthalpy Offset.

5.1.2 Enthalpy Offset

The enthalpy offset calculates and returns an array of:

$$\text{Offset H}_i = -H_i^{ig(25°\,C)} + H_i^{fig(25°\,C)} \tag{5.2}$$

for all components.

where: $H^{ig(25°C)}$ *= ideal gas enthalpy at 25°C.*

$H^{fig(25°C)}$ *= ideal gas enthalpy with heat of formation of the component at 25°C.*

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHOffsetH Class	Vapour & Liquid

5.2 Entropy Reference States

All entropy calculations are determined with respect to a reference enthalpy which are defined in the following methods.

Property Methods

The entropy reference state calculation methods are shown in the table below.

Calculation Method	Phase Applicable	Property Class Name
Ideal Gas Entropy Offset	Vapour & Liquid	**COTHOffsetIGS Class**
Entropy Offset	Vapour & Liquid	**COTHOffsetS Class**

5.2.1 Ideal Gas Entropy Offset

The Ideal Gas entropy calculates and returns an array of:

$$S_i^{ig} + \text{offset S}_i \tag{5.3}$$

for all components.

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHOffsetIGS Class	Vapour & Liquid

The term, offset S_i, is calculated by Section 5.2.2 - Entropy Offset.

5.2.2 Entropy Offset

The entropy offset calculates and returns an array of:

$$\text{Offset S} = 0 \tag{5.4}$$

for all components.

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHOffsetS Class	Vapour & Liquid

5.3 Ideal Gas Cp

The ideal gas C_p calculates and returns an array containing the ideal gas C_p of all components.

5.4 Standard State Fugacity

The fugacity of component, i, in the mixture is related to its activity coefficient composition through the following equation.

$$f_i = \gamma_i x_i f_i^{std} \tag{5.5}$$

where: γ_i *= activity coefficient of component i*

f_i^{std} *= standard state fugacity of component i*

x_i *= mole fraction of component i*

The standard state fugacity, f_i^{std}, is defined at the temperature and pressure of the mixture. As, γ_i, approaches one in the limit $x_i \rightarrow 1$, the standard state fugacity may be related to the vapour pressure of component *i*.

$$f_i^{std} = P_i^{sat} \phi_i^{sat} \exp\left[\int_{P_i^{sat}}^{P} \frac{V_i}{RT} dP\right] \tag{5.6}$$

where: P_i^{sat} *= vapour pressure of component i at the temperature of the system*

ϕ_i^{sat} *= fugacity coefficient of pure component i at temperature T and pressure* P_i^{sat}

P = pressure of the system

Vi = liquid molar volume of component i at T and P

R = gas constant

T = temperature of system

The Poynting factor accounts for the effect of pressure on liquid fugacity and is represented by the exponential term in the above equation. The correction factor generally is neglected if the pressure does not exceed a few atmospheres. The liquid volume has little effect on pressure and the above equation simplifies to:

$$f_i^{std} = P_i^{sat}\phi_i^{sat}\exp[(P - P_i^{sat})V_i/ (RT)] \qquad (5.7)$$

The vapour phase fugacity can be calculated by any method when liquid activity coeffiecients are used.

Property Methods

The standard state fugacity calculation methods are shown in the following table.

Calculation Method	Phase Applicable	Property Class Name
LnStdFugacity	Liquid	**COTHIdealStdFug Class**
LnStdFugacity	Liquid	**COTHPoyntingStdFug Class**
LnStdFugacity	Liquid	**COTHPhiStdFug Class**
LnStdFugacity	Liquid	**COTHPoyntingPhiStdFug Class**

5.4.1 Standard State without Poynting Correction

This method calculates the standard state fugacity for all components. The effects of the poynting correction and ϕ_i^{sat} in **Equation (5.5)** are neglected.

For condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat} \qquad (5.8)$$

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHIdealStdFug Class	Liquid

Notes

For non-condensible components in the presence of any condensible components, Henry's law is used as shown below.

$$f_i^{std} = H_{i,\ j} \tag{5.9}$$

In a system of all non-condensible components and no condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat} \tag{5.10}$$

5.4.2 Standard State with Poynting Correction

This method calculates the standard state fugacity for all components. The effect of the poynting correction is included and accounts for the effect of pressure on the liquid fugacity. The effect of the fugacity coefficient, ϕ_i^{sat}, in **Equation (5.5)** is neglected.

For condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat} \exp[(P - P_i^{sat})V_i / (RT)] \tag{5.11}$$

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHPoyntingStdFug Class	Liquid

Notes

For non-condensible components in the presence of any condensible components, Henry's law is used as shown below.

$$f_i^{std} = H_{i,\ j} \tag{5.12}$$

In a system of all non-condensible components and no condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat} \exp[(P - P_i^{sat})V_i / (RT)] \tag{5.13}$$

5.4.3 Ideal Standard State with Fugacity Coefficient

This method calculates the standard state fugacity for all components. The effect of the fugacity coefficient, ϕ_i^{sat}, is included although the poynting factor in **Equation (5.5)** is neglected.

For condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat} \phi_i^{sat} \tag{5.14}$$

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHPhiStdFug Class	Liquid

Notes

For non-condensible components in the presence of any condensible components, Henry's law is used as shown below.

$$f_i^{std} = H_{i,j}\exp[(P - P_i^{sat})V_i/(RT)] \tag{5.15}$$

In a system of all non-condensible components and no condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat}\exp[(P - P_i^{sat})V_i/(RT)] \tag{5.16}$$

The fugacity coefficient, ϕ_i^{sat}, is calculated from the specified vapour model.

5.4.4 Ideal Standard State with Fugacity Coeff & Poynting

This method calculates the standard state fugacity for all components. The effects of the fugacity coefficient, ϕ_i^{sat}, and the poynting correction in **Equation (5.5)** are included.

For condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat}\phi_i^{sat}\exp[(P - P_i^{sat})V_i/(RT)] \tag{5.17}$$

Property Class Name and Phases Applicable

Property Class Name	Phase Applicable
COTHPoyntingPhiStdFug Class	Liquid

Notes

For non-condensible components in the presence of any condensible components, Henry's law is used as shown below.

$$f_i^{std} = H_{i,j} \exp[(P - P_i^{sat}) V_i / (RT)] \tag{5.18}$$

In a system of all non-condensible components and no condensible components, the standard state fugacity is calculated as:

$$f_i^{std} = P_i^{sat} \exp[(P - P_i^{sat}) V_i / (RT)] \tag{5.19}$$

The fugacity coefficient, ϕ_i^{sat}, is calculated from the specified vapour model.

6 Flash Calculations

6.1 Introduction

Specified variables can only be re-specified by you or via the *Recycle Adjust***,** or *SpreadSheet* operations. They will not change through any heat or material balance calculations.

Rigorous three phase calculations are performed for all equations of state and activity models with the exception of the Wilson equation, which only performs two phase vapour-liquid calculations.

COMThermo uses internal intelligence to determine when it can perform a flash calculation on a stream, and then what type of flash calculation needs to be performed on the stream. This is based completely on the degrees of freedom concept. When the composition of a stream and two property variables are known, (vapour fraction, temperature, pressure, enthalpy or entropy, one of which must be either temperature or pressure), the thermodynamic state of the stream is defined.

COMThermo automatically performs the appropriate flash calculation when sufficient information is known. Depending on the known stream information, one of the following flashes are performed: T-P, T-VF, T-H, T-S, P-VF, P-H, or P-S.

6.2 T-P Flash Calculation

The independent variables for this type of flash calculation are the temperature and pressure of the system, while the dependent variables are the vapour fraction, enthalpy and entropy.

Using the specified models, rigorous calculations are performed to determine the coexistence of immiscible liquid phases and the resulting component distributions by minimization of the Gibbs free energy term. For Vapour Pressure models or the Semi-empirical methods, the component distribution is based on the Kerosene solubility data (Figure 9 A1.4 of the API Data Book).

If the mixture is single-phase at the specified conditions, the property package calculates the isothermal compressibility (dv/dp) to determine if the fluid behaves as a liquid or vapour. Fluids in the dense-phase region are assigned the properties of the phase that best represents their current state.

Use caution in specifying solids with systems that are otherwise all vapour. Small amounts of non-solids may appear in the “liquid” phase.

Material solids appear in the liquid phase of two-phase mixtures, and in the heavy (aqueous/slurry) phase of three-phase system.

6.3 Vapour Fraction Flash

Vapour fraction and either temperature or pressure are the independent variables for this type of calculation. This class of calculation embodies all fixed quality points including bubble points (vapour pressure) and dew points. To perform bubble point calculation on a stream of known composition, simply specify the Vapour Fraction of the stream as 0.0 and define the temperature or pressure at which the calculation is desired. For a dew point calculation, simply specify the Vapour Fraction of the stream as 1.0 and define the temperature or pressure at which the dew point calculation is desired. Like the other types of flash calculations, no initial estimates are required.

All of the solids will appear in the liquid phase.

The vapour fraction is always shown in terms of the total number of moles. For instance, the vapour fraction (VF) represents the fraction of vapour in the stream, while the fraction, (1.0 - VF), represents all other phases in the stream (i.e. a single liquid, 2 liquids, a liquid and a solid).

6.3.1 Dew Points

Given a vapour fraction specification of 1.0 and either temperature or pressure, the property package will calculate the other dependent variable (P or T). If temperature is the second independent variable, the dew point pressure is calculated. Likewise, if pressure is the independent variable, then the dew point temperature will be calculated. Retrograde dew points may be calculated by specifying a vapour fraction of -1.0. It is important to note that a dew point that is retrograde with respect to temperature can be normal with respect to pressure and vice versa.

6.3.2 Bubble Points/Vapour Pressure

Vapour pressure and bubble point pressure are synonymous.

A vapour fraction specification of 0.0 defines a bubble point calculation. Given this specification and either temperature or pressure, the flash will calculate the unknown T or P variable. As with the dew point calculation, if the temperature is known, the bubble point pressure is calculated and conversely, given the pressure, the bubble point temperature is calculated. For example, by fixing the temperature at 100°F, the resulting bubble point pressure is the true vapour pressure at 100°F.

6.3.3 Quality Points

Bubble and dew points are special cases of quality point calculations. Temperatures or pressures can be calculated for any vapour quality between 0.0 and 1.0 by specifying the desired vapour fraction and the corresponding independent variable. If HYSYS displays an error when calculating vapour fraction, then this means that the specified vapour fraction doesn't exist under the given conditions, i.e., the specified pressure is above the cricondenbar, or the given temperature is to the right of the cricondentherm on a standard P-T envelope.

Enthalpy Flash

Given the enthalpy and either the temperature or pressure of a stream, the property package will calculate the unknown dependent variables. Although the enthalpy of a stream cannot be specified directly, it will often occur as the second property variable as a result of energy balances around unit operations such as valves, heat exchangers and mixers.

If an error message appears, this may mean that an internally set temperature or pressure bound has been encountered. Since these bounds are set at quite large values, there is generally some erroneous input that is directly or indirectly causing the problem, such as an impossible heat exchange.

Entropy Flash

Given the entropy and either the temperature or pressure of a stream, the flash will calculate the unknown dependent variables.

Solids

COMThermo flash does not check for solid phase formation of pure components within the flash calculations.

Solids do not participate in vapour-liquid equilibrium (VLE) calculations. Their vapour pressure is taken as zero. However, since solids do have an enthalpy contribution, they will have an effect on heat balance calculations. Thus, while the results of a temperature flash will be the same whether or not such components are present, an Enthalpy flash will be affected by the presence of solids.

6.4 Flash Control Settings

Flash control settings are used to control tolerances, iteration numbers, and some other flash options. You can set flash options through applications that support COMThermo. These include HYSYS, HYCON, and HTFS amongst others.

Flash control values are stored in the flash control object and can be set through interface functions. The Flash XML file is described by the COMThermo property manager. It identifies the flash control settings and sets it into the flash control object where flash can now get the controls.

In flash control, there are two kinds of controls:

Control	Description
Fixed Control	Fixed controls are hard coded controls that have fixed names and default values. If the user does not set the controls, the default values are used.
Additional Control	Additional controls are called SecantSetting controls. SecantSettings such as Temperature and Pressure are set by default, as others can be defined by COMThermo flash and/or the user. If the user defines a control (the name given by the user), in the user created flash object users can use the same name to get the values of that control set in the flash XML file.

Refer to the Flash Control Settings in the Flash XML File section in the Programmer's guide of the COMThermo development kit for more information.

7 Property Packages

7.1 Introduction

A summary of the property packages used within the COMThermo framework are grouped into the following sections:

- **Section 7.2 - Vapour Phase Models**
- **Section 7.3 - Liquid Phase Models**

Each section consists of tables which include the file name, description, property names, and class names within COMThermo.

7.2 Vapour Phase Models

Property package information for vapour phase models is shown in the following sections.

Ideal Gas

PV=nRT can be used to model the vapour phase but is only suggested for ideal systems under moderate conditions.

XML File Name	Name	Description
Ideal_vapour	Ideal Gas	**Ideal Gas Equation of State**

Property Name	Class Name	Description
Enthalpy	COTHIGEnthalpy	Ideal gas enthalpy.
Entropy	COTHIGEntropy	Ideal gas entropy.
Cp	COTHIGCp	Ideal gas heat capacity.
LnFugacityCoeff	COTHIGLnFugacityCoeff	Ideal gas fugacity coefficient.
LnFugacity	COTHIGLnFugacity	Ideal gas fugacity.
MolarVolume	COTHIGVolume	Ideal gas molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHIGZFactor	Ideal gas compressibility factor.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.

Property Name	Class Name	Description
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Peng-Robinson

This model is ideal for VLE calculations as well as calculating liquid densities for hydrocarbon systems. However, in situations where highly non-ideal systems are encountered, the use of Activity Models is recommended.

XML File Name	Name	Description
pr_vapour	Peng-Robinson	**Peng-Robinson Equation of State** using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHPREnthalpy	Peng-Robinson enthalpy.
Entropy	COTHPREntropy	Peng-Robinson entropy.
Cp	COTHPRCp	Peng-Robinson heat capacity.
LnFugacityCoeff	COTHPRLnFugacityCoeff	Peng-Robinson fugacity coefficient.
LnFugacity	COTHPRLnFugacity	Peng-Robinson fugacity.
MolarVolume	COTHPRVolume	Peng-Robinson molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHPRZFactor	Peng-Robinson compressibility factor.
amix	COTHPRab_1	Peng-Robinson amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas offset enthalpy
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

HysysPR

The HysysPR EOS is similar to the PR EOS with several enhancements to the original PR equation. It extends its range of applicability and better represents the VLE of complex systems.

XML File Name	Name	Description
hysyspr_vapour	HysysPR	**HysysPR Equation of State** using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHPR_HYSYS_Enthalpy	Peng-Robinson enthalpy.
Entropy	COTHPR_HYSYS_Entropy	Peng-Robinson entropy.
Cp	COTHPR_HYSYS_Cp	Peng-Robinson heat capacity.
LnFugacityCoeff	COTHPR_HYSYS_LnFugacityCoeff	Peng-Robinson fugacity coefficient.
LnFugacity	COTHPR_HYSYS_LnFugacity	Peng-Robinson fugacity.
MolarVolume	COTHPR_HYSYS_Volume	Peng-Robinson molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHPRZFactor	Peng-Robinson compressibility factor.
amix	COTHPRab_1	Peng-Robinson amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas offset enthalpy
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Peng-Robinson-Stryjek-Vera

This is a two-fold modification of the PR equation of state that extends the application of the original PR method for moderately non-ideal systems. It provides a better pure component vapour pressure prediction as well as a more flexible mixing rule than Peng robinson.

XML File Name	Name	Description
prsv_vapour	PRSV	**Peng-Robinson Stryjek-Vera** using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHPRSVEnthalpy	PRSV enthalpy.
Entropy	COTHPRSVEntropy	PRSV entropy.
Cp	COTHPRSVCp	PRSV heat capacity.
LnFugacityCoeff	COTHPRSVLnFugacityCoeff	PRSV fugacity coefficient.
LnFugacity	COTHPRSVLnFugacity	PRSV fugacity.
MolarVolume	COTHPRSVVolume	PRSV molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHPRSVZFactor	PRSV compressibility factor.
amix	COTHPRSVab_1	PRSV amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Soave-Redlich-Kwong

In many cases it provides comparable results to PR, but its range of application is significantly more limited. This method is not as reliable for non-ideal systems.

XML File Name	Name	Description
srk_vapour	SRK	**Soave-Redlich-Kwong Equation of State** using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHSRKEnthalpy	SRK enthalpy.
Entropy	COTHSRKEntropy	SRK entropy.
Cp	COTHSRKCp	SRK heat capacity.
LnFugacityCoeff	COTHSRKLnFugacityCoeff	SRK fugacity coefficient.
LnFugacity	COTHSRKLnFugacity	SRK fugacity.
MolarVolume	COTHSRKVolume	SRK molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHSRKZFactor	SRK compressibility factor.
amix	COTHSRKab_1	SRK amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Redlich-Kwong

The Redlich-Kwong equation generally provides results similar to Peng-Robinson. Several enhancements have been made to the PR as described above which make it the preferred equation of state.

XML File Name	Name	Description
rk_vapour	Redlich-Kwong	**Redlich-Kwong Equation of State** using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHRKEnthalpy	RK enthalpy.
Entropy	COTHRKEntropy	RK entropy.
Cp	COTHRKCp	RK heat capacity.
LnFugacityCoeff	COTHRKLnFugacityCoeff	RK fugacity coefficient.
LnFugacity	COTHRKLnFugacity	RK fugacity.
MolarVolume	COTHRKVolume	RK molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHRKZFactor	SRK compressibility factor.
amix	COTHRKab_1	SRK amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Zudkevitch-Joffee

This is a modification of the Redlich-Kwong equation of state, which reproduces the pure component vapour pressures as predicted by the Antoine vapour pressure equation. This model has been enhanced for better prediction of vapour-liquid equilibrium for hydrocarbon systems, and systems containing Hydrogen.

XML File Name	Name	Description
zj_vapour	Zudkevitch-Joffee	**Zudkevitch-Joffee Equation of State**

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHZJLnFugacityCoeff	ZJ fugacity coefficient.
LnFugacity	COTHZJLnFugacity	ZJ fugacity.
MolarVolume	COTHZJVolume	ZJ molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHZJZFactor	ZJ compressibility factor.
amix	COTHZJab_1	ZJ amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Kabadi-Danner

This model is a modification of the original SRK equation of state, enhanced to improve the vapour-liquid-liquid equilibrium calculations for water-hydrocarbon systems, particularly in dilute regions.

XML File Name	Name	Description
kd_vapour	Kabadi-Danner	**Kabadi-Danner Equation of State** using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHKDEnthalpy	KD enthalpy.
Entropy	COTHKDEntropy	KD entropy.
Cp	COTHKDCp	KD heat capacity.
LnFugacityCoeff	COTHKDLnFugacityCoeff	KD fugacity coefficient.
LnFugacity	COTHKDLnFugacity	KD fugacity.
MolarVolume	COTHKDVolume	KD molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHKDZFactor	KD compressibility factor.
amix	COTHKDab_1	KD amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Virial

This model enables you to better model vapour phase fugacities of systems displaying strong vapour phase interactions. Typically this occurs in systems containing carboxylic acids, or compounds that have the tendency to form stable hydrogen bonds in the vapour phase. In these cases, the fugacity coefficient shows large deviations from ideality, even at low or moderate pressures.

XML File Name	Name	Description
virial_vapour	Virial	**The Virial Equation of State**

Property Name	Class Name	Description
Enthalpy	COTHVirial_Enthalpy	Virial enthalpy.
Entropy	COTHVirial_Entropy	Virial entropy.
Cp	COTHVirial_Cp	Virial heat capacity.
LnFugacityCoeff	COTHVirial_LnFugacityCoeff	Virial fugacity coefficient.
LnFugacity	COTHVirial_LnFugacity	Virial fugacity.
MolarVolume	COTHVirial_Volume	Virial molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
ZFactor	COTHVirial_ZFactor	Virial compressibility factor.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Lee-Kesler-Plöcker

This model is the most accurate general method for non-polar substances and mixtures.

XML File Name	Name	Description
lkp_vapour	Lee-Kesler-Plöcker	**Lee-Kesler-Plöcker** EOS using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEnthalpy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHLKPLnFugacityCoeff	LKP fugacity coefficient.
LnFugacity	COTHLKPLnFugacity	LKP fugacity.
MolarVolume	COTHLKPMolarVolume	LKP molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHLKPZFactor	LKP compressibility factor.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Braun K10

This model is strictly applicable to heavy hydrocarbon systems at low pressures. The model employs the Braun convergence pressure method, where, given the normal boiling point of a component, the K-value is calculated at system temperature and 10 psia (68.95 kPa).

XML File Name	Name	Description
braunk10_vapour	Braun K10	Braun K10 Vapour Pressure Property Model.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHBraunK10LnFugacityCoeff	Braun K10 fugacity coefficient.
LnFugacity	COTHBraunK10LnFugacity	Braun K10 fugacity.
MolarVolume	COTHBraunK10Volume	Braun K10 molar volume.
MolarDensity	COTHCOSTALDDensity	Costald molar density.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

7.3 Liquid Phase Models

The property package information for the liquid phase models is shown in the following sections.

Ideal Solution

Assumes the volume change due to mixing is zero. This model is more commonly used for solutions comprised of molecules not too different in size and of the same chemical nature.

XML File Name	Name	Description
idealsol_liquid	Ideal Solution	**Ideal Solution Model**

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
LnFugacityCoeff	COTHIdealSolLnFugacityCoeff	Ideal Solution fugacity coefficient.
LnFugacity	COTHIdealSolLnFugacity	Ideal solution fugacity.
LnActivity Coeff	COTHIdealSolLnActivityCoeff	Ideal solution activity coefficient.
LnStdFugacity	COTHIdealStdFug	Ideal standard fugacity with or without poynting correction.
LnActivityCoeffDT	COTHIdealSolLnActivityCoeffDT	Ideal solution activity coefficient wrt temperature.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHIdealSolGibbsEnergy	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.

Property Name	Class Name	Description
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Regular Solution

This model eliminates the excess entropy when a solution is mixed at constant temperature and volume. The model is recommended for non-polar components where the molecules do not differ greatly in size. By the attraction of intermolecular forces, the excess Gibbs energy may be determined.

XML File Name	Name	Description
regsol_liquid	Regular Solution	**Regular Solution Model.**

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
LnFugacityCoeff	COTHRegSolLnFugacityCoeff	Regular Solution fugacity coefficient.
LnFugacity	COTHRegSolLnFugacity	Regular solution fugacity.
LnActivity Coeff	COTHRegSolLnActivityCoeff	Regular solution activity coefficient.
LnStdFugacity	COTHIdealStdFug	Ideal standard fugacity with or without poynting correction.
LnActivityCoeffDT	COTHRegSolLnActivityCoeffDT	Regular solution activity coefficient wrt temperature.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	Viscosity.

Property Name	Class Name	Description
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHCavettGibbs	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

van Laar

This equation fits many systems quite well, particularly for LLE component distributions. It can be used for systems that exhibit positive or negative deviations from Raoult's Law; however, it cannot predict maxima or minima in the activity coefficient. Therefore it generally performs poorly for systems with halogenated hydrocarbons and alcohols.

XML File Name	Name	Description
vanlaar_liquid	van Laar	Two-parameter temperature dependent **van Laar Model**

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
LnFugacityCoeff	COTHVanLaarLnFugacityCoeff	Van Laar fugacity coefficient.
LnFugacity	COTHVanLaarLnFugacity	Van Laar fugacity.

Property Name	Class Name	Description
LnActivity Coeff	COTHVanLaarLnActivityCoeff	Van Laar activity coefficient.
LnStdFugacity	COTHVanLaarStdFug	Ideal standard fugacity with or without poynting correction.
LnActivityCoeffDT	COTHVanLaarLnActivityCoeffDT	Van Laar activity coefficient wrt temperature.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHCavettGibbs	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Margules

This was the first Gibbs excess energy representation developed. The equation does not have any theoretical basis, but is useful for quick estimates and data interpolation.

XML File Name	Name	Description
margules_liquid	Margules	Two-parameter temperature dependent **Margules Model**

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
LnFugacityCoeff	COTHMargulesLnFugacityCoeff	Margules fugacity coefficient.
LnFugacity	COTHMargulesLnFugacity	Margules fugacity.
LnActivity Coeff	COTHMargulesLnActivityCoeff	Margules activity coefficient.
LnStdFugacity	COTHMargulesStdFug	Ideal standard fugacity with or without poynting correction.
LnActivityCoeffDT	COTHMargulesLnActivityCoeffDT	Margules activity coefficient wrt temperature.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHCavettGibbs	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.

Property Name	Class Name	Description
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Wilson

First activity coefficient equation to use the local composition model to derive the Gibbs Excess energy expression. It offers a thermodynamically consistent approach to predicting multi-component behaviour from regressed binary equilibrium data. However the Wilson model cannot be used for systems with two liquid phases.

XML File Name	Name	Description
wilson_liquid	Wilson	Two-parameter temperature dependent **Wilson Model**

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
LnFugacityCoeff	COTHWilsonLnFugacityCoeff	Wilson fugacity coefficient.
LnFugacity	COTHWilsonLnFugacity	Wilson fugacity.
LnActivity Coeff	COTHWilsonLnActivityCoeff	Wilson activity coefficient.
LnStdFugacity	COTHWilsonStdFug	Ideal standard fugacity with or without poynting correction.
LnActivityCoeffDT	COTHWilsonLnActivityCoeffDT	Wilson activity coefficient wrt temperature.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHCavettGibbs	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.

Property Name	Class Name	Description
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

General NRTL

This variation of the NRTL model uses five parameters and is more flexible than the NRTL model. Apply this model to systems with a wide boiling point range between components, where you require simultaneous solution of VLE and LLE, and where there exists a wide boiling point or concentration range between components.

XML File Name	Name	Description
nrtl_liquid	General NRTL	**The General NRTL Model** with five-coefficient temperature dependent parameters.

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
ActTempDep	COTHNRTLTempDep	HYSYS NRTL temperature dependent properties.
LnFugacityCoeff	COTHNRTLLnFugacityCoeff	NRTL fugacity coefficient.
LnFugacity	COTHNRTLLnFugacity	NRTL fugacity.
LnActivity Coeff	COTHNRTLLnActivityCoeff	NRTL activity coefficient.
LnStdFugacity	COTHNRTLStdFug	Ideal standard fugacity with or without poynting correction.
LnActivityCoeffDT	COTHNRTLLnActivityCoeffDT	NRTL activity coefficient wrt temperature.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.

Property Name	Class Name	Description
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHCavettGibbs	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

UNIQUAC

This model uses statistical mechanics and the quasi-chemical theory of Guggenheim to represent the liquid structure. The equation is capable of representing LLE, VLE, and VLLE with accuracy comparable to the NRTL equation, but without the need for a non-randomness factor.

XML File Name	Name	Description
uniquac_liquid	UNIQUAC	**UNIQUAC Model** with two-coefficient temperature dependent parameters.

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
LnFugacityCoeff	COTHUNIQUACLnFugacityCoeff	UNIQUAC fugacity coefficient.
LnFugacity	COTHUNIQUACLnFugacity	UNIQUAC fugacity.
LnActivity Coeff	COTHUNIQUACLnActivityCoeff	UNIQUAC activity coefficient.

Property Name	Class Name	Description
LnStdFugacity	COTHIdeallStdFug	Ideal standard fugacity with or without poynting correction.
LnActivityCoeffDT	COTHUNIQUACLnActivityCoeffDT	UNIQUAC activity coefficient wrt temperature.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHCavettGibbs	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Chien-Null

This model provides consistent framework for applying existing Activity Models on a binary by binary basis. It allows you to select the best Activity Model for each pair in your case.

XML File Name	Name	Description
cn_liquid	Chien-Null	Three-parameter temperature dependent **Chien-Null Model**.

Property Name	Class Name	Description
Enthalpy	COTHCavettEnthalpy	Cavett enthalpy.
Entropy	COTHCavettEntropy	Cavett entropy.
Cp	COTHCavettCp	Cavett heat capacity.
LnFugacityCoeff	COTHCNLnFugacityCoeff	CN fugacity coefficient.
LnFugacity	COTHCNLnFugacity	CN fugacity.
LnActivity Coeff	COTHCNLnActivityCoeff	CN activity coefficient.
LnActivityCoeffDT	COTHCNLnActivityCoeffDT	CN activity coefficient wrt temperature.
LnStdFugacity	COTHIdealStdFug	Ideal standard fugacity with or without poynting correction.
ActTempDep	COTHCNTempDep	HYSYS CN temperature dependent properties.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	Viscosity.
ThermalConductivity	COTHThermCond	Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
Helmholtz	COTHCavettHelmholtz	Cavett Helmholtz energy.
InternalEnergy	COTHCavettInternalEnergy	Cavett Internal energy.
GibbsEnergy	COTHCavettGibbs	Cavett Gibbs energy.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.

Property Name	Class Name	Description
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Antoine

This model is applicable for low pressure systems that behave ideally.

XML File Name	Name	Description
antoine_liquid	Antoine	UNIQUAC activity model with two-coefficient temperature dependent parameters.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHAntoineLnFugacityCoeff	Antoine fugacity coefficient.
LnFugacity	COTHAntoineLnFugacity	Antoine fugacity.
LnActivity Coeff	COTHAntoineLnActivityCoeff	Antoine activity coefficient.
MolarDensity	COTHCOSTALDDensity	COSTALD molar density.
MolarVolume	COTHCOSTALDVolume	COSTALD molar volume.
Viscosity	COTHViscosity	HYSYS Viscosity.
ThermalConductivity	COTHThermCond	HYSYS Thermal conductivity.
SurfaceTension	COTHSurfaceTension	Surface Tension.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Braun K10

This model is strictly applicable to heavy hydrocarbon systems at low pressures. The model employs the Braun convergence pressure method, where, given the normal boiling point of a component, the K-value is calculated at system temperature and 10 psia (68.95 kPa).

XML File Name	Name	Description
braunk10_liquid	Braun K10	Braun K10 Vapour Pressure Property Model.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHBraunK10LnFugacityCoeff	Braun K10 fugacity coefficient.
LnFugacity	COTHBraunK10LnFugacity	Braun K10 fugacity.
LnActivity Coeff	COTHBraunK10LnActivityCoeff	Braun K10 molar volume.
MolarDensity	COTHCOSTALDDensity	Costald molar density.
MolarVolume	COTHCOSTALDVolume	Costald molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Esso Tabular

This model is strictly applicable to hydrocarbon systems at low pressures. The model employs a modification of the Maxwell-Bonnel vapour pressure model.

XML File Name	Name	Description
essotabular_liquid	Esso Tabular	Esso Tabular vapour Pressure Property Model.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHEssoLnFugacityCoeff	Esso fugacity coefficient.
LnFugacity	COTHEssoLnFugacity	Esso fugacity.
LnActivity Coeff	COTHEssoLnActivityCoeff	Esso activity coefficient.
MolarDensity	COTHCOSTALDDensity	Costald molar density.
MolarVolume	COTHCOSTALDVolume	Costald molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Chao-Seader

This method for heavy hydrocarbons, where the pressure is less than 10342 kPa (1500 psia), and temperatures range between -17.78 and 260°C (0-500°F).

XML File Name	Name	Description
cs_liquid	Chao-Seader	**Chao-Seader Model** is a semi-empirical property method

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHChaoSeaderLnFugacityCoeff	Chao-Seader fugacity coefficient.
LnFugacity	COTHChaoSeaderLnFugacity	Chao-Seader fugacity.
MolarVolume	COTHRKVolume	Redlich-Kwong molar volume.
ZFactor	COTHRKZFactor	Redlich-Kwong compressibility factor.
amix	COTHRKab_1	Redlich-Kwong EOS amix.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Grayson-Streed

This model is recommended for simulating heavy hydrocarbon systems with a high hydrogen content.

XML File Name	Name	Description
gs_liquid	Grayson-Streed	**Grayson-Streed Model** is a semi-empirical property method.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHGraysonStreedLnFugacityCoeff	Grayson-Streed fugacity coefficient.
LnFugacity	COTHGraysonStreedLnFugacity	Grayson-Streed fugacity.
MolarVolume	COTHRKVolume	Redlich-Kwong molar volume.
ZFactor	COTHRKZFactor	Redlich-Kwong compressibility factor.
amix	COTHRKab_1	Redlich-Kwong EOS amix.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

HysysPR

The HysysPR EOS is similar to the PR EOS with several enhancements to the original PR equation. It extends the range of applicability and better represents the VLE of complex systems.

XML File Name	Name	Description
hysyspr_liquid	HysysPR	Peng-Robinson EOS using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHPR_HYSYS_Enthalpy	Peng-Robinson enthalpy.
Entropy	COTHPR_HYSYS_Entropy	Peng-Robinson entropy.
Cp	COTHPR_HYSYS_Cp	Peng-Robinson heat capacity.
LnFugacityCoeff	COTHPR_HYSYS_LnFugacityCoeff	Peng-Robinson fugacity coefficient.
LnFugacity	COTHPR_HYSYS_LnFugacity	Peng-Robinson fugacity.
MolarVolume	COTHPR_HYSYS_Volume	Peng-Robinson molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
ZFactor	COTHPRZFactor	Peng-Robinson compressibility factor.
amix	COTHPRab_1	Peng-Robinson amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Kabadi-Danner

This model is a modification of the original SRK equation of state, enhanced to improve the vapour-liquid-liquid equilibrium calculations for water-hydrocarbon systems, particularly in dilute regions.

XML File Name	Name	Description
kd_liquid	Kabadi-Danner	Kabadi-Danner EOS using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHKDEnthalpy	Kabadi-Danner enthalpy.
Entropy	COTHKDEntropy	Kabadi-Danner entropy.
Cp	COTHKDCp	Kabadi-Danner heat capacity.
LnFugacityCoeff	COTHKDLnFugacityCoeff	Kabadi-Danner fugacity coefficient.
LnFugacity	COTHKDLnFugacity	Kabadi-Danner fugacity.
MolarVolume	COTHKDVolume	Kabadi-Danner molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHKDZFactor	Kabadi-Danner compressibility factor.
amix	COTHKDab_1	Kabadi-Danner amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Peng-Robinson

This model is ideal for VLE calculations as well as calculating liquid densities for hydrocarbon systems. However, in situations where highly non-ideal systems are encountered, the use of Activity Models is recommended.

XML File Name	Name	Description
pr_liquid	Peng-Robinson	Peng-Robinson EOS using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHPREnthalpy	Peng-Robinson enthalpy.
Entropy	COTHPREntropy	Peng-Robinson entropy.
Cp	COTHPRCp	Peng-Robinson heat capacity.
LnFugacityCoeff	COTHPRLnFugacityCoeff	Peng-Robinson fugacity coefficient.
LnFugacity	COTHPRLnFugacity	Peng-Robinson fugacity.
MolarVolume	COTHPRVolume	Peng-Robinson molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHPRZFactor	Peng-Robinson compressibility factor.
amix	COTHPRab_1	Peng-Robinson amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Peng-Robinson-Stryjek-Vera

This is a two-fold modification of the PR equation of state that extends the application of the original PR method for moderately non-ideal systems. It provides a better pure component vapour pressure prediction as well as a more flexible Mixing Rule than Peng robinson.

XML File Name	Name	Description
prsv_liquid	PRSV	Peng-Robinson-Stryjek-Vera EOS using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHPRSVEnthalpy	PRSV enthalpy.
Entropy	COTHPRSVEntropy	PRSV entropy.
Cp	COTHPRSVCp	PRSV heat capacity.
LnFugacityCoeff	COTHPRSVLnFugacityCoeff	PRSV fugacity coefficient.
LnFugacity	COTHPRSVLnFugacity	PRSV fugacity.
MolarVolume	COTHPRSVVolume	PRSV molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHPRSVZFactor	PRSV compressibility factor.
amix	COTHPRSVab_1	PRSV amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Soave-Redlich-Kwong

In many cases it provides comparable results to PR, but its range of application is significantly more limited. This method is not as reliable for non-ideal systems.

XML File Name	Name	Description
srk_liquid	SRK	Soave-Redlich-Kwong EOS using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHSRKEnthalpy	SRK enthalpy.
Entropy	COTHSRKEntropy	SRK entropy.
Cp	COTHSRKCp	SRK heat capacity.
LnFugacityCoeff	COTHSRKLnFugacityCoeff	SRK fugacity coefficient.
LnFugacity	COTHSRKLnFugacity	SRK fugacity.
MolarVolume	COTHSRKVolume	SRK molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHSRKZFactor	SRK compressibility factor.
amix	COTHSRKab_1	SRK amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Virial

This model enables you to better model vapour phase fugacities of systems displaying strong vapour phase interactions. Typically this occurs in systems containing carboxylic acids, or compounds that have the tendency to form stable hydrogen bonds in the vapour phase. In these cases, the fugacity coefficient shows large deviations from ideality, even at low or moderate pressures.

XML File Name	Name	Description
virial_liquid	Virial	Virial Equation of State.

Property Name	Class Name	Description
LnFugacityCoeff	COTHPR_LnFugacityCoeff	Peng-Robinson fugacity coefficient.
LnFugacity	COTHPR_LnFugacity	Peng-Robinson fugacity.
LnStdFugacity	COTHIdealStdFug	Ideal standard fugacity.
MolarVolume	COTHSolidVolume	Molar solid volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHPR_ZFactor	Peng-Robinson compressibility factor.
Enthalpy	COTHPR_Enthalpy	Peng-Robinson enthalpy.
Enthalpy	COTHSolidEnthalpy	Insoluble solid enthalpy.
Entropy	COTHPR_Entropy	Peng-Robinson entropy.
Entropy	COTHSolidEntropy	Insoluble solid entropy.
Cp	COTHPR_Cp	Peng-Robinson heat capacity.
Cp	COTHSolidCp	Insoluble solid heat capacity.
amix	COTHPRab_1	Peng-Robinson amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.

Zudkevitch-Joffee

This is a modification of the Redlich-Kwong equation of state, which reproduces the pure component vapour pressures as predicted by the Antoine vapour pressure equation. This model has been enhanced for better prediction of vapour-liquid equilibrium for hydrocarbon systems, and systems containing Hydrogen.

XML File Name	Name	Description
zj_liquid	Zudkevitch-Joffee	Zudkevitch-Joffee Equation of State.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEntropy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHZJLnFugacityCoeff	Zudkevitch-Joffee fugacity coefficient.
LnFugacity	COTHZJLnFugacity	Zudkevitch-Joffee fugacity.
MolarVolume	COTHZJVolume	Zudkevitch-Joffee molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHZJZFactor	Zudkevitch-Joffee compressibility factor.
amix	COTHZJab_1	Zudkevitch-Joffee amix.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

Lee-Kesler-Plöcker

This model is the most accurate general method for non-polar substances and mixtures.

XML File Name	Name	Description
lkp_liquid	Lee-Kesler-Plöcker	Lee-Kesler-Plöcker EOS using Mixing Rule 1 for all properties.

Property Name	Class Name	Description
Enthalpy	COTHLeeKeslerEnthalpy	Lee-Kesler enthalpy.
Entropy	COTHLeeKeslerEnthalpy	Lee-Kesler entropy.
Cp	COTHLeeKeslerCp	Lee-Kesler heat capacity.
LnFugacityCoeff	COTHLKPLnFugacityCoeff	LKP fugacity coefficient.
LnFugacity	COTHLKPLnFugacity	LKP fugacity.
MolarVolume	COTHLKPMolarVolume	LKP molar volume.
Viscosity	COTHViscosity	HYSYS viscosity.
ThermalConductivity	COTHThermCond	HYSYS thermal conductivity.
SurfaceTension	COTHSurfaceTension	HYSYS surface tension.
ZFactor	COTHLKPZFactor	LKP compressibility factor.
IGCp	COTHIdealGasCp	Ideal gas heat capacity.
OffsetIGH	COTHOffsetIGH	Ideal gas Offset enthalpy.
OffsetH	COTHOffsetH	Offset enthalpy with heat of formation.
OffsetIGS	COTHOffsetIGS	Ideal gas offset entropy.
OffsetS	COTHOffsetS	Offset entropy.
MolarDensity	COTHSolidDensity	Solid molar density.
MolarVolume	COTHMolarVolume	Solid molar volume.
Enthalpy	COTHSolidEnthalpy	Solid enthalpy.
Entropy	COTHSolidEntropy	Solid entropy.
Cp	COTHSolidCp	Solid heat capacity.

8 Utilities

8.1 IIntroduction

The utility commands are a set of tools, which interact with a process by providing additional information or analysis of streams or operations. In HYSYS, utilities become a permanent part of the Flowsheet and are calculated automatically when appropriate.

8.2 Envelope Utility

Currently there are two utilities in HYSYS that are directly related to COMThermo:

- HYSYS Two-Phase Envelope Utility
- COMThermo Three-Phase Envelope Utility

They can be accessed through the Envelope utility in HYSYS. Refer to Section 14.10 - Envelope Utility in Chapter 14 - Utilities in the **Operations Guide** for more information.

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